Regionally Based Assessment of Persistent Toxic Substances

Global Report 2003

UNITED NATIONS

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PREFACE

The Global Environment Facility through its Contaminated Based Operational Programme (OP10) supports projects that can lead to implementation of more comprehensive approaches for restoring and protecting the International Waters environment. The Programme assists initiatives that help characterise the nature, extent and significance of these contaminants. In furthering this process, UNEP, with the generous financial support of the Global Environment Facility Australia, Canada, France, Germany, Sweden, Switzerland and the United States of America undertook this regionally based assessment of persistent toxic substances (PTS). A major objective was to identify priorities for future interventions by the GEF under OP10. Additionally, the assessment will greatly assist the GEF in shaping the strategic priorities of its third phase. The project achieves this by:

- Delivering a measure of the nature and comparative severity of damage and threats posed at national, regional and ultimately at global levels by PTS.
- Providing the GEF, UNEP and others with a science-based rationale for assigning priorities for action among and between chemical-related environmental issues and for determining the extent to which differences in priority exist among regions.
- Evaluating the sources of PTS, their levels in the environment and consequent impacts on biota and humans, their modes of transport over a range of distances, the existing alternatives to their use and remediation options, the global capacity for their good management and the barriers that prevent such management.
- Stimulating research through the identification of data gaps.

This report is based upon the information presented in the twelve regional reports developed during the regional phase of the project. The project was managed by UNEP Chemicals in Geneva, Switzerland. UNEP would like to thank the Steering Group members that met periodically and provided thoughtful and meaningful direction during the implementation of the project.

Many scientists, representatives of governments, industry and non-government organisations and other interested parties participated in providing data, and in the technical and priority setting meetings that were held across all relevant regions. Unfortunately, we cannot list all the persons but offer our thanks and appreciation to their contribution and effort in the development of the regional and global reports. The lead authors for this report deserve special mention for overcoming the challenge of drafting and finalising the document. Their task was a difficult one given the mountains of data that required sorting and analysis. We thank them for their patience, wisdom and steadfast commitment toward the successful completion of this report.

This global assessment of PTS is the first of its kind. The many major data gaps that were encountered and the short time period allowed provided many challenges. However, we are pleased to present the initial Regionally Based Assessment of PTS and hope it will be useful to governments, non-governmental organizations, intergovernmental organizations and others in their efforts to protect people and the environment from the risks of toxic chemicals.

Since this project was initiated, governments negotiated and adopted the Stockholm Convention on Persistent Organic Pollutants. We hope that this assessment will be a useful contribution to the work of the Parties of that treaty in protecting our health and environment, and will also support efforts under other international agreements such as the Rotterdam Convention, the Basel Convention, the UNECE LRTAP Convention, the Global Programme of Action for Protection of the Marine Environment and the Regional Seas Agreements.

Klaus Töpfer
Executive Director
United Nations Environment Programme

ABBREVIATIONS AND ACRONYMS

ACP	Arctic Contamination Potential
ADI	Acceptable Daily Intake
ALRT	Atmospheric Long Range Transport
AMAP	Arctic Monitoring and Assessment Programme
APEs	Alkylphenol Ethoxylates
BCF	Bioconcentration Factor
BHC	Benzenehexachloride
BPH	Benzo(a)pyrene oxidation
CEEC	Central and Eastern Europe
CEP	Caspian Environment Programme
CIS	Commonwealth of Independent States
CSIRO	Commonwealth Scientific & Industrial Research Organisation
CTD	Characteristic Travel Distance
DDD /DDE	Metabolites of DDT
DDT	Dichlorodiphenyltrichloroethane
DLPCBs	Dioxin-like PCBs
EDCs	Endocrine Disrupting Chemicals
EMAN	Ecological Monitoring and Assessment Network
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe
EPER	European Pollutant Emission Register
ERL	Effects Range Low
ERM	Effects Range Median
EROD	7-ethoxyresorufin-O-deethylase
EUSES	European Union System for the Evaluation of Substances
FAO	Food and Agriculture Organisation of the United Nations
FERTIMEX	Fertilizantes Mexicianos, S.A.
GEF	Global Environment Facility
GEMS	Global Environment Monitoring System
GLBTS	Great Lakes Bi-national Toxics Strategy
HCB	Hexachlorobenzene
HELCOM	Helsinki Commission/The Baltic Marine Environment Protection Commission
HCHs	Hexachlorocyclohexanes
HIPS	High Impact Polystyrene
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
HxBB	Hexabromobiphenyl

IARC	International Agency for Research on Cancer
IFCS	Intergovernmental Forum on Chemical Safety
IMO	International Maritime Organisation
INFOCAP	Information Exchange Network on Capacity Building for the Sound Management of Chemicals
IPPC	Integrated Pollution Prevention and Control
I-TEQ	International Toxicity Equivalence
K_{AW}	Air/Water Partition Coefficient
K_{OA}	Octanol/Air Partition Coefficient
K_{ow}	Octanol/Water Partition Coefficient
LC_{50} Median	Lethal Concentration
LD_{50} Median	Lethal Dose
LOAEL	Lowest Observable Adverse Effect Level
LRT	Long Range Transport
LRTAP	Long Range Transport Air Pollutants
LRTP	Long Range Transport Potential
MDL	Minimum Detectable Level
MEDPOL	Mediterranean Pollution Monitoring and Research Programme
MEA	Multi Lateral Environmental Agreements
MEMAC	Marine Emergency Mutual Aid Centre
MRL	Maximum Residue Limit
MSCE-East	Meteorological Synthesizing Centre-East
MSWI	Municipal Solid Waste Incinerator
NAFTA	North American Free Trade Agreement
NARAPs	North American Regional Action Plans
ND	Not detected
NEPC	National Environment Protection Council
NGOs	Non-Governmental Organisations
NHATS	National Human Adipose Tissue Survey
NIS	Newly Independent States
NOAA	National Oceanic and Atmospheric Administration
NOAEL	No Observable Adverse Effect Level
NOEL	No Observable Effect Level
NPRI	National Pollutant Release Inventory
NWT	Northwest Territories
OCs	Organochlorines
OCPs	Organochlorine Pesticides
OECD	Organisation for Economic Co-operation and Development

OPs	Organophosphates
OSPAR	Commission for the Protection of the Marine Environment of the North-East Atlantic
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo- p-dioxins
PCDFs	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
PFOS	Perfluorooctane sulfonate
PIC	Prior Informed Consent
POPs	Persistent Organic Pollutants (group of twelve as defined in the Stockholm Convention 2001)
PRTRs	Pollutant Release and Transfer Registers
PVC	Polyvinylchloride
REACH	Registration, Evaluation and Authorisation of Chemicals
RENPAP	Regional Network on Pesticide Production in Asia and Pacific
ROPME	Regional Organisation for the Protection of the Marine Environment
ROWA	Regional Organisation of West Asia
SAICM	Strategic Approach to International Chemicals Management
SCCPs	Short-chain chlorinated paraffins
SMOC	Sound Management of Chemicals
SPM	Suspended particulate matter
SPREP	South Pacific Regional Environment Programme
SR	Special Range
t	Tonnes
TBBPA	Tetrabromobisphenol A
TCDD	Tetrachlorodibenzo-*p*-dioxin
TEL	Tetraethyllead
TEQ	Toxicity Equivalents
TML	Tetramethyllead
TOMPS	Toxic Organic Micropollutants Survey
TPT	Triphenyltin
TRI	Toxics Release Inventory
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organisation
WFD	Water Framework Directive
WHO	World Heath Organisation
WMO	World Meteorological Organization

EXECUTIVE SUMMARY

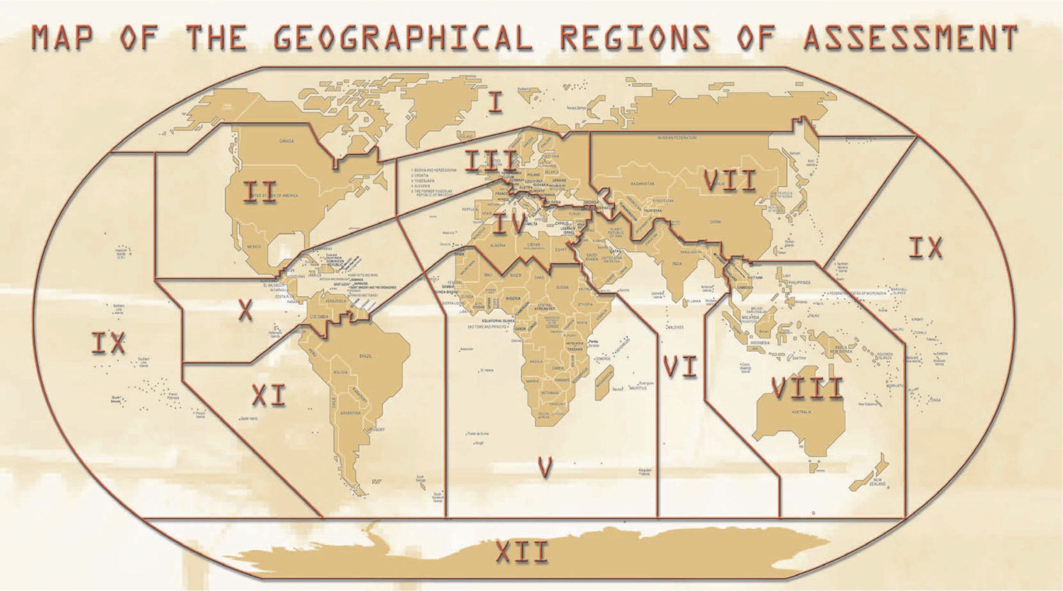
In 1997 the United Nations Environment Programme (UNEP) Governing Council decided that immediate international action should be initiated to protect human health and the environment through measures which will reduce and/or eliminate the emissions and discharges of an initial set of twelve "persistent organic pollutants" (POPs). The present project was initiated in mid-1998 at a time when the negotiations for an international legally binding instrument for implementing international action on certain persistent organic pollutants had just started and while the outcome of the negotiations was still purely conjectural. It was initiated by GEF after discussions with UNEP to address a broader set of issues and substances than those which finally were agreed under the Stockholm Convention on POPs. This project therefore deals with "persistent toxic substances" or PTS and is deliberately looking at a wider group of chemicals than the twelve "POPs" under the Stockholm Convention.

The Regionally Based Assessment of Persistent Toxic Substances (RBA PTS) Project was designed to gather data and assess the sources, environmental concentrations, the transboundary movement and effects of a selected number of PTS. The objective of the project is to provide a measure of the threats and damage to the environment and human health posed by these substances. It is intended that the results of the project will guide the Global Environment Facility (GEF) and other funding agencies toward priorities for future action to mitigate the effects of these PTS.

The project was designed to be based in the regions and draw on the resources and expertise at the country level. Regional teams were set up to be responsible for delivering the data gathering and assessment and UNEP provided central project management and coordination functions. A steering group made up of representatives of interested international organisations, environmental and industrial non-governmental organisations and scientists provided assistance to the project manager in guiding and delivering the project.

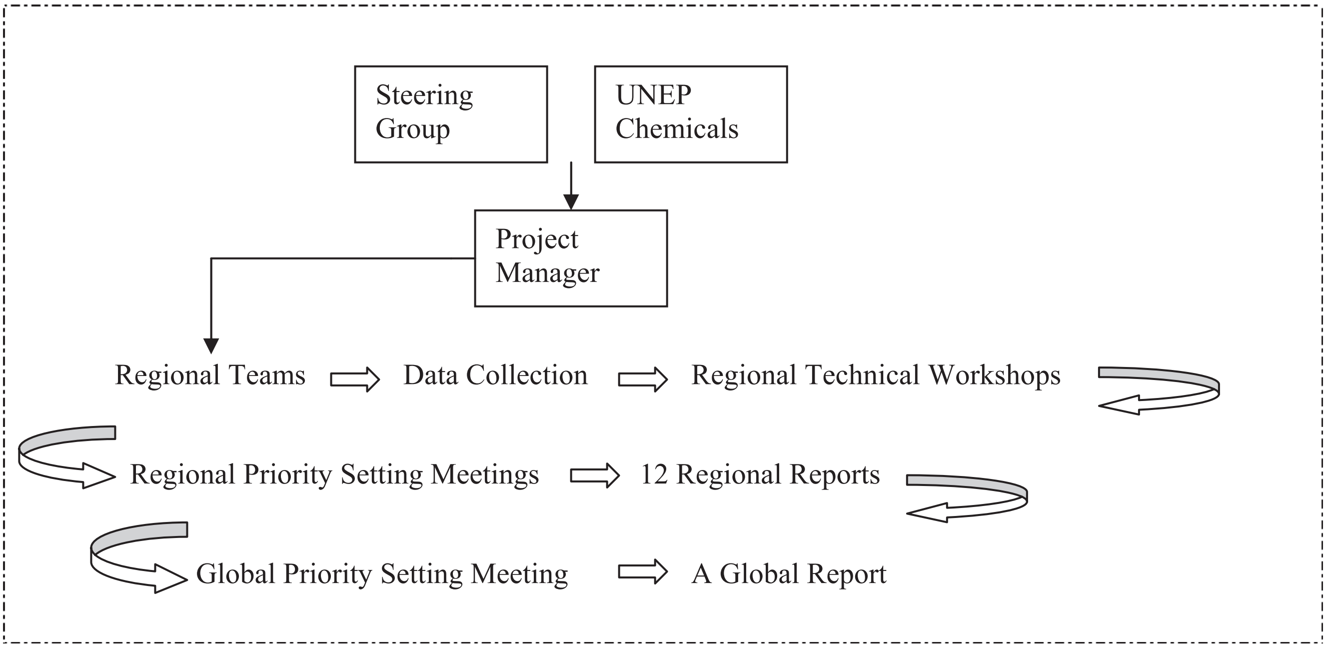
For this project the globe was partitioned into twelve regions. The regions were linked to important international waters in keeping with the focus of the project. The twelve regions were:

I – Arctic
II - North America
III – Europe
IV – Mediterranean
V - Sub-Saharan Africa
VI - Indian Ocean
VII - Central and North East Asia
VIII - South East Asia and South Pacific
IX - Pacific Islands
X - Central America and the Caribbean
XI - Eastern and Western South America
XII - Antarctica



Methodology

As this was a regionally based assessment, most of the work occurred in the various regions and effectively at the country level. A key feature of the data gathering part of the project was that an invitation was extended very widely for data. Information was sought from governments, research institutions, academics, non-governmental groups and industry. A Regional Coordinator and an accompanying team of four to five persons were selected. The process for the assessment is explained in the box below.



The regional teams were responsible for data gathering and assembly. One tool that was developed to assist in this data gathering was a standard data input form or questionnaire. It was clear that when dealing with complex and disparate data from a wide variety of sources, there is no simple and effective system which will easily and adequately handle the information.

Technical workshops were held with wide participation of experts within each region. Regional Priority Setting Meetings were organised in which participants agreed on the key priorities related to PTS amongst the stakeholders. A Global Team of six experts, along with the Project Manager, was composed to develop the global report mainly from the findings of the regional reports. A Global Priority Setting Meeting allowed feedback and further input via comments and submissions into the draft report.

Chemicals assessed

The term ‘PTS’ does not imply any particular level of risk but rather is a broad consideration for substances that persist in the environment, are found in areas far removed from sources and display some level of toxicity. Persistent toxic substances may be manufactured intentionally for use in various sectors of industry, one important sub-group being pesticides, while others may be formed as by-products during a variety of processes (industrial, non-industrial and natural) including combustion.

All regions considered the 12 designated “Stockholm POP” chemicals. They were also able to select additional chemicals that were of concern within the region. This project was primarily concerned with data gathering and not with assessing which chemicals are or could be considered PTS and the inclusion of a chemical for assessment does not imply that it meets any particular criteria of toxicity, persistence or effect. Additionally, the assessment of any given chemical in this project does not imply in any way that the chemical should be subject to inclusion in the list of Stockholm POPs.

The chemicals considered under the project are listed below. Not all the other chemicals were necessarily assessed by every region during the regional assessment.

List of chemicals assessed

STOCKHOLM POPS	OTHER CHEMICALS
ALDRIN	HEXACHLOROHEXANE
ENDRIN	POLYAROMATIC HYDROCARBONS
DIELDRIN	ENDOSULPHAN
CHLORDANE	PENTACHLOROPHENOL
DDT	ORGANIC MERCURY COMPOUNDS
HEPTACHLOR	ORGANIC TIN COMPOUNDS
TOXAPHENE	ORGANIC LEAD COMPOUNDS
MIREX	PHTHALATES
HEXACHLOROBENZENE	PBDEs
POLYCHLORINATED BIPHENYLS	CHLORDECONE
DIOXINS (PCDDs)	OCTYLPHENOLS
FURANS (PCDFs)	NONYLPHENOLS
	ATRAZINE
	SHORT-CHAIN CHLORINATED PARAFFINS
	PFOS
	HEXABROMOBIPHENYL

Conclusions

Many PTS are a historical problem, i.e., their massive and worldwide use occurred during a time of ignorance of the environmental problems potentially caused by them. In addition, the extensive commercialisation and industrialisation that was undertaken some fifty years ago, increased the demand and pace for the production of chemicals and the development of poor processes even in waste management. **The root causes** discerned for the expression of PTS are outlined below:

- Persistence
- Low water solubility
- High toxicity
- Unsustainable production/consumption
- Cost of chemicals
- Perceived effectiveness
- Ignorance

The **capacity to monitor** PTS differs widely across regions. While undertaking sophisticated monitoring programmes and having adequate legislative action to enforce environmental protection, the developed regions still require further financial resources and increased monitoring facilities. However, the gap is wide with regards to the needs of the developing regions. In Sub-Saharan Africa, Central America and the

Caribbean, the Indian Ocean and parts of Asia, the monitoring of PTS is mainly ad hoc and relies on analyses from research and on accidents. There is need for practical technology transfer and an increase in available financial resources to provide sustainable development of control mechanisms. Regional partnerships between developed and developing countries and among the latter should be encouraged.

Barriers do exist that mitigate against the implementation to solutions and alternatives to PTS. These include the following:

- Lack of comprehensive scientific data
- Lack of monitoring and inventory capacity
- Lack of suitable legislative framework
- Ineffective enforcement of regulations
- Illegal trade and use
- Inappropriate use and abuse
- Lack of awareness and information
- Commercial pressures
- Lack of clear responsibilities and limited coordination
- Lack of financial resources
- Lack of availability and acceptance of alternatives

While many **alternatives** to PTS have been researched, it is not necessarily easy to find suitable, workable systems to replace the desired qualities of these chemicals. The quality of persistence, low water solubility toxicity and the cost efficiency of processes that may release or emit PTS are difficult to replace. However, there are real examples that do exist where alternative measures have been instituted and have generated the desired result that was provided by the replaced PTS. Examples include:

For pesticides – Integrated Pest Management; Integrated Vector Management; Replacement of chlorinated pesticides; Organic farming.

For industrial chemicals and unintended by-products – Environmentally sustainable production; Best available technology; Destructive technology without unwanted emissions.

Priority Environmental Source Issues

A lack of data was a serious constraint with the compilation of many of the regional reports, especially from regions with developing countries and countries with economies in transition. Quantitative comparisons of production and releases by source type and chemical across regions was very difficult, as the lack of data, method of reporting, completeness, reported time trends in reductions and or increases, allowed mostly qualitative horizontal comparisons.

The general and comparative sensitivity of specific regions was not considered (i.e. would a small source of PAH in Region I be more important, than a relatively large source in a region just to the south?). Key observations, considerations, conclusions and suggestions that follow are outlined below:

- Obsolete stocks and reservoirs of released PTS (such as contaminated sediments and soils, and stocks of obsolete pesticides) are located in a number of regions and are major current sources. This aspect has been identified as a serious concern in developing as well as developed regions, thereby sharing a common environmental issue. This presents a potential of collaboration on remediation and other technologies between developed and developing nations, including nations with economies in transition.
- Even though much has been done to reduce emissions, industrial activity, (both in developed and developing regions as well as countries with economies in transition) must still be considered as a major source of PCDD/PCDF, and probably other related PTS. The characterisation and location of these activities on a global basis needs to be better understood, for a strategic application of interventions to be cost and time effective.

- Open burning and biomass burning are probable, but largely unknown sources of PAH and PCDD/PCDF in developing regions, or regions with a mixed economy. Open burning and biomass burning in many areas exposes biota and human populations, due to their close proximity (land fills, domestic heating, close location to water etc), and needs to be much better understood. Large cities as such can also be considered as a concentration of both various PTS sources and exposure routes, specifically involving the human population. Large cities are normally also located close to fresh water, and often with coastal areas, two areas of major concern due to pollution potential and sensitivity of the ecosystems.
- The developed regions can be considered as the major sources of intentionally produced industrial PTS (chlorinated paraffins, PBDE, PFOS and others). This is then transported via the environment, as well as through trade, to other regions. A better understanding is needed, as double counting (produced in one country, and used in another) could give the false impression about specific chemicals. The issue of secondary sources, such as e-waste, also needs to be better understood, as production, transport, primary use, and waste treatment (secondary use), will all be potential sources (to a greater or lesser extent).
- Very little is still known about the sources of organometalics in all the regions, although mercury is being addressed by the Global Mercury Assessment. Not enough information was available to make any qualitative statements about this issue, but concern is still obvious from the various regional reports.
- PCB remains a large problem in almost all the regions, although it should be recognised that PCB is one of the specific issues that will be addressed by the National Implementation Plans under the Stockholm Convention.
- DDT and the lack of a clear and effective alternative continue to hamper development, as well affecting the health of millions of people in many regions. Combined and continued efforts (such as with the WHO) is needed to address this insidious issue, as well as to raise the understanding of the problems in other regions.
- The source profile (Table 2.9) indicates that much more is known about most PTS sources in the developed regions, but in developing regions, major data gaps exist regarding the non-intentional and intentionally produced industrial PTS. Capacity and means to address the related issues remain a primary aspect that will need attention to assist developing regions in this regard.
- It must be recognised that the source profile is likely to change with more information from various activities, including the NIPs. Part of the lack of information can be ascribed to little capacity within developing regions to address source aspects. It will therefore be very useful if the source profile could be regularly updated, providing a clear means to understand the global issues, as well as to provide guidance on interventions, research and prioritisation.
- The source profile is also likely to change, as changes in sources within the various regions, through mitigation measures or through economic and social development are likely to occur.
- Perhaps one of the most useful outcomes of the Global Source Characterisation was the beginning of the relative understanding of the contributions and problems faced by the various regions. If the enhancement of this understanding can be done through the maintenance and expansion of some of the momentum and networks that has been generated through this effort, much value will be derived on a number of levels, inter alia research, capacity building, intervention planning and public trust.

The majority of the issues identified above, are in most cases regional specific. This means that addressing these priorities within the identified regions, will contribute significantly towards reducing the releases on a global scale. Addressing the issues on a regional level, within the scope of a global strategy, will enable better application of resources on mitigation measures, sustainable development, environmental protection and, human health improvement. Future developments however, could change the pattern. Increased industrialisation of developing regions could alter the global source profile, if appropriate technologies are not instituted.

Priority environmental concentration issues

As expected, the situation is very different across the regions. There are regions with a tradition in gathering information on PTS since the 70's, whereas in others there are important data gaps or even no information exists for some PTS. Therefore, priorities across regions may be based on facts (existing information and reported hot spots) or suspicions that environmental levels are high due to the existence of a variety of sources. From the regional reports the following picture of concerns can be obtained:

- The levels of PTS pesticide chemicals that were widely used across the regions in the past are now declining because regulatory measures, such as banning, use restrictions, etc. This is the case of DDT, heptachlor and chlordane. The use of mirex and toxaphene, which has been limited to certain regions, follow the same trends. These are in general PTS of secondary concern, except in the Polar Regions where there is evidence of still increasing levels.
- PTS pesticide chemicals that are still in use show detectable levels in practically all environmental compartments and, in some cases, are quite high. Even when they are banned in some regions there are also examples of elevated environmental levels in recent records, demonstrating illegal use or transport between regions. Examples include lindane and endosulphan.
- Industrial PTS chemicals which have been banned or subject to control in some regions (and environmental levels shows a clear decline since regulatory measures were taken), may still continue to be used in developing countries, where levels are even increasing as is the case of PCBs. Effective assessment, control of use and remediation will be a priority.
- Unintentionally produced PTS are of concern in the developed world, where levels reported are high, and obviously of great concern. Data are scarce in the developing world, representing a big data gap, although open burning may be of high concern. This is particularly the case with PCDD/PCDFs and PAHs.
- New candidate chemicals for global concern are insufficiently covered to draw a complete picture, while there are clear evidences of ecotoxicological effects for some of them. Gathering information becomes a priority. This is the case of PCP, brominated compounds, alkylphenols, etc.

For a better assessment of the PTS levels and effects, two major gaps need to be adequately filled, and this becomes also a priority:

Data generation and gathering should be extended throughout the regions, particularly for some PTS and compartments, and more important, in a harmonised manner, to allow data to be compared over time and between studies, countries and regions.

Regionally adapted benchmarks, namely environmental quality guidelines and human tolerable daily intakes, should be defined and more widely used to compare measures of environmental levels with environmental or health effects.

Integration of information on environmental measurements of sources and pathways with physical and biological models is required to aid the design and implementation of monitoring, research, and management, including mitigation.

Recommendations

While many recommendations were made in reports at the regional level, an attempt has been made to extract considerations that can be translated to achieving a global strategy. It is expected that any future actions that would consider the data from these reports will ensure that only validated information is captured in the decision process. Some positive considerations which developed during the implementation of this project should be incorporated into any relevant post project exercise.

Network – The use of the network established should be incorporated into any relevant post project enterprise. A good relationship exists among all the regional coordinators and teams that will provide synergy for any future project.

Regional Direction - The use of a regional strategy to attain global results has proven successful for the implementation of this project. This pattern should be replicated for future initiatives.

Emerging Chemicals - It will be appropriate for UNEP to concentrate on work associated with the twelve selected PTS under the Stockholm Convention. However, certain other emerging chemicals are a cause for concern globally and these should be considered in future programmes.

The Stockholm Convention has legally binding obligations for the Parties. These obligations consider the activities required to address the reduction and control of the selected twelve chemicals under the

Convention. This report recognises the ultimate responsibility of the Parties to the Stockholm Convention, and presents certain recommendations on the Stockholm POPs for possible consideration at the Conference of the Parties. These include:

- **Ratification of Environmental International Conventions –** The three major International Conventions pertaining to chemical management (Stockholm, Rotterdam and Basel) present a unique opportunity for all countries to be involved regionally and internationally in chemical management exercises that can only enhance the reduction of the levels and effects of PTS in the environment. In particular, the ratification of the Stockholm that directly considers the reduction and ultimate elimination of twelve POPs should be considered with priority.
- **Global strategy for Implementation of NIPs –** All countries that have signed the Stockholm Convention that are considered 'GEF eligible' have access to funds to create National Implementation Plans (NIPs) under the Stockholm Convention. These Plans are being administered by several Executing International Agencies. Even though there are disparities between countries, it is recommended that a global strategy be crafted to ensure efficiency, foster synergy between Agencies and to promote regional collaboration during the development of NIPs
- **A global assessment of the strategies to eliminate the use of DDT for malaria control -** Many countries are now battling to reduce if not eliminate the use of DDT for malaria vector control. A global assessment would include a close collaboration with industry and the WHO should recommend the best alternatives that now exist. The assessment would be used to promote the development of alternatives and to pursue the use of other less caustic chemicals and non-chemical solutions.

Below are post project initiatives suggested for future action based on the results of the assessment. These initiatives involve, in the main, chemicals outside of the twelve selected Stockholm POPs.

▪ Update of the Regionally Based Assessment of PTS

Many pieces of data and aggregated analyses were not captured under the current assessment. As such, it is considered prudent that the assessment be updated on a regular basis. This exercise could be carried out every 3-5 years resulting in a periodic assessment of the status of the selected chemicals with room for possible addition or subtraction.

▪ Filling of data gaps

Consistently throughout the regional reports, it was established that major data gaps existed that prevented the scientific acknowledgement of intuitive concerns for certain chemicals. These gaps varied from region to region and from chemical to chemical. Unfortunately, it is difficult to prioritise the importance of these data gaps on a global scale given the differences between regions. However, an effort to glean information based on regional priorities should be considered with expediency.

▪ Conduct of a global assessment of PCDD/PCDFs and PAHs emissions from open burning

It is being shown from the RBA PTS that open burning is a major concern in all habitable regions under the project. However, there is limited knowledge of the extent of the problem. The NIPs being developed by each signatory to the Stockholm Convention includes an assessment of the needs associated with the reduction of emissions of dioxins and furans. However, this could be aided by a global programme to ascertain measurements for various open burning sites. The intention is to establish with a fair degree of accuracy, estimated emissions from these various sources using models based on representative measurements taken from major, established open burning sites.

▪ A resource centre for new PTS chemicals

In order to be at the cutting-edge of the emerging concerns from certain PTS, UNEP Chemicals will develop a resource centre for those chemicals for which limited information is available especially in the developing world. These substances will include all the emerging chemicals identified in this report outside of the

Stockholm POPs. The centre would be interactive and developed as a network with a clearinghouse function. Such a centre would collate data from the developed and developing world, collaborate in ongoing work analysing these chemicals in terms of production, use and environmental concentrations and provide publications to share the emerging information in a wide circulation throughout all countries.

■ A global strategy for increasing public awareness on PTS issues

Consistently, the recurring message in the recommendations for all the regional reports is the need for broad public awareness programmes especially among civil society to increase the knowledge and sensitivity on the dangers of these chemicals. The increased awareness of what these chemicals are in the first instance and the danger involved from exposure will go a long way in ensuring reduced risk to public health and the environment. Working with SAICM (The Strategic Approach to International Chemicals Management) and the IOMC (The Inter-Organization Programme for the Sound Management of Chemicals), emphasis is placed on informing the public through audio-visual means and wherever possible, in the local language and using appropriate awareness strategies.

■ A global source profile

Currently, the Stockholm Convention obliges Parties to the Convention to carry out source profiles for those substances under that Convention. In order to keep track of what is happening, a global profile of selected priority chemicals would be undertaken on a timely basis to provide useful information on the production, emissions and releases of certain PTSs. Such a programme would rely on relevant, existing, global and regional data centres as well as the global monitoring network being established. It would make use of the wide network already developed through the RBA PTS Project as a means of collecting vital country and regional information for assessment. The SAICM should consider this recommendation as part of its portfolio.

■ A global strategy for technology transfer

In the past the transfer of technology has on occasion not been appropriate given the differences in geography, development of supporting institutions, culture and language. In order to ensure maximum benefit from the transfer of technology to reduce the release and emissions of PTS and subsequent effects to the environment, an agreed strategy would be developed that has the acceptance of all stakeholders. It is recommended that the SAICM consider in its work the importance of technology transfer and the need for it to reflect national requirements and situations, and to consider developing guidance on this matter.

■ Development of capacities and predictive capability of the LRT of PTS

For most of the regions of the globe no quantitative region-specific tools for transport assessment exist. The three major reasons for that are: Lack of region-specific process and understanding; lack of sufficient/and or sufficiently good data for model input and a lack of capacity for developing and using transport models within the regions. This knowledge gap not only prevents a quantitative treatment of PTS fate, but may often impede even a conceptual qualitative understanding of PTS transport behaviour in regions other than the Northern temperate environment. Therefore, there is need to gain a quantitative understanding and predictive capability of the transport and accumulation behaviour of various PTS under a variety of geographic and climatic circumstances, that reflect the diversity of the entire global environment. To achieve this, the following should be undertaken: a) Conduct studies aimed at a quantitative understanding of fate processes that are both unique and important for the transport behaviour of PTS under various regional circumstances. Specifically, identify PTS fate processes of importance in polar, arid and tropical ecosystems and investigate them with the aim to derive quantitative information suitable for inclusion into regional and global fate and transport models for PTS. Such fate processes may include phase partitioning, air-surface exchange, contaminant focussing and degradation processes; b) Ensure there are resources and capacity for monitoring PTS in remote environments. Models and a quantitative understanding of fate processes can not substitute for field data, but are dependent on them; c) Support the development, improvement, evaluation and use of regional and global PTS transport models of variable complexity; and d) Build capacity within the regions for studying and modelling PTS transport processes.

1 INTRODUCTION

1.1 BACKGROUND

There is considerable concern amongst Governments, Non-Governmental Organisations, scientists and the wider community over potential adverse effects on the environment and human health from exposure to chemicals. The long life times and potential for long-range transport of certain chemical pollutants requires that concerted international action is put in place to effectively control exposures since such chemicals released in one place may have impacts at a considerable distance from the source.

In 1997 the United Nations Environment Programme (UNEP) Governing Council decided that immediate international action should be initiated to protect human health and the environment through measures which will reduce and/or eliminate the emissions and discharges of an initial set of twelve “persistent organic pollutants” (POPs). International negotiations resulted in the adoption of the Stockholm Convention on Persistent Organic Pollutants in May 2001. The 12 substances initially addressed in the Stockholm Convention are: aldrin, endrin, dieldrin, chlordane, DDT, toxaphene, mirex, heptachlor, hexachlorobenzene, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Criteria are set out by which other chemicals will be considered for addition to the Convention.

The present project was initiated in mid-1998 at a time when the negotiations for an international legally binding instrument for implementing international action on certain persistent organic pollutants had just started and while the outcome of the negotiations was still purely conjectural. It was initiated by GEF after discussions with UNEP to address a broader set of issues and substances than those which finally were agreed under the Stockholm Convention on POPs. This project therefore deals with “persistent toxic substances” or PTS and is deliberately looking at a wider group of chemicals than the twelve POPs under the Stockholm Convention. PTS is a descriptive term and does not reflect a narrow definition of chemical properties or a legal definition but rather is used as an umbrella term for compounds that show persistence in the environment (and hence may have effects at some distance from their source and for some time after they are released) and which are toxic. The project was designed to compile and evaluate existing data on PTS. It was not intended to be a formal risk or hazard assessment. Inclusion of a chemical as PTS within this project does not imply that there is necessarily any given level of risk or imply a need for a specific action (regulatory or otherwise) but that the chemical properties in terms of persistence and potential toxicity mean that further assessment at the regional or international level may need to be undertaken as a basis for such action, as appropriate.

Persistent toxic substances may be manufactured intentionally for use in various sectors of industry. One important sub-group is pesticides, others may be formed as by-products from a variety of processes (industrial, non-industrial and natural) including combustion. To date, scientific assessments have often been focused on specific local and/or regional environmental and health effects, in particular "hot spots" such as the Great Lakes region of North America or the Baltic Sea in Europe.

1.2 OBJECTIVES

The objective of this project, as stated in the project brief, was to deliver a measure of the nature and the comparative severity of damage and threats posed at national, regional and ultimately at global levels by Persistent Toxic Substances (PTS).

In order to address this overall objective a number of sub-objectives were developed:

- ⇒ **To establish a regionally based network of experts and teams to gather and evaluate data on PTS**
- ⇒ **To set up a framework for broad-based stakeholder input within regions to determine regional priority issues related to PTS**
- ⇒ **To gather available data on sources of selected PTS within each region**
- ⇒ **To gather available data on concentrations of PTS in the environment, including animals and humans**
- ⇒ **To gather available information on the effects of PTS on humans and ecosystems**

- ⇒ **To gather available information on the long-range transport of PTS**
- ⇒ **To gather from the regions available information on the management of PTS and barriers to improved management**
- ⇒ **To develop regional reports containing the findings of the work**
- ⇒ **To hold a global priority setting meeting to review the results and priorities of the global assessment**
- ⇒ **To develop a global report synthesizing the results from the regions and identifying key priority areas, recommendations for future action and data gaps.**

1.3 SCOPE OF PROJECT

The project was designed to meet the objectives outlined above using a regionally based team approach and using existing data available within the regions.

The project combines two aspects of the PTS issue – it is underpinned by a science-based assessment and as such it has gathered, analysed and presented information and also drawn together stakeholders in the regions to discover their priority issues related to PTS. The project has been carried out independently of actions related to the negotiation and implementation of any international, regional or national agreements or policies and while it may help to provide information to such processes it was not designed and implemented with that objective.

The scope and impact of PTS are very broad with sources from many activities and practices, a wide range of chemicals, multiple pathways of exposure and highly variable behaviour in the environment as well as a wide variation in toxicities. The persistence and widespread occurrence and low absolute levels of PTS present challenges to those authorities and scientists studying PTS. Analytical data can be expensive to acquire and may have limited application. Providing a firm foundation for assessment and possible action to prevent and mitigate potential effects of PTS requires a holistic approach to data gathering, assembly and assessment often based on limited data. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation.

1.4 METHODOLOGY

The project was designed to be based in the regions and draw on the resources and expertise at the country level. Regional teams were set up to be responsible for collecting the data, implementing technical workshops and making the regional assessment. UNEP provided central project management and coordination functions and guidance was provided from the centre in order to facilitate a consistent approach. A Steering Group made up of representatives of relevant international organisations, environmental and industrial non-governmental organisations and scientists provided assistance to the Project Manager in guiding and delivering the project.

1.4.1 The Regions

For this project the globe was partitioned into twelve regions. The twelve regions were linked to important international waters in keeping with the focus of the project and designed to provide a manageable structure for the project execution. The twelve regions were:

I – Arctic

II - North America;

III – Europe

IV – Mediterranean

V - Sub-Saharan Africa

VI - Indian Ocean

VII - Central and North East Asia (Western North Pacific)

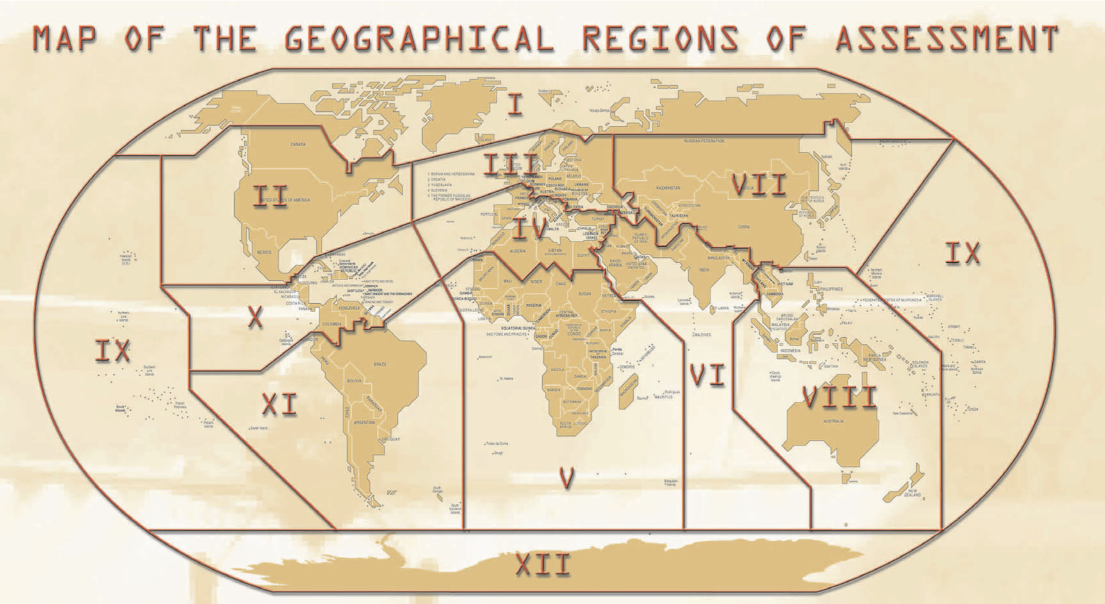
VIII - South East Asia and South Pacific

IX - Pacific Islands

X - Central America and the Caribbean

XI - Eastern and Western South America; and

XII - Antarctica.



1.4.1.1 Region I – Arctic

The regional boundaries used were those set for the Arctic Monitoring and Assessment Project (AMAP). The region includes the Arctic regions of the eight circumpolar countries: Canada, Denmark (Greenland); Finland, Iceland, Norway, Russia, Sweden and the United States of America (USA). Climate varies considerably with maritime climates along the coast of Norway, adjoining parts of the Russian coast and a narrow coastal strip of Alaska. A continental climate is found from northern Scandinavia to Siberia and eastern Alaska to the Canadian Arctic archipelago.

Much of the Arctic region is lightly populated and not industrialised, however, heavy industry in or near the Arctic parts of Russia and Scandinavia, historical equipment uses and waste disposal practices may be significant sources of PTS. In addition various PTS have found uses within the Arctic region.

1.4.1.2 Region II – North America

Region II consists of the Canada the USA and Mexico except the Arctic parts of Canada and the USA (Region I) and Hawaii (Region IX). Climatic variation is large from Arctic in the north to tropical in the south.

The USA and Canada are developed, industrialised countries with sophisticated industry and regulation, Mexico is a developing country with increasing industrialisation.

1.4.1.3 Region III – Europe

The Europe region for this project consists of Armenia, Austria, Azerbaijan, Belarus, Belgium, Bulgaria, Czech Republic, Denmark, Estonia, Finland, Georgia, Germany, Hungary, Ireland, Latvia, Liechtenstein, Lithuania, Luxembourg, Netherlands, Norway, Poland, Republic of Moldova, Romania, Russian Federation, Slovakia, Sweden, Switzerland, Ukraine, United Kingdom of Great Britain and Northern Ireland. It excludes those parts of the countries assessed under Region I (Arctic).

Region III spans three climatic zones – the circumpolar zone in the north, the subtropical zone south of the Alps including the Dinaric alps and the Balkans and the temperate zone warm in the central and southern area and cool in the north.

The countries included in Region III range from highly industrialised economies (such as Germany and the UK) to countries with economies in transition including some with aged industrial infrastructure to those with greater reliance on agriculture and a developing economic structure.

The chemical industry, metal production and processing and agriculture are all significant parts of the economy.

1.4.1.4 Region IV – Mediterranean

Region IV consists of countries clustered around the Mediterranean Sea: Albania, Algeria, Andorra, Bosnia-Herzegovina, Croatia, Cyprus, Egypt, France, Greece, Israel, Italy, Jordan, Lebanon, Libyan Arab Jamahiriya, Malta, Monaco, Morocco, Palestine, Portugal, San Marino, Slovenia, Spain, Syrian Arab Republic, The Former Yugoslav Republic of Macedonia, Tunisia, Turkey and Yugoslavia.

The climate is generally characterised by mild wet winters and hot dry summers with more than 90% of annual precipitation falling in winter.

Much of the population and urban development occurs along the coastal strip. Large variations are observed in the levels of development, ranging from highly industrialised economies of such as France, Italy and Spain through industrialising countries such as Greece and Turkey to developing countries in the south.

1.4.1.5 Region V – Sub-Saharan Africa

The region consists of the following countries and island states: Angola, Benin, Botswana, Burkina Faso, Burundi, Cameroon, Central African Republic, Chad, Comoros, Congo (Brazzaville), Cote d'Ivoire, Democratic Republic of Congo, Djibouti, Equatorial Guinea, Eritrea, Ethiopia, Gabon, The Gambia, Ghana, Guinea-Bissau, Guinea, Kenya, Lesotho, Liberia, Madagascar, Malawi, Mali, Mauritania, Mauritius, Mozambique, Namibia, Niger, Nigeria, Rwanda, Sao Tome and Principe, Senegal, Seychelles, Sierra Leone, Somalia, South Africa, Sudan, Swaziland, Tanzania, Togo, Uganda, Zambia and Zimbabwe.

The region can be divided into three major regions – the Northern Plateau, the Central and Southern Plateau and the Eastern Highlands. The equatorial belt has rainfall whereas the northern and southern African countries and those in the Horn of Africa are typically arid or semi arid.

In general the African economy is fragile and largely agricultural and high debts contribute to comparatively low levels of industrialisation and development. Most industrial areas are located close to lakes, rivers and estuaries.

1.4.1.6 Region VI – Indian Ocean

The region consists of Bahrain; Bangladesh; Bhutan; India; Iran; Iraq, Kuwait; Maldives; Nepal; Oman; Pakistan; Qatar; Saudi Arabia; Sri Lanka; the United Arab Emirates and Yemen. Climate varies considerably across this region covering mountain environments through to coastal and desert environments.

The economies and levels of development and income also vary strongly across the region with some countries deriving high incomes from oil production and others with largely agricultural and undeveloped economies.

1.4.1.7 Region VII – Central and North East Asia

The region consists of eleven countries: Afghanistan, China; Japan; Republic of Korea; Democratic People's Republic of Korea; Russian Federation (excluding the Arctic part – Region 1 and western part – Region III); Mongolia; Kazakhstan; Kyrgyzstan; Tajikistan; Turkmenistan; and Uzbekistan. Region VII includes a continental landmass, several major islands and various bodies of water with mountains, plains and deserts.

The major part of the population is concentrated in the eastern half of the region. The region has countries which are in the process of rapid development with increasing industrialisation and mineral and oil production, highly industrialised economies in transition and fully developed industrial economies. In addition some areas are at an earlier stage of development.

1.4.1.8 Region VIII – Southeast Asia and the Pacific

The region consists of: Australia, Brunei Darussalam, Cambodia, Indonesia, Lao People's Democratic Republic, Malaysia, Myanmar, New Zealand, Papua New Guinea, Philippines, Singapore, Thailand, and Viet Nam.

Climate ranges from tropical (Southeast Asia and Papua New Guinea) through to semi temperate conditions in the continental plateau and the mountains. The climate in Australia is generally arid or semi arid, it is temperate in the south and tropical in the north. New Zealand is temperate with some regional contrasts.

The sub-region remains very diverse in terms of economic development, political systems, ethnicity, culture, and natural resources. Singapore, for example, is an OECD country and Brunei Darussalam, an oil-rich microstate, Myanmar, Lao People's Democratic Republic, and Cambodia are essentially agrarian economies, while Malaysia, Thailand, the Philippines, Indonesia, and Viet Nam are rapidly industrializing. Australia and New Zealand are developed countries with mixed economies and substantial agricultural sectors.

1.4.1.9 Region IX – Pacific Islands

The region is very diverse. Twenty two countries and territories were included in this region: American Samoa; Cook Islands; Federated States of Micronesia; Fiji; French Polynesia; Guam; Kiribati; Marshall Islands; Nauru; New Caledonia; Niue; Northern Mariana Islands; Palau; Pitcairn Islands; Samoa; Solomon Islands; Tokelau; Tonga; Tuvalu; Vanuatu; Wallis and Funtuna; and various other US territories.

The islands are spread across more than 30 million square kilometres of which more than 98% is ocean. Of 7500 islands about 500 are inhabited. Countries and territories range from single islands to groupings of more than 100. Some islands are mountainous, others are low lying atolls. Economies tend to be based on agriculture and fishing.

1.4.1.10 Region X – Central America and the Caribbean

Region X consists of the countries of: Antigua and Barbuda; Bahamas; Barbados; Belize; Bermuda; Colombia; Costa Rica; Cuba; Dominica; Dominican Republic; El Salvador; Grenada; Guatemala; Guyana; Haiti; Honduras; Jamaica; Nicaragua; Panama; Puerto Rico; Saint Kits and Nevis; Saint Lucia; Saint Vincent and the Grenadines; Suriname; Trinidad and Tobago, and Venezuela. In general the climate is tropical.

The economies of many countries used to be largely agricultural. However, development of mining in Venezuela, Guyana and Suriname, tourism in the Caribbean and, latterly, increasing manufacturing have somewhat reduced the dominance of agriculture.

1.4.1.11 Region XI – Eastern and Western South America

This region consists of eight countries: Argentina; Bolivia; Brazil; Chile; Ecuador; Paraguay; Peru and Uruguay. Climate varies considerably across the region from tropical in the north through more temperate to desert with high mountains with alpine conditions.

The economies range from relatively undeveloped through those based on exploitation of mineral and other natural resources through to the large economy of Brazil (in the top 10 countries worldwide in terms of GDP).

1.4.1.12 Region XII – Antarctica

This region was not defined by national boundaries but rather by setting geographical limits. The region included all land and ocean – south of 50°S from 50°W to 30°E; south of 45°S from 30°E to 80°E; south of 55°S from 80°E to 150°E; and south of 60°S from 150°E to 50°W, as well as Ile St Paul and Ile Amsterdam, Macquarie Island and Gough Island.

The region is remote, land mass has cold desert conditions with much of the land permanently covered by ice. Islands within the region range from permanently snow covered to more temperate conditions with more developed terrestrial ecosystems.

There is no indigenous population or industrial activity.

1.4.2 Structure (regional teams)

The basic functional unit for the project delivery was the "Regional Team"[1]. Each Regional Team consisted of a regional coordinator appointed by UNEP and a team of four or five team members selected by the coordinators and approved by the Steering Group. The regional team was responsible for project planning and execution at the regional level.

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[1] The approach in three regions was significantly different. The assessment of Region I was carried out by a contractor working for the Arctic Monitoring and Assessment Programme (AMAP) and was based on the existing AMAP report (AMAP 1998), the Arctic report for the RBA was reviewed. In region II a contractor compiled the report and only a priority setting meeting was undertaken. The work of Region XII was delegated to the Scientific Committee on Antarctic Research (SCAR) who in turn subcontracted the work.

A network of experts was assembled at the country level. These experts were drawn from academia, Government, industry and non-Governmental Organisations and provided data and information to the regional teams for use in the assessment, in part through participatory regional workshops. Establishing and operating the network presented some challenges but after initial teething troubles some regions found the process valuable and effective. This was especially true where there was little previous experience in working with such networks and where basic infrastructural weaknesses were an issue.

Central project management and direction was provided by UNEP Chemicals in Geneva to ensure that regions were working in a compatible manner and to provide guidance on common issues that arose.

Due to the particular circumstances of the Arctic and Antarctic no regional meetings were held.

1.4.3 Approach

This project was based on the collection, synthesis and analysis of existing data. There is a considerable quantity of existing data available relating to the sources, environmental levels, transport and effects of a variety of PTS.

The project was based on a regional structure to ensure that, in so far as possible, the conclusions and priorities were based on the specific situation and circumstances in the different regions.

It is important to evaluate what is known in the regions, what are the perceived priorities and where the major data gaps and deficiencies are. This will provide GEF and UNEP with a soundly-based rationale for assigning priorities for future action on chemical issues and help to direct a focused and cost-effective programme of future work by countries and regions.

The Regional Teams were responsible for data gathering and assembly. One tool that was developed to assist in this data gathering was a standard data input form or questionnaire. Some Teams made more use of the standard questionnaires than others. It was clear that when dealing with complex and disparate data from a wide variety of sources with no control or influence over the studies from which data were being collected, there is no simple and effective system that will easily and adequately handle the information. In some regions comparatively greater use was made of data in the general scientific literature (in the case of Region XII all data came from this source).

A key feature of the data gathering part of the project was that an invitation was extended very widely for data. Information was sought from governments, research institutions, academics, non-governmental groups and industry. The nature of the project was such that although the reports and findings were widely disseminated there was no formal process of review by governments.

Workshops were organised in the relevant regions to bring together interested parties, to brief them on the project and to gather feedback and data relevant to the project. In general a two-stage approach was taken to have a workshop on sources and concentrations of PTS in the environment and a second on toxicological and ecotoxicological impacts and transboundary movement of PTS.

Regional Priority Setting Meetings were organised in which participants were involved in a process designed to discover what the key priorities related to PTS amongst the stakeholders were. Participation was taken from representatives of governments, industry, NGOs, and scientists from within each respective region. This process drew both on analytical and related data as well as the perceptions of risk and harm amongst stakeholders.

To assist with the process of setting priorities, a simple scoring system was developed. The participants were asked to assign a “score” to the chemicals. The score could be 0, 1 or 2 and relating to different aspects of PTS knowledge: sources; levels; effects and gaps. A score indicated no concern (0), local concern (1), and regional concern (2), while for gaps 0 indicated that supporting data were available, 1 that the data were limited, and 2 that data were largely missing.

The holding of and outputs from the Regional Priority Setting Meetings provide a powerful tool in the study of PTS and how the problems are perceived in the Regions by a broad group of stakeholders. The results from this exercise gave an overview of the various aspects of the occurrence of PTS within a Region and integrated perceptions and data. Nevertheless, precaution should be taken when looking at this dataset as a basis to prioritise PTS and hence to orientate future research and actions. Inevitably, the judgements expressed by participants usually reflected their specific experience, knowledge and perception of the problems and often for a specific country only. Such a simple scoring system restricts the depth of information and the results should be used as a part of a wider assessment and not taken as definitive for a region.

The findings of the project were summarised in 12 regional reports (see reference list). The overall findings, key themes and examples from the regional reports have been assembled into this report but for a full picture of the work carried out and data gathered, the regional reports should be used alongside this global report. The project was separate from and independent of activities related to the negotiation and subsequent implementation of the Stockholm Convention although findings from this work may be of relevance to entities working on the Stockholm Convention.

1.4.4 Persistent Toxic Substances - PTS

This project is concerned with a group of chemicals that are termed "Persistent Toxic Substances" or PTS. There is no formal or legal definition of PTS but rather the concept was developed during the project development phase to encompass chemicals that could be of concern due to their potential toxicity to ecosystems or humans. These chemicals exhibited characteristics of environmental persistence so that long-term exposures might result and effects may be felt some distance from the point of production or release.

The project was developed with the explicit intention to consider a broader range of chemicals and issues than the 12 POPs that were the subject of the negotiations to develop a legally binding agreement which led ultimately to the Stockholm Convention. The number of possible chemicals that could meet the definition of being PTS is very large. In order to ensure that the project was both consistent and at the same time able to be responsive to the priorities of the regions the following approach was taken: all regions would consider the 12 designated "Stockholm POP" chemicals, they would also be able to select additional chemicals that were of concern within the region.

In order to help the regions in selecting PTS chemicals a listing was compiled and provided to the regions for their consideration. This list was drawn from chemicals which could be grouped as PTS and which had been considered for action or assessment in other programmes. Information relevant to the process for deriving the list and a discussion of the selection of PTS at the planning workshops and in the project initiation is described in the Guidance Document issued at the beginning of the project (UNEP 2000).

This project was primarily concerned with data gathering and not with assessing which chemicals are or could be considered PTS. The inclusion of a chemical for assessment does not imply that it meets any particular criteria of toxicity, persistence or effect. It is crucial to recognise that the exclusion of chemicals from this assessment does not imply that there are not other potential PTS that may be important.

The project provides information on those chemicals that were considered and is based on the information and data provided during the project period. Supplementary data and further studies may change the relative priorities and may change the interpretation of the data available. The work is therefore to be seen as a step in the process of evaluating PTS and not as a definitive study and all conclusions are drawn with that in mind.

The chemicals considered in each region are shown in Table 1. Most regions considered chemicals selected from the list of provided by UNEP but some added additional chemicals as well. Since only limited data are available in some regions, the fact that a chemical was not considered does not necessarily mean that it is not present or not necessarily a priority. The listing is broken down to show those chemicals defined as "Stockholm POPs", and "other PTS" which are grouped according to their primary use or designation – as pesticides, industrial chemicals or unintentionally produced PTS.

Some chemicals will have multiple uses and these may all need to be considered. Hexachlorobenzene may be used as a pesticide, an industrial chemical and can also be unintentionally produced, while PAHs are usually produced unintentionally but are also produced for use as an industrial chemical.

Table 1 Chemicals considered in the regions.

		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
"Stockholm POP" pesticides	Aldrin	●	●	●	●	●	●	●	●	●	●	●	●
	Chlordane	●	●	●	●	●	●	●	●	●	●	●	●
	DDT	●	●	●	●	●	●	●	●	●	●	●	●
	Dieldrin	●	●	●	●	●	●	●	●	●	●	●	●
	Endrin		●	●	●	●	●	●	●	●	●	●	●
	Heptachlor	●	●	●	●	●	●	●	●	●	●	●	●
	Mirex	●	●	●	●	●	●	●	●	●	●	●	●
	Toxaphene	●	●	●	●	●	●	●	●	●	●	●	●
	Hexchlorobenzene (HCB)	●	●	●	●	●	●	●	●	●	●	●	●
POP industrial chemicals	Polychlorinated biphenyls (PCBs)	●	●	●	●	●	●	●	●	●	●	●	●
POP unintentionally produced	Dioxins (PCDDs)	●	●	●	●	●	●	●	●	●	●	●	●
	Furans (PCDFs)	●	●	●	●	●	●	●	●	●	●	●	●
Other PTS – pesticides	Atrazine			●			●			●	●		
	Lindane (γHCH)[1]	●	●	●	●								●
	Hexachlorocyclohexanes (HCH)[1]	●	●			●	●	●	●	●	●	●	●
	Chlordecone		●	●					●				
	Pentachlorophenol		●	●	●	●	●	●	●	●	●	●	
	Endosulphan		●	●		●	●		●	●	●	●	
	Organotin	●	●	●	●	●	●	●	●	●	●		●
Other PTS - industrial	Organolead	●	●	●		●	●		●	●			
	Hexabromobiphenyl (HxBB)		●	●					●				
	Polybrominated diphenyl ethers (PBDE)		●	●	●			●	●				
	Phthalate esters		●	●	●	●	●		●	●			
	Short-chain chlorinated paraffins (SCCPs)		●	●					●		●		
	Nonyl/octyl phenols		●	●	●				●		●		
	Perfluorooctane sulfonate (PFOS)		●										
Other PTS – unintentionally produced	Organomercury	●	●	●	●	●	●	●	●	●	●	●	●
	Polycyclic aromatic hydrocarbons (PAH)		●	●	●		●	●	●	●		●	●

Note 1 – potential confusion arises since lindane is an isomer of the HCH grouping, some data refer specifically to lindane, other data are more general and related to HCH. Treatment by the regions was not always consistent.

1.5 PURPOSE AND STRUCTURE OF GLOBAL REPORT

The outputs from the Regionally Based Assessment (RBA) include:

- ⇒ **Twelve regional reports addressing the findings of the project at the regional level including regional priorities developed by stakeholder meetings;**
- ⇒ **A network of scientists and other stakeholders;**
- ⇒ **A large body of data related to PTS sources, environmental concentrations and effects;**
- ⇒ **This global report.**

The global report synthesizes the key findings from the regional reports and draws conclusions on the principal issues and data gaps. This report is designed to be a stand-alone document summarising the findings of the project. Detailed data and information is contained in the regional reports and summarised in this report with key themes supported by example data sets and key case studies. The report is structured in the following sections:

Chapter 1 is the introduction providing an outline of the background to the project, the methods applied and the common themes running through the project. Chapter 2 addresses sources of PTS in the regions summarising the key findings including regional priorities related to sources of PTS and key data gaps. Chapter 3 considers data on concentrations of PTS in the environment, animals and humans as well as evidence for toxic effects on ecosystems and humans. Regional priorities are summarised and key data gaps identified. Chapter 4 is concerned with the fate and transport of PTS providing a summary of work and knowledge within the regions regarding the transboundary transport of PTS and key features of the chemicals and regions that will affect transport and fate. The models used to estimate these transport pathways are explored. Chapter 5 addresses the root causes of PTS, the capacity and needs of the regions to manage PTS, the barriers to sustainable management of chemicals, alternatives and the measures for reduction. Chapter 6 contains overall conclusions, priority issues and data gaps along with recommendations for future actions.

1.6 LIMITATIONS AND CAVEATS

A project of this scale and size addressing an issue as complex and wide-ranging as PTS at the global level is limited by a number of factors which should be considered in the reading of the report.

1.6.1 Administration

The project set out to build a network of scientists and experts from countries across the globe working together in 12 regional groupings to generate the information which forms the core of this work. The process of identifying the key individuals and institutions is by no means simple and although the team cast the invitation as widely as possible, there are likely to be individuals with valuable data and insights to contribute who were not initially identified, were otherwise engaged or who may be able to contribute to follow-on work.

In some regions there was little experience in working across national boundaries and the availability of suitable infrastructure to enable smooth and simple communication and project management was highly variable. Consequently, for some regions it was harder to complete the tasks and to gather all possible data. The achievement of organising teams of experts and coordinating workshops on technical findings and priority setting should not be underestimated.

1.6.2 Data quantity and quality

The field of PTS chemicals is very broad indeed. The quantity and quality of data vary widely. Some regions, for example North America and Europe, have a huge volume of data and the sorting, sifting and selection of relevant data becomes a major problem. In other regions, for example Africa and South America, there were instances where there was no relevant information available on some of the chemicals and the problems become more related to trying to work with a very incomplete picture. Even in the “data rich” regions, many gaps were identified and full information was not available. The significance of the gaps and their impact on limiting the overall assessment varies widely but should be borne in mind in reading the report and making use of the data and conclusions.

It is clear that not all data was made available to the project and there will inevitably be omissions. No systematic process of data validation was included. However, many of the data sets will have been validated when they were developed or published under other programmes, while additional validation was at the discretion of the regional teams. Data management was a major challenge for this project. The computer based system that was developed in a relative short period, had to consider disparate data relating to many matrices, a wide range of different experimental designs and no consistency in sampling, analysis and reporting protocols. Clearly this is an inevitable consequence of relying on existing data rather than setting out to design a data generation programme from the start. Important lessons have been learned about the extreme difficulty in developing and implementing a meaningful and effective data management system for a project such as this.

1.6.3 Priority setting

In a field as complex as PTS where information and data are incomplete and of variable coverage and quality, the process of setting priority issues must be viewed as an interactive process. Information is inevitably less than perfect and decisions are influenced by many factors. Priority lists developed by the participants in particular workshops are based on the interaction of factors and information available to those present and may be expected to be revised in the light of additional information, analysis and consideration.

1.6.4 Relationship to other initiatives

Many initiatives are underway related to improved chemical management and reduction of harm to human health and the environment that might be caused by chemicals. This project is an assessment of data related to Persistent Toxic Substances which are a subset of chemicals and the report should be viewed in the wider context of assessments and initiatives which are being developed and implemented. It provides data and may be valuable to decision makers as a part of the overall process of assessing risks and setting priorities for action.

The project did not attempt to identify new chemicals that could give rise to concern Such activities are underway in other fora and should be considered.

1.6.5 Chemical classification

It is important to recognise that there is a defined process contained in the Stockholm Convention to propose and assess chemicals as possible Persistent Organic Pollutants. This project is entirely separate from that process and no judgement, explicit or implicit, was made regarding whether the compounds addressed beyond the 12 Stockholm POPs are or may in future be classified as POPs under the Stockholm Convention.

1.7 REFERENCES

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Pacific Islands (Region IX) Regional Report, 2002. UNEP/GEF: Regionally Based Assessment of Persistent Toxic Substances.

South East Asia and South Pacific Regional Report, 2002. UNEP/GEF: Regionally Based Assessment of Persistent Toxic Substances.

Sub-Saharan Africa (Region V) Regional Report, 2002. UNEP/GEF: Regionally Based Assessment of Persistent Toxic Substances.

UNEP 2000, Guidance Document for the Collection, Assembly and Evaluation of Data on Sources, Environmental Levels and Impacts of Persistent Toxic Substances. UNEP, Geneva.

2 SOURCE CHARACTERIZATION

2.1 BACKGROUND INFORMATION ON PTS SOURCES

The information and analysis presented in this chapter are based on data gathering and interpretation of existing information, as done in a coordinated fashion in each of the 12 Regions (Region I – XII Reports). For most of these Regions, data gathering consisted mainly of questionnaires related to information on sources and also by contributions from participants at technical workshops.

Source characterization and source inventories represent crucial steps in developing appropriate risk control strategies for PTS. This approach will present an informed and motivated basis from which to derive important global sources in order of importance and so target source reduction measures effectively and incorporate effective risk reduction measures.

For the purpose of the RBA, we use the term “source” in relation to the entry of a PTS into the compartment of the environment under consideration. For a chemical that is manufactured, we consider the complete chemical life-cycle from production through use and any final disposal. Therefore, any intentional release (such as agricultural application of pesticide) or unintentional release (such as fugitive emissions) during manufacture, transport, use or from stockpiles and waste of a chemical to air, water, soil, sediment or biota is included as a source. For “unintentionally produced PTS” we are guided by where the PTS enters the environment. In both cases there is scope for some overlap. It is also relevant to consider potential sources such as stockpiles, reservoirs and waste sites from which uncontrolled releases may occur. Once released, the chemical can be transported through various means to other areas. It also needs to be understood that stockpiles and wastes can and does include chemicals other than the identified PTS.

Release to the environment can already start during production, but can also occur during storage, transport, use and disposal. In addition, unintentional by-product formation (mainly PCDD/PCDF) can also occur during production and disposal processes and, specifically for PCDD/PCDF, if thermal processes are used (UNEP 1999).

There are different types of sources of PTS as considered by the RBA. It includes both intentional and unintentional production, and can further be classified into point and diffuse (non-point) sources, as well as secondary sources. Because of the wide range of chemicals considered by the RBA, it comes as no surprise that many different sources are also involved that will result in the introduction of these chemicals into the environment. Point and diffuse sources include releases from industrial and domestic sites, traffic, waste disposal operations such as incinerators, and landfills. Secondary sources include the spreading of sludge on land and remobilisation of previously deposited compounds from soils and water-bodies. Some sources can be regulated (such as industrial point sources and agricultural application) while other diffuse emissions (in this regard, emissions are understood to include releases to all media) represent unregulated and/or difficult to regulate inputs (fugitive releases from landfills, domestic open burning of waste, forest fires, etc.).

The UNEP/GEF preparatory workshops for the RBA project (UNEP 1999a), listed a preliminary screening list of important potential PTS sources. An augmented list is presented in Text Box 2.1. For more detail on known conversion rates or release factors of PCDD/PCDF, the UNEP Standardised Toolkit (UNEP 2001) can be consulted.

An investigation of the information in text Box 2.1 provides an indicative list of the direct and/or indirect involvement of water. In most cases manufacturing and processing plants are located close to, or are dependant on local water supply – mostly rivers and lakes – with a concomitant potential for pollution by PTS. In addition, much of the agricultural production also depends on access to water from rivers and reservoirs, also with the threat of polluting these sources with PTS pesticides. These observations regarding water will be followed throughout this report. Note should also be taken of the overlaps between the different categories. Production of electronic equipment that incorporates PTS (such as PBDE) could result in releases elsewhere when the products are treated as waste (see Annex II).

Text Box 2.1. Major source categories of potential releases of PTS to the environment.

Manufacturing

This sector includes chemical manufacturing of PTS, as well as the manufacturing of products that involves the use of materials that may be contaminated with PTS – for example:

- textile manufacturing
- chlorinated chemical production *i.e.* of chloro-aromatics (phenols, benzenes), oxy-chlorinators
- Cl_2-production using graphite electrodes
- oil refining and catalyst regeneration
- pulp and paper (elemental chlorine bleaching)
- pesticide production and formulation

Thermal Processes

Processes that involve high temperatures and usually combustion can lead to the formation and release of a suite of complex PTS, particularly PAH, PCDD/PCDF, PCB and HCB. Key variables to consider include the effectiveness of combustion, the addition of pollution controls and the nature of the materials being introduced. Also, in many parts of the world uncontrolled combustion processes and combustion process facilities not equipped with adequate air pollution control systems are likely to be a major source of these pollutants.

Thermal Manufacturing Processes

- metallurgical processes, primary processes, mainly copper, steel and aluminium, also zinc recovery from steel and other scrap recovery processes including aluminium, steel, copper, zinc, magnesium, lead and others (i.e. cable burning)
- coke production and carbo-chemical processes (especially using brown coal/lignite)
- mineral processing (especially cement kilns), asphalt mixing, production of lime, ceramic, glass, brick and other similar processes carried out at small-scale

Controlled Combustion Processes

- municipal (non-hazardous) waste incineration
- industrial waste combustion, including treated wood waste combustion
- hazardous waste incineration
- medical/clinical waste,
- sludge (non-hazardous) incineration
- coal combustion (large volumes)
- oil combustion (large quantities)
- wood/biomass (large and small scale quantities) combustion
- landfill gas/biogas
- crematoria and animal carcass burning

Uncontrolled Combustion

- biomass such as forest, bush, agricultural harvest residues (eg straw and sugar cane leaves)
- accidental fires, eg houses, industrial complexes etc
- landfill fires, unintentional and intentional
- combustion of other wastes, i.e. flaring of drilling mud, landfill gas etc., building waste and construction debris, domestic (backyard) waste burning
- plastic container/barrel burning

- hazardous waste/contraband CDs and DVDs/tires/rubber/cable
- e-waste - end-of-life electronic products
- general open burning

Product application and use

- agricultural applications of pesticides (see Table 2.1)
- application of pesticides outside agricultural lands, for disease vector control, locust control, vegetation control and others
- preservatives for wood, leather, textiles
- textile and leather dying
- industrial bleaching processes, especially using chlorine
- transformers and electrical equipment
- solvent use and all processes which involve solvents, i.e. dry-cleaning, de-greasing etc.
- PCB-paint use, PCP-paint
- storage of products containing PTS, such as e-waste and contaminated feed

Transport

During the transport of PTS products and products containing PTS, accidents and spillages can and do occur.

Recycling Processes (excluding thermal)

- metals (incl. vehicle) recycling by-products such as shredder (mainly PCB), waste oil, scrap yards with stockpiles, refrigerator recycling, electronic scrap and circuit board recycling *etc*.
- paper recycling, especially de-inking sludges
- sewage sludge (including paper sludge) and effluent applications *i.e.* on land as agricultural fertilizer, for composting.
- solvent recovery processes and especially residue sludge from it
- waste oil recovery
- plastics recycling including extrusion
- metal flyash recycling

Waste Disposal (non-thermal waste disposal)

- landfills (controlled and uncontrolled) of various waste types (municipal, hazardous *etc*.), contaminated incinerator ash, sludge, metal ash, also leaching from those landfills
- storage/stocks of transformers containing PCB-oil
- ocean dumping of solid/sludge/liquid wastes
- dumps of obsolete pesticides, but likely to contain non Stockholm POP pesticides as well
- donations of pesticides to developing countries can result in toxic waste dumps.

Reservoirs (potential for re-release subsequent to initial accumulation)

- soil and sediments
- waste and obsolete stockpiles
- PCP-treated wood i.e. telephone poles, railroad ties, etc.

Pesticides constitute an important PTS use category where chemicals are applied, in most cases, directly and intentionally to the environment. A summary of main sources of PTS pesticides to the various environmental compartments is shown in Table 2.1. It must be noted however, that there is less data concerning the airborne load of pesticides when compared with the other compartments. The data included in this report related to pesticides are therefore related to sources that can contaminate soil, freshwater and marine waters.

Table 2.1. Some of the main sources of pesticides to the various abiotic environmental compartments

Air	Soil	Freshwater	Marine water
Agricultural usage	Stockpiles	Agricultural usage	Agricultural runoff
Spraying/land application	Production and waste (DDT and dicofol)	Runoff from agricultural use	Major rivers and coastal drains
Production	Misuse	Production (DDT/dicofol)	

2.2 PTS PRODUCTION, USE AND EMISSIONS

2.2.1 Global PTS production data

A database of historical, present, and predicted global usage or sale of selected persistent pesticides including aldrin, dieldrin, endrin, technical HCH, lindane, DDT, chlordane, endosulphan, heptachlor, and toxaphene was prepared by Voldner and Li (1993, 1995), Li et al. (1996, 1997), and Barrie et al. (1997). This information was linked with the global distribution of agricultural activities to determine usage distribution. The reported global cumulative usage for selected pesticides is presented in Table 2.2.

Table 2.2. Global cumulative usage of selected pesticides for various periods of time (Barrie et al. 1997)

Pesticides	Usage (tonnes)	Period	Source
DDT	1500000	1948-1993	Voldner and Li 1995
Technical HCH	550000	1948-1993	Voldner and Li 1995
Technical lindane	720000	1948-1993	Voldner and Li 1995
Toxaphene	450000	1948-1993	Voldner and Li 1993
Technical HCH	40000 29000	1980 1990	Li et al. 1996
Technical lindane	5900 4000	1980 1990	Li et al. 1996
α-HCH	28000 20400	1980 1990	Li et al. 1996
γ-HCH	11900 8400	1980 1990	Li et al. 1996
Interpolated			
DDT	2600000 990000	1950-1993 1970-1993	Voldner and Li 1995
Toxaphene	1330000 670000	1950-1993 1970-1993	Voldner and Li 1993

Similar data are available for the global flux of PCDD/PCDF. In a publication that only became available after the completion of the Regional reports, Fiedler (2002) calculated the annual global flux, based on PCDD/PDDF releases to air for 21 developed countries as between 9964 g TEQ “at best”, to a maximum of 21391 g TEQ, based on 1999 data.

For PCB, the global production (excluding the production by the former USSR) has been estimated at 1.5 million tonnes (UNEP 1998). For the Russian Federation, the total production has been estimated at 180000 tonnes (AMAP 2000), thereby bringing the worldwide production to a total of 1.68 million tonnes. Polycyclic aromatic hydrocarbons are formed mainly through combustion (about 90%). More information on PAH is available from the Region II and III Reports.

Demand for PBDE has decreased significantly in Europe over the last 10 years, although global demand is continuing to climb with the vast majority 97% (8290 tonnes) used in North America in 1999. Production in Europe was estimated to be 210 tonnes in 1999.

Additional information for this report was also obtained from AMAP (2002), Global Emissions Inventory Activity (GEIA, 2003), and GloPeRD (2003). Note should also be taken about possible double counting, and the uncertainties that are inherent with production estimates. Products can be produced in one Region and exported to another, where they can be counted again. With the Regional Reports mostly looking at their own Regions, this possibility exists when compiling data from all the Regions.

2.2.2 PTS pesticides

The PTS pesticides considered in this report include those that are defined by the Stockholm Convention, as well as others that have drawn attention due to their high volume of use and their regular detection in the environment. The PTS pesticides as defined by the Stockholm Convention are aldrin, chlordane, DDT, dieldrin, toxaphene, mirex, endrin, heptachlor and HCB. Note should again be taken that some of these chemicals have more than one use or source category.

Figure 2.1. DDT is still being used for malaria control in some countries in Africa.

Although HCB was initially used as a pesticide, the principal current sources of HCB in the environment are estimated to be the manufacture of chlorinated solvents (probably only in some older technologies), the manufacture and application of HCB-contaminated pesticides, and waste combustion processes (Bailey 2001). A substantial portion of HCB measured in the atmosphere is thought to come from volatilisation of "old" HCB on the soil from past agricultural use and contamination. Only a small fraction of the HCB generated as a by-product may be released depending on the process technology and waste-disposal practices employed. For example, according to the US Toxic Chemical Release Inventory (TRI), releases of HCB from the ten largest processing facilities in North America were 460 kg, most of this to air, compared with almost 542000 kg transferred offsite as waste for treatment in regulated facilities.

The other identified PTS pesticides include atrazine, endosulphan, lindane, PCP, organotin (including TBT and TPT), and chlordecone. Annex 1 contains more information regarding the chemicals. The various uses and applications of all the PTS pesticides differed considerably between the Regions.

2.2.3 Unintentionally produced PTS

2.2.3.1 PCDD/PCDF

There has been an increasing number of observations, which appears to indicate that dioxins may have been present in the environment for considerably longer than the onset of industrial activity (*e.g.* Alcock *et al.*, 1998), and that they may be formed through non-anthropogenic activities. For example, studies at Lancaster University have detected the presence of PCDD/PCDF in environmental samples collected and stored from the late-1800s (Alcock *et al.*, 1998). The researchers believe this is consistent with the emission of trace quantities of PCDD/PCDF from combustion of coal/wood and/or metal smelting activities prior to the increasing use of chlorine in industry during this century. Results are highly consistent with reports of PCDD/PCDF in Mississippi clay, German kaolinite and Australian sediments. Taken together, these studies provide a strong indication that natural processes can form PCDD/PCDF. There is little doubt though, that the vast majority of PCDD/PCDF are formed through anthropogenic activity. However an unknown amount may be formed via natural processes and this could have consequences for dioxin inventory estimates (adapted from the Region III Report).

Fig 2.2. Incomplete combustion practices and increasingly diffuse sources are some of the main PCDD/PCDF releases to the environment, although there are also non-anthropogenic sources.

2.2.3.2 PAH

Combustion sources are thought to account for over 90% of the environmental burden of PAHs. In particular, stationary point sources account for around 90% of these inputs (Howsam and Jones 1998). Inputs to the atmosphere are dominated by emissions associated with residential heating, (coal, wood, oil and gas burning) industrial processes (coke manufacture).

Non-combustion processes such as the production and use of creosote and coal-tar, (and the remediation of sites contaminated with these substances), though poorly quantified, are potentially very significant primary and secondary sources. Nations undergoing rapid industrialisation may well prove to be an increasingly significant source of PAH in global terms with the increase in number of mobile and industrial sources (adapted from Region III report).

2.2.3.3 PCB

Because the vast majority of PCB is intentionally produced, PCB will be discussed in section 2.2.4

2.2.4 Intentionally produced industrial PTS

Since the combined list of intentionally produced PTS identified by the 12 Regions is quite extensive, only those that are mentioned consistently are discussed in this section. More information can be obtained from the individual regional reports.

2.2.4.1 PCB

PCB have been used in capacitors and transformers, hydraulic fluids, adhesives, plasticizers, heat transfer fluids, wax extenders, lubricants, cutting oils and flame-retardants. PCB enter water mainly from discharge points of industrial and urban wastes into rivers, lakes, and coastal waters (adapted from Region II and III Reports).

2.2.4.2 HCB

See section 2.2.2

2.2.4.3 PBDE

Polybrominated diphenyl ethers (PBDE) represent important additive flame-retardants with numerous uses within industrial and domestic electronic equipment and textiles. PBDE are similar in behaviour (hydrophobic, lipophilic, thermally stable) to PCB. Growing evidence suggests that PBDE are widespread global environmental pollutants and that they are capable of bio-accumulation in food chains. Despite several years of increasing interest in these compounds, our understanding of the principal environmental sources remains limited. Reservoirs of commercial mixtures associated with products have not been broadly quantified on a national scale and possible release to different environmental compartments remains uncertain (adapted from Region II and III Reports).

2.2.4.4 PCP

The identified main sources into the environment are: treatment of wood (sapstain control agent), impregnation of heavy-duty textiles and fibres (fungicide), use and disposal of treated wood and textiles (including imported goods), contaminated sites (former PCP production and wood preservation plants) and treatment of contaminated soil and groundwater, natural sources or burning processes.

2.2.4.5 Short-chain chlorinated paraffins

Short-chain chlorinated paraffins (SCCPs) are part of a family of chemicals referred to as chlorinated paraffins. Chlorinated paraffins are complex mixtures of straight chain chlorinated hydrocarbon molecules with a range of chain lengths (short C_{10-13}, intermediate C_{14-17} and long C_{18-30}) and degrees of chlorination (between 40 - 70 % weight basis). These compounds were first produced as extreme pressure additives around 1930. In 1985, the estimated world production of chlorinated paraffins was ~300000 tonnes (WHO 1996). SCCPs comprise the smallest fraction of the global production.

The widespread use of SCCPs are potential sources of environmental contamination, particularly to the aquatic environment. SCCPs may be released into the environment from improperly disposed metal-working fluids containing SCCP or from polymers containing SCCPs. The potential for loss during production and transport is expected to be less than that during product use and disposal (adapted from Region III Report).

2.2.4.6 Organic tin

The main primary source of TBT is leaching from sea ship hulls. Related activities that cause emissions of TBT are sea ship traffic, docking activities and dumping of dredged material. In addition, sources include industrial discharges from production/formulation of all organic tin compounds, atmospheric deposition of organic tin compounds, TBT used for wood conservation: application, leaching, dumping of conserved wood as waste, antiseptic or disinfecting use of TBT and disposal of harbour sediments contaminated with organic tin compounds (OSPAR 2000). (Adapted from Region III Report).

2.2.4.7 Organic mercury

Methyl mercury may be volatised or emitted into the air from combustion sources such as incinerators and power plants. Municipal solid-waste incinerators and coal-burning power plants are both substantial sources of methyl mercury, the latter because mercury is a contaminant in coal. Although inventories have estimated inputs of these constituents, estimates of associated methylmercury formation have not been made. On the basis of the limited data available, it appears that the most significant mercury releases are those to air from combustion activities (particularly coal-fired power stations), primary metals production and the chlor-alkali industry (OSPAR 2000). (Adapted from Region III Report).

2.3 REGIONAL DATA AVAILABILITY

2.3.1 PTS pesticides

Table 2.3 is an assessment of the information from the 12 Regional reports, which shows the availability of substantial information to specific pesticide sources. This will include inventories, estimates and calculations. A '+' is not given if the chemical is only mentioned in reports, without the provision of further information. This will be different from the data gap analysis, as a data gap score indicates a need for information, rather than an evaluation of available information.

Table 2.3 Data availability concerning pesticide sources from the 12 regions, as well as additional information from submissions during and after the Global Priority Setting Meeting, March, 2003, Geneva.

Pesticide/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Aldrin	-	+	+	-	-	+	+	-	-		+	-
Chlordane	-	+	+	-	-	-	+	-	-	-	-	-
DDT	+	+	+	+	-	+	+	+	-	+	+	-
Dieldrin	-	+	+	-	-	-	-	-	-		+	-
Endrin		+	+	-	-	-	-	-	-	-	+	-
Heptachlor	-	+	+	-	-	-	-	-	-	+	-	-
Hexachlorobenzene	-	+	+	+	+	+	+	-	-		+	-
Atrazine		+	+		+	-			+	+		
Chlordecone		+	+					-				
Endosulphan		+	+		-	-		+	+	-	-	
HCH	-	+	+	+		+	+	-	+	+	+	-
Mirex	-	+	+	-	-	-	-	+	-	+	-	-
Pentachlorophenol		+	+		-					+	+	
Toxaphene	-	+	+	-	-	-	+	-	-	+	-	-

+ Substantial information available

- Considered by Region

Blank: not considered by Region

2.3.1.1 Region I (Arctic):

Sources of PTS pesticides in the Arctic Region are not well documented, partly due to the fact that their use in the Arctic has been very limited. Arctic sources are the result of accidental spills or deliberate and inappropriate disposal of contaminants. Pesticides have been deliberately used for insect control (e.g. the main pesticide being DDT for the control of biting flies and mosquitoes in or near populated areas). DDT was first applied directly into the Yukon River for mosquito and black fly control in July 1948 (Bright et al, 1995a). Over much of the Arctic, the levels of Stockholm POPs cannot be related to known use and/or releases from potential sources within the Arctic and can only be explained by long-range transport from other Regions.

2.3.1.2 Region II (North America):

There is good information related to the USA as the USEPA Toxics Release Inventory (TRI) provide publicly available information on releases and transfers to air, water and land through a mandatory reporting mechanism (CEC 2002). In Mexico, production from the agrochemical industry was traditionally carried out through Fertilizantes Mexicanos, S.A. (FERTIMEX). The data reporting mechanism of Mexico is not comparable and hence the information related to pesticides in the North America Region is mostly gathered from the USA and Canada.

2.3.1.3 Region III (Europe):

During the last decade a large amount of progress has been made in the production of atmospheric emission inventories of several PTS compounds within Europe. However there is still a lack of comparability in inventories produced by various organisations for the same compound group, except DDT, HCB, lindane and pentachlorophenol. Many international organisations are working on the issue of unwanted and expired pesticide stocks. These include FAO, UNEP Chemicals, WHO, UNIDO, as well as industry and NGOs. The problem of obsolete pesticides in Central and Eastern Europe (CEEC) and the Newly Independent Sates (NIS) is particularly severe, with a quantity in excess of 80000 tonnes reported.

2.3.1.4 Region IV (Mediterranean):

The production and uses of PTS compounds are banned or severely restricted for many of the countries in the Mediterranean Region. Aldrin, dieldrin, heptachlor, chlordane and HCH are prohibited in the EU for plant protection whereas for other applications, a written authorisation for import may be granted. Endrin and mirex are not subjected to the PIC procedure although many countries have banned its use. Algeria (chlordane, DDT and heptachlor) and Morocco (DDT) have also requested specific exemptions in the framework of the Stockholm Convention. For many countries in the Region, the main pesticide sources are related to stockpiles and inventories due to former production and/or import. DDT and their derivatives are still being used in the Region as precursors of dicofol production but the total amounts being used are in the range of a thousand tonnes. Importantly, the compounds present in the main environmental compartments are due to previous chronic usage and from accidental spills. In general, there is a lack of adequate data sets to perform a quantitative source assessment.

2.3.1.5 Region V (Sub-Saharan Africa):

Pesticides constitute one of the major sources of PTS in the Region. The main categories of sources identified in the Region were production and imports, use of PTS pesticides, and obsolete stocks. Except for atrazine being produced in South Africa, PTS pesticides are generally imported and not produced in this Region, but pesticide formulation plants exist in some countries of the Region. Sub-Sahara Africa imports less than 5% in terms of value of total pesticides import of the world. Twenty-two RBA countries each import more than \$5 million worth of pesticides annually. The most widely used PTS pesticides are organochlorine pesticides namely: DDT, endosulphan, chlordane, lindane, heptachlor, toxaphene, HCB and aldrin and atrazine. There is a likelihood of illegal use of PTS pesticides (likely to include DDT) in the Region. The FAO estimates that there might be more than 120000 tonnes of these chemicals stocked or discarded over many parts of Africa, with some of these being donations from developed countries.

2.3.1.6 Region VI (Indian Ocean):

Sources of PTS (including pesticides) in the Indian Ocean Region are not well documented. In most cases, these are the results of spills from small manufacturing/formulation units, storage, excessive agricultural application, abuse, and inappropriate disposal of the waste generated from manufacturing units. In countries like India, Pakistan, Sri Lanka, Nepal, Bhutan, Bangladesh, Myanmar and six countries of the Gulf Region, PTS pesticides such as aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB toxaphene, mirex are either banned or not registered. Therefore, the presence of these pesticides in the environment may be due to excessive use in the countries in the past. The only information on production, import and quantity of stockpiles on a limited number of chemicals were available from a few countries. No information on release of pesticides at the manufacturing stage that is done in some countries is available. Pesticides releases from excess use in agriculture and the run-off contaminating the various national river basins may be of local concern in this Region.

2.3.1.7 Region VII (Central and North-East Asia):

Most of the PTS pesticides are banned in the Region. However, some of them are still being manufactured and applied within the Region. Several countries have requested exemption from the Stockholm Convention for DDT; China, for the production and use of DDT as an intermediate and for vector control; the Republic of Korea for use as a de minimis contaminant in dicofol (maximum concentration 0.1%) and the Russian Federation for production and use for vector control. In the Commonwealth of Independent States (CIS) countries, the application of pesticides and agricultural chemicals has been a serious issue. In addition, in the CIS countries and in the Russian Federation, obsolete pesticides are a significant problem. Documentation and monitoring of obsolete pesticides are lacking, therefore the location of burial of obsolete pesticides and their quantities are not always known. The burial of obsolete pesticides, such as in Kyrgyzstan, has also led to leakage and exposure of these chemicals to the environment. Due to inadequate control over chemical imports into some of the countries of Region VII, large volumes of banned chemicals with expired validity dates have been imported into the Region.

2.3.1.8 Region VIII (South-East Asia and South Pacific):

Information on the importation, use and emissions of PTS pesticides are limited in the Region except for Australia and New Zealand. Agricultural activities including the use and disposal of wastes are the main sources of PTS pesticides in the Region. Much of the attention has been on regulatory measures to phase out or to ban the use of PTS pesticides. Except for DDT, endosulphan, mirex and lindane, many of the pesticides have been banned or have not been used for the last 10 years. Attention has been on regulatory measures to phase out or to ban the use of PTS pesticides.

2.3.1.9 Region IX (Pacific Islands):

None of the PTS pesticides are manufactured within the Region. They have been used in the past, although the level of usage has been generally low by world standards. Information was mainly obtained through direct enquiry to government agencies, and also from the South Pacific Regional Environment Programme (SPREP) survey on Persistent Organic Pollutants in the Pacific (Burns et al, 2000). The primary uses were in crop production, termite control, general household and public health applications and for vector control. Malaria is a significant problem in the Solomon Islands, Vanuatu and New Caledonia. However, spraying for mosquitoes is also practised in most other countries for the control of dengue fever. The most significant sources of PTS in the Region are currently the use of DDT in the Solomon Islands, stockpiles of obsolete pesticides and numerous contaminated sites.

2.3.1.10 Region X (Central America and Caribbean):

Pesticides are mostly imported into the countries (Colombia, Suriname, Venezuela and the Caribbean countries) forming part of this Region. Large quantities of pesticides are imported for use in the agricultural sector and for vector control. Agriculture plays an important role in the economies of all countries of the Region. However, land available for agriculture is being reduced, and available agricultural lands are expected to be more productive. Large quantities of pesticides are used to achieve this goal as well as to meet the requirements of the products exported to international markets. Further, because attempts have been made to provide local sources of food, the agricultural sector has been diversified. This has led to the cultivation of crops such as tomatoes, vegetables, plantains, ginger, etc., which is accompanied by a suite of sometimes new and additional pesticides.

2.3.1.11 Region XI (Eastern and Western South America):

In general, quantitative information on PTS including pesticides in this Region is scarce and fragmentary. Chlorinated pesticides (e.g. cyclodienes, DDT) have been intensively used in the Region in the past. As a consequence, several official stockpiles and disposal sites exist waiting for final treatment or remediation. Most of these sites are more than twenty years old and there is a risk of releases if affordable cleaning technologies are not available. Illegal trade and disposal of chlorinated pesticides are also relevant aspects related to sources. Lindane and endosulphan are two potentially relevant PTS of emerging concern due to their widespread use in the Region. Pentachlorophenol and its salts also have to be considered even though their use and distribution are more limited within the Region.

2.3.1.12 Region XII (Antarctica):

Antarctica and the adjacent islands and oceans have a very small human population. Pesticides are neither produced nor applied in the Region. There appears to be no data suggesting that any permanent habitation in Antarctica is a local source of pesticide PTS.

2.3.2 Unintentionally produced PTS

Table 2.4 is an assessment of information from the 12 Regional Reports that shows the availability of substantial information to specific sources of unintentionally produced chemicals. Although PCB, HCB and PCP can also be formed unintentionally, they will be discussed under intentionally produced PTS.

Table 2.4 Data availability regarding unintentionally produced chemicals from the 12 Regions

Chemical/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
PCDD/PCDF	+	+	+	+	-	-	+	-	-	-	-	-
PAH	-	+	+	+	-	-	-	-	-	-	-	+

The scoring criteria are the same as for Table 2.3

2.3.2.1 Region I (Arctic)

There is good (but not complete) information available on PCDD/PCDF levels and sources from this Region. Primary sources seem to be smelting activities (in particular on the Kola Peninsula and Norilsk) and the paper and pulp industries. Pulp and paper industry emissions of 2,3,7,8-TCDD in circumpolar countries were reduced during 1990s. Uncontrolled local incineration of waste in the Arctic is a PCDD/PCDF source of unknown magnitude. Low-temperature combustion sources of PAHs exist throughout the circumpolar Arctic. More information on petrogenic PAH is also available from the AMAP 1998 report.

2.3.2.2 Region II (North America)

Good information on sources is available from the USA and Canada, and adequate information on sources for Mexico, of PCDD/PCDF. The USA and Canada have well developed inventories of PCDD/PCDF and PAH sources. Open burning however, has now been highlighted as of increased significance as a growing source. (Region II Report).

2.3.2.3 Region III (Europe)

For both classes of compounds, good inventories are available for most countries of the Region. Considerable effort has been expended in Western Europe to try and quantify and rank PCDD/PCDF primary sources and emissions to the environment, principally the atmosphere, so that cost-effective source reduction measures can be taken. There have, however, been limited attempts to define inputs of PCDD/PCDF to land. Inputs via imported contaminated goods (such as feedstuff) and contamination of food have also received considerable attention.

Within the Region, PAH releases to air have been estimated for each country. Total emissions to air within the Region have been estimated to be over 385 tonnes. Estimates of emissions to water have been made for some countries, but no data is reported for inputs to soils.

2.3.2.4 Region IV (Mediterranean)

France seems to have the best data for PCDD/PCDF emissions, while a number of other countries have restricted or incomplete data, and others have none. The countries with the least amount of information seem to be from the southern part of the Region. For PAH, some data concerning pollution of the Mediterranean is available, mostly related to marine transportation, accidents and land-based sources (estimates vary between 0.3 – 1000 PAH tonnes per year for marine transportation).

2.3.2.5 Region V (Sub-Saharan Africa)

Hardly any data exists on PCDD/PCDF or its sources. The National Implementation Plans under the Stockholm Convention, that includes inventories, has only been started during 2002/3. The countries where some research activities have been noted are Nigeria, South Africa and Namibia. The observation was made that open burning remains a serious issue in Africa. Exploratory calculations done, based on population numbers and assumptions regarding domestic waste production and burning, indicate a daily TEQ release to air of about 60 g TEQ for the whole Region. However, further analyses are required to define the extent of PCDD/PCDF emissions from open burning. Nothing could be traced on PAH.

2.3.2.6 Region VI (Indian Ocean)

Although some of the sources seem to be well known, no quantitative estimates regarding PCDD/PCDF release were available. Municipal solid waste, industrial waste and medical waste incineration in India and some of the other countries were identified as likely major sources of PCDD/PCDF. Other likely sources were industrial processes such as paper and pulp, PVC, and iron and steel sintering. Some countries in the Gulf Region had releases of PCDD/PCDF quantified from an aluminium and chlor-alkali plant, municipal waste burning, a PVC plant, refinery, steel industry and waste incinerators. No information on PAH was available, other than for PAH in oil lakes and sludges from Kuwait. Saeed (2002) calculated that a total of 372 MT of PAHs are left in the oil lakebeds assuming the PAHs content of oil as 240 mg/kg.

2.3.2.7 Region VII (Central and North-east Asia)

Well-established inventories on PCDD/PCDF sources exist for Japan and Korea, but not for most of the other countries in the Region. Major industries in the Russian Federation part of the Region were also identified as potential sources. In the Russian Federation, the combustion of hazardous waste (approximately 42 million tonnes in 1998) is a potential source of these substances (6-7 kg TEQ/year; including European and Arctic Russia). Municipal solid waste combustion/incineration and PCDD/PCDF contaminants in agricultural chemicals and PCB oils were also identified as sources of concern. Some work has also been done on PCB, HCB, PCP as an unintended by-product from combustion processes and as contaminants in other chemical products. Little data was presented on PAH.

2.3.2.8 Region VIII (South-East Asia and South Pacific)

Two countries in the Region have published emission inventories for dioxins. In addition, three countries in the Region have embarked on UNEP/GEF-funded projects to establish dioxin emission inventories. It is estimated that dioxin emissions in Australia range from 150gTEQ/year to 2300gTEQ/year. Sources of dioxins and furans include prescribed burning, bush fires, residential wood fires, sinter production, coal and oil combustion, metal production, medical waste incinerators, and cement production. The total annual emissions to air, land and water for 1998 in New Zealand was estimated to be in the range 41 to 109 g I-TEQ.

The major likely sources of dioxin and furan emissions in this Region are from both industrial and non-industrial sources. These include waste incineration, industrial processes, open burning of domestic solid wastes, landfill fires, forest fires and other open burning of biomass. In Viet Nam, the extensive use of dioxin-contaminated herbicides during the Viet Nam War was reported to be a major source of dioxin emissions. An estimated total of about 170 kg of TCDD was reported to have been applied, although more recent investigations have indicated that this is probably under-estimated.

Only Australia has an inventory on PAH sources, while Brunei conducted some research on levels in air during forest fires. According to the Environment Australia 2001 report, the total PAH emission from residential firewood combustion is approximately 625 tonnes/year.

2.3.2.9 Region IX (Pacific Islands)

A rough estimate of dioxin emissions for some countries in the Region has been made in 1994, using information on fuel use and biomass combustion. A total of almost 2 g TEQ/year was estimated, although the data is now historical. Very limited information on PAH was provided.

2.3.2.10 Region X (Central America and the Caribbean)

Although many of the activities known to produce PCDD/PCDF take place in the different countries of Region X, there are no specific studies on sources or emissions However, domestic and hazardous waste burning and forest and scrub fires have been identified as potential major sources.

There are no inventories of PAH sources or estimates of emissions for the Central America and Caribbean Region. An indicative overview of sources and sub-sources of PAH is provided in the Regional Report. Used oil is known to be a source of PAHs and it may also be a source of PCBs. This waste product is of considerable concern in every country in the Region, as is on-field stubble burning and the use of creosote in timber.

2.3.2.11 Region XI (Eastern and Western South America)

A preliminary regional estimate was calculated considering the correlation between CO_2 emission from fossil fuels and the cement industries, and TEQ (PCDD/PCDF) emissions to air for some industrialized countries. Based on further calculations and assumptions, the total (all media) regional PCDD/PCDF emissions would be in the order of 1300 g TEQ/year for this Region, with Brazil and Argentina responsible for about 70% of this total. There are no PAH emission measurements for the Region. Estimates of PAH emissions, however, indicate a total emission of 111-500 tonnes polycyclic organic matter/year for Argentina, and 467-6607 tonnes/year for Brazil.

2.3.2.12 Region XII (Antarctica)

Mention is made of only one local source of PCDD/PCDF, at McMurdo Station. The only other source would then be from outside the Region, unless other stations also have incinerators. The introduction of PAH to the Region is a combination of global input, low-level and long-term natural and anthropogenic sources and catastrophic incidents with no long-term trend and seem generally well characterised.

2.3.3 Intentionally produced PTS

Table 2.5 is an assessment of information from the 12 Regional Reports, which shows the availability of substantial information to specific sources of intentionally produced chemicals.

Table 2.5 Data availability concerning intentionally produced chemicals from the 12 Regions according to the Regional Reports, as well as additional information from submissions during and after the Global Priority Setting Meeting, March, 2003, Geneva .

Chemical/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
PCB	+	+	+	+	-	-	+	+	-	-	-	+
HCB	-	+	+	-	-	-	+	-	-	-	-	-
Chlorinated paraffins		+	+					-	-			
Hexabromo-biphenyls		+	+					-				
Phthalates		+	+	-	-	-		-	-			
Nonyl/octyl phenols		+	+	-				-		-		
Perfluorooctyl sulfonates (PFOS)		+	+									
Organotin	-	-	+	-	-	-	-	-	-	-		-
Organomercury	-	+	+	-	-	-	-	-	-	-	-	-
Organolead	-	+	+		-	-		-	-			

The scoring criteria are the same as for Table 2.3

2.3.3.1 Region I (Arctic)

There is good (but not complete) information available on PCB sources in this Region, particularly for sources in the Russian Federation where an inventory of production, use and known contaminated sites has recently been completed. This inventory covers all of Russia and not just the Arctic areas AMAP, 2000). PCB has been used in sealants, and in electrical condensers and transformers used for both civilian/commercial and military purposes. The countries in this Region are at various stages of inventory, clean-up and disposal of these sources and stocks. PCB-contaminated waste oil was applied to soils to control dust in Arctic settlements (e.g. Fairbanks). Open use is currently banned in all circumpolar countries, but there are still large amounts present in the Arctic in permitted use. Although anthropogenic sources of metals were discussed in the Report, no information as to the sources of the organic compounds was provided.

2.3.3.2 Region II (North America)

Good information on sources is available from the USA and Canada, and adequate information on sources for Mexico, on PCB and HCB. Of these, HCB was commercially manufactured, but is now only produced as an intermediary during chemical synthesis. Information on production, use and releases also exist for SCCPs, hexabromobiphenyl, polybrominated diphenyl ethers, phthalates, octyl- and nonyl-phenols, perfluorooctyl sulfonates, organolead and mercury. Less information was available on TBT, which is not inventoried by the USA, Canada or Mexico. Specific mention was made regarding Mexico that, although less data is available from that country, this is due to a lack of monitoring rather than an absence of sources of the chemicals.

2.3.3.3 Region III (Europe)

PCB releases to air have been estimated for each country of the Region, with a total emission to air estimated to be over 74 tonnes. Emissions to water are predicted to be large, although there is a paucity of estimates within this Region as a whole. No data has been reported on emissions to land. Total HCB emissions to air within the Region have been estimated to be over 8200 tonnes. Hexabromobiphenyls are not currently produced and only limited data is available for TBT. The other chemicals have either very little data, or have not been addressed in the report.

2.3.3.4 Region IV (Mediterranean)

Total PCB production in some of the European countries (France, Italy and Spain) was in the range of 300000 tonnes for the period 1954-84. There is a lack of quantitative information concerning the amount and status of remaining stocks of PCB containing equipment. Most of the PCB destruction capacity of the Region is located in France. PCB emissions show a decreasing trend with time in the EMEP countries of the Region. Some hot spots have arisen from the destruction of electrical and military equipment during regional conflicts such as the Balkans and the Israel-Lebanon wars.

Emissions of PBDE from the various countries of the Region are proportional to their consumption of electrical and electronic equipment. Hence, economic development patterns indicate an increasing trend in emissions, although the absolute levels are relatively low at present. Release from antifouling painting in commercial shipping is the source of TBT in the Region. The present release rates estimates are in the order of some 240 tonnes per year. Emissions of brominated flame-retardants into the atmosphere are very much linked to the consumption of electrical and electronic equipment but little data on sources is available. However, as for the other intentionally produced chemicals, these are estimates regarding sources rather than substantial data.

2.3.3.5 Region V (Sub-Saharan Africa)

As a Region, very little data is available on any of the intentionally produced PTS. None of these chemicals are likely to be manufactured in this Region. The observation was made, however, that the major industrial complexes were all located close to freshwater bodies, one of the most depleted resources in Africa.

2.3.3.6 Region VI (Indian Ocean)

Although some information on PCB was available for some countries, these were estimates rather than known releases. In addition to PCBs associated with electricity, PCB is also released during ship breaking operations and the re-rolling of paint contaminated scrap metal. Unauthorised offshore use of 84 tonnes per year of organotin compounds is reported in Sri Lanka but the conditions regarding this use were not presented. Some quantification was done on the use of phthalates but no information as to releases was provided.

2.3.3.7 Region VII (Central and North-east Asia)

Japan had a good inventory of PCBs as a source compared with some of the other countries from the Region. Information also seems to be well established for the Russian Federation, although it cannot be considered as complete especially for the Asian part of the country. Some data was available for HCB from the Russian Federation and Japan, but less on PBDE. TBT production and use information was available for Hong Kong, SAR and Japan, but not for the rest of the Region. Similar data was also available on organic mercury, especially for Japan, but mercury products are being manufactured in China, Mongolia, the Russian

Federation, Kazakhstan, Kyrgyzstan, Tajikistan and Uzbekistan. No other chemicals were considered in this Report.

2.3.3.8 Region VIII (South-East Asia and South Pacific)

PCB is well managed and inventoried in Australia and New Zealand, but less so in other countries of the Region. These other countries are at various stages of an inventory. Although it was never manufactured in this Region, there are still many electrical components that contain PCB. Some steps have been taken to eliminate these sources. Other PTS chemicals such as SCCPs, nonyl- and octyl-phenols, phthalates, PBB and PDBE are used in the Region, but little is known about their sources.

Little data is available on the organometals, although known sources exist. The main sources of organotins are considered to be antifouling paints, ship-scrapping activities in some areas and sewage disposal. There is, however, no available inventory of organotin emissions. In Papua New Guinea, mercury (organic and inorganic) was found in scalp hair of individuals, with dietary fish as a suspected source. The annual loading of mercury into the Gulf of Thailand was reported to be about 5.4 metric tons per year, and mercury is widely used in gold mining in the Philippines.

2.3.3.9 Region IX (Pacific Islands)

No manufacturing of any of the PTS is done. PCB is probably the major PTS to be considered although in many instances steps have been taken to eliminate stockpiles of transformers and oils.

2.3.3.10 Region X (Central America and the Caribbean)

None of the countries in the Region have full national inventories of PCB's stocks and uses. This is attributed to a lack of knowledge about PCBs and the implications associated with their use, a lack of human and financial resources and poor legislative framework. Panama and the Dominican Republic have reported that PCB oil is used by a minority of the population as a popular remedy against arthritis and flexural pains.

No information is available on PBDE, organic mercury, lead or tin. TBT could be a concern as all countries of the Region experience ship traffic. Panama would be the country exposed to the heaviest ship traffic, with approximately 15000 ships per year crossing the Panama Canal. SCCPs are not produced in the Region but are imported in goods or as raw material for local industries. No information on quantities is available. Phthalates and the octyl- and nonyl-phenols are known to be imported, but little data is available.

2.3.3.11 Region XI (Eastern and Western South America)

Detailed inventory information is still incomplete but there are some country estimates. Brazil with 130000 tonnes of PCB, Chile with 700 tonnes, Peru 1000 tonnes and Uruguay with 81 tonnes of PCB-containing oil is documented. There is very little available data for sources of organometallic compounds, especially for organic tin.

2.3.3.12 Region XII (Antarctica)

PCB sources on the continent are again the research stations and notably, the McMurdo Station. There is also a comparatively large amount of data for environmental levels of PCBs. No other regional PTS sources are mentioned.

2.4 SUMMARY OF REGIONAL PRIORITIES ON SOURCES

2.4.1 PTS Pesticides

A scoring mechanism was utilised as a tool to prioritise the 18 selected persistent toxic substances (including pesticides) according to sources and source data gaps. The scoring results based on a collective effort of all the participants of the Technical Workshops held in different regions, have been prioritised according to the level of concern and data gap and are listed in the following table.

Table 2.6 Regional priorities on sources/data gaps concerning PTS pesticides in the 12 Regions

Pesticide/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Aldrin	0/2	0/0	0/0	0	0/1	0/0	0/1	0/0	1/2	1/2	1/2	
Chlordane	1/1	0/0	0/1	0	1/0	0/0	1/1	0/0	1/2	1/2	1/2	
DDT	1/1	0/0	1/0	1	2/1	1/1	2/1	2/0	2/2	1/2	1/2	
Dieldrin	0/2	0/0	1/0	0	1/1	0/0	0/1	1/0	1/2	1/2	1/2	
Endrin	0/2	0/0	0/0	0	0/1	0/0	0/1	0/0	1/2	1/2	1/2	
Heptachlor	1/1	0/0	1/0	0	0/0	0/0	0/1	0/0	1/2	1/2	1/2	
Hexachlorobenzene	1/1	1/1	2/1	1	0/0	0/0	1/2	0/0	1/2	1/2	1/2	
Atrazine	0/2	1/1	1/1		2/1	1/1		1/2	1/2	1/2		
Chlordecone	0/2	0/0			0/0			0/0	0/2	0/2		
Endosulphan	0/1	2/1		1	2/2	2/1		2/0	1/2	1/2	1/1	
Lindane (γ-HCH)	1/1	2/1	2/1	1	1/2	1/1	2/1	0/0	1/2	1/2	1/1	
Mirex	0/2	0/0	0/0	0	0/0	0/0	0/1	0/0	1/2	1/2	0/2	
Pentachlorophenol	0/2	2/1	2/2	1	0/2	0/0	1/2	0/1	1/2	1/2	2/2	
Toxaphene	1/1	0/0	1/2	0	0/0	0/0	0/1	0/0	0/2	0/2	0/2	

Scores: Score=0 –chemical is of no concern/supportive data is collected

Score=1 –chemical has local concern/supportive data is limited

Score=2 –chemical has regional concern/supportive data is lacking

Single score–only for sources

No score–not considered by that Region

In interpreting the scores, it is important to note that different scores for chemicals indicate that the chemicals are of different levels of concern. For example, a chemical having a source score of ‘2’ is a chemical of regional concern compared to a chemical having a source score of ‘1’ indicating a chemical of local concern. The scoring system does not provide any information on the ranking or prioritisation of chemicals having the same source scores in the table above. In other words, the chemicals have been grouped according to score, but they are not ranked within each group. The priority assessment was based on a combination of hard data on chemicals as well as potential threats and data gaps.

2.4.2 Unintentionally produced PTS

Table 2.7 Regional priorities on sources and data gaps for unintentionally produced PTS in the 12 regions.

Chemical/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
PCDD/PCDF	1/1	2/1	2/2	2	2/2	2/2	2/2	2/1	2/2	2	2/2	
PAH	1/1	2/1	2/2	1	1/2	2/2	2/2	2/0	2/2	2	2/1	

Scores as for Table 3.6

2.4.3 Intentionally produced PTS

Table 2.8 Regional priorities on sources and data gaps concerning intentionally produced PTS in the 12 regions

Chemical/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
CB	2/1	2/1	2/1	2	2/2	1/2	2/2	2/0	2/2	2	2/1	
HCB	1/1	1/1	2/1	1	0/0	0/0	1/2	0/0	1/2	1	1/1	
Chlorinated paraffins	0/2	1/1	2/2		1/1			0/2	0/2			
PBDE	1/1	1/2	2/2	1	0/0		1/2	0/1	1/2	1		
Phtalates	0/2	2/1		1	0/1	2/1		0/1	2/2	2		
Nonyl/octyl phenols	0/2	2/1		1	0/1			0/2	0/2	2		
Perfluorooctyl sulfonates (PFOS)	0/2	1/1										
Organotin	1/1	1/1	1/2	1	0/0	1/1	1/1	1/0	2/2	1	1/1	
Organomercury	1/2	2/1	1/2	1	1/1	2/1	1/2	0/0	1/2	1	1/1	
Organolead	1/2	2/1	1/1		1/2	1/1		1/0	2/2	1		
PCP	0/2	2/1	2/2	1	0/2	0/0	1/2	0/1	1/2	1	2/2	

Scores as for Table 3.6

2.5 SUMMARY OF REGIONAL DATA GAPS

2.5.1 Region I (Arctic)

Numerous local sources of PTS exist but have not been studied. Surveys of local sources of contamination by PTS within the Arctic are needed to quantify the emissions and leakage and to determine the relative importance of regional and extra-regional sources. For example, in some locations in the Russian Federation, there are high HCH levels in lake water and high DDT levels are now seen in snow, rivers, seawater, coastal sediments, and in a few samples of invertebrates, fish, reindeer, lemming, seabirds, seal, and beluga. These findings indicate possible fresh releases or improper disposal but the high concentrations reported must be verified. The Russian Arctic is probably the least well-known in terms of PTS sources within the Region but is probably a larger source than the European and North American Arctic sub-Regions combined. From the Regional Report, the source data from the Russian Federation is the least well substantiated but a PCB inventory has been made.

2.5.2 Region II (North America)

The national substance inventories have become valuable databases. However, the national database in Mexico is still in its developmental stage and many required databases are limited or lacking. In addition, the following critical points were identified (Region II Report): Environmental management, emergency management, training, monitoring and oversight, collection and disposal of packaging, agricultural runoff water and illegal PTS sales.

The national databases in Canada and the USA were not designed to address all sources and: (1) do not include all important substances; (2) identify all on-site releases and off-site transfers from a facility; (3) some releases are estimated not measured; (4) do not indicate the ultimate environmental fate of materials which porting facilities release or ship off-site for disposal or other disposition; (5) do not provide information on the toxicity or potential health effects of substances which reporting facilities release or transfer; and (6) do not identify exposure risk to human or ecological populations from substances released or transferred by reporting facilities.

2.5.3 Region III (Europe)

Within the Region as a whole there is a large amount of data relating to industrial point source emissions to the atmosphere. Due to restrictions on the manufacturing and more stringent control of releases, emissions from primary sources have been declining during the last 20 years. Understanding of secondary source inputs and the potential for environmental recycling of individual compounds continues to be limited and few measurements are available. Obsolete stocks of pesticides represent a potential source of PTS material particularly within the Central European Countries and Newly Independent States. Exact quantities and components of the stockpiled wastes are unknown at present, but quantities are thought to be in excess of 80000 tonnes.

For the compounds of emerging concern (e.g. PBDE, SCCPs) emission sources to all environmental compartments are very poorly characterised, few formal inventories have been established and there is limited understanding of the principal contemporary source categories. For PBDE, evidence of increasing concentrations in human tissues from Sweden would suggest that emissions into the Region have been rising during the last 20 years. Unlike sources to air, sources to land and water are very poorly quantified for all the PTS compounds. Prioritisation of source inputs within the Region as a whole highlight that the following compounds represent ongoing releases in the Region which are of great concern with respect to the environment and health: HCB, PCBs, PCDD/PCDF, PCP, PBDE, and SCCPs.

2.5.4 Region IV (Mediterranean)

Great gaps exist in the data for PTS sources in the Mediterranean Region. For PTS pesticides, including lindane, the sources are multiple and diffuse. Although there is a decreasing tendency in the use of these compounds in the Region, there is a lack of control regarding the existing stockpiles of obsolete pesticides. In Eastern Europe, there are data gaps with respect to pesticide stockpiles due to poor coordination of work on this issue. In some locations upstream to the Black Sea basin, related rivers and regions close to Turkey and the Middle East, there is an important diffuse (non point) source of obsolete pesticides as run-off from agriculture. These include DDT and HCH. DDT and its derivatives are still being used in the Region as precursors of dicofol production; the total amounts being used are in the range of thousands of tonnes.

For the intentional and unintentionally produced PTS, substantial data were only available for PCB and PAH, with data incomplete or only estimates available for the other PTS. Most of the countries have not performed any comprehensive survey at present. Industrial sources are extremely difficult to quantify due to the lack of co-operation from most of the industrial associations active in the Region. Environmental control units in the countries do not have the capabilities to monitor industrial sources in a comprehensive fashion and are only faced with the outcome of the industrial mismanagement practices.

2.5.5 Region V (Sub-Saharan Africa)

Based on pesticide import data from FAO, South Africa, Nigeria, Cote D’Ivoire, Kenya, Ethiopia, Ghana, Sudan, Tanzania, Mozambique and Mali are the highest users of pesticides in the Region. Pesticides are mainly used in agriculture on lands. The total area that might experience application is estimated at almost a million hectares. The major agricultural areas for many countries have also been identified and reported. Ethiopia, Madagascar, Mozambique, Somalia, South Africa, Sudan, Tanzania and Zimbabwe have especially large areas under cultivation and pasture, but smaller countries (such as islands) might have a much higher percentage allocated. PTS pesticides are also used outside agricultural areas, for purposes of disease vector control, vegetation control, food collection and others. Stocks of obsolete pesticides are a serious problem in Africa (more than 112000 tonnes). Some of these chemicals were donations from developed countries. Countries having the largest quantities are South Africa, Botswana, Ethiopia, Mali and Mozambique. PTS pesticides of concern in terms of data gaps on volume of use were DDT, atrazine and endosulphan.

Although very limited data were available, countries were ranked according to certain economic indicators which were used as surrogates for PTS production such as PCDD/PCDF. Countries that were identified as probably having the largest PTS problems were South Africa, Nigeria, Cote d'Ivoire, Kenya, Ethiopia, Ghana, Sudan, Tanzania, DRC, Zambia, Cameroon and Uganda. Data gaps were a serious constraint during this assessment.

2.5.6 Region VI (Indian Ocean)

A number of the PTS pesticides have been banned in many countries of the Region. However, data gaps exist on unused quantities stockpiled and on what has been disposed. Information on quantities of PTS released from waste disposal sites and contaminated sites in India, Pakistan and Gulf Region Countries is required. PTS pesticides that are banned and not produced, but still imported and used at present, may cause local concern. Endosulphan and atrazine are of local concern because of evidence of small amount of import, existing stockpiles in all the above countries and production in India. Endosulphan may be considered as a chemical of regional concern whereas atrazine is of local concern due to relative amounts involved. Pesticide PTS in terms of source and data gaps are of no concern in Gulf countries and Yemen. DDT, though a restricted chemical, is manufactured and used in India and exported to Bhutan, Pakistan and Nepal for vector control. It is of local as well as regional concern. The intention is to phase out DDT in due course.

This Region also identified major data gaps on phthalates and other PTS released from waste and hazardous waste disposal sites and contaminated sites in a number of countries. In addition, a lack of data on PTS sources namely, PCB, PCDD/PCDF and PAH in major oil producing countries (Gulf Region Countries) exists.

2.5.7 Region VII (Central and North-East Asia)

In general, inventories of PTS sources are not well documented in the Region, in particular for developing countries and countries with economies in transition. There is basically little information available on PTS in Democratic Peoples' Republic of Korea, and inventories of PTS sources in the Russian Federation have mainly been devoted to the industrially developed European part of the Russian Federation, in comparison to scarcity of reliable data on the sources of PTS in the Asian territory of the Russian Federation (Siberia and Far East). Little information is available on the quantity and location of obsolete pesticides in the CIS countries. In some cases, obsolete pesticides have not been properly labelled and therefore the identities of pesticides are often unknown. For some countries, although some PTS sources have been or are being monitored, the list of PTS monitored is often shorter than the Stockholm Convention's list of 12 POPs, therefore resulting in data gaps. For example, in the Russian Federation, there is almost a complete lack of data on HCB stocks. In Kazakhstan, there are no source inventories particularly focussed on PTS. In Tajikistan, there is little or no monitoring of PCDD/PCDF and PAH, and monitoring systems for obsolete pesticide stocks in Uzbekistan have not been established. PCDD/PCDF sources have also been poorly investigated in the developing countries. Emission inventory compilation is necessary. In the Region, open burning and forest fires could be a significant contributor of PCDD/PCDF and PAH emissions to the atmosphere. However, almost no information is available. In the Russian Federation, forest fires annually destroy huge taiga massifs, some of which have been treated with pesticides.

2.5.8 Region VIII (South-East Asia and South Pacific)

In general, there are limited available data on inventory of PTS emissions in the Region. There are also limited available data on industrial, agricultural and other activities to allow estimates of emissions of PTS to be made. Most of the PTS pesticides have been banned or are not widely used in recent years with the exception of endosulphan. Although no emission inventory is available for the PTS pesticides, the trend of decreasing environmental levels reported in some countries indicates that the emissions of PTS pesticides are generally declining. PCBs have also been banned and are being phased out. There is also lack of emission inventories of other emerging PTS of concern such as nonyl- and octyl-phenols, PBB, PDBE and phthalates. More work is needed to establish comprehensive PTS inventories in most countries.

2.5.9 Region IX (Pacific Islands)

In terms of data gaps related to PTS, missing is information on stockpiles and contaminated sites in countries and territories not already covered by existing surveys.

2.5.10 Region X (Central America and the Caribbean)

There are significant data gaps in the information compiled. In Caribbean countries, data on the importation of pesticides have not been compiled for the individual pesticide of concern and therefore, it is difficult to create a clear picture of the extent of the problem through importation data. However, several countries are in the process of compiling information in this form.

Information on the sources of PCDD/PCDF has been compiled on the basis of known processes generating these unintentional products. Reference to the production of PCDD/PCDF through burning of plastics, landfilling operations, burning of fuels and incineration have been more by association rather than by any quantification or collected data on emissions. The quantity of PTS emitted through the burning of organic materials during forest and scrub fires, and crops (sugar cane) have not been estimated.

Data gaps also exist for confirming the presence of PAHs and PCBs in used oil, motor vehicle emissions and industrial estate processes. The activities of industrial estates have also been identified as sources PTS releases to air, water, soil and waste. Supporting data are absent in the majority of cases.

2.5.11 Region XI (Eastern and Western South America)

Source information is not complete for the Region. Full quantitative measurements are unavailable and inventory information is fragmentary. Some official information on sources is not available for public access.

2.5.12 Region XII (Antarctica)

PTS pesticides are neither produced nor applied in the Region. There appears to be no data suggesting that any permanent habitation in Antarctica is a local source of PTS (except for PAH).

2.6 SUMMARY OF PRIORITY REGIONAL SOURCES AND DATA GAPS

2.6.1 Region I (Arctic)

Over much of the Arctic, the levels of PTS, including PTS pesticides, cannot be related to known use and/or releases from potential sources within the Arctic and can only be explained by long-range transport from lower latitudes. Old and disused military sites are also likely sources, with the Russian Arctic probably the least well known. Open burning has also been raised as a probable major source.

2.6.2 Region II (North America)

The Great Lakes basin as a whole might be considered to be a hot spot (WWF 2000). Significant progress has been made since the signing of the Great Lakes Bi-national Toxics Strategy (GLBTS) by Canada and the United States in 1997. Both parties have engaged in a wide range of activities to address sources of “Level I” substances including five cancelled pesticides, namely, chlordane, aldrin/dieldrin, DDT, mirex, and toxaphene. Abandoned waste sites located in the USA, Canada and Mexico also present some problems. The Superfund sites in the USA are well documented, some have already been cleaned up, others are being attended to and most have approved cleanup plans.

The Sydney Tar Ponds and Coke Ovens site is one of the largest and most hazardous chemical waste sites in eastern Canada. More than 80 years of discharges from the coke ovens of an adjacent steel plant have contaminated the 51 acre (23 hectare) site and the adjoining Muggah Creek.

In Mexico, required databases are limited or lacking. Access to information is difficult requiring intensive searches to determine, when possible, the character, quantities and movements of PTS.

2.6.3 Region III (Europe)

Europe is the largest chemical-producing Region in the world, accounting for 38 % of the total; Western Europe alone accounts for 33 % (Region III Report). There is a large amount of data relating to industrial point source emissions to the atmosphere, but sources to land and water are very poorly quantified for all the PTS compounds in general. Obsolete stocks of pesticides particularly within the Central European Countries and Newly Independent States are of major concern in the Region.

2.6.4 Region IV (Mediterranean)

The main PTS pesticide sources (including lindane) are production and agricultural application and therefore multiple and diffuse. There is a lack of control regarding the existing stockpiles in the countries of the Mediterranean Region. Although the use of lindane is severely restricted in the Region, in countries like France and Spain the estimated atmospheric emissions are quite large. DDT is still being used in the Region as a precursor of dicofol, but information about the amounts being used is uncertain. Some hot spots have arisen as a consequence of mismanagement of former production sites. This is particularly true for lindane. In the case of toxaphene and other pesticides, the dumping of obsolete stocks in the southern countries of the

Region is deemed to have created potential hot spots. Commercial harbours in the North-western and Adriatic areas constitute potential TBT hot spots. PAH emissions from marine fuel combustion are another major source in the Mediterranean Sea itself.

2.6.5 Region V (Sub-Saharan Africa)

Pesticides constitute one of the major sources of PTS. Except for atrazine produced in South Africa, PTS pesticides are generally imported and not produced in the Region, but pesticide formulation plants exist in many countries. The most widely used PTS pesticides are mainly organochlorine pesticides namely: DDT, endosulphan, chlordane, lindane, heptachlor, toxaphene, HCB, aldrin and atrazine. There is also the likelihood of illegal use of PTS pesticides (likely to include DDT) in the Region. A serious problem facing the Region is the issue of stocks and reservoirs of obsolete, discarded and banned PTS pesticides. The identified industrial complexes in Nigeria and South Africa, and probably to a lesser extent in other countries of the Region, has the potential of being serious intentionally and unintentionally produced PTS pollution sources, as old technology and lack of pollution control systems is expected to be the norm. Open burning of all types of waste was also identified as a possible major source, not necessarily associated with industry. Once again the association of these pollution sources (both pesticide and non-pesticide PTS) to water was highlighted.

Fig 2.3. Visible pesticide aggregate (yellow) in soil associated with an obsolete pesticide dump in Vikuge, Tanzania; a legacy of international aid.

2.6.6 Region VI (Indian Ocean)

Although a number of the PTS pesticides have been banned in many countries of the Region, data gaps exist on unused quantities of obsolete chemicals and the rate of their disposal. Stockpiles of obsolete pesticides in India, Pakistan, Sri Lanka, Nepal, Bhutan, Myanmar, Iran and Bangladesh are of concern. Information on quantum of PTS released from waste disposal sites and contaminated sites (including PTS pesticides) in India, Pakistan and Gulf Region Countries is also needed. Pesticides releasing from excess use in agriculture and the subsequent run off that contaminates the various national river basins may be of local concern in this Region. Countries like Bhutan, Nepal and Yemen have also reported the import and export of low quality pesticides and banned pesticides. Other high major PTS sources identified are: waste incinerators, the pulp and paper industry and chlorine based manufacturing units as a source of emission of PCDD/PCDF in India, Pakistan and Gulf Region countries, ship-dismantling sites in coastal areas in India (300 ships per year), Bangladesh and Pakistan for PCBs contamination, the vast oil lakes in Kuwait (PAH), and PCB contaminated transformers.

2.6.7 Region VII (Central and North-East Asia)

In this Region, the former Soviet Union contains the major hot spots for obsolete pesticides. Members of the Commonwealth of Independent States (CIS) have a large quantity of PTS that is obsolete and redundant. A conservative estimate suggests there is more than 150000 tonnes of obsolete pesticides. There is also a problem with the lack of control of imported obsolete pesticides and burial of these pesticides in some CIS countries. In some countries such as Democratic Peoples' Republic of Korea, there is a severe lack of information concerning PTS sources, including PTS pesticides. In the coastal areas of China, which have undergone rapid development such as the Pearl River Delta, it is estimated that 76000 – 100000 tonnes of organochlorine pesticides were used annually from 1972 to 1982 (Hua and Shan, 1996). There is also evidence from the distribution profiles of DDT and its degradation products that current input of fresh DDT, as an impurity of other pesticides, may still continue in some areas of the Pearl River Delta. PCB, PAH and PCDD/PCDF emissions remain a significant PTS source in the Region due to industrial activities, as well as forest fires.

2.6.8 Region VIII (South-East Asia and South Pacific)

There are limited available data on import, use and inventory of PTS emissions for this Region. Many of the PTS pesticides with the exceptions of DDT, endosulphan, mirex and lindane have been banned or were not used in many of the countries of the Region for more than 10 years. Mirex is used only in very limited quantities in Australia while DDT, endosulphan and lindane are still in use in some countries. In the southern part of Viet Nam, between 1962 and 1971, Agent Orange and other herbicides were sprayed for defoliation. It has been noted that soils in the vicinity of former facilities related to the Agent Orange spraying programme have elevated dioxin levels. High levels of DDT have been found at former cattle dip sites in Australia. Most of the PTS pesticides have been banned or have not been widely used in recent years in the Region with the exception of endosulphan. More work is needed to establish comprehensive PTS inventories in these countries. Other hot spots identified were sites of forest fires as sources of PCDD/PCDF and PAH emissions.

2.6.9 Region IX (Pacific Islands)

The current usage of PTS pesticides is low in this Region and should be eliminated over the next 10 years or so. The most significant sources of PTS are currently the use of DDT in the Solomon Islands, the stockpiles of obsolete pesticides, and contaminated sites. There is a lack of information on stockpiles and contaminated sites in countries and territories not covered by the SPREP survey (Burns et al, 2000).

2.6.10 Region X (Central America and the Caribbean)

PTS pesticides are not manufactured within the Region but are imported for agricultural and public health reasons. In Caribbean countries, data on the importation of pesticides have not been compiled for the individual pesticides of concern and therefore it is difficult to create a clear picture of the extent of the problem through importation data. One of the more significant concerns of PTS is the reservoir of obsolete pesticides located in several countries. These pesticides include aldrin, chlordane, endrin, heptaclor, toxaphene, and chlordecone. Endosulphan and atrazine are currently used. The development of reliable sources and emission inventories is urgently needed.

The use of PCBs in electrical transformers was shown to be the single largest source of PCBs in the Region. Stocks of PCBs in all the countries are waiting full recording through inventory processes and then disposal. Although not quantified, there are important potential sources of dioxins and furans. The burning of plastics and other chlorine containing compounds were identified as a potential major source of dioxins and furans. Spontaneous ignition at landfill sites and in some cases deliberate burning of municipal garbage were also regarded as significant sources of dioxins and furans. The petroleum industry including extraction of crude oil and refining operations are a probable main source of PAHs in the Region. These operations have led to contamination of water, soil and air. Large quantities of oily wastes generated through oil used as lubricating fluid in combustion engines have been discarded into the environment.

2.6.11 Region XI (Eastern and Western South America)

PTS source information is far from adequate for the Region. Full quantitative measurements are unavailable and inventory information is fragmentary. Some official information on sources is not available for public access. Illegal trade and disposal of chlorinated pesticides are also relevant aspects related to sources. Chlorinated pesticides (e.g. cyclodienes, DDT) have been intensively used in the past. The Region has very few officially recognized contaminated sites, mostly in heavily populated industrial areas, i.e. Sao Paulo (Brazil), Buenos Aires (Argentina), Santiago and Concepción (Chile). However, official numbers grossly underestimate the real situation due to illegal or non-reported contaminated sites throughout the Region. Most of these sites are more than twenty years old and there is a risk of emission if affordable cleaning technologies are not available. Lindane and endosulphan are two potentially relevant PTS of emerging concern due to their widespread use. Pentachlorophenol and its salts also have to be considered even though their use and distribution are more limited.

In spite of the fact that detailed source information is fragmentary, in terms of relative importance PCB and probably PCDD/PCDF appear as some of the most relevant PTS for the Region. PCB's sources are mostly confined to heavily industrialized and urbanized areas with high-energy demands and some disposal sites.

2.6.12 Region XII (Antarctica)

Pesticides are neither produced nor applied in Antarctica, and there appears to be no data suggesting that any permanent habitation in Antarctica is a local source of PTS pesticides. The major sources of PTS are likely to be from outside the Region.

2.7 SUMMARY OF MAJOR PTS SOURCES BY REGION

The above exposition, taken from the individual Regional reports (I-XII), considered the sources within each Region. Only Regions I and XII considered sources adjacent to their Regions as major contributors. Therefore, there is also a need to compare the inter-Regional sources to characterise the major global sources for each PTS. This will be attempted in the following sub-sections.

2.7.1 PTS pesticides

2.7.1.1 POP pesticides

The current magnitude of the manufacture of the Stockholm POP pesticides except for limited production of chlordane and DDT does not constitute a major global source, when compared with historical production data. Under the Stockholm Convention, the manufacture of these compounds is severely restricted. The major current sources of Stockholm POP pesticides seem to be from obsolete stocks.

Specifically, Regions III (80000 tonnes) and V (120000 tonnes) have major stockpiles which can be considered as real or potential sources. Although there are initiatives to deal with these stockpiles, the time that it will take to reduce the amounts will take one or more decades. These stockpiles should continue to receive serious consideration until such time as the stocks are reduced. Attention should also be given to site clean-up, as soil and water contamination that has occurred over years of storage and neglect will also take considerable time to be remediated.

2.7.1.2 Other PTS pesticides

The production and use of the remaining PTS pesticides, specifically the high volume agricultural application of atrazine, endosulphan and lindane, has a different profile. Although there are limited atrazine production facilities in some of the developing Regions (such as in Region V - South Africa and Region VI - India), atrazine is also manufactured in Regions II and III. However, it remains one of the most used PTS chemicals, with many Regions evaluating atrazine at various levels of concern.

The second major use PTS pesticide is endosulphan. Very little information was provided on this chemical regarding manufacture from any of the Regions in the Regional Reports (except India), although most Regions did indicate significant use. However, not enough information was provided to identify any Region specifically as a major production or use source.

The third major use pesticide is lindane. Again very little production data were available from the Regional reports, but India and China were countries reporting its manufacture. From the Reports, Regions II and III have largely banned or severely restricted its use. Therefore the developing and mixed economy Regions are the major areas where it is applied, such as Regions IV, V, VI, VII, X and XI, with very little use reported for Regions VIII and IX.

2.7.2 Unintentionally produced PTS

2.7.2.1 PCDD/PCDF

Due to the major economic activities being located in Regions II, III and VII (the G7 are all located in these three Regions), and based on the data given in 2.1, it can be assumed that currently, these three Regions together constitute the major global PCDD/PCDF source.

For PCDD/PCDF however, the reductions being achieved in Regions II and III, together with increased industrialisation of developing Regions, might move these developing and mixed economy Regions into the category of a significant global source. These include Regions IV, VI and XI.

Open burning has been identified as a probable major source in the mixed economy and developing Regions such as IV, V, VI, VII, VIII, IX and X. The lack of data from the developing and mixed economy Regions remains however, a major constraint in determining the relative contributions from each Region, especially when comparing the highly characterised industrial sources in Regions II, III and VII.

The PCDD/PCDF contribution from forest and grass fires is relatively unknown, but if shown to be a major source, Regions V, VII, VIII and XI need to be considered as important areas of emission.

2.7.2.2 PCB

The major stockpiles of PCB in Regions III and VII qualify these two Regions as globally important sources. It must be remembered though that major stocks are found in almost all the other Regions, such as V, IV, VI, VIII, IX and X. The biological sensitivity of Regions I and XII should also not be overlooked as a long term environmental sink and therefore a source of exposure, due to accumulated PCB in these Regions.

2.7.2.3 PAH

It is very difficult to identify specific Regions as major PAH sources. Oil production Regions and oil consumption Regions do not always overlap. Therefore transport of oil to other Regions, and the general use of oil and oil products also contribute towards sources of PAH away from oil production areas. The oil production has restricted locations in Regions I (Alaska and the Russian Arctic), V, VI, VII, VIII, and X. Oil, and other sources of PAH, such as wood and coal combustion, as well as forest and grass fires, are located in various Regions.

Ongoing reductions in emissions achieved in Regions II and III again might change the emission pattern, in the same way as for PCDD/PCDF, thereby elevating some Regions into a global source position.

2.7.3 Intentionally produced PTS

Since the majority of the intentionally manufactured PTS capacity is located in Regions II, III and VII, these three Regions are the global sources (through production, emissions and trade) of chemicals such as PFOS, phthalates, PBDE, octyl/nonyl phenols and SCCPs. The remaining Regions (excluding XII due to very low use) could be considered as secondary sources, due to subsequent releases from use and products. This profile is not complete and should be considered as based on information from the Regional Reports in the main. The future update and refinement of the profile should be considered.

A summary of section 2.7 is presented Table 2.9.

Table 2.9. Current global source profile of PTS chemicals#.

Chemical/Region	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Obsolete PTS pesticides		+	+	+	+	+	+	+		+	+	
DDT					+	+	+	+			+	
Atrazine		+	+		+	+		+		+		
Lindane			+	+	+	+	+				+	
Endosulphan					+			+		+	+	
PCDD/PCDF		+	+		+	+	+	+		+	+	
Open burning*		+			+	+	+	+		+	+	
Biomass fires**					?		+	+		?	+	
PCB		+	+	+		+	+			+	+	
PAH		+	+	+		+				+	+	
HCB		+	+				+				+	
Chlorinated paraffins		+	+									
PBDE		+	+	+								
Phthalates		+	+									
Nonyl/octyl phenols		+	+									
PFOS		+	+									
TBT			+	+			+					
Organomercury		+	+				+					

$^{\#}$ Based on information from the 12 Regional Reports, as well as submissions during and after the Global Priority Setting Meeting, March, 2003, Geneva.

? Recognised as potential major sources

* Since open burning of waste is a source of multiple PTS, this separate category was introduced to highlight this source where it has been identified in the Regional Reports as a concern.

** Biomass burning (mainly grass and forest fires, as well as wood fires) has also received mention in a number of Regional Reports, and is also considered a source of multiple PTS (PAH, PCDD/PCDF etc).

2.8 CONCLUSION

Based on the information presented in the Regional Reports and the analysis on sources given in Sub-Section 2.2, the following general observations are made:

- The Regions where the most chemicals are produced (pesticides as well as intentional and unintentional industrial chemicals), are Regions II and III (mainly developed nations), and to a lesser extent Regions IV, VII and VIII (composed of both developed and developing countries). Given that Region VIII seems to have no active PTS pesticide production, this Region need only be considered for PCDD/PCDF production. On the map these Regions (II, III, IV and VII) constitute a band of productions sites, mostly in the northern hemisphere
- Regions with comparatively little PTS production are V, VI, IX, X and XI though developing countries. These Regions still contain countries with appreciable production such as India, Brazil, Nigeria and South Africa. Regions with almost no sources are the Polar Regions (I and XII).

- Almost all Regions have PAH sources (except XII with some minor localised sources from research stations, spills and accidents), but the major sources Regions (oil and biomass combustion) are II, III, IV, VI, VII, VIII and X.
- Since almost all the PTS pesticides have to be imported into Regions V, VIII, IX, X and XI, these Regions can be considered as net importers of PTS pesticides.
- Very little data were available on organometalics. This was a feature of both developing as well as developed Regions. Mention has been made though, of the Global Mercury Assessment that was completed during the course of the project.
- Since hardly any active imports of intentionally produced PTS occurs into the polar Regions (I and XII), these two Regions can be considered as net PTS sinks. The close geographic association of Region I to the proposed net-producing Regions II, III and VII, contrast with the remoteness of Region XII. This Region has some of the lowest known environmental levels of most of the PTS considered in this Report. The possibility also exists that their might be differences in the relevant contributions of the oceanic and atmospheric pathways between these two Regions. For Region I, the atmospheric pathway dominates but such information is not yet firmly established for Region XII.
- Most of the past PCB, production sites, past and present production activities of PTS pesticides, and most of the worlds industrial activities likely to be sources of intentional and unintentional PTS chemicals are located in Regions II, III and VII. This contiguous band of Regions could be considered as global net sources of PTS. These should be considered as both sources of direct releases to the environment, as well as trade sources to most of the other Regions, where secondary releases take place (such as pesticide application, PCB use, e-waste treatment or secondary stocks).
- Up to a certain point, the Regional levels of concern and data gap scores support the above observations. Almost all the Regions scored 2/2 for PCDD/PCDF and PAH. However, for the intentionally produced industrial PTS, the scores were generally higher in the Regions that produce them, than in the Regions that receive them. Some of the Regions gave some very low scores to these chemicals, such as 0/0 for PBDE in Region V. This can possibly be explained by both a lack of knowledge, and the low amount of these industrial chemicals that are perceived to be imported into such Regions.
- On the other hand, the concern with PCDD/PCDF and PAH in almost all the Regions, does suggest that at least internal (but likely also external) sources are a major concern. Regions that expressed concern about biomass burning (eg. forest fires) as a source of PCDD/PCDF are V, VII, VIII, X and XI.
- Open burning has been identified as a likely or potential major PTS source in many of the Regions. The uncontrolled nature of this source (materials, temperature, conversion rates etc.) makes it a difficult issue to address due to the inherent data gaps (see UNEP 2001, for information on conversion rates). A characterisation of this source within these limits would probably provide a better base of assessing applications of BAT and BEP, as well as its impact on Regional and global flux. The Expert Group on BAT and BEP established by the INC of the Stockholm Convention is developing guidelines and guidance to reduce/minimise releases of TCDD/TCDF.
- The source profile, as reflected in Table 2.9, summarises the available information on sources of PTS chemicals on a global basis. Although the Table is based on incomplete data, it does show a pattern of sources including the differences between developing and developed Regions. As such, it can be updated by addressing the major issue of data gaps, possibly including open burning using other information such as those forthcoming from the various country NIPs. This will provide a useful and adaptable tool for assessment, decision-making and action at national, regional and global levels of chemicals management.

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3 ENVIRONMENTAL LEVELS, TRENDS AND EFFECTS

3.1 BACKGROUND INFORMATION ON LEVELS OF PTS

A considerable amount of data is available on the occurrence of PTS in the different regions of the world, although with a very uneven distribution in terms of compartmental, geographical and temporal coverage. An open literature survey from 1990 to 2002 has shown more than 85000 references for the compounds considered in the present assessment. A summary is presented in Figures 3.1 and 3.2 regarding different PTS and compartments.

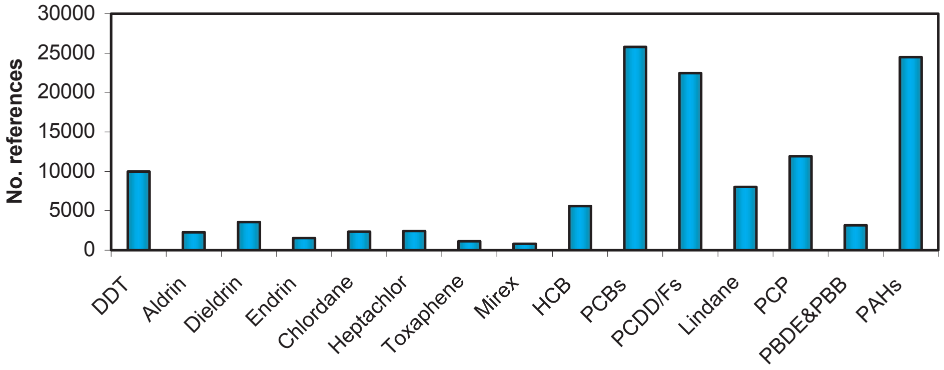

Figure 3.1. No. of references in the open literature (1990-2002) for different PTS

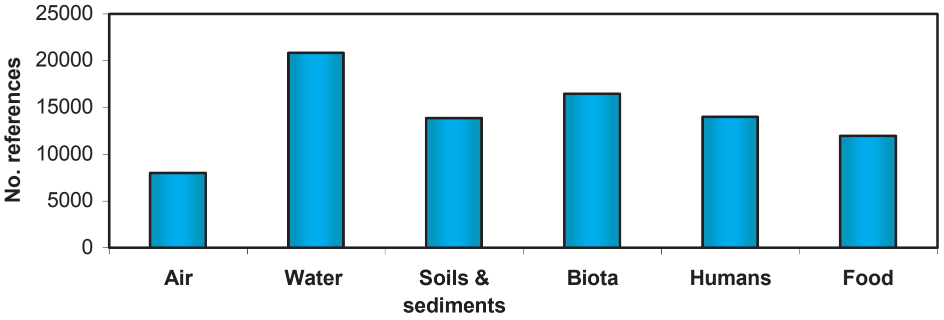

Figure 3.2. No. of references in the open literature (1990-2002) for different compartments

Data on PTS loadings greatly differ among biotic and abiotic compartments, as exemplified in Figure 3.3. Differences are also observed at regional level (Figure 3.4) where data is focused on certain PTS either reflecting regional main concerns or the available analytical capabilities. Moreover, data are often patchy, and typically the result of one-off studies rather than systematic, comparable and long-term monitoring. Surveillance networks are operational only in regions belonging to the developed world (e.g. North America, Europe, Japan and Australia), including the polar ones, but even in these regions, monitoring activities do not cover most of the PTS considered in this assessment.

On the other hand, measuring and reporting protocols vary widely in the published data. For example, the tissue basis of the measurement in biota samples (e.g. fresh mass, dry mass, total lipid, or a particular organ) introduces a large range of variability and not always is it possible to inter-convert values (e.g. bring all data to a whole organism dry mass or total lipid basis). Furthermore, there have been changes in analytical methodology, which made comparison with older results problematic in some cases. Advances in the analysis of some PTS, for example, have introduced new forms of conveying the results like in the case of PCBs and PAHs, which have been first reported as total equivalents and later as individual components. Finally, the quality of data, particularly the older ones, is also difficult to assess. These have been major drawbacks in preparing the global report.

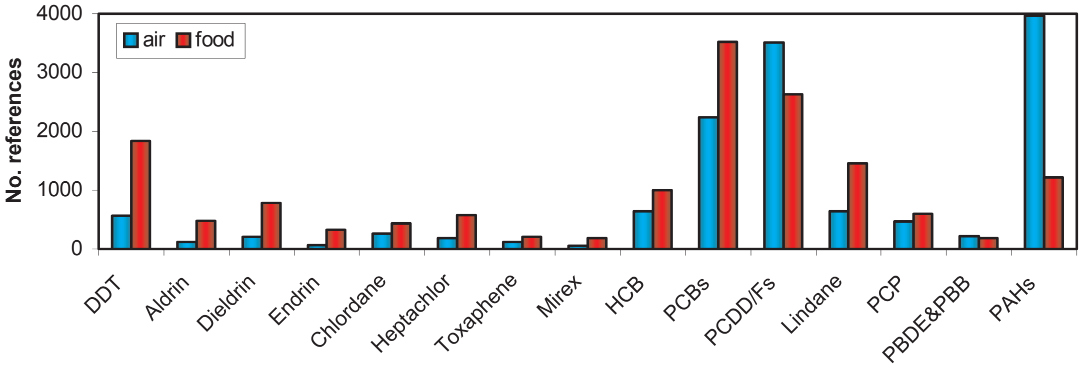

Figure 3.3. No. of references in the open literature (1990-2002) for PTS in air and food

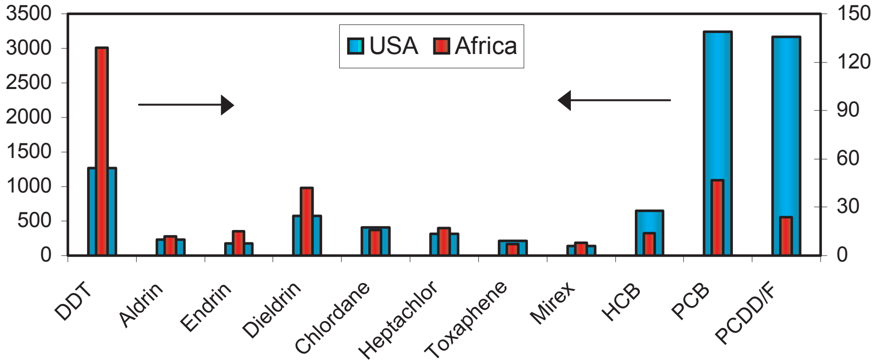

Figure 3.4. No. of references in the open literature (1990-2002) for PTS in USA and Africa

The data summarised in this chapter are based on the twelve Regional reports and data contained in the questionnaires from the Project. Despite the different use made by the regions of these questionnaires, this has been the first attempt to put together the available information on PTS at the global level. Future efforts on PTS sources, environmental levels, and national capacity, will benefit from the development of compatible national databases on PTS. The total number of questionnaires approved in the UNEP Data base (www.chem.unep.ch/pts) is shown in Figure 3.5. As can be observed, data refer mainly to pesticides, in particular to DDT (25% of the total number of questionnaires), and to a lesser extent to industrial chemicals such as PCBs and HCB.

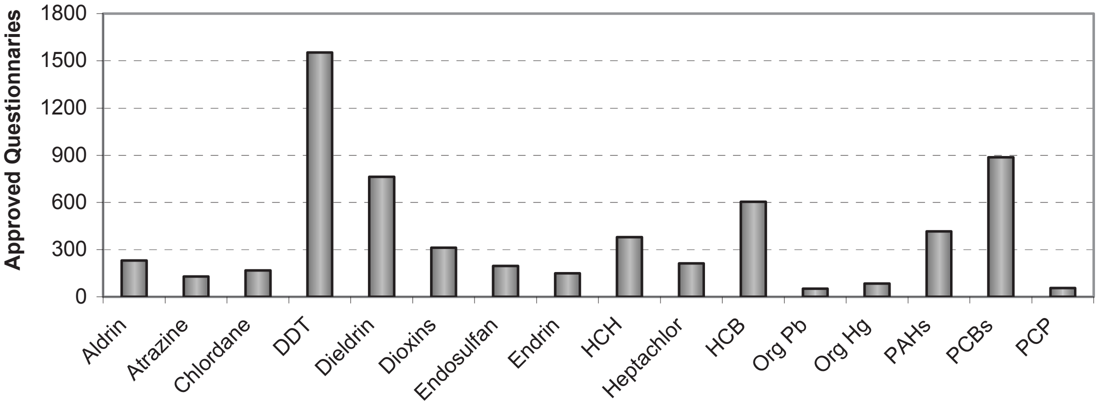

Figure 3.5. Available data set of PTS in the UNEP Data base.

The aim of the data reported in the following sections is to provide information about the occurrence and levels of PTS in the different environmental compartments. Data are mainly from the last decade and where possible, the temporal variability is also assessed. Considering the usual concentration ranges and the drawbacks indicated above, it is difficult to go further in the assessment of levels and effects in different parts of the world.

3.2 CONCENTRATION DATA AND TRENDS

3.2.1 Abiotic compartments

3.2.1.1 Air and Precipitation

The atmospheric compartment is one of the most important pathways of transport for several PTS in the environment. A large amount of data is now available on levels of PTS in air, particularly organochlorine (OC) compounds and polycyclic aromatic hydrocarbons (PAHs). On a global basis, the most frequently reported OC compounds are hexachlorocyclohexanes (α- and γ-HCH) and PCBs. Data on PAHs in air are also available for several regions. This indicates that they are of concern, particularly in urban areas, which are known as important sources for these compounds.

One of the most relevant evidence from the existing data is that some PTS have been globally everywhere in the atmosphere. Practically all regions of the world have reported some levels of DDT, HCHs, PCBs and PAHs in air. Obviously, ranges and trends depend on the vicinity of sources. However, regular monitoring of airborne contaminants is unevenly distributed across the globe. Some developed countries have long experience in collecting data on PTS in air and precipitation but other geographical areas are not covered by any monitoring programme.

Highest concentrations of pesticides in air have been reported in the tropical-temperate regions, particularly in India, Asia and Africa. Lower levels have been recorded in the Polar Regions. For example, concentrations of OCs in Arctic air from northern Canada and Norway are generally one order of magnitude lower than in air from southernmost locations in the same countries. Table 3.1 shows the range of concentrations in the UNEP regions extracted from the completed questionnaires and regional reports. Although direct comparative analysis is very difficult since several concentrations are reported on a different basis, it is interesting to note significant differences between regions. Of special concern is data for Region VI which cannot be considered representative for the whole area

The global picture of industrial PTS and by-products is very different and probably highly dependent on the status of use and control of emissions of these compounds. PAHs concentrations have been reported in dry deposition in a number of urban areas as well as in remote places. Levels are highly dependent on the location (urban or rural) and related to emissions produced by sources including biomass burning.

Despite the variety of components analysed, some seasonal and spatial trends are apparent. Concentrations are consistently higher in winter than in summer and in urban rather than in rural areas. The higher values are found in particular places like stack gases, tunnels of motorways, open burning sites, etc. A comprehensive overview of levels in urban areas can be found in the Mediterranean regional report (UNEP, 2002e). Concentrations of PAHs (Σ10-18 PAH components) in aerosol samples from different cities are between 4 and 310 ng/m^3, with benzo[a]pyrene ranging from 0.2-22 ng/m^3.

Table 3.1 Ranges of reported data for selected PTS in air (ng/m3)

UNEP Region	HCHs	DDT	PCBs
I	0.002-0.3	0.0001-0.016	0.003-0.102
II	--	--	--
III	474		
IV	0.003-77		0.17-2
V	0.0005-0.118	0.0084-0.011	
VI	10-780	0.076-52.8	
VII		0.004-0.116	0.009-2.3
VIII	0.120-120	0.014-3.6	nd-17
IX	0.03-0.27	0.002-1.3	0.01-2.3
X		0.216-0.992	
XI	1-1.5	1-1.5	1.0-3.0
XII		0.11-0.23	

Data on dioxins and furans in air have been reported in the industrialised world since the 80's. Ambient concentrations show a high variability from urban to rural and from contaminated to uncontaminated sites. The analytical challenges and high cost of air measurements of dioxins and furans severely restrict the number of available data. Typical concentrations in Europe and Mediterranean regions range from <1 to 14800 fg TEQ/m^3, in rural and contaminated areas respectively. In Asia reported values range from 7-1486 fg TEQ/m^3. In South America reported values range between 3 and 394 pg TEQ/m^3 (in airborne particulate matter). The lack of any data for areas such as Sub-Saharan Africa and Indian Ocean Regions is a major data gap. Reported data in other regions fall within those ranges but the variability means that assessment and conclusions are difficult without supporting information (UNEP, 2002f, g).

Very few data in the scientific literature deal with large geographical areas. Good examples include the work of Iwata et al. (1993, 1995) and Lohmann et al. (2001) where PCBs and other chlorinated compounds were analysed in air samples in the atmosphere of the Pacific and Atlantic oceans. Both studies cover a large geographical area and both conclude that, in general, values are higher in the Northern hemisphere for PCBs and dioxins and furans (Figures 3.6 and 3.7).

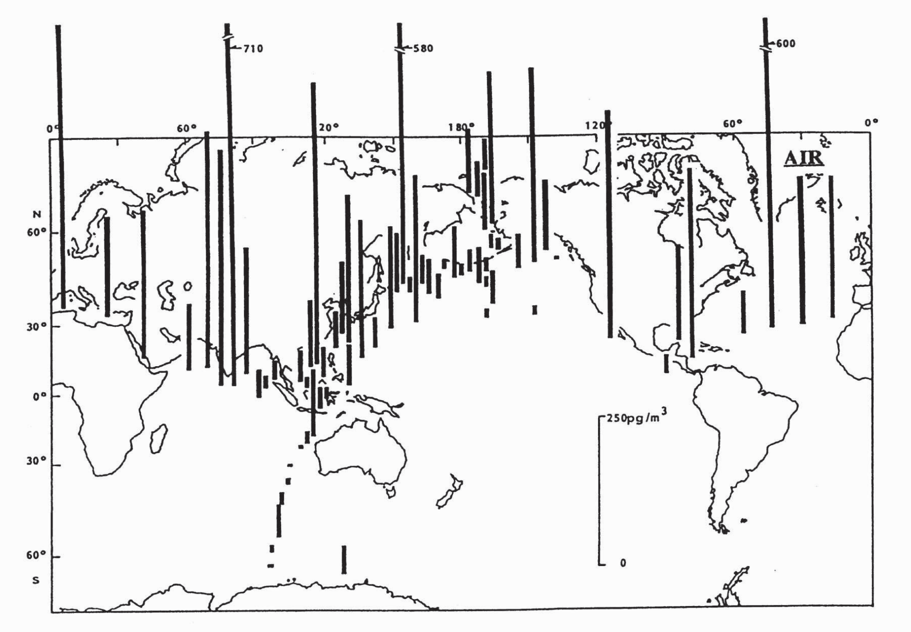

Figure 3.6. PCBs in air samples in the Northern and Southern hemispheres (Iwata et al., 1993)

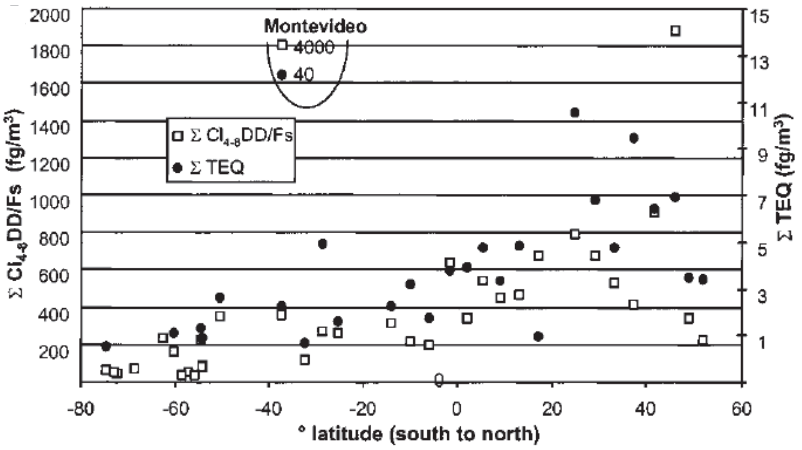

Figure 3.7. Dioxins and furans in air samples along an Atlantic Ocean transect (Lohmann et al., 2001)

Deposition Rates

Deposition values show a wide variability. In general, it can be stated that depositional fluxes from the atmosphere are higher for those pesticides still in use, such as lindane, whereas those of banned pesticides have been decreasing. Reported depositional fluxes are generally only available for developed regions and it will be important to complete this data base with data coming from the less developed regions.

In the area of Great Lakes, downward fluxes for pesticides in 1997 and 1998 ranged from 0.01 ng/m^2/day to 40 ng/m^2/day, with in- use pesticides such as γ-HCH accounting for the highest fluxes. Volatilization fluxes for those pesticides banned from use were almost 10 times greater than those for currently used pesticides, reaching –37 ng/m^2/day at their highest. PCBs and HCB downward fluxes ranged from 0.02 ng/m^2/day to 11 ng/m^2/day across the basin.

The situation in the European region is not so straightforward. While a decrease of α-HCH air concentration was reported (from 90 pg/m^3 in 1992 to 25 pg/m^3 in 1999), no similar decrease occurred for lindane (EMEP, 1998). Contrasting results have been observed for the Mediterranean region where the opposite has been noted. According to Chevreuil et al. (1996), total lindane deposition decreased from 210 to 34 ng/m^2/day through the 90's, but no similar decrease was observed for α-HCH (3.6-7.4 ng/m^2/day). In the Asian Region the deposition fluxes of HCHs and DDTs are within the range of 0.6-9.4 ng/m^2/day and 0.4-15.0 ng/m^2/day, respectively.

Atmospheric deposition of PCBs can reflect local sources, like heavily human-impacted environments. High values have been reported in the Baltic Sea (10-15 ng/m^2/day). However, mixing and long range transport may also account for an increased deposition. In this respect, both the European and the Mediterranean regions have similar values of PCBs deposition ranging from 1.2 to 5.6 ng/m^2/day, probably due to the generalised mechanisms of atmospheric circulation in the area.

The absolute values for PAHs deposition are clearly higher than the other reported PTS by 1 < 3 orders of magnitude. Values as high as 5.2 μg/m^2/day have been reported in Europe. Bulk deposition of PAHs and PCDD/PCDFs has been measured in the UK (Toxic Organic Micropollutants Survey) (Halsall et al., 1995). The annual average of ΣPAH deposition in Manchester and Cardiff during 1991/92 was 5.2 and 4.1 μg/m^2/day, respectively. In general, urban fluxes are higher compared to rural locations (Gevao et al., 1998), reflecting the importance of the urban centres as a source of PAHs, and the large decline in many atmospheric PAH species moving away from urban areas.

3.2.1.2 Freshwater environments

Freshwater environments include basically rivers and lakes. Pollutant loads are highly influenced by the respective hydrological regimes and if sampling is not adequately performed, data is hardly representative. In this respect, the assessment of levels and trends of contaminants in freshwater systems is, in general, severely hampered by the lack of proper data collection. This situation may be surprising given that the freshwater biota has received much attention over the last few decades (see section 3.2.2.2).

DDT and other polychlorinated pesticides

The highest levels of HCHs in freshwaters are found in the Indian and South-East Asia and South Pacific regions. Cyclodiene pesticides have occasionally been determined and endosulphan has been widely reported in certain regions (e.g. Central America and South-East Asia) in concentrations ranging up to 100 ng/L. However, care must be taken because data quality is quite different depending on the region. In this regard, it is interesting to note that in general, the highest reported levels of PTS pesticides in freshwaters come from developing countries.

The most frequently detected pesticides in all regions are DDTs and HCHs. The highest DDT concentrations have been reported for regions VII (Central and North-east Asia), X (Central America and the Caribbean) and XI (Eastern and Western South America) (Figure 3.8). In all these regions, DDT continues to be used for different purposes, even where regulatory measures have been taken.

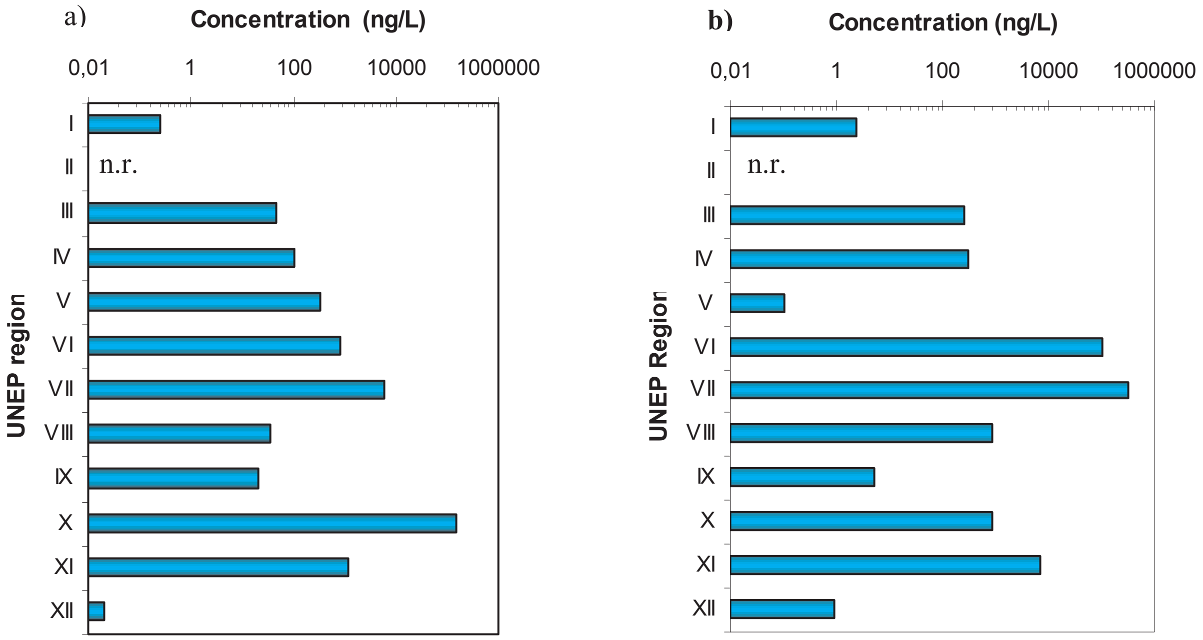

Figure 3.8. DDT (a) and HCHs (b) concentration ranges reported in freshwaters across the regions (n.r.: not reported).

On a regional basis, the following features can be highlighted. In the Arctic Region the higher concentrations of chlorinated pesticides (up to 55 ng/L of HCHs) have been found in the Russian rivers (e.g. Ob and Yenisey) (AMAP, 2000). In the European Region, episodically high concentrations of DDT and lindane have been found in the lower course of the Danube River. For example, the mean river water concentration of DDT in Slovakia was 0.047 µg/L, but findings up to 0.26 µg/L were reported. Lindane and other HCH isomers were detected in two of the nine Danube tributaries examined, both of them on the Romanian territory (lindane - river Olt, 0.15 µg/L and river Arges 0.25 µg/L). This would indicate occasional unauthorised uses of organochlorine pesticides in some parts of the region and also suggests Romania as a potential "hot spot" for environmental contamination with chlorinated pesticides in the Danube River basin. Residues of HCB were also detected quite frequently in the Danube River (35 % positive samples) (UNEP, 2002d).

In the Mediterranean region, cyclodiene pesticides (dieldrin, aldrin, endrin, heptachlor) have been reported in river water samples collected during the 80's and 90's in many countries with a wide range of values (<0.1 – 228 ng/L), but only in France as part of a continued monitoring activity. DDT levels in the Mediterranean freshwater environment range ND-103 ng/L, the highest values being detected in developing countries within the region. The same trend can be observed for lindane (1-320 ng/L).

Recently, endosulphan has been found at levels of 0.23-0.49 µg/L in Lake Kinneret waters (Israel) and at 0.03-1.70 µg/L in the coastal lagoon of Mar Menor (Spain) (UNEP, 2002e). Chlordane and toxaphene have only rarely been reported in the Mediterranean region (UNEP, 1995). Earlier studies on water samples collected in 1982-1983 in the mouth of Ebro River (Spain) determined concentrations of α- and γ-chlordane in the range of 11-64 and 21-110 pg/L, respectively (Cid et al., 1990). Yamashita et al. (2000) found concentrations also at the pg/L level in the Nile River waters and the Manzala coastal lagoon.

Data gathered up to now indicate that Sub-Saharan African fresh waters (rivers, lakes, ground, estuaries and rainwater) are contaminated by a broad spectrum of PTS. From these data, the following ranges of concentrations in rivers (ng/L) were found: endosulphan (ND - 4843), atrazine (0.38 - 44000), PCBs (ND - 0.3), dieldrin (ND - 921), DDT (ND - 350), HCB (ND - 9.4), heptachlor (ND - 5.3), chlordane (0.02) and HCH (ND - 0.1). mirex was not detected in rivers in S. Africa and Nigeria. The reported concentration ranges (ng/L) for lakes (Malawi, Nakuru, etc.) from the period 1990-to date is as follows: endosulphan (ND – 11.4), dieldrin (5 - 10), DDT (0.06 - 8.1), heptachlor (ND –0.07), chlordane (0.02 – 1.9) and HCH (ND - 0.1) (UNEP, 2002f).

These results come from individual studies done in some countries and do not reflect the general situation of the region. However, these reported concentrations are amongst the highest values reported for freshwater environment at the global level. It is of concern that monitoring activities and analytical capabilities are lacking in this region and only few countries report PTS levels in freshwater.

Chlordane, DDTs, HCHs, HCB and toxaphene were found in water samples of Region VII (Japan, Kazakhstan, Russian Federation and Republic of Korea). HCH values in the range of 1-322000 ng/L have been reported in Kazakhstan. In East Russia, the Amur River periodically showed relatively high levels of α-HCH (<5-1840 ng/L), γ-HCH (<5-620 ng/L) and DDT (<50-450 ng/L) (Kucklick et al., 1993).

Lake Baikal (Russia) deserves particular attention. Organochlorine pesticides were analysed in early 90's and total DDTs, total HCHs, chlordane and toxaphene in (dissolved+particulate) phases of water were reported to be (0.047+0.006), (1.340+NA), (0.028+0.006) and (0.064+NA) ng/L, respectively (Kucklick et al., 1993) (NA = not analysed). In another report, reported levels of HCB were of 0.007-0.028 ng/L (Iwata et al., 1995).

Tanabe and co-workers reported the concentration of DDTs, HCHs and chlordanes in freshwater from several Asian countries and Australia (Iwata et. al., 1994). Extremely high concentrations of HCHs were found in one Malaysian river (900 ng/L) while other areas in Region VIII showed much lower levels (0.08 – 22 ng/L). Concentrations of HCHs in water in Australia were found to be low (0.079 – 0.87 ng/L) in the 20 areas studied. DDT was found to be abundant in inland waters of most countries in Region VIII. Particularly high levels of DDT were found in municipal sewage waters in Ho Chi Minh City, Viet Nam (25 ng/L). Chlordanes were found to be generally low in most parts of the region ranging from 0.002 to 2.8 ng/L.

In the Pacific Island Region, the only reliable water values are from recent studies of a Saipan contaminated site, a Guam well monitoring data and a large-scale Japanese study of Asia and Oceania which analysed six water samples from Solomon Islands. These provide cause for concern as the highest values for HCHs (5.3 ng/L) and PCBs (1.1 ng/L in Solomon Islands and 32000 ng/L in Saipan) exceed Australia and New Zealand (ANZ) standards for water (4 ng/L and 1 ng/L, respectively). The high DDT value of 21 ng/L greatly exceeds the recommended ANZ guideline of 1 ng/L (UNEP, 2002j).

In the Eastern and Western South America Region, lindane and its isomers are frequently detected in high levels (mean: 622 ng/L), exceeding Canadian guidelines by 3 to 400 times (10 ng/L). Excluding the highest sites, the general mean decreases to 146 ng/L but this is still above the accepted guidelines (UNEP, 2002m).

DDT is also frequently reported with surprisingly high concentrations in this region. For example, the general mean (1267±1920 ng/L) duplicates that of the more soluble HCHs. Reports from northern freshwater environments in Argentina and Brazil indicate very high levels (1000-6000 ng/L), more than 3 orders of magnitude above the US EPA guideline (1 ng/L). This suggests higher inputs possibly related to sub-tropical agricultural use and vector control. However, this variability probably includes also methodological uncertainties, especially in older reports. As observed for HCHs, excluding the highest samples, the DDT average decrease to a few tens of ng/L, but still remains 1-2 orders of magnitude higher than the guidelines.

It is clear from the presented data that with few exceptions organochlorinated pesticides levels in water are low. Highest values come frequently from developing countries and in some cases from accidents or spills released by pesticide producers in the developed world. In general, for PTS pesticides levels are higher in the Northern hemisphere

It is also a general trend that elimination of use of PTS pesticides results in declining levels in freshwaters, even for those regions where levels reported during the 70-80's were high. However, in several regions, DDT still continues to be used and therefore freshwater levels are still high. Two regions showed high levels of DDT (Central and North East Asia and Eastern and Western South America). Recent use of pesticides such as lindane and endosulphan, are frequently detected in quite high concentrations in waters of regions VI, VII, VIII and X.

PCBs

Information is scarce and only few countries have representative data. From the collected data, it appears that PCB concentrations in freshwaters are low, usually below detection limits, which can be explained by their low water solubility. However, concentrations of PCBs in Arctic lake and river waters in Canada are in the range of 0.15-4.83 ng/L, exceeding the USEPA Great Lakes Water Quality guideline for protection of aquatic life of 17 pg/L (AMAP, 2000). Levels of PCBs in lakes, rivers, dams and streams from Nigeria, South Africa, Zimbabwe, Kenya and Cote d'Ivoire (1990/1992) were in the range of ND - 2000 ng/L, being much higher than those reported for 1970-1989. PCB levels in Lake Baikal were of 0.18-0.590 ng/L (Iwata et al., 1995).

In general, high concentrations are found in urban and near industrial sites, mainly in urban-industrial effluents. However, highest concentrations in water refer to spills or accidents. For instance, the most relevant problem in the Mediterranean region concerning the aquatic environment was probably the contamination of several aquifers in the Balkans area during the Kosovo war. However, the ecological disaster with greatest repercussion was the pollution of the Krupa River (Slovenia) in 1983, resulting from wastes dumped during the manufacture of transformers by Iskra in Semič. Despite the remediation measures applied since 1990, the groundwaters still contained, in 1997, 100 ng/L of PCBs compared to 380 ng/L in 1988.

PCDD/PCDFs

Practically no data is reported for PCDD/PDDFs in waters across the globe, or they are below detection limits. An exception to this rule is the reported data from the Republic of Korea, where the ranges are 0.001-1.061 pg TEQ/L. In 2000 the Japan national dioxin survey average level in water (rivers, lakes and coastal sea water) in 2116 sites was reported to be, 0.31 pg-TEQ/L with a range of 0.012 to 48 pg-TEQ/L (national dioxin survey, ministry of the environment, Japan). The levels in 83 sites (3.9 % or total) exceeded the water quality standard (1pg-TEQ/L) of Japan. The 1996 studies on several New Zealand rivers revealed no PCDD/PCDFs in the water samples (the limit of detection was 2 pg/L for 2,3,7,8-TCDD) (UNEP, 2002h, i).

3.2.1.3 Seawater

Oceanic waters are the final receptors of land based pollutant sources and, similar to the atmospheric compartment, can be an important pathway for global transport of several PTS. Coastal waters are particularly affected by inputs of PTS via discharges of sewage and industrial effluents and rivers, whereas atmospheric deposition is the major pollutant source in open seawaters (Scrimshaw and Lester, 1996). As a consequence, the concentrations of PTS exhibit strong decreasing gradients off-shore, so that it is necessary to distinguish between coastal and open waters in the global assessment of PTS levels.

The occurrence of persistent and hydrophobic organic pollutants in the marine environment is of concern because they may be distributed over large areas and accumulates in organisms and biomagnified through the food web. However, some regions have not reported data on PTS concentrations in marine waters, i.e sub-Saharan Africa and South American Region. It is probable that none of the coastal countries have conducted research on marine water, neither for academic nor for safety/environmental purposes.

DDT

Usually, DDT is present at lower concentrations in pelagic Arctic seawater, but in the Russian Arctic, concentrations of DDT and PCBs are high. These data are consistent with measurements based on suspended particulate matter in seawater and with reports of elevated DDT and PCBs in suspended sediments of some Russian rivers (e.g., the Ob River). If confirmed by future measurements, this would imply major inputs of DDT and PCBs to the Arctic Ocean from Russian sources.

Open sea waters were sampled in 1993-94 in the Western Mediterranean, including the straits of Sicily and Gibraltar (Dachs et al., 1997). DDT levels were of 0.1-0.7 pg/L and 0.4-2.8 pg/L in the particulate and dissolved phases, respectively. In the continental shelf, the values were 1 and 4 pg/L, respectively.

In the Indian Ocean region, the levels of pp'-DDT were found in the range of 13.3-56.0 ng/L. Among DDT metabolites, pp'-DDE was found to be present in every alternate station with increasing concentration (2.5-20.3 ng/L), whereas op'-DDE could be detected occasionally in the northern part of the region. The baseline levels of total DDT residues in the coastal waters of the Arabian Sea were established to be 100-440 ng/L (Shailaja et al., 1992). A few chlorinated pesticides have been detected in marine water analysis done in India.

In Central America and the Caribbean, there are several reports of total DDTs in sea waters ranging from n.d. values up to a few µg/L. These values are among the highest reported in the literature, probably reflecting the use of DDT in the region and supporting data on the levels found in freshwater resources.

In 1993, Iwata et al. reported DDT values in surface seawater representative of a large geographical area covering several regions. The results shown in Figure 3.9 clearly indicate that the highest levels were found in the coastal waters of the Indian Ocean Region.

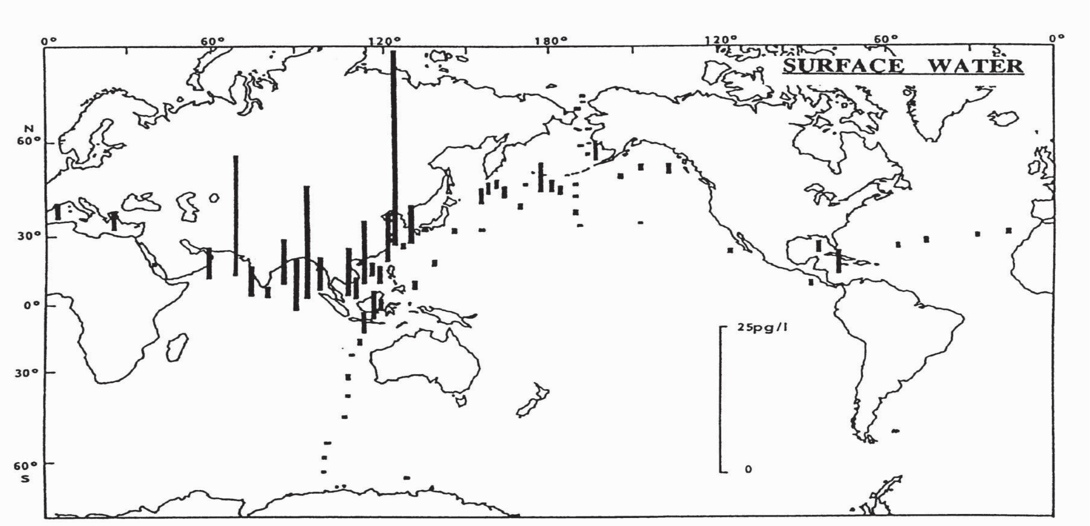

Figure 3.9. Distribution of total DDT concentrations in surface seawater (Iwata et al., 1993).

HCHs

Lindane is more water soluble than most of the other chlorinated hydrocarbons discussed in this report and, therefore, a major input to the sea is via rivers from the application areas. Some surveys have been carried out in estuaries and coastal waters. There are indications of a slight decrease in the riverine input of lindane to the Irish Sea. Lindane concentrations are higher in the southern North Sea and the German Bight than in the north-western North Sea. Concentrations of α-HCH ranged from 0.1 to 0.7 ng/L (mean value 0.28 ng/L), and γ-HCH from 0.1 to 4.0 ng/L (mean value 1.1 ng/L).

Lindane, α-HCH and β-HCH were detected in significant amounts (1-30 ng/L) in various marine wetlands of Greece (Albanis et al., 1995). Similar levels were reported in coastal waters of Alexandria (Abd-Allah, 1999). Lindane levels off shore in the Eastern Mediterranean ranged from 0.06 to 0.12 ng/L, whereas values one order of magnitude lower were found in the Western basin. In the Eastern Atlantic, the values are in the pg/L level (40 and 100 pg/L for α- and γ-HCH, respecively) (Lakaschus et al., 2001).

Seawater samples were collected along the central west coast of India at a depth of 20 m during 1987 ORV Sagar Kanya cruise. The levels of γ-HCH ranged from 0.26 to 9.4 ng/L. Recently, higher values of lindane (up to µg/L) were reported in the Central American Region (UNEP, 2002g, k).

Surprisingly, high levels of ΣHCH are found in the Arctic Ocean (Figure 3.10), especially in the Beaufort Sea and Canadian Arctic Archipelago. ΣHCH levels measured in the late 80's to early 90's appear to increase in a smooth gradient with latitude from the tropical western Pacific Ocean to the Arctic Ocean. Wania and Mackay (1996) have suggested that this is evidence of the 'cold-condensation' effect. Other less volatile OCs (e.g., chlordanes, PCBs, DDT) were present at lower concentrations in the Bering/Chukchi Seas than at more temperate latitudes. Recent data confirm that the relative abundance in pelagic Arctic seawater is α-HCH > HCB > γ-HCH ≈ toxaphene > chlordanes ≈ PCBs > DDTs (Bidleman et al., 1990). An exception seems to be the Russian Arctic seas, where the order is reversed.

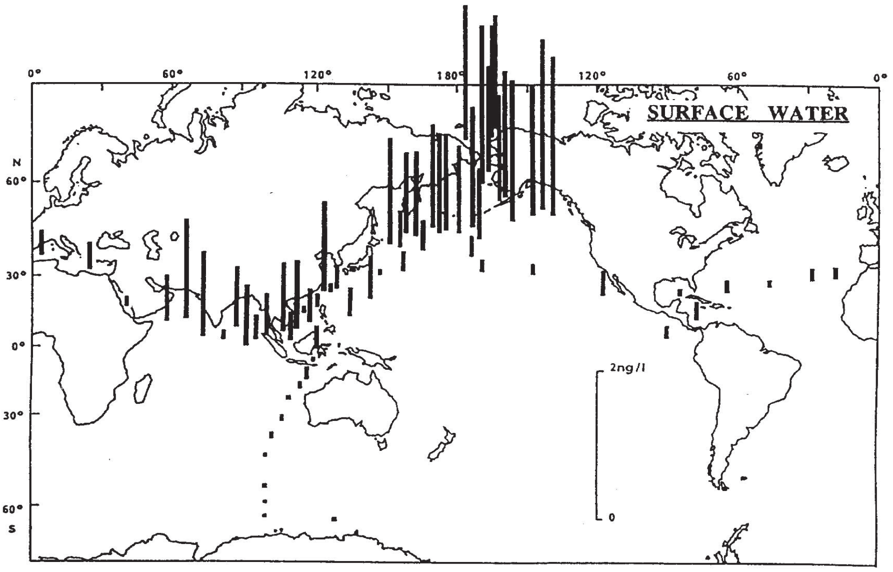

Figure 3.10. Distribution of total HCHs concentrations in surface seawater (Iwata et al., 1993).

PCBs

The comparison of results among authors is generally hampered by the different analytical standards used and the lack of distinction between the dissolved and particulate fractions. Predictably, the highest concentrations of PCBs were reported in urban and industrial coastal wastewaters as well as in river discharges. Accordingly, decreasing concentration gradients have been found in transects offshore from these sources.

Concentrations of PCBs in filtered ocean water are usually reported to be in the low pg/L range and this makes reliable quantification difficult. A large survey conducted by Iwata et al. (1993) showed a rather uniform distribution of PCBs in surface waters off the Atlantic, Pacific and Indian Oceans, with relatively higher levels in the temperate Northern Hemisphere (Figure 3.11).

Particular studies have been performed in the European and in the Mediterranean Seas. In general, the concentrations of PCBs for all the investigated areas in the Mediterranean Sea were similar except in the Ligurian Sea where concentrations were higher. PCB concentrations in the suspended particulate matter from coastal and open Western Mediterranean waters were in 1990 5-35 pg/L, the same order of magnitude as those reported in other regions, e.g. North Sea and North Atlantic. An extensive review of data obtained during the 80's has been published by Tolosa et al. (1995).

In a more recent study covering the whole Western basin, a spatial gradient was also observed from the continental shelf (3.5-26.6 pg/L) towards the open sea (1.7-6.6 pg/L). A relatively important enrichment (8.4 pg/L) was found in open sea stations located in higher productivity frontal zones.

Total PCBs in sea water in Japan, analysed in 1999 ranged from less than 0.01 ng/L for each isomer to 150 ng/L with a detection frequency of 131 among 171 samples (Ministry of the Environment, Japan). In the Pacific Islands, of 25 seawater samples, all were below 0.25 ng/L of total PCBs. Indeed, the Antarctic data for surface seawater showed concentrations varying from 35-69 pg/L total PCBs (Tanabe et al., 1983).

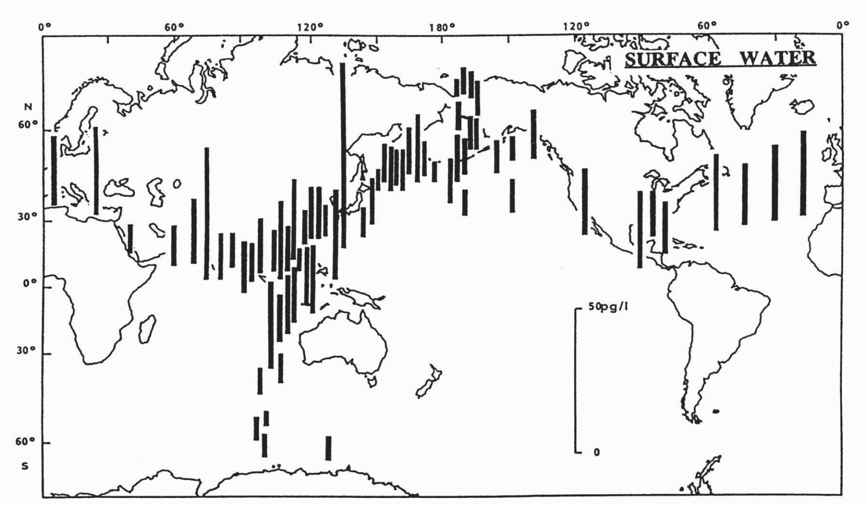

Figure 3.11. Distribution of total PCBs concentrations in surface seawater (Iwata et al., 1993).

PCDD/PCDFs

Information on dioxin levels in seawater is scarce, but a few point source emissions have been studied, such as in Frierfjorden (North Sea), in Region II. Dioxin concentrations seem ten to twenty times higher in samples from the Northern North Sea than in samples from the Barents Sea.

In both river and coastal sea waters of Japan, the sum of dioxins and furans reported by the Ministry of the Environment in 1997 gave an average concentration of 0.37 pg-TEQ/m^3 at 12 sites with variations between 0.005 and 3.9 pg-TEQ/m^3. Data from local governments at 21 sites ranged from n.d. to 0.4 pg-TEQ/m^3 with an average concentration of 0.061 pg-TEQ/m^3 (UNEP, 2002h). In general, dioxin levels in coastal waters were one order of magnitude lower than those in rivers.

PAHs

Concentrations of PAHs in seawater vary considerably depending on the proximity to sources. The highest values are found in coastal waters as a result of terrestrial inputs and maritime transport (e.g. harbours). Atlantic sea water concentrations range from 0.3 ng/L for individual lower molecular weight PAHs (two and three ring compounds) to less than 0.001 ng/L for the high molecular weight PAHs (five or more ring compounds). Higher concentrations were generally found in coastal and estuarine samples with total PAH concentrations ranging from not detectable to 8500 ng/L.

In the Danube, Dnieper and Dniester River Estuaries and other point sources of pollution located offshore Romania and Bulgaria, the concentrations of PAHs in suspended particulate matter (SPM) are ca. 1600 pg/L. This is higher than in other estuaries of the western Mediterranean (ca. 560 pg/L).

In 1997, levels of PAHs in samples from the North Aegean Sea were found to be of 10 to 30 ng/L. Along the Turkish coast and the Ionian Sea, concentrations vary over a wider range (0.02 to 40 µg/L), with high concentrations caused most probably from direct discharges from the ships (Sakellariadou et al.,1994).

Data on individual PAHs in the water column of the Western Mediterranean have also been reported (Dachs et al., 1997). PAHs (Σ16) associated to SPM were evenly distributed in subsurface waters, and their concentrations ranged from 200 to 750 ng/L, with peaks at the Rhone and Ebro river plumes (570-970 ng/L). The vertical profiles exhibited a decreasing concentration trend with a relative increase of the more polycondensed compounds derived from pyrolytic sources. The PAH contents in the dissolved phase of the open sea were of 0.4-0.9 ng/L , with values around 2 ng/L in coastal areas.

In the East Asia Region (Republic of Korea) concentrations reported for PAHs in seawater ranged from 25.9 to 10197 ng/L. In the Russian sector of the Arctic region (Pechora and Kara Seas) 10-69 ng/L of the sum of 23 PAH compounds have been reported (AMAP, 2000).

Organotin compounds

Organotin compounds have not been studied in many regions of the world; most of the information derives from the MEDPOL work in the Mediterranean Region, where pollution with TBT compounds is a recognised problem in marinas and harbours. The areas investigated were the French Mediterranean and Northern Tyrrhenian coasts, the Nile Delta area, and the Southern coast of Turkey.

The results of this survey can be considered as representative of the various contaminated sites occurring in the Mediterranean region before TBT regulation (Gabrielides et al., 1990). The concentrations of TBT in seawater from harbours and marinas on average vary between 100 and 1000 ng/L. The mariculture areas exhibited less contamination by TBT with concentrations <20 ng/L which is considered the NOEL for mollusc larval development. In conclusion, the survey showed conclusively that high and potentially toxic concentrations of TBT occur in the vicinity of harbours and marinas where there are high densities of ships and pleasure craft.

A campaign conducted by IFREMER in 1997 confirms that contamination of the French coast is still a problem. Seventy-five percent of the measurements were above the threshold of 1 ng/L, which is known to cause toxic effects to some marine species (Michel and Averty, 1999).

3.2.1.4 Soils

Soils are natural sinks for persistent and lipophilic compounds which adsorb to the soil organic carbon and, once adsorbed, remain relatively immobile (Buckley-Golder et al., 1999). Besides accidental spills, soils can receive inputs of PTS via different pathways, the most important being: atmospheric deposition, chemicals application, and amending with sewage sludges or composts. Levels can vary considerably over small areas moving away from the sources due to the limited mobility of the adsorbed pollutants. Concentrations in soil will reflect a long-term input history of the site.

DDT

DDT in soils has been detected in all regions of the globe but the assessment is difficult because of the lack of representativeness of data. Concentrations range from no detection in remote locations to few mg/kg in areas where DDT is still in use. Some examples are described below.

DDTs (DDT+DDE) in soils from the Czech Republic ranged from 0.003-5.2 mg/kg. In India, monitoring of 224 soils collected from cotton-wheat crops, rice fields, local orchards and vegetable fields exhibited DDT concentrations ranging from 0.005-0.049 mg/kg (ICAR, 2002). A survey of 63 soil samples carried out in the Pearl River Delta (China) showed DDT values of 0.015-0.125 mg/kg (av. 0.068 mg/kg) (Zhang et. al., 2001).

The Cattle Tick Dip Site Management Committee in Australia released data on levels of DDT in the contaminated sites (Miller et al., 2002). DDT levels were found to be as high as 106 mg/kg in some areas. These soils were also found to contain chlordane and dieldrin in low concentrations (to 2 ng/g). However, DDT levels were on the declining trend since DDT usage was banned in 1987 in Australia.

Soil samples taken in the three most important rice producing areas of Cuba showed DDT residues, in 1983, in the range of 0.06 – 0.35 mg/kg. In Panama, several studies revealed the presence of organochlorine pesticides in soil. In samples of soil cultivated with rice showed methoxychlor, heptachlor, DDT, DDE and lindane. Levels of the insecticides were in the range of 0.01-0.84 mg/kg (UNEP, 2002k).

HCHs

As in the case of DDT, concentrations of HCHs in soils are very diverse, depending on the proximity to the sources. A survey carried out in soils from the Pearl River Delta (China) averaged 0.02 mg/kg of HCHs (range from 2-30 ng/g). HCH levels in Kazakhstan were reported to be very high, 1.0-1.9 mg/kg. Concentrations in soils near Lena River (Russia) were 0.001-0.017 mg/kg (Regional Administration, and Committee of Natural Resources, Russian Federation, 2001).

Lindane has also been a major problem in the Balkan countries in relation with some abandoned stockpiles. A preliminary study of HCH levels conducted during the 90's showed concentrations of 40-225 mg/kg of HCHs in the topsoil around a chemical plant in Durres (Albania). Sediment samples from the main collector draining to the Adriatic Sea exhibited concentrations of 1878 mg/kg of total HCHs at a distance of 100m, and of 226 mg/kg before discharging to the sea.

PCBs

PCBs in soils have received little attention until recently, when a global survey was conducted by an European Group (GLOBAL SOC PROJECT). A wide range of levels was reported. Higher concentrations are detected in areas where PCBs use was important and where PCBs were disposed without any precaution. For example, in Eastern Europe several sites reach levels of 53 mg/kg (Kocan et al., 1999).

In Central America (Panama), PCBs were detected in several studies around transformer sites in levels up to 185 mg/kg. However, in background areas, soil levels are in the range of 0.026 and 97 µg/kg, highly dependent on soil organic matter contents (Meijer et al., 2003). Higher concentrations are found in the Northern hemisphere where the major use has taken place (Figure 3.12).

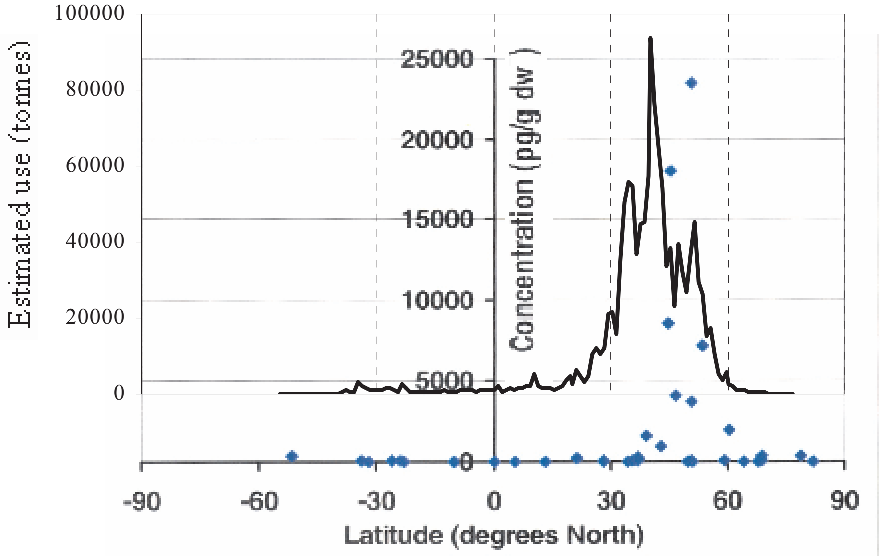

Figure 3.12. PCBs concentration in background soils across the globe, inlcuding the estimated usage of PCB (Meijer et al., 2003)

Sewage sludges are monitored for PCBs in Europe were they are widely used in agriculture. The EU establishes a max. concentration of 0.8 mg/kg of PCBs (Σ7). The values found in 50 wastewater plants in the east of France were between 0.04 – 1.13 mg/kg and 0.5 mg/kg in the region of Paris. The mean value in sludges disposed through agriculture was of 0.19 mg/kg (UNEP, 2002e).

PCDD/PCDFs

In Europe, a number of intensive surveys have been carried out. In almost all countries a broad range of dioxin concentrations was detected, as illustrated in Table 3.2, with consistent urban-rural gradients. In general, data come from studies where the concentrations of PCDD/PCDFs were measured around areas influenced by potential point sources, such as waste incinerators or industrial plants.

Soils under the influence of strong emitting sources present the higher levels of PCDD/PCDFs (up to 100 ng I-TEQ/g dw). The lowest values found in rural sites are below 1 pg I-TEQ/g dw. In Seveso area (Italy), the levels measured in 1995-96 ranged from 0.91 ng I-TEQ/kg to 16 ng I-TEQ/kg.

In Japan, the average level of PCCD/PCDFs in soils (3031 sites) was 6.9 pg-TEQ/g, ranging from 0 to 1200 pg-TEQ/g (National Dioxin Survey, Ministry of the Environment, Japan, 2000). Buckland et al. (1998) summarised the New Zealand study on ambient concentrations of PCDD/PCDFs shown in Table 3.2. Soils from the Amazon basin contained 0.02-0.4 ng I-TEQ/kg PCDD/ PCDFs, and 0.1-7.7 µg/kg of PCBs.

Table 3.2. Summary of dioxin concentrations in soils (pg TEQ/g dw)

Country	Contaminated	Urban	Other types	Rural
Austria	332			<1-64
Belgium			2.7-8.9	2.1-2.3
Germany	30000	10-30		1-5
Ireland			<1-8.6	4.8
Luxembourg			1.8-20	1.4
The Netherlands	98000			2.2-16
Sweden	11446			<1
United Kingdom	1585		<1-87	<1-20
France		200-1700	20-3500	
Italy		1000-6200	60-4310	5310
Spain	100-10800	150-24200	270-2240	120-8400
Portugal		2040-16400		790-850
Greece	34000-1144000			
Russia		av. 312		0.22-0.75
Kazakhstan	0.001 - 550	0.12 - 370		
New Zealand		260-6670		0.17-1.99

Figure 3.13 shows the estimated deposition rates of PCDD/PCDFs in several soils (Hites et al., 1996). Estimations are higher in densely populated and industrialised areas of North America and Asia.

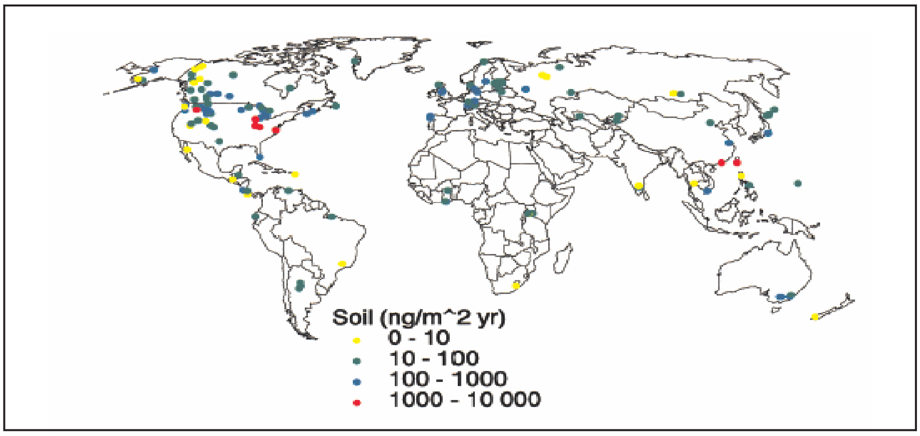

Figure 3.13. Estimated PCDD/PCDFs deposition rates (Brzuzy and Hites, 1996)

PAHs

Reported mean contents of PAHs in urban soils are within the range of about 1- 3 µg/g but values of 30 to 50 µg/g have been found in some locations. The average PAHs level in rural European soils is rather uniform with median values of about 0.3 – 0.4 µg/g. In the Novi Sad region (FRY) soils were found to contain up to 2.4-8.5 µg/g of PAHs (∑16) (av. 5.48 µg/g) after the war period (UNEP, 2002e).

3.2.1.5 Sediments

Sediments would be the natural sink for PTS upon release to the aquatic environment due to their low solubility in water. Much of the PTS used in agriculture as well as in vector control will find their final destination in sediments where limited breakdown and slow natural decomposition will occur. Probably one of the largest existing PTS databases, biased towards developed regions, is related to sediment levels. However, there are problems in assessing the data because sample procedures and treatments (e.g. sample sieving) as well as the sediment characteracteristics (e.g. % organic carbon) are frequently not reported.

3.2.1.5.1 Continental sediments

DDT

DDT has been widely reported in sediment samples from rivers and lakes. Concentration values range from not detected to thousands of µg/kg dw. Usually, concentrations are high in areas where DDT is still used. The highest reported levels come from sediments in Indian rivers, but it was recognised that more recent values range from 63 – 260 µg/kg dw. High levels were also reported in the East Asia Region, in the former USSR, with total concentrations of DDT compounds in bottom sediments in Ural River between 0.02-64.5 µg/kg, and in Miass River between 0.29-64.5 µg/kg (UNEP, 2002h). The Sub-Saharan African Region reported DDT in lake sediments ranging from 13 – 223 µg/kg dw, although the spatial coverage of the data is poor. A screening for persistent chlorinated hydrocarbons was carried out in December 1995 in the main coastal lagoons on the Pacific side of Nicaragua (Carvalho et. al., 1999). Total DDT in these lagoons averaged 4.5 and 3.4 µg/kg dw, which may be considered a baseline level for the region. Sediments of the Esteros Naranjo-Paso Caballos system at Chinandega district showed much higher levels, 270 ng/g dw for total DDT. Torres et al. (2002) analysed sediment samples from Paraíba do Sul-Guandu system (Brazil). This river is the only source of potable water for more than 10 million in the metropolitan area of Rio de Janeiro. The average concentration of ΣDDT was around 225 µg/kg.

DDT has also been found in remote areas where use has been very limited, like in the Arctic, but where the predominant pathway for PTS inputs to lakes and ponds is thought to be via atmospheric transport and deposition from sources in temperate, industrialised regions. Concentrations of DDT in surface sediments range from <0.25-5.25 µg/kg dw but declined significantly with latitude from 9.7 µg/kg dw in sediments from two lakes in northern Ontario to 0.10 µg/kg dw in Ellesmere Island (AMAP, 2000).

Cyclodiene pesticides and HCHs

Cyclodiene pesticides have been extensively reported in sediments collected across the globe, particularly during the 80's. Levels of heptachlor (0.01-0.93 µg/kg dw) and total chlordane (sum of γ and α-chlordane) (0.4-18.5 µg/kg dw) were reported in sediments from the Nile River and the Manzala Lake. More recently, low levels of cyclodiene pesticides (<0.25-6.7 µg/kg dw) were found in sediments collected in 1999 from Alexandria harbour and Lake Maryut, whereas values up to 44 µg/kg dw were reported for total chlordane (sum of γ and α-chlordane) in the harbour sediments (UNEP, 2002e).

Cyclodiene pesticides were found in sediments along the Ebro River sediments at concentrations ranging from 0.02 to 1.7 µg/kg dw (mean 0.4 ± 0.6 µg/kg dw). Aldrin was found only in 46% of the samples (Fernandez et al., 1999). In Israel, levels were <0.5 µg/kg dw in coastal, estuarine and river sediments, but noticeable in surface sediments of Lake Kinneret for dieldrin (1.6-9.9 µg/kg dw) and heptachlor (2.1-59.9 µg/kg dw). Dieldrin was also found in 4 out of 9 sampling locations of river sediments in Cyprus in a survey carried out from 1997-1998. The values ranged from 1.7-133 µg/kg on a dry basis (UNEP, 2002e).

HCHs were detected during the 80's in coastal sediments from the Western, Central and Eastern part of the Mediterranean, with mean values ranging from 0.5 to 2.5 µg/kg dw. Mirex has not been detected in sediments from the Mediterranean Region (UNEP, 2002e).

In India, Sarkar et al. (1997) compared the organochlorine pesticide residue levels in different estuarine sediments along the west coast of India in Arabian Sea (Saraswati, Purna, Netravati, Beypore, Ponnani) with those offshore (10-15 km away from the river mouth). The levels at the mouth of estuaries were total HCHs 0.85-7.87 µg/kg, aldrin 0.10-0.26 µg/kg, dieldrin, 0.70-3.33 µg/kg, endrin 0.42-0.95 µg/kg, whereas those in the offshore sediments were, HCHs 0.10-6.20 µg/kg, aldrin0.09-0.26 µg/kg, dieldrin, 0.20-1.41 µg/kg, endrin 0.39-0.78 µg/kg, and endosulphan ND-9.0 µg/kg. On the other hand, the levels of contamination in sediments along the east coast of India at river mouth and coastal region were, total HCHs 20-100 and 15-

120 µg/kg, aldrin ND-350 and ND-150 µg/kg, dieldrin ND-250 and ND-175 µg/kg, respectively (Sarkar and Everaarts, 1998). As shown, the concentrations of different contaminants in sediments along the east coast were much higher than those along the west coast.

HCB

HCB is widely distributed in freshwater sediments, either close to industrial areas or remote sites. High concentrations have been found in the Mediterranean region. The higher values have been reported for the Gulf of Fos and the Rhone Delta (30-39 µg/kg dw). Concentrations in the Ebro Delta were one order of magnitude lower. In the coastal shelf the values were below 1 µg/kg (Tolosa et al., 1995). HCB was also found in shallow sediments of the Venice Lagoon (Italy) at concentrations ranging from 0.85-1.11 µg/kg dw, in 4 out of 9 sampling locations of river sediments in Cyprus, at levels ranging from 0.1-4.8 µg/kg dw, and in sediments from the Nile River (3.8-4.5 µg/kg dw) (UNEP, 2002e).

HCB was also detectable at low concentrations (< 0.1-5.4 µg/kg dw) in almost all samples of freshwater surface sediments from Alaska, Northern Canada, Greenland, Norway, Finland, and Russia, the higher values being found in Finnish sediments (AMAP, 2000).

PCBs

PCBs have been detected in Arctic lake sediments. Concentrations of a total of 12 congeners were in the range of 2-40 µg/kg dw, with a significant latitudinal decline of penta- to octachlorobiphenyls, with increasing north latitude (Muir et al., 1996). This is consistent with predictions of the ‘cold condensation’ hypothesis.

PCBs have also been determined in a series of lake sediment cores, collected in UK and Finland, in order to investigate the temporal trends of these pollutants along their production period and further use restriction. The details of these studies are described in section 3.2.3.1 (temporal trends).

In the Sub-Saharan Africa Region, reported data are very scarce. Total PCBs in lake sediments range from 70-320 µg/kg dw, with an apparent increase from recent data (UNEP, 2002b).

In the South American Region, PCB concentrations in sediments are relatively high but the database is strongly biased by contaminated sites in Argentina, the Río Santiago (998 µg/kg and Brazil (580 µg/kg). Excluding these sites, the general PCB mean decrease from 58±149 to 9.1±7.7 µg/kg is lower than the Canadian guideline for protection of aquatic life (34.1 µg/kg). However, polluted sediments from the Río de la Plata estuary often exceed this Canadian value (UNEP, 2002k).

PCDD/PCDFs

PCDD/PCDFs have been determined in a limited number of lake sediment cores in Canada and Finland, and in surface sediments from Arctic lakes in Norway and Sweden. The profiles show low concentrations ranging from 1.4 to 4.2 pg TEQ /g dw in the surface slices (AMAP, 2000). Marvin et al. (2002) conducted a survey in Lake Ontario (Canada) to assess spatial and temporal trends in sediment PCDD/PCDFs contamination. The analysis showed on average 91 pg TEQ/g (2.81 ng/g) but four sites had concentrations in excess of 200 pg TEQ/g.

In Europe, the first data on PCDD/PCDF levels in Po River sediments have been recently published, giving concentrations from 1-2 ng TEQ/kg dw to 10-11 ng TEQ/kg dw (Fattore et al., 2001). Sediment concentrations of dioxins in Lake Baikal and Selenga river in Irkutsk region (Russia) were reported to be 0.03 and 0.05 pg TEQ/g, respectively, while those of the sediments near a discharging point from a pulp and paper mill plant were 7.7 pg TEQ/g. In lake sediments from Japan, PCDD/PCDF levels ranged from 16.1 to 50.7 with an average of 33.1 pg-TEQ/g. In general, levels of PCDDs/PCDFs in river sediments sampled were higher in industrial and urban areas. Concentrations of PCDD/PCDFs in sediments from New Zealand were in the range of 0.081 – 2.71 ng I-TEQ/kg (UNEP, 2002h, i).

3.2.1.5.2 Marine sediments

Marine sediments have been widely monitored as they constitute an important sink for certain PTS entering the sea through rivers and urban and industrial wastewaters. The impact of these discharges on coastal waters is geographically limited to the continental shelf, as beyond their zone of influence, concentrations drop rapidly reflects the enhanced sedimentation processes which take place at the freshwater-seawater interface. In fact, 80% of the terrestrial sediments are trapped on the continental shelf and only the finest particles are transported by currents to deep sea basins. Therefore, the attention has been mainly focused on coastal sediments.

DDT

In general, concentrations of all OCs in Arctic marine sediments are extremely low. Most sites have concentrations less than 1 ng/g dw. However, data are lacking on OCs in marine sediments from the Canadian and Alaskan Arctic except for a limited number of samples from the southern Beaufort Sea and Bering Sea.

DDTs have been monitored in the Mediterranean region. A large number of bottom sediments collected in the Western basin revealed the widespread occurrence of these pollutants in the region and allowed the identification of some "hot spots". DDT levels in coastal sediments were mainly within 47 - 227 ng/g whereas in the deep basin were of 0.5-1.2 ng/g dw.

Coastal sediments of the Sub-Saharan Africa Region have received little attention with respect to PTS. DDT levels in sediment samples from the South-east Asia and South Pacific Region were generally low even though some sites showed extremely high levels. For example, one site in Australia showed 1700 ng/g of DDT while most other parts of the country showed levels lower than 20 ng/g. In the Pacific Islands Region, the allowed level for total DDTs is 1880 ng/g and samples (e.g. Tonga and Solomon Islands) are reported to contain from not detected to 1024 ng/g.

PCBs

PCBs are widely distributed in Arctic sediments but at low levels, generally below 2 ng/g dw, with no apparent geographic trend (AMAP, 2000). A mapping of PCBs in sediment samples (around 100) collected from different areas of the Western Mediterranean basin revealed the widespread occurrence of these pollutants in the region and allowed a mass balance assessment (Tolosa et al., 1995 and 1997). Localised inputs or "hot spots" have been identified near sewage outfalls from highly industrialised and populated cities (229 ng/g Σ9 PCB cong). Other substantially PCB-contaminated sediments arise from freshwater discharges like the Rhône and Ebro rivers (34 ng/g Σ9 PCB cong). The levels in the deep basin were 2-6 ng/g dw.

A survey conducted recently revealed the presence of PCBs in Kuwait sediments more than in other Gulf States. Data reported as Aroclor 1254 range from 50-24500 pg/g in Kuwait sediments; from <7.8-190 pg/g in Saudi Arabia; from 20 pg/g in Qatar; varied between 13-130 pg/g in UAE (Al-Majed et al., 2000) and between 4-139 pg/g dw in Oman (Al-Wahebi, 2002). In India, PCBs were analysed in surface sediments of river Ganges, along its entire length, and the average concentration was 4.1±4.4 ng/g dw (Senthilkumar et al., 1999). In the east coast of India PCBs were found at levels from ND-1.4 ng/g in sediments from river mouths and from ND to 1.09 ng/g in the coastal region (Sarkar and Everaarts, 1998).

In the Pacific Islands Region, measured PCBs in sediments range from not detected to several thousands of ng/g in heavily polluted sites. In New Zealand, in the South-east Asia and South Pacific Region, the sum of 25 PCB congeners was in the range of 0.12 – 8.80 ng/g dw for sediment samples. Cullen et al. (1992) summarised studies on PTS levels in sediments carried out in the 70's and 80's in Australia. PCBs were found in marine sediments at concentration ranges of not detected to 1300 ng/g.

Sampling of marine sediments for PCBs in Antarctica has typically been undertaken in regions of known contamination. Most work has been carried out in the vicinity of McMurdo Research Station in the Ross Sea. Risebrough et al. (1990) found typical total PCB concentrations in surface sediments of 500 ng/g. Kennicutt et al. (1995) also analysed PCBs in sediments from Winter Quarters Bay, near the McMurdo Station, and from Arthur Harbour on the Antarctic Peninsula. They reported total PCB concentrations ranging from 250-4300 ng/g and 2.8-4.2 ng/g, respectively. Concentrations decreased rapidly away from sources of contamination.

PCDD/PCDFs

Levels of PCDD/PCDFs have been determined in marine sediments from northern Norway (near Kirkenes), in the Mackenzie River Delta area, and in the Barents Sea. PCDD/PCDFs in the Barents Sea were 10 to 20 times lower than those in the northern North Sea where TCDD TEQs ranged from 5.5 to 17.2 pg/g. PCDD/PCDF isomer patterns were very similar for both the Barents Sea and North Sea samples and indicative of combustion sources. TCDD TEQ levels in most marine or estuarine sediments exceeded

Canadian environmental quality guidelines for protection of aquatic life of 0.09 pg/g dw but did not exceed the Norwegian Environmental Authority ‘background’ levels of 30 pg TEQ/g.

The Gulf of Finland, a sub-basin of the Baltic Sea, was found to be severely polluted, with PCDD/PCDF concentrations as high as 101000 pg/g dw and 479 pg TEQ/g dw. In Finland, chlorophenols were manufactured in 1939-1984 and used as a wood preservative (mainly 2,3,4,6-tetrachlorophenol). The chemical plant was situated next to the Kymijoki River, which discharges into the Gulf and may be linked to the contamination since PCDD/PCDFs may be formed as a by-product.

Sediments sampled in the Catalan coast (Spain) in the late 80’s - early 90’s, showed concentrations in the range 0.4-8 ng I-TEQ/kg dw (Eljarrat et al., 2001). The influence of a sewage sludge dumping site increased these levels to 57 ng I-TEQ/kg dw. In Portugal, data are only available from three river sediments in Oporto region. PCDD/PCDF concentrations range from 0.54 to 3.39 ng I-TEQ/kg dw. In general, profiles show higher concentrations of higher chlorinated congeners, particularly OCDD and OCDF. In Japan, the levels of dioxins and furans in coastal sediments ranged, in 1997, from 0.012 to 49.3 pg-TEQ/g dw (av. 17.1). Data on PCDD/PCDFs in sediments in the southern hemisphere are practically unknown, although the absence of many industrial sources suggests that levels should be lower than in the northern hemisphere.

All these data together point out a generalised pollution pattern in sediments by PCDD/PCDFs, with levels higher in the coastal environment close to the river mouths and outfalls from industrialised areas. Some dated sediment cores provide a picture of large temporal variations in sedimentation of PCDD/PCDFs, with a peak of pollution in the 60’s – 70’s followed by a drop.

PAHs

PAHs are commonly found in marine sediments in relatively high levels compared to other PTS and are derived from petrogenic or pyrogenic sources. In Europe, PAH concentrations up to 35.2 µg/kg dw have been found in the southern Baltic Sea. Somewhat elevated concentrations were observed in the eastern Gulf of Finland as well as in the northern Gulf of Bothnia (up to 17.0 µg/kg dw and 20.9 µg/kg dw, respectively).

PAHs are widespread in coastal zones in the Mediterranean region and clearly associated with urban and industrial inputs. An increasing trend of pyrolytic PAHs in transects from the coastal areas towards the open sea indicates the predominance of atmospheric inputs in the latter, which account for 80-90% of the total PAHs in the deep basins.

Extensive studies have been conducted on the determination of PAHs in the sediment from Arabian Gulf. The levels found in 1991 in sediments from different countries of the region were: Kuwait, 30.4 µg/kg dw; Saudi Arabia, 36.4-761 µg/kg dw; Bahrain, 47.5-97.5 µg/kg dw; UAE, 10.9-21.8 µg/kg dw; and Oman, 4.5-36.5 µg/kg dw. However, there were pockets of high contamination in the coastal area receiving industrial effluents where the levels ranged from 5.6 to 1334 µg/kg dw. The contamination screening survey conducted in 1998 by ROPME revealed PAHs in sediments from Kuwait (97.7 µg/kg dw) and from Saudi Arabia (6.9 µg/kg dw) (UNEP, 2002g).

In South America, most reports correspond to harbours and ports in heavily impacted areas and thus present a wide variability (0.1-286000 µg/kg). Most affected areas correspond to the intensive traffic in the Paraná, Uruguay and Río de la Plata rivers, especially close to heavily populated areas such as Buenos Aires and Montevideo, the Argentine Patagonian coastal area, where crude oil extraction and transport are very active, and the Tiete River and surrounding environments close to Sao Paulo in Brazil.

In the Antarctic Region, the information on environmental levels of PAHs generally refer to local sources which are unrepresentative of the region as a whole. Generally, PAH concentrations in marine sediments vary from undetectable to about 10 µg/kg. At sites of local contamination, corresponding values can be much higher: ≥60000 µg/kg in long-term contaminated sediments. There appears to be no temporal trend in the environmental loading of PAHs, as the PAH output has a long history. The introduction of PAH in the region is an irregular combination of global input, low-level and long-term natural and anthropogenic sources, and catastrophic incidents. In the Arctic region, the baseline values in the Norwegian and Russian sectors are in the range of 10-160 µg/kg (Σ 24 PAHs) but concentrations up to 8000 µg/kg have beeen found in contaminated sites (e.g. harbours) (AMAP, 2000).

Organotin compounds

The 1988 MEDPOL pilot survey on TBT reported levels in sediments from harbours in the range of 30 – 1375 ng/g (Gabrielides et al., 1990). The RNO monitoring program in France determined concentrations of 2-197 ng/g of TBT in the Atlantic Bays (Brest and Arcachon) and of 9-127 ng/g in the Mediterranean ports (RNO, 1996). Studies have also been performed in many Mediterranean coastal sites (e.g. Egypt, Malta, France, Spain, Italy, etc.) (Bressa et al., 1997; Barakat et al., 2002; Díez et al*.,* 2002). Reported values of 1 to 2067 ng Sn/g dw for TBT, indicate that antifouling paints are still of concern in marinas, harbours and, particularly in sites adjacent to vessel repair facilities. However, the large predominance of the organotin degradation products over the parent compounds in the Western Mediterranean suggests that there are almost no recent inputs of these compounds.

TBT levels in India, at Kochi, Marmagao, and Mumbai were 244-872, 33-2333, and 93-536 ng/g, respectively (UNEP, 2002g). The levels of TBT reported in surface sediments from the Pearl River Delta (China) were from 1.7 to 379.7 ng/g (Zhang et al., 2002). High TBT concentrations (328.7-377.7 ng/g) were found in sediments from the Front Channel of the Pearl River (Zhujiang) where more than 30 shipyards and ship-repairers were located. It was therefore suggested that shipping activities, especially at shipyards, were mostly responsible for the TBT contamination in the region.

3.2.2 Biotic compartments, including humans

3.2.2.1 Terrestrial environment

Terrestrial biota (vegetation and animals) will be considered here as the bioindicator of environmental pollution. Biota linked to food production is considered in section 3.2.2.4.

3.2.2.1.1 Vegetation

Several studies have analysed vegetation for monitoring purposes. The concentrations of organic pollutants in biomonitors reflect the ambient air concentrations during the time of exposure of the plant but a range of factors will affect the concentration. Therefore, a large number of samples is required in order to minimise the effect of point sources and overcome the inherent variability. Moreover, different plants may not be directly comparable for global assessments.

Leafy vegetables and, particularly, conifer needle species and bark have been used in several regions as biomonitors of PTS contamination (Buckley-Golder et al., 1999; Weiss et al., 2000; Calamari et al., 1994; Simonich et Hites, 1995; Holoubek et al., 2000). The advantage of biomonitors, such as pine needles, is that they are widely spread and samples can be easily obtained. As there is a database of measurements taken from a wide range of locations over long periods of time, the analytical results from different locations or years can be compared. However, a linear correlation between PTS concentrations in pine needles, or any other vegetation, and the high volume samplers or deposition samples cannot be established.

A series of papers (e.g. Kylin et al., 1994; Strachan et al., 1994; Sinkkonen et al., 1995) has outlined the use of pine (*Pinus sylvestris*) needles to determine the regional contamination of organochlorines in Northern Europe. The study of the pathway of benzo(a)pyrene (BaP) migration from bulk deposition to soil and vegetation, with special emphasis on the forest ecosystem, was performed in Lithuania (Milukaite, 1998).

Twenty-five remote forest sites covering Austria and located far away from settlements, factories and public roads were investigated. Three exposed alpine mountains sites situated at one slope but at different altitudes were included to investigate the influence of altitude on the concentrations detected (Weiss et al., 1998).

Selected PTS compounds (PAHs, PCBs, OCPs, PCDD/PCDFs) are monitored in the air, soils and needles from sampling sites located in Czech boundary high-mountain ecosystems (Holoubek et al., 1998), and in Poland (Migaszewski, 1999). Studies from Bavaria and Hesse in Germany reported that mean dioxin concentrations in pine needles ranged from 0.53 to 1.64 pg I-TEQ/g dw.

In Austria, the background concentrations of dioxins in spruce needles were in a very narrow range between 0.3 and 1.9 pg I-TEQ/g dw. The data of dioxins levels presented in the EU SCOOP report and related to France, Greece, Italy and Spain indicated a typical range of 0.09 – 1.22 pg I-TEQ/g dw, with a maximum value of 64 pg I-TEQ/g dw in a contaminated site. HCB, HCHs and DDT have also been measured in pine needles in Greece and more extensively in Italy, Croatia and France. The results are summarised in Table 3.3 (UNEP, 2002e).

Table 3.3. Concentration of some organochlorinated compounds in pine needles from several countries. The values are expressed in ng/g dw

Sampling site	HCB	α-HCH	γ-HCH	pp'-DDE	pp'-DDT	ΣPCBs
Croatia	0.3-1.5	0.2-7.4	0.5-7.4	0.8-2.6	0.0-0.7	1.4-10 (Aroclor)
France (Paris)		7-27	59-69			190-680 (av. 340)
Greece	5.0-7.2					
Italy (North):						
- Industrial	2.2-5	1.4-26	3.9-10	1.6-12.4	2.6-11	30-360
- Alps	0.5-3	1.1-4.5	0.6-4.9	0.6-3.2	0.6-5.0	

Most recent Sub-Saharan samples show residue levels lower than those found in the 80's when DDT was most intensively used. In certain cases however, high concentrations of PTS have still been reported. Some examples are 233 ng/g of DDT (pine needles) and 2700 ng/g PCBs (plants from refuse dumps) in Nigeria (Osibanjo, 1994). The wide range (in some cases high) of environmental concentrations observed in most of the areas of each country indicates that Sub-Saharan Africa is widely contaminated by PTS. The levels will tend to increase in countries still using PTS in relatively large quantities (e.g. Nigeria, South Africa and Zimbabwe), countries that have not enforced the ban or restriction and countries without regulatory control on the use of PTS chemicals.

Aquatic plants, viz. water hyacinth, have also been used as biomonitors. High levels of PCBs have been reported in South Africa (1300 ng/g dw) and Nigeria (2700 ng/g dw). Dieldrin was detected at a much lower concentration in water hyacinth in Nigeria (43 ng/g dw). Plants in Lake Nymba Ya Mungu, in Tanzania, viz. *Pistia stratiotes*, showed the following levels of PTS: dieldrin 27 ng/g, lindane 4.5 ng/g and aldrin 25 ng/g dw (Paasivirta et.al., 1988). Plants in higher Kenya lakes proved to contain from traces to 107 ng/g dw of total DDT. A study done in Hartbeespoort Dam Lake in South Africa (Greichus et al., 1977) revealed that algae contained higher levels of PCBs (2500 ng/g dry weight) than water hyacinth (1300 ng/g dw).

Standley et al. (1995) and Espinosa et al. (1998) used leaves and bark from deciduous trees and mangrove leaves, for estimating atmospheric transport of organochlorine pesticides from nearby regions in Costa Rica and Colombia, respectively.

The use of biomonitors has been particularly appropriate for assessing the long range transport of PTS in polar regions. Vegetation samples are much easier to collect than air samples especially in remote locations. In these regions, the terrestrial ecosystem is poorly developed and there are no large plants. Most data are derived from analysis of lichens and bryophytes. The presence of land-breeding marine birds and mammals will also provide a strong linkage between the terrestrial community and the marine ecosystem at coastal locations. It should also be noted that most of the terrestrial vegetation is very slow-growing and that biomass often accumulates in the absence of significant grazing and slow microbial breakdown. Thus, vegetation samples used for PTS analysis may represent decades of accumulation (AMAP 2000).

The presence of some pollutants, such as PAHs and organometals, will often include a significant local component associated with long-term human habitation close to the site. Thus, significant contamination of soils and vascular plants by PCBs is observed in the immediate vicinity and within a 20 km radius of abandoned and recently active military radar (DEW line) sites in the Canadian Arctic. There is evidence for transfer of PCBs from plants to lemmings at former DEW line radar sites. This raises the possibility that 1) military sites of other circumpolar countries which contained significant amounts of electrical equipment could also have contaminated soils and dump sites and 2) terrestrial mammals and birds could be contaminated because of feeding, even infrequently, on resident plants or animals at these locations.

3.2.2.1.2 Animals

Wildlife is very diverse among regions and the results are difficult to compare. Moreover, they are not adequately sampled for an assessment of spatial or temporal trends. However, analysis of animals can provide a good indication of the diffused contamination over a certain period of time. Representative studies are summarised below.

Spatial coverage of OC levels in major terrestrial species in the Arctic is good only for caribou/reindeer (Rangifer), where adequate numbers of samples have been analysed from all major Canadian herds as well as herds in northern Norway, Svalbard, and Sweden. A few reindeer samples from several sites have also been analysed in Russia.

In caribou/reindeer, PCBs, HCB and HCH isomers are the dominant PTS in samples from Canada and Svalbard but PCBs are more prominent in samples from Russia. A significant west to east increase in PCBs, HCB, HCHs and PCDD/PCDFs was also found in caribou from the Canadian Arctic with highest mean levels in Cape Dorset and Lake Harbour herds and lowest in the Inuvik herd.

Comparison of OC levels in the lichen → caribou → wolf food chain, from three Canadian herds indicated biomagnification of most OCs and highly selective bioaccumulation of PCB congeners. PCBs are also the predominant OCs in red fox and wolf samples from Canada. Concentrations of PCBs and chlordane observed in Arctic fox liver are among the highest observed in liver of any Arctic mammal. The PCB levels (8.6-208 µg/g fat) are in the same range as observed in polar bear and comparable or higher than in other marine mammals.

Higher levels of PCBs and other OCs, particularly mirex, were also found in waterfowl, especially in molluscivores and piscivores, in the eastern compared to the western Canadian Arctic. In the case of birds, however, most overwinter at temperate latitudes and the east-west trends in OCs may reflect, therefore, migratory patterns and winter-feeding locations rather than regional contamination differences.

Of the birds of prey for which analytical results are available, the lowest OC levels are found in Icelandic gyrfalcon. This is mainly because they are non-migratory birds and so their exposure is primarily of Arctic origin. Migratory species such as merlin, white-tailed sea eagle, and peregrine falcon have much higher ΣDDT and ΣPCB levels, reflecting accumulation of OC's at wintering grounds farther south, as well as accumulation in the Arctic from preying on migratory birds. There was a significant trend of decreasing OC levels in white-tailed sea eagle eggs with increasing latitude (from 61°30'N to 69°N) along the Norwegian coast.

The higher levels of OCs in the eastern Canadian Arctic are probably the result of the predominant west to east/northeast atmospheric circulation pattern, which delivers these contaminants from industrialised regions of central and eastern North America to the Arctic via long-range atmospheric transport. The north-south trends seen in Norway and Sweden are probably the result of long-range transport from industrialised parts of Europe, combined with southerly/southwesterly atmospheric circulation patterns.

In Europe, an important part of the programme of the German Environmental Specimen Bank is focused on the terrestrial ecosystem especially in the areas of the national parks of mud flats in Schelswig-Holstein and Lower Saxony (North Sea) and the areas of Sarland and the Halle/Leipzig/Bitterfeld as urban-industrialised regions (Marth et al., 2000). Soil samples, earthworms and deer livers (*Capreolus capreolus*) as well as city dove eggs (*Columbia domestica*) were analysed for the PTS under list in these model regions.

The European otter (*Lutra lutra*) is a common species on the Euroasian continent that has received attention because of the dramatic decline of some populations early in the 50`s. In the beginning of the 80's, PCBs were suggested to be an important reason for this decline, based on the results of various studies showing levels in the different countries of 16-130 µg/g (Sjőasen et al., 1997). DDT values were in the range 0.9 – 18 µg/g.

Red foxes, barn swallows and rabbits have been studied in Italy. pp'-DDE concentrations in fox samples (*Vulpes vulpes*) in Central Italy varied between 0.55 µg/g and 4.17 µg/g ww in muscle (0.14 - 0.67 µg/g in fat) (Corsolini et al., 2000). In barn swallows (*Hirundo rustica*) collected in 1995 from agricultural areas in Northern Italy, mean pp'-DDE in liver and muscle were 95 and 75 ng/g ww, respectively (Kannan et al., 2001).

Exposure of red foxes (*Vulpes vulpes*) to PCBs in Central Italy was determined by analysis of adipose tissue samples collected from 1991-1992. PCBs ranged 0.6-8.0 ng/g ww (mean: 2 µg/g) (Corsolini et al., 1995). PCBs were also detected in adipose and muscle tissues of red foxes sampled 1992-1993 in three areas of the Tuscany region variously impacted by industrial and agricultural activities. Mean concentrations on lipid basis were 7.6 – 38 µg/g in muscle and 7.2 – 7.6 µg/g in fat (Corsolini et al., 2000). Barn swallows (*Hirundo rustica*) collected in 1995 from agricultural areas around Milan, Northern Italy contained mean values of 1230 ng PCBs/g ww in liver and 716 ng PCBs/g ww in muscle (Kannan et al., 2001).

African wildlife includes *Crocodylus sp*., *Gyps sp*., *Bos taurus*, *Capra hirus*, etc. The levels of dieldrin in animals from Malawi, Nigeria and Kenya did not exceed 70 ng/g for the 90's corresponding to the period during which the use of these pesticides was restricted. However, high concentrations of DDT have been found in zebu (1917 ng/g) and hen (777 ng/g) in Madagascar (1996), in crocodile (34420 ng/g) and wildlife (25900 ng/g) in Zimbabwe. This could be correlated with house treatment of DDT for malaria control and with aldrin + dieldrin for termite control. Moreover, high levels of lindane (6305 ng/g) and toxaphene (3119 ng/g) found in wildlife (South Africa) may indicate that animal contamination by PTS could be a major problem in Sub-Saharan Africa (UNEP, 2002f).

In the Indian Ocean Region, wild birds have received particular attention. In a study on resident and migratory birds collected from South India, organochlorine contamination pattern varied depending on their migratory behaviour (Tanabe et al., 1998). Resident birds living in the same region for their entire life span contained relatively greater concentrations of HCHs (14-8800 ng/g ww) than DDTs (0.3-3600 ng/g ww). Chlordane compounds and HCB ranged 0.1-4.3 and <0.1-1.2 ng/g ww, respectively. Local migratory birds that migrate between Himalayan and South Indian region contained DDTs 67-13000 ng/g ww and HCHs 280-4100 ng/g ww. Short distance migrants, those breeding in central China (e.g. common redshank), eastern Russia (Mongolian plover) and Middle East countries (white cheeked tern) contained DDTs and HCHs 17-1800 and 19-470 ng/g ww, respectively.

Long distance migratory birds, which have their breeding ground in Europe, Russia, Middle east, Papua New Guinea and Australia (e.g. white winged tern and terek sandpiper, common sandpiper, curlew sandpiper, lesser crested tern) contained DDTs and HCHs at levels of 9.2-3.300 and 19-5500 ng/g ww, respectively. Chlordane and HCB residues were higher in short and long distance migrants (0.3-10 and 0.2-1.8 ng/g ww, respectively) than in resident birds (0.1-4.3 and <0.1-1.1 ng/g ww, respectively). Among various HCH isomers, β-HCH was the most predominantly noticed contaminant in all the bird species. Some resident and migratory birds contained relatively larger proportions of α- and γ-isomers suggesting later exposure. Global comparison of organochlorine concentration indicated that resident birds in India had the highest residue of HCH isomers and moderate to high residues of DDTs, predominantly containing pp´-DDE. It was considered that migratory birds wintering in India acquire considerable amounts of HCHs and DDT.

The pattern of PCB contamination of birds was also dependent on their migratory behaviour (Tanabe et al., 1998). Resident birds living in the same region for their entire life contained PCBs from <20 to 65 ng/g ww. In local migrant birds that migrate between Himalayan and South Indian region, the concentration of PCBs ranged 30-640 ng/g ww. Short distance migrants contained 40-4400 ng/g ww, whereas long distance migratory birds contained PCBs at levels of 27-1400 ng/g ww.

Wild birds examined in India contained dioxins and furans in the muscle and liver tissue (Kumar et al., 2001). The levels of dioxins and furans in the muscle tissue of eagle were 24 and 19 pg/g fat; prairie kite 240 and 130 pg/g fat; osprey 200 and 150 pg/g fat; back winged kite 97 and 59 pg/g fat; spotted owlet 270 and 9.2 pg/g fat respectively. Spotted owlet contained very high levels of dioxins 1800 (1300-2700 pg/g fat) and furans 850 (620-1000 pg/g fat) in liver tissue.

There is limited amount of data available on the occurrence of PTS, particularly pesticides, in birds in Australia (Miller et al., 1999). Although the data are limited, the concentrations of DDT appear to be the highest ranging from <0.01 to 519 µg/g (fat) with HCB next in concentrations ranging from <0.01 to 8.62 µg/g (fat), HCH next with concentrations ranging from <0.001 to 1.61 µg/g (fat), and dieldrin with lowest concentrations ranging from <0.0006 to 0.82 µg/g (fat) assuming 10% fat content. Levels in the 70’s and 80’s were in the range <0.01 up to 519 µg/g in fat.

3.2.2.2 Freshwater environment

3.2.2.2.1 Fish

Freshwater fish are good indicators of the quality of the waters where they live. On a lipid weight basis, PTS levels in freshwater fish are generally higher than those in terrestrial herbivores and are similar to or higher than levels in mammalian carnivores. The ultimate purpose in determining the levels of toxic chemicals in fish is to obtain an indication of the potential risks posed to humans. Since fish flesh is the principal item consumed, research on concentrations of PTS has focused primarily in this area although this is not the most sensitive part to toxic flows. The different units used for reporting data, e.g. on wet weight, dry weight and lipid basis, prevents their global assessment. Therefore, the examples given below have been selected to illustrate the existing information in each region.

A comprehensive study has recently been performed in Canada where levels of persistent bioaccumulative toxic substances (e.g., PCBs, DDT, toxaphene and mercury) were determined in top predator fish and their food webs. Samples were taken from lakes stretching over three thousand kilometres across Canada from northern Alberta to Labrador, and south a thousand kilometres from Labrador to upstate New York. A total of 34 lakes were studied over a three year period. Twenty-four of the lakes had lake trout as the top predator and this specie was the largest group analysed for contaminants (324 samples) (Muir et al., 2002).

In Europe, most monitoring of rivers is at the national level, but multinational or regional activities also exist, although data on biota is rather scarce (e.g. Rhine and Danube). For organic pollutants, no systematic measurements are done in fish and thus, no comprehensive data are available in the literature.

DDT

The Arctic char (*Salvelinus alpinus*), the lake trout (*Salvelinus namaycush*) and the lake whitefish (*Coregonus clupeaformis*) have been analysed in the Arctic lakes, clearly showing lower levels of DDTs when compared to levels in the Great Lakes (AMAP, 2000). Values range from 1.3-12.3, 0.2-15 and 0.3-44 ng/g ww, respectively. Elevated ΣDDT concentrations were found in fish from Wabush Lakes in Labrador presumably due to past use for biting fly control. In some isolated lakes in Ontario. pp'-DDE/ΣDDT ratios did not vary significantly among lakes which suggests that these were old DDT sources. However, the extent of contamination by DDT was surprising given that these fish were collected 30 years after cessation of use (Muir et al., 2002).

Recent data of DDT available for different freshwater fish species (e.g. cyprinids) in Italy range from 17 ng/g ww (River Po, eel) to 4030 ng/g fat weight in various fish species also in River Po. In Croatia, levels of DDT in various rivers and fish species are between 1 and 147 ng/g. In Egypt, DDT in fish species from various rivers (mostly Nile) range from 1 to 850 ng/g (UNEP, 2002e).

The finfish of Lake Victoria (Kenya) was studied in the years 1990 and 1992. The levels obtained were 3 - 460 ng/g for DDT. It should be noted that Lake Victoria feeds the river Nile that in turn feeds Lake Nubia. Generally, fish from Kenyan rivers have high DDT levels (85 –1185 ng/g). Nigerian rivers also have high DDT contamination in fish (3-161ng/g) (Osibanjo et.al 1994). Levels of total DDT in organisms of Lake Baikal were reported to be 0.28-0.3 mg/kg lipid for omul (fish), and 54-62 mg/kg lipid for Baikal Seal (Kucklick,. et al., 1993).

Analysis of four fish species from freshwater lake in Jaipur (India) revealed that the DDT residues were low in muscle tissue. In 1999, none of the fresh water fish samples collected from Kerala and Assam (India) contained DDT residues (Agnihotri, 1999). However, 75% of samples of fish rohu and catla collected from Calcutta market were contaminated with DDT and 29.2% exceeded the MRL value.

DDT concentrations in amphibian and fish samples in the Republic of Korea were reported as 170 ng/g and 4200 ng/g DDT, respectively. In China, the concentrations of DDT in freshwater fish were reported as 5-40.1 ng/g, in Russia as 280-300 µg/kg and Japan 7-18 ng/g.

In Nicaragua, Lake Xolotlán has deserved some attention because it receives the superficial runoff from its extensive drainage basin which is intensively cultivated. However, DDT or its metabolites were present in low concentrations in all the fish samples analysed. In Brazil, the vast majority of data on chlorinated compounds in freshwater fish refers to the Tietê River (São Paulo State) and the Amazonas. However, levels were below the maximum permitted by the Codex Alimentarius.

Cyclodiene pesticides and toxaphene

Toxaphene is the major OC contaminant in all freshwater fish and invertebrates that have been analysed from the Canadian Arctic and West Greenland as well as from the European Arctic (Paasivirta and Rantio, 1991). However, assessment of circumpolar trends in concentrations of persistent OCs in fish is difficult because of the limited number of samples per location analysed. Highest toxaphene levels are generally seen in fish that are strictly piscivorous such as lake trout and burbot (10.3-238 ng/g ww). The limited data suggest that compounds such as endosulphan, methoxychlor, and pentachloroanisole are not present at high levels in

Arctic fish in comparison with persistent OCs. Toxaphene was also a major OC in fish from Russian rivers (30-1300 ng/g) (AMAP, 1998).

Concentrations of aldrin, dieldrin and heptachlor in fish (*S. galileum*) from different sites in Lake Kinneret (Israel) were found in the range 0.5-106 ng/g (Zimand, 2002). In Egypt, the levels of pesticides were generally lower and much below the acceptable tolerance levels for human consumption (Dogheim et al., 1999; Yamashita et al., 2000).

The finfish of Lake Victoria (Kenya) was studied in the years 1990 and 1992. The levels obtained were 7 - 70 ng/g for dieldrin, 1 - 47 ng/g for lindane and 20 ng/g for aldrin. Generally, fish from Kenyan and Nigerian rivers have high PTS contamination as follows: dieldrin (nd-173ng/g), lindane (4-295 ng/g and 0.2-598 ng/g) and endosulphan (nd-110 ng/g and 3-904 ng/g).

Levels of chlordane and toxaphene in organisms of Lake Baikal were reported to be 0.09-0.141 and 0.93-1.3 mg/kg lipid for omul (fish), and 0.2-0.22, 1.5-1.7 and 2.2-2.3 mg/kg lipid for Baikal Seal, respectively (Kucklick,. et al., 1993).

Calero et al. (1993) found toxaphene in 81% of the fish samples from Lake Xolotlán (Nicaragua) in concentrations ranging from 24 to 1131 ng/g ww and, besides this, α-HCH, heptachlor, heptaclor-epoxide, aldrin and dieldrin were not detected.

HCB

Data are available for different fish species from River Po (*Rutilus pigus*, *Perca fluviatilis*, etc.), showing contamination in the range of about 4-21 ng/g ww. Mean levels of about 7 and 4 ng/g fat have been reported, respectively, for rainbow trout and eel from the same river (Galassi et al., 1994 and 1996).

In France, the concentrations of HCB in the rouch (*Rutilus rutilus*) collected in 1991 in the Seine river were in the range of 3.8-274 ng/g dw (Chevreuil et al., 1995). HCB has also been found in trout from isolated lakes in the Pyrenees (Spain) (0.10-0.22 ng/g ww), where only atmospheric inputs can be expected (Sanchez et al., 1993). HCB analysis in Japan was also detected in fish with frequencies of 10 % and maximum values of 2 ng/g ww.

HCHs

Levels of HCHs in Arctic freshwater fish (e.g.Arctic char and lake whitefish) are in the range of 0.2-3.0 ng/g, much lower than those found in industrialised areas. A number of fish (roach and perch) collected in 1991 in the Seine, Marne and Yonne Rivers (France) exhibited concentrations of lindane of 11-29 ng/g ww (Bintein and Devillers, 1996).

Fish samples collected in 1993 from the Nile River near Cairo showed concentrations of α-, β- and γ-HCH of 0.5, 1.5 and 0.2 ng/g ww, respectively. Lindane levels have declined in the Nile River and coastal lakes in recent years (Badawy and Wahaab, 1997; Yamashita et al., 2000).

The finfish of Lake Victoria (Kenya) was studied in the years 1990 and 1992. The levels obtained were 1 - 47 ng/g for lindane. Fish from Kenyan and Nigerian rivers exhibited lindane levels of 4-295 ng/g and 0.2-598 ng/g, respectively (Osibanjo et al., 1994). HCH was also present at low levels in several freshwater fish samples collected in different regions of India including markets. In China and Russia, freshwater fish contained HCH at levels of 2-240 ng/g and 20-21 ng/g, respectively.

PCBs

With the exception of the Arctic char, there is insufficient geographical coverage of any freshwater species to permit examination of circumpolar trends of PCBs. However, a north-south trend in PCB concentrations was previously observed in burbot liver collected from a series of lakes and riverine sites in central and north-western Canada (Muir et al., 1990).

Char and lake trout from Arctic lakes clearly have lower levels of PCBs (0.1-35.8 ng/g ww) when compared to levels in the Great Lakes. Lake trout from smaller remote lakes in Alberta and NW Ontario, which receive contaminants solely from the atmosphere, have PCB levels similar to Arctic salmonids, indicating that proximity to sources rather than north latitude is a critical factor in explaining spatial trends. Char from northern Norway and Finland had lower levels than char from southern Sweden (Lake Vättern), which is highly impacted by industries and towns.

The Canadian study referred above, reports PCB concentrations in approximately 860 fish and invertebrate samples. PCB concentrations (sum of 57 congeners) ranged from 1.4 to 1000 ng/g ww in lake trout and were generally much lower in other fishes. Median concentrations of ΣPCB in (whole) pike and walleye ranged from 5.2 to 38 ng/g ww, respectively (Muir et al., 2002).

These types of studies have also been performed in German rivers (e.g Elbe, Meuse, Rhine) (Gregor and Hajslova, 1998). Barbel, roach and perch were some of the species studied. Considering results obtained for barbel, the Czech part of Elbe may be considered among the heaviest PCB-contaminated waters in Europe.

Levels of PCBs were investigated in muscle of three cyprinids of the Po River: nase (*Chondrostoma söetta*), chub (*Leuciscus cephalus*) and barbel (*Barbus plebejus*) were in the range from 1174 to 5130 ng/g lipid, significantly lower than those found in a different selection of species in early 90's (Galassi et al., 1994, Viganò et al., 2000).

In Egypt, fish from various rivers (mostly Nile) exhibited PCBs levels from <1 to 52 ng/g ww (Dogheim et al., 1996; Abd-Allah and Abbas, 1994). The finfish of Lake Victoria (Kenya), studied in 1990 and 1992 showed levels of 20 - 332 ng/g for PCBs. Fish from Nigerian rivers exhibited PCB levels of 8-130 ng/g. Levels of total PCB and toxaphene in biota of Lake Baikal were reported to be 0.73-1.6 µg/g lipid for omul (fish) and 24-28 µg/g lipid for Baikal Seal (Kucklick et al., 1993).

PCBs congeners were determined in dolphin blubber and liver tissue and prey fish from the river Ganges (India) collected during 1994-96 (Senthilkumar, 1999). The concentrations found in blubber were 1100-13000 ng/g ww (av. 4000) and in liver tissue 180-390 ng/g ww. PCBs in fish from different locations in the river Ganges ranged from 100 to 270 ng/g ww.

In Japan in 1999, 40 fish samples among 70 showed PCB data more than the quantification limit, ranging from n.d. to 780 ng/g ww. PCBs in some amphibian and fish samples in the Republic of Korea were reported as 0.3 µg/g and 57.4 µg/g, respectively. In China, PCBs were reported as 2-267 ng/g for fish samples and in Russia as 730-1600 ng/g.

Fish from the Río de la Plata had higher PCB levels, compared with samples collected upstream along 1500 km on the Paraná and Iguazú rivers. The study of the sabalo (*Prochilodus lineatus*) showed consistent spatial patterns (Colombo et al., 1990). PCB concentrations are highest close to Buenos Aires sewer and industrial area (mean= 3.8±2.0 µg/g) and decrease in the Upper Paraná and Iguazú.

In contrast to the Argentinean results, Focardi et al. (1996) determined PCBs levels in fish muscle sampled at the Biobío River (central region of Chile) and observed upstream values around 530 ng/g of lipid, one order of magnitude higher than those of marine fish. The basin is characterised by pulp and paper mills, petrochemicals, forestry and diversified agriculture. The value of 1842 ± 1005 ng/g found for *M. cephalus* sampled in the river mouth may reflect the additional influence of the heavy local industrial activity.

PCDD/PCDFs

In the Great Lakes, considerable emphasis has been placed on the analysis of PCDDs and PCDFs. Recently, Kolic et al. (2000) reported on patterns and relative abundances PCDD/PCDF in fish found in the Ontario Great Lakes region. In the northernmost Great Lakes, Superior and Huron, the TEQ values for dioxin-like PCBs (DLPCBs) and PCDD/PCDFs are relatively low in comparison to the Lake Ontario fish samples. When comparing the PCDD/PCDF TEQ values at locations with the same fish species against those determined in an earlier study, there has been a general decrease in PCDD/PCDF levels in the Ontario region lakes.

There is a relatively large data set on PCDD/PCDFs in freshwater fish from Canada, Norway, and northern Finland and Sweden. TCDD levels are low (typically < 1 pg/g) in comparison to levels in fish sampled near bleached kraft mills or to species in the lower Great Lakes or the Baltic Sea.

High levels of dioxins and dioxin-like PCBs in eel from Dutch freshwater were reported in a screening of Dutch fishery products (van Leeuwen et al., 2002). Anticipating the new European MRL for dioxins and furans in fish (4 g PCDD/PCDF-TEQ/g ww), an extensive survey was carried out on PCB and dioxin contamination of eel from the Netherlands.

The dioxins and furans levels in aquatic organisms in rivers, lakes and coastal environment of Japan were from n.d. to 1.33 with the average of 0.46 pg-TEQ/g ww, from 0.34 to 0.44 with the average of 0.38 pg-TEQ/g ww and from n.d. to 2.90 with the average of 0.83 pg-TEQ/g ww, respectively.

Some of PCDD/PCDF concentrations in amphibian organisms and fish in the Republic of Korea were reported as 4.37 pg/g and 3.3 pg/g, respectively, for amphibia samples, and 2.23 pg/g and 6.91 pg/g, respectively, for fish samples.

3.2.2.2.2 Fish-eating birds

Fish-eating birds are the top predators in the aquatic food chain and can be used to assess chemical contamination in freshwater and marine environments. In addition, because of their mobility, the study results can be representative of a fairly large area, depending on the foraging pattern of the species. This feature may be desirable in some cases but may introduce interpretation difficulties in others.

A number of studies have focused on the use of eggs of aquatic birds as biomonitors. As an example, gulls have been shown to be a very useful monitoring matrix. Herring Gulls (*Laurus argentatus*) have been extensively monitored in the Great Lakes. DDT, dieldrin and mirex, and other chlorinated organics such as PCBs, HCB, dioxins and furans are routinely measured (Environment Canada 2000). Today, the Herring Gull continues to be recognised as one of the major indicator species for environmental contamination in the Great Lakes. The programme is one of the longest running wildlife monitoring programs for contaminants in the world.

Twenty-five years of monitoring has shown that concentrations were highest in the early and mid-70’s and that levels from all sites have decreased greatly since that time. Herring Gull eggs from sites in Lake Superior and Lake Erie were generally the least contaminated with PCBs, DDE and dieldrin compared to the other lakes.

The lower contaminant levels in gull eggs from Lake Superior were probably due to the lower levels of development, industry and human population along its shores, in comparison with the lower Great Lakes. However, contaminant levels in Lake Superior eggs have not decreased as fast as levels found in eggs from other regions of the Great Lakes, probably because of the relatively higher contribution of atmospheric sources.

Herring Gull eggs have also been collected from breeding colonies on the islands of the North Sea and Baltic Sea. A lot of very useful results from German Environmental Specimen Bank were published during recent years (Marth et al., 2000).

Audouin’s Gull (*Larus audouinii*) eggs have also been extensively monitored in the Mediterranean. Comparison between Western and Eastern basins has found levels significantly and consistently higher in the Western than in the Eastern basin.

Trends for total PCBs and DDTs are similar but in the latter case, the differences are even larger indicating a higher impact of industrial PTS sources for the Western basin. In general, median PCB levels show an intermediate position between the heavily industrialised North Atlantic and the pristine Arctic.

Other species widely studied are cormorants (*Phalacrocorax sp.*), bald eagles (*Haliaeetus sp.*), osprey (*Pandion haliaetus*), etc. The Osprey is a good indicator specie because, unlike some other top predators, it is remarkably tolerant of humans and will nest often near inhabited zones.

DDT

DDT has received particular attention in relation with the eggshell thinning effect and the devastating impact on fish-eating bird populations. OCs were measured in birds’ eggs collected in 1997 from the Danube Delta and it was found that DDT was the main contaminants in all samples (Aurigi et al., 2000).

Fassola et al. (1998) report on organochlorine pesticide levels in eggs of the little egret, *Egretta garzetta*, and the black-crowned night-heron, *Nycticorax nycticorax*, collected in 1993-1994 from heronries near Pavia, northern Italy. Levels of pp’-DDE in eggs of avocet and fish-eating birds (cormorant, gull, egret,…) of the River Po Delta were in the range of 206-1281 ng/g ww (Focardi, in UNEP 2002e). Eggs of *Egretta garzetta*, collected in the Göksu Delta (Turkey), were also analysed for DDT (3126 ng/g dw) (Ayaş et al., 1997).

DDT were also determined in eggs of Dalmatian Pelican (*Pelecanus crispus*) as well as in eels (*Anguila anguila*) the main pelican prey, collected at the wet lands of Amvekikos Gulf (Greece) during 1992-93. The biomagnification factors (BMF) of pp'-DDE in pelican eggs in relation to eels gave a value of 3.5 (Albanis et al., 1995). DDT were also measured in unhatched Audouin gull eggs from Aegean Sea (NE Mediterranean) colonies in 1997 and 1998 (1-1035 ng/g dw) (Goutner et al., 2001) and in four Greek wetlands using the cormorant *Phalacrocorax carbo* as a suitable bioindicator (Konstantinou et al., 2000).

Cyclodiene pesticides and HCHs

Levels of aldrin (0.1 – 3.4 ng/g dw), endrin (0.0 – 6.9 ng/g dw), heptachlor (0.1 – 3.0 ng/g dw), heptachlor epoxide (1 – 57 ng/g dw), α-HCH (0.4 – 11 ng/g dw), β-HCH (155 - 308 ng/g dw) and lindane (0.4 – 19 ng/g dw) were measured in unhatched Audouin gull eggs from Aegean Sea (NE Mediterranean) colonies in 1997 and 1998, whereas dieldrin was below the detection limit. Differences between years in the same regional colonies were attributable to temporal changes in diet (Goutner et al., 2001).

Lower residue values of aldrin (0.01 – 0.3 ng/g dw), heptachlor (0.3 – 0.9 ng/g dw), heptachlor epoxide (3.8 – 8.6 ng/g dw) and lindane were found in four Greek wetlands, using the cormorant *Phalacrocorax carbosinesis* as a bioindicator (Konstantinou et al., 2000).

α-HCH, β-HCH and lindane were determined in eggs of Dalmatian Pelican (*Pelecanus crispus*) as well as in eels (*Anguila anguila*), the main pelican prey collected at the wet lands of Amvakikos Gulf for a two year period, 1992 and 1993. The concentrations of these compounds in pelican eggs were 7.9 ± 3.2, 16.4 ± 5.4 and 7.6 ± 2.9 ng/g ww, respectively, and 6.5 ± 2.5, 10.1± 4.2 and 4.2± 1.6 ng/g ww in eels (Albanis et al., 1995b).

PCBs

PCB levels in eggs of avocet and fish-eating birds (*Phalacrocorax*, *Sterna* and *Larus sp.*) of the River Po Delta were in the range of 477 - 7085 ng/g ww (Focardi, 2002). Koci et al. (2000) determined PCB residues (145-656 ng/g ww) in eggs of a series of migratory birds (*Sterna* and *Pelecanus sp.*) inhabiting the Karavasta Lagoon, a natural protected area in Albania.

PCB levels were measured in unhatched Audouin gull eggs from Aegean Sea (NE Mediterranean) colonies in 1997 and 1998 (Goutner et al., 2001) and in four Greek wetlands, using the cormorant (*Phalacrocorax carbo*) eggs as a suitable bioindicator (Konstantinou et al., 2000). The median total of the PCBs (IUPAC Nos. 8, 20, 28, 52, 101, 118, 138, 180) were significantly different among the areas (12.2 - 68.4 ng/g dw).

Bird eggs from common gulls (*Larus dominicanus*) were analysed by Muñoz and Becker (1999) in order to correlate PCB levels with respect to their different throphic status and anthropogenic influence in different colonies sampled along the Chilean coast. PCBs levels were higher by a factor of two in central Chile (71-87 ng/g ww) compared to eggs collected in southern Chile (31-49 ng/g ww) reflecting the impact of anthropogenic sources. Nevertheless, average data of 6 PCB congeners indicate that levels are at least one order of magnitude lower than those reported for gulls' eggs in the northern hemisphere.

Focardi et al. (1996) analysed tissue residues of PCBs and other chlorinated pesticides in muscle and liver samples of three species of birds collected in the Biobío river basin (central Chile) in an attempt to evaluate a possible pollution gradient from the Andes (Santa Barbara) to the sea (380 km). Levels of PCBs were higher in the most urbanised area (Concepción) with an important industrial activity (3047-4398 ng/g lipid). The similar compositional pattern observed for PCB congeners in both areas indicates a common source for these PTS.

PFOS

The class of chemicals called fluorinated surfactants have been generating growing interest among environmental chemists. The presence of perfluorooctanesulfonic acid (PFOS) in liver samples of fish-eating birds has recently been reported. Table 3.4 shows some current representative concentrations of PFOS in the environment (Giesy and Kannan, 2001; Kannan et al., 2001). Future research is needed on the bioaccumulation potential of this chemical because of its widespread distribution and persistence.

Table 3.4. Current Representative Concentrations of PFOSs in the Environment

Animal	Location	PFOS concentration	Units
Herring Gull blood	Great Lakes	66-79	ng/mL
Herring Gull plasma	Great Lakes	277-453	ng/mL
Cormorants	Lake Huron	340	ng/L
Cormorants	Lake Superior	92	ng/L
Bald Eagle Plasma	Midwest US	2-2570	ng/mL
Albatross sera	Pacific Midway Is.	3.5-20	ng/mL
Cormorant egg yolk	Washington DC	24-254	ng/g
Chinook fish liver	Great Lakes	110	ng/g
Ringed Seal Plasma	Canadian Arctic	<3-12	ng/mL
	Baltic Sea	16-230	ng/mL
Gray Seal Plasma	Canadian Arctic	11-49	ng/mL
	Baltic Sea	14-76	ng/mL
Polar Bear Liver	Alaska	180-680	ng/g
Polar Bear Blood	Alaska	26-52	ng/g

3.2.2.3 Marine environment

The marine environment has probably been the most extensively monitored ecosystem, although it provides very different conditions in the context of measurements of PTS in biota. Organisms inhabiting coastal areas have often been proposed as sentinels for monitoring PTS of land-based origin because they may concentrate indicative hydrophobic compounds in their tissues, directly from water through respiration and also through the diet.

"Mussel Watch Programmes" which examine chlorinated hydrocarbon compounds in bivalves around the world, offer a way to identify persistent hot spots, as well as to investigate temporal trends in the marine environment over the long term. Benthic marine organisms have also been sampled for a range of PTS. Their restricted mobility and contact with substrate makes them useful as monitors of local pollution. Feeding and growth exhibit strong seasonal patterns, implying that capacity for uptake of PTS will vary through the year. Interpretation of PTS loading in individuals can be complex.

In the pelagic system, vegetation comprises microscopic phytoplankton with short turnover times. Zooplankton, however, tend to be large and often long-lived. Predators include cephalopods, fish, birds and mammals. With the exception of cephalopods, these predators are typically long-lived. Many species of birds and mammals migrate from high to lower latitudes and back, so that their pollutant loadings will integrate inputs from both outside and within the regions in the case of PTS with long turnover times. Even at lower levels in the food web, the mobility of pelagic organisms means that they will integrate environmental PTS loadings over large spatial and temporal scales.

In the following sections, information on three representative levels in the food web, namely bivalves, fish and marine mammals, will be summarised.

3.2.2.3.1 Marine invertebrates

Bivalves have been extensively used to assess the occurrence of PTS in the coastal marine environment. The NOAA´s International Mussel Watch Program has significantly contributed to extend this methodology world-wide for pollution assessment. To this end, a variety of species have been used, namely mussels, oysters, clams, etc. The data obtained should provide a basis for the comparison of the distribution of PTS at a global level, but unfortunately, they are very sparse. The PTS reported below are those more frequently and widely monitored as described in the Regional Reports. Crustaceans have also been widely monitored, particularly in highly productive areas like the coastal lagoons of the subtropical Mexican Pacific or in Antarctica (krill). However, the peculiar ecology of the latter makes it difficult to compare with pelagic crustacea at lower latitudes.

DDT

Concentration ranges in mussels (*Mytilus sp.*) collected in different coastal areas of the world are shown in Table 3.5. Although circumpolar coverage for marine invertebrates is poor, the results in bivalves generally indicate higher levels of DDTs (DDT+DDE+DDD) in Russian waters than in samples from Iceland or Greenland In contrast, the European Atlantic coasts and the Mediterranean are routinely monitored as part of some national monitoring programs (e.g. France, Italy,…). In general, pp'-DDE was the predominant component in all organisms, and the concentrations are too diverse to detect any trend, except the occurrence of local hot spots. Only few studies have been reported in Sub-Saharan Africa, mainly focused in Cameroon and Nigeria. In the Southeast Asia and South Pacific Region (e.g. Thailand, Philippines, Malaysia, Australia, etc.) the bivalve mainly used for monitoring is *Perna viridis*.

In the Atlantic and Pacific Coasts of Central America, the initial monitoring phase of the NOAA´s International Mussel Watch was carried out in 1991-1992 (Farrington et al., 1995). The general levels measured were within the ranges found in other moderately contaminated coasts. According to this study DDTs were the most prevalent organochlorine compound found in biota. DDTs were also the dominant chlorinated pesticide in the samples analysed within the South America Mussel Watch Program. Concentrations were higher in Recife and Santos Bay (Brazil) and Río de la Plata (Argentina). Asiatic clams (*Corbicula fluminea*) were used as sentinel organisms (Farrington and Tripp, 1995).

Cyclodiene pesticides

Much data on chlorinated pesticides date from the 80's with fewer from the last decade, probably because of the ban of all these compounds in most countries. More recent data is shown in Table 3.5. Mussels (*Mytilus sp.*) have been analysed in the Mediterranean. Green mussels (*Perna viridis*) have been largely sampled in the coasts of Republic of Korea and West Malaysia, with aldrin, heptachlor and endosulphan the predominant analytes. In the Pacific Islands (Fiji, Tonga, Solomon,…), endrin and aldrin were below the detection level in shellfish.

Table 3.5. Representative levels of PTS in bivalves from different regions of the world (Reported data during the 90's, in µg/kg ww)

	DDTs	"Drins"	HCHs	PCBs	PAHs
Arctic					
-Greenland	0.24-0.81		0.39-0.82	0.59-1.40	
- Russia	1.29-2.17		0.26-0.28	3.46-5.29	
Europe					
-Atlantic coast	0.7-45		4.2 (av.)	1-12	25 (av. dw)
Mediterranean	0.2-157	0.01-2.4	2.5 (av.)	2-30	82 (av. dw)
Morocco	7-29		0.5-6.4		3.4-34.6 (dw)
Sub-Saharan Africa	37-113		0.8-144		
Arabian Gulf				0.5-3.8	4-23 (dw)
Rep. of Korea	3.6-350	0 - 13.5			
Japan		0-160			
Southeast Asia	0.1-38	0-15.7	0.01 – 20	0.01 – 0.43	
New Zealand	0-3			0.11 – 12.9	
Pacific Islands	0.3-52	<0.1-0.6	0.1-0.9		
Central America					
-Pacific coast	2-134			3.4 – 29	120-250 (dw)
-Atlantic coast	2.4-199	1.6 (av.)	2.8-4.2	1.7-144	
South America					
-Pacific coast	0.8-10	<0.01-4.73			10-200 (dw)

The International Mussel Watch Program carried out at the Central and South America coasts revealed the occurrence of "drins" and chlordane in some samples, the latter being the most abundant (0.46-16.0 µg/kg) (Farrington and Tripp, 1995). Recent studies performed in the Caribbean (Jamaica) have shown decreasing levels of dieldrin whereas those of endosulphan (3.6 ± 1.4 µg/kg) were increasing (Mansingh, 2000).

HCHs and HCB

Among the HCH isomers, lindane is usually the predominant component. The large survey of mussels performed during 1995-99 in the French Atlantic and Mediterranean coasts (over 700 samples) showed α/γ-HCH ratios of 0.25 (RNO, 2001). In the South-western Pacific coast, the higher levels of HCHs in green mussels (*Perna viridis*) were found in the Gulf of Thailand (Monirith et al., 2000).

HCB has been widely distributed in the Western Mediterranean. Concentrations in the range of 0.2 – 3.0 µg/kg ww were found in mussels collected in early 90's in the Western basin (UNEP, 2002e). Another study has reported that the organochlorine pesticide with the highest frequency of occurrence and concentration in mangrove oysters (*Crassostrea corteziensis*) along the Pacific Coast of Mexico was HCB, which is used alone or in combination with other fungicides in mixed seed protectants. High HCB concentrations were found in oysters from lagoons bordered by extensive agricultural lands (183 - 911 µg/kg). Values were low in areas with limited agricultural activities (1.1-2.0 µg/kg) (UNEP, 2002c).

A number of shellfish species from Pacific Islands have been analysed with HCB contents of <0.1-0.1 µg/kg (Fiji, Tonga and Solomon) (UNEP, 2002j).

PCBs

Few studies report PCB levels in Arctic and Antarctic invertebrates which will accumulate their entire PCB loading within the regions and will probably be sensitive to local inputs. In the Arctic, the results seem to indicate higher levels of PCBs in biota from Russian waters than in samples from Iceland or Greenland (Table 3.5). In Antarctica, concentrations in bivalve tissues showed high levels of PCB contamination close to the McMurdo station (380-430 µg/kg), but not at remote sites (5-22 µg/kg) (Kennicutt et al., 1995).

In the Mediterranean, the levels of PCBs found in mussels (*Mytilus sp.*) indicate that rivers and wastewater discharges are the major sources of PCBs in coastal areas, and that the values are higher in the Western than in the Eastern coast. PCBs were also found in green mussels (*Perna viridis*) in the South-western Pacific coast, with rather low levels (Monirith et al., 2000).

Mangrove oysters (*Crassostrea corteziensis*) collected in 1996 at 14 mangrove sites along the Pacific Coast of Mexico extending southward from the state of Sonora to Jalisco (about 1100 km) showed low concentrations of PCBs in non urban areas (3.4 - 29 µg/kg) while high concentrations were found near to suburban centres (390 - 655 µg/kg). Compared with earlier data, it appears that the levels were increasing in these areas. The mangrove bivalve *Anadara tuberculosa* was also used for monitoring PCBs along the Pacific Coast of Costa Rica. The concentrations in 137 samples were in the range of 8.3-266 µg/kg dw (UNEP, 2002k).

In South America, the Mussel Watch reported baseline PCB concentrations ranging from 200-700 µg/kg lipids in unpolluted sites; 1000-3000 µg/kg in samples from moderately contaminated sites, and 4000-13000 µg/kg lipids in most affected bivalves. Sampling sites showing high PTS levels in the region include Recife (Brazil), Río de la Plata (Argentina) and Punta Arenas (Chile) (Farrington and Tripp, 1995).

TBT

Since the discovery of TBT in bivalves from the Arcachon Bay (France) it has been extensively monitored in Mediterranean harbours and marinas. The first survey in Spain was conducted in 1988 in the NE coast (Tolosa et al., 1992). Concentrations of TBT in clams (*Tapes decussata*) and mussels (*Mytilus galloprovincialis*) were found to be 900 µg/kg and 200 µg/kg ww, respectively. A survey conducted ten years later (Morcillo et al., 1997) still showed elevated concentrations of TBT. In the SW of Spain, levels of TBT in bivalves were generally <400 µg/kg (Gomez-Ariza et al., 1995). Mussels collected along the Portuguese coast exhibited, in certain places, values of 200-838 µg/kg of TBT and no traces of MBT and DBT, indicating recent inputs of the compound. TPhT was also found at high concentrations (up to 800 µg/kg). Mussels and clams collected in the Alexandria harbours were also analysed and exhibited concentrations of 97-420 µg/kg and 93-320 µg/kg of TBT, respectively (Abd-Allah, 1995).

In the Republic of Korea, levels of TBT reported in bivalves were in the range of 16-2800 µg/kg, whereas in Japan levels were much lower. The levels of organotins in mussels and shrimps from the Pearl River Estuary were found to be 13.2 µg/kg and 3.6 µg/kg, respectively (Zhang et al., 2002).

Organomercury compounds

Mercury has been a subject of special concern in the Mediterranean where generally concentrations in organisms have been higher than those found in the Atlantic. These higher concentrations were attributed to the higher natural background levels of mercury and not to anthropogenic contamination. In 1996, a large survey of methyl mercury in bivalves along the French coast was carried out. Mussels and oysters were collected in 96 stations included in the National Monitoring Network (Claisse et al., 2001). The concentrations found were similar in both species and ranged from 8 to 238 mg/kg dw with a mean of 64 ± 35 mg/kg. The higher values were found along the Brittany coast and the Rhone delta although they were all below the WHO guideline and the maximum permissible level in sea food. In the Arabian Gulf, methyl mercury was also determined along with total mercury. The level of methyl mercury in bivalves from Kuwait was 0.045 mg/kg and, in Saudi Arabia, ranged from 0.011-0.045 mg/kg ww.

PAHs

Concentrations of PAHs in bivalves exhibit a large variability, the highest values being usually associated with coastal urban and industrial areas. Data given for the 14 priority PAHs in *Mytilus sp*. from the Nothwestern Mediterranean Sea (Table 3.5) include values up to 390 µg/kg dw in mussels collected inside harbours (Baumard et al., 1998). In the Eastern basin, values ranged up to 750 µg/kg dw (UNEP, 2002e).

In a study carried out at 14 mangrove sites along the Pacific Coast of Mexico, using the oyster *Crassostrea corteziensis*, concentrations were found in the range of 120-250 µg/kg except in the area of Ensenada lagoons where the values measured were 1820 - 3520 µg/kg. PAHs were also included in the South America Mussel Watch Program (Farrington and Tripp, 1995). In less polluted areas, background levels in bivalves were below 10 µg/kg lipids and above 200 µg/kg in some impacted sites such as Punta Arenas (Chile), Recife (Brazil), Concepción (Chile) and Bahía Camarones, Río de la Plata and Bahía Blanca (Argentina).

A number of accidental oil spills have been monitored using bivalves. Kennicutt et al. (1995) undertook extensive sampling of inter-tidal limpets in response to the grounding of the Bahia Paraiso (Antarctica). Total PAHs loading in whole tissue samples reached 125000 µg/kg dw in the initial phase of the spill, decreased about ten-fold over the 7 weeks following the spill and declined to about 180 µg/kg dw two years later. Cripps and Shears (1997) found that limpets from uncontaminated sites in the Southern Ocean will have PAH tissue concentrations of <100 µg/kg dw.

The maximum levels of PAHs in bivalves from different Arabian Gulf countries, soon after the Gulf War were from 2.8-54.1 µg/kg dw. Mussels (*Mytilus sp.*) were also used to survey the spatial and temporal evolution of the Aegean Sea oil spill in the Galicia coast (Spain). Concentrations of 330-2440 µg/kg dw of 12 parent PAHs were found just after the spill (December 1992) and 75-564 µg/kg dw one year later (Porte et al., 2001). An extensive monitoring of mussels was also carried out after the Exxon Valdez oil spill (ASTM, 1995).

3.2.2.3.2 Fish

A high diversity of fish species from all parts of the world and representing different habitats, has been analysed for PTS. Territorial species, particularly coastal and benthic fish, are usually selected for monitoring purposes as in the case of bivalves. PTS loads in pelagic and migratory fish are less informative but may provide an overall idea about the global distribution of PTS in the marine environment. Organochlorinated compounds, particularly DDTs and PCBs but also cyclodiene pesticides, HCHs, HCB, dioxins, furans and PAHs have been the most intensively investigated pollutants. A major problem in assessing levels is the diversity of units used in reporting data. Therefore, only a general overview is given in the following sections.

DDT

Cod fish (*Gadus morhua*) has been widely monitored in the Arctic whereas a variety of other fish have been studied in the Antarctic. The concentrations of DDTs in the liver of Atlantic cod and the common dab (*Limanda limanda*) ranged from 56-253 and 12-54 µg/kg ww, respectively. Weber and Goerke (1996) sampled various species of fish off the Antarctic Peninsula between 1987 and 1991, especially

Chaenocephalus aceratus, *Chamsocephalus gunnari* and *Gobionotothen gibberifrons*. Concentrations of pp'-DDE were 2-40 µg/kg lipid and were one to two orders of magnitude lower than in North Sea fish. Focardi et al. (1992) present data for a range of Antarctic fish species but mainly *Chionodraco hamatus* and *Pagothenia bernacchii*, sampled in 1987-90. Concentrations in liver were about ten times the levels in muscle and ranged from 25.0 to 52.7 µg/kg dw for pp'-DDE in the two species and 14.6 to 8.1 µg/kg dw for pp'-DDT.

Long-term monitoring of DDT in biota samples has been carried out in the Baltic since the 70's. Many authors consider the Baltic herring (*Clupea harengus*) to be a good indicator of the Baltic Sea ecosystem pollution by PTS (Roots, 1996; Falandysz et al., 1997). The concentrations of DDTs in herring muscle vary between 61-710 µg/kg lipid, decreasing to the north and west.

In the Mediterranean Sea, the red mullet (*Mullus sp.*), a benthic and territorial fish of commercial interest in the region, has been selected as a biomonitor. In general, pp'-DDE was the predominant component in all samples and the concentrations are too variable to detect any trend except the occurrence of local hot spots. Concentrations were in the range of 2-15 µg/kg ww of total DDTs (DDT+DDE), with values up to 230 ng/g ww in the NW coast and <1 µg/kg ww in Corsica and Sardinia Islands (Porte et al., 2001).

DDTs were also measured in a variety of mesopelagic (*Lepidorombus* and *Phycis sp.*) and deep sea fish species (*Lepidion*, *Coryphaenoides*, *Bathypterois* and *Mora moro sp.*) collected in the Western Mediterranean. The concentrations (0.4-10.2µg/kg ww) can be considered as the background values for the region (Porte et al., 2000; Garcia et al., 2000).

The Adriatic Sea has been investigated for the occurrence of chlorinated hydrocarbons. DDTs were determined in several fish species (*Gobius sp.*, *Mullus barbatus*, *Diplodus annularis*, *Oblada melanura* and *Merluccius merluccius*) collected from three areas in the Eastern coastal waters. Average levels were in the range 37-124 µg/kg ww (Bayarri et al., 2001). *Mullus barbatus* was also the indicator species used in the Aegean Sea. A large survey conducted from 1986 to 1995 in both the Greek and Turkish coasts determined a relatively low level of pollution in this area. Conversely, concentrations of DDT in Black Sea fish are high by comparison with those reported for other regional seas (Tanabe et al., 1997).

Levels of pp'-DDE were also measured in bluefin tuna (*Thunnus thynnus*) and swordfish (*Xiphias gladius*) collected off the Italian coast in 1999. Mean concentrations of pp'-DDE in tuna was 49 µg/kg in muscle. In swordfish, pp'-DDE values ranged 45-69 µg/kg wet wt in muscle (Kannan et al., 2001).

The recent available data from the contaminant screening survey in Arabian Gulf States (Al-Majed et al., 2000) showed that the mean concentrations of chlorinated pesticides in fish muscle were low. In Kuwait for instance, five different fish species were examined and the range of DDE and DDT was found to be 1.6-26 and 0.03-2.3 µg/kg dw, respectively.

Bottom-feeding fish were studied from the Bay of Bengal off India as part of a monitoring programme. Concentrations of DDTs ranging from 1.31 to 115.9 µg/kg ww in four species were found. The levels in other areas of the Indian south-east coast were from ND-2.38 µg/kg (Rajendran et al., 1992). Fish samples from the Japan Sea were found to contain 20 - 1200 µg/kg of DDTs.

Fish samples collected in Australia, Viet Nam and Indonesia seem to have higher levels of DDT than other parts of the Southeast Asia and South Pacific region. Levels were in the range of 22-28 µg/kg ww, whereas in Thailand and Cambodia levels were 6.2-8.1 µg/kg ww (Kannan et al., 1995; Monirith et al., 1999). Total DDT was relatively low in Malaysian fish (0.1-6.0 µg/kg ww) and decreasing compared to earlier studies (Hossain et al., 2001).

DDT levels in fish samples from the Pacific Islands ranged from 0.1-24 µg/kg ww, although some very high values have been reported for some samples probably indicating some local hot spots (Kannan et al., 1995).

DDT levels in commercial fish samples have been reported in Colombia (ΣDDT 0.7 – 0.78 µg/kg ww) and in Honduras (0.2-2.6 mg/kg lipids) (UNEP, 2002k). DDT residues in fish tissues collected along South America coast (mainly in Brasil and Argentina) show wide variability (88 – 27125 µg/kg lipids) depending on the species and the collection sites.

Cyclodiene pesticides

Cyclodiene pesticides have been determined during the last 20 years in a large number of fish in coastal areas of Spain, Egypt, Morocco, in the middle and north Adriatic Sea, Greece, Turkey, etc. (UNEP, 1990). Concentrations of aldrin, dieldrin, endrin and heptachlor in *Mullus barbatus* were in the low µg/kg range. Values of 0.1-1.0 µg/kg ww were reported, for example, in samples collected along the coasts of Greece and Turkey (Giouranovits et al., 1994; Kucuksezgin et al., 2001).

In the south-east coast of India, aldrin levels were 0.3 to 4.2 µg/kg in fish tissues (Shailaja and Singhal, 1994). Aldrin, dieldrin, heptachlor and, less frequently, endrin, were also found in fish samples from Malaysia and Pacific Islands with concentrations in the range of <0.1-9.5 µg/kg ww. Values from the Guam Island were very high, probably reflecting a local hot spot (Kannan et al., 1995; Hossain et al., 2001).

Toxaphene and chlordane

Toxaphene was found to be the major OC contaminant in muscle of cod from the Canadian Arctic. The levels in Atlantic cod liver from the Barents Sea were lower than those found in cod from the Norwegian Sea and from the northern parts of the North Sea. The lowest OC concentrations were found in livers of cod from different stocks in Icelandic and Faeroese waters. On the other hand, relatively high levels of OCs were found in Greenland halibut liver and muscle. Levels in muscle are three to five times higher than levels in sea run char muscle and 15-20 times higher than Arctic cod.

In turn, chlordane and mirex have been found in various species of fish collected between 1987 and 1991 off the Antarctic Peninsula, especially *Chaenocephalus aceratus*, *Chamsocephalus gunnari* and *Gobionotothen gibberifrons*. Concentrations were similar in liver and adipose tissue for all species, being 0.5-12.5 µg/kg lipid for mirex and 0.5-6 µg/kg lipid for trans-nonachlor (Weber and Goerke, 1996).

Chlordane was a major pesticide in fish samples from the Japan Sea (6.6 - 510µg/kg). It was also found in fish samples collected in the different Pacific Islands at levels of <0.01-2.1 µg/kg ww. Fish samples collected in Australia seem to also have high levels of chlordane (51µg/kg ww) compared to the other parts of the Southeast Asia and South Pacific Region (0.1-2.6 µg/kg) (UNEP, 2002i).

HCHs

An extensive survey of red mullet (*Mullus barbatus*) carried out between 1986-91 in 8 coastal stations of the Aegean Sea revealed concentrations of α and γ-HCH of 0.1-0.5 µg/kg ww and 0.6-3.5 µg/kg ww, respectively. Lindane was also found in red mullet collected between 1993-99 in the Cyprus coast (0.6-1.3 ng/g dw).

Fish samples from the Japan Sea were found to contain 2.1 – 3100 µg/kg of HCHs. HCHs were also widespread in fish from the Southeast Asia and South Pacific Region, with values within the range of 0.3 – 1.8 µg/kg ww (Kannan et al., 1995). In Malaysia however, higher levels were found (0.3-8.3 µg/kg ww) (Hossain et al., 2001). HCH levels in fish samples from the Pacific Islands were low ranging from <0.01-4.2 µg/kg ww (Kannan et al., 1995).

HCB

Concentrations of HCB in various species of fish off the Antarctic Peninsula (*Chaenocephalus aceratus*, *Chamsocephalus gunnari* and *Gobionotothen gibberifrons*) collected between 1987-91 were about 20 µg/kg lipid, similar to levels found in North Sea fish. The level was interpreted as a result of cold condensation increasing environmental levels (Weber and Goerke, 1996). Focardi et al. (1992) present data for other fish species sampled in the Ross Sea region in 1987-90. Most data refer to two species, *Chionodraco hamatus* and *Pagothenia bernacchii* and average concentrations in the liver were 8.4 µg/kg dw and 3.4 µg/kg dw, respectively.

HCB has been determined since the 70's in the Baltic herring (*Clupea harengus*), which has been considered a good bioindicator. In the Mediterranean, the indicator species has been the red mullet. Measurable amounts of HCB have been found in all samples collected along the NW Mediterranean coast, with levels in the range of 0.24-2.80 µg/kg ww. HCB was also measured in a variety of deep sea fish species (*Lepidion*, *Coryphaenoides*, *Bathypterois* and *Mora moro sp.*) collected in the Western Mediterranean. The concentrations (0.1-0.7µg/kg ww) can be considered as the background values for the region (Porte et al., 2000).

Fish samples from the Japan Sea were found to contain HCB (1.3 – 120 µg/kg). HCB was detected in all fish samples collected in the Southeast Asia and South Pacific Region with much higher values in Australia (4.2 µg/kg ww) than in other parts of the region (0.0-0.2 µg/kg ww). In the Pacific Islands HCB levels in fish were very low ranging from <0.10-0.3 µg/kg ww with some values up to 3.3 µg/kg ww (Kannan et al., 1995).

PCBs

Low PCB levels were found in Greenland halibut muscle from the Norwegian and Barents Sea. In Antarctica, Larsson et al. (1992) analysed the liver of fish *Pagothenia bernachii* and found concentrations of total PCBs of 70 µg/kg fat. Weber and Goerke (1996) analysed various species of fish in the Antarctic Peninsula region (*Chaenocephalus aceratus*, *Chamsocephalus gunnari* and *Gobionotothen gibberifrons*). Concentrations of individual compounds were measured (e.g. PCB-153 0.5-7.4 µg/kg lipid) and found to have a slight increase from 1987 to 1991 suggesting that loadings of PCBs reflected global re-distribution.

PCBs have been determined since the 70's in the Baltic herring (*Clupea harengus*). Muscle concentrations are highest in southern Baltic proper and decrease to the north and west. Lowest concentrations were found off the Estonian coast (120 µg/kg lipid) and highest near the Polish coast (2800 µg/kg lipid). Concentrations of PCBs in Black Sea fish are high by comparison with those reported for other regional seas (Tanabe et al., 1997).

The distributions of PCBs in different Mediterranean fish indicate that rivers and wastewater discharges are the major sources of PCBs in western Mediterranean coastal areas. PCBs are higher in coastal areas close to large cities receiving river discharges (av. 527 µg/kg dw). The levels in the French Atlantic coast are slightly higher than in the Mediterranean (RNO, 2001). Levels of PCBs (Σ19 cong.) in benthic fish collected along the Atlantic coast of Portugal were in the range of 1-12 µg/kg ww (Ferreira et al., 1998).

The accumulation of PCBs in red mullet, mackerel and anchovy from the Adriatic revealed detectable differences among species and sites. Higher concentrations were found in the northern area and in mackerel (94 -177 µg/kg ww) (Bayarri et al., 2001). PCB levels in fish collected from the Egyptian Mediterranean coast ranged from 18 to 32 µg/kg (Abd-Allah et al., 1998). Most recent data show concentrations much higher in the Western than in the Eastern Mediterranean coast. Representative concentrations of PCBs in Mediterranean pelagic and deep sea fish are 1.0 – 16 µg/kg ww (Porte et al., 2000).

PCBs were also analysed in bluefin tuna and swordfish off the Italian coast. Concentrations of total PCBs in livers of *Thunnus thynnus* ranged from 224 to 1660 µg/kg ww (mean: 934). Mean PCB values in pooled samples of liver and muscle of swordfish (*Xiphias gladius*) were 745 and 329 µg/kg ww, respectively (Kannan et al., 2001).

PCBs are the major organochlorine residues in fish tissues collected in the South America coast (mainly Brazil and Argentina) showing variability that depends on the environmental features (30- 47550 µg/kg lipids). Fish samples from the Japan Sea were found to contain 3.8 – 950 µg/kg of PCBs. Fish samples collected in Australia seem to have high levels of PTS compared to other parts of the region. In particular, PCBs were more than 10 times higher (55 µg/kg ww) (Kannan et al., 1995). PCB levels in fish samples from the Pacific Islands ranged from 1-23 µg/kg ww although high values have been reported for some samples probably indicating local hot spots (Kannan et al., 1995).

PCDD/PCDFs

Data on PCDD/PCDFs are very limited compared to OC pesticides and PCBs. The dioxin concentrations in 7 pools of herring muscle along the Finnish coast varied between 165 and 329 pg-TEQ/g lipid, corresponding to 2.9-24 pg/g ww. The highest concentrations were found in the inner part of the Gulf of Finland (Vartiainen et al., 1997).

PCDD/PCDFs in samples of selected fish species from the Adriatic Sea ranged between 0.23-1.07 pg TEQ/g (Bayarri et al., 2001). In general, levels were greater for those species at higher levels in the trophic web (mackerel > red mullet > anchovy). PCDD/PCDFs were also analysed in *Thunnus thynnus* and *Xiphias gladius* collected off the Italian coast in 1999. Concentrations were less than the limits of detection which varied from 1-75 pg/g ww (Kannan et al., 2001). Cod fish and sharks collected in the Japan Sea exhibited concentrations of PCDD/PCDFs in the range of 0.10 - 0.95 pg TEQ/g and 0.15 - 1.2 pg TEQ/g, respectively.

PAHs

Concentrations of PAHs in marine biota indicate a high degree of contamination of certain areas. Baumard et al. (1998) determined the 14 priority PAHs in fish livers (*Serranus* and *Mullus sp.*) of specimens collected off the French and Spanish Mediterranean coasts and found values of 27-87 and 15-49 µg/kg dw, respectively. Similar determinations carried out in deep sea fish from the NW Mediterranean basin (*Mora sp.*) showed liver concentrations of 7-16 µg/kg ww (Solé et al., 2000).

PAHs were determined in fish soon after the Gulf War. The maximum levels of PAHs in fish from Kuwait, Saudi Arabia, Bahrain, UAE and Oman were 136, 196, 135, 18.4, 38.2 µg/kg dw, respectively (Fowler et. al., 1993). A recent contamination screening survey conducted in 1998-2000 by ROPME (Al-Majed et al., 2000) detected PAHs in fish muscle from 4.7-13.5 µg/kg dw from Kuwait, 2.8-11.9 µg/kg dw from Saudi Arabia, 0.7-8.7 µg/kg dw from Qatar and 1.5-9.6 µg/kg dw from UAE. One of the most extensive surveys of PAHs in fish was carried out after the Exxon Valdez oil spill occurred in Alaska (1989) (ASTM, 1995).

Organotin compounds

Watanabe et al. (1998) conducted a study in 1993-94 on the organotin compounds in tissues of fish captured in the Gulf waters. Fish of seven species caught from the shore of Saudi Arabia, Bahrain, UAE and the Strait of Hormuz were analysed. The levels of TBT were nd-21 µg/kg ww in muscle and from nd -50 µg/kg ww in liver tissues, increasing along the Arabian shore from the north to the Strait of Hormuz. TPT in muscle ranged from n.d. to 7 µg/kg ww and in liver from n.d. to 40 µg/kg ww.

In Japan, TBT and TPT were detected in some marine fishes (10 and 13 out of 70 samples, respectively) with levels up to 160 and 100 µg/kg ww, respectively. The reported TBT concentrations of fish samples from China were in the range of 4.8-18.8 µg/kg (Zhang et al., 2002).

Organomercury compounds

Mercury (organic and inorganic) was monitored in marine organisms since the inception of the MEDPOL programme as initial results indicated that mercury concentrations in Mediterranean species were generally higher than those found in organisms from the Atlantic. A total of 115 samples of fifteen kinds of fish caught in different European coastal areas were analysed during 1997. The mean content of total mercury and organic mercury in pooled samples were 111±100 ng/g and 95±87 ng/g, respectively. The highest values of total mercury (119±111 ng/g) and organic mercury (103±96 ng/g) were found in bathypelagic fish.

Total mercury and methyl mercury concentrations were measured in tuna fish and sharks from the South Adriatic Sea. The highest mean levels of total mercury were found in *Squalus acanthias* (6.5 µg/g ww). In the other species, mean mercury levels were notably lower (0.46 µg/g ww for *Auxis rochei*: 0.38 µg/g ww for *Prionacee glauca*). The analytical data showed that mercury was present mainly in the organometallic form with percentages between 69 and 100% (Storelli et al., 2001).

In 1993-1994, after the Gulf War, a total of 72 fish samples of 28 species were collected in the region and total mercury and methyl mercury were determined in muscle (Al-Majed et al., 1998). The average concentration of total mercury was found to be 0.80-mg/kg dw with a range of 0.250-3.201 mg/kg dw. The mean value of methyl mercury was 0.76 mg/kg dw with a range of 0.144-2.944 mg/kg dw. More recently, Al-Majed and Preston (2000) determined total and methyl mercury in zooplankton and various fish species (N=330) collected from Kuwait Bay and Northern area of Kuwait. The total mercury concentration in zooplankton ranged from 0.004-0.035 mg/kg dw with methyl mercury less than 25% of the total. Total and methyl mercury in fish differed between species and ranged from 0.073 mg/kg in *Liza subviridis* to 3.923 mg/kg in *Epinephelus coiodes*.

3.2.2.3.3 Marine mammals

Marine mammals are usually migratory species, so that their pollutant loading will integrate PTS inputs from different regions. Then, the main significance of the values found relates to the fact that they are at the top of the trophic web and therefore represent the higher levels that biota may achieve in the marine environment.

Data are available for concentrations of major PCB congeners, DDT, chlordane-related compounds, HCH isomers, and HCB in Arctic and Antarctica marine mammals. Less frequently measured are the toxaphene components and cyclodienes (dieldrin, endrin). PCDD/PCDFs have been determined in seals from Arctic Canada, northeast Greenland and Svalbard, but information on their spatial trends is limited.

Whales, seals and dolphins from other regions (e.g. the Eastern and Western Pacific coasts, the Caribbean and Mediterranean Seas, etc.) have also been analysed. Relevant data is decribed below and in Table 3.6.

DDT

Harp and ringed seals have been the most studied species in the Arctic. A west to east increase in DDT levels from North America to western Russia has been observed in blubber samples. DDT levels in harp seals from northeastern Greenland were found to be about two to three-fold lower than those from northern Norway and western Russian waters. Highest levels of DDTs in Arctic ringed seals were found in samples from the Yenisey Gulf (Table 3.6).

Table 3.6. Levels of DDTs and PCBs in blubber samples of marine mammals (in μg/kg ww)

	seals		whales	dolphins	
	DDTs	PCBs	PCBs	DDTs	PCBs
Arctic	225-3600	241-2870			
Antarctica	116	100			
Mediterranean					
Italian coast				4400-635000 (dw)	6900-1345000 (dw)
Atlantic Ocean					
Caribbean Sea	1300 – 2300		700 – 1600	1400-7400	2000-5000
Argentina				1670- 4320 (fat)	1980 – 3300 (fat)
Pacific Ocean					
Costa Rica				2700-6500	1500-6400
China, Japan				2600-160000 (fat)	800-4800 (fat)
Philipines					2400-8600
Australia	720-2500		390-800	980-3340	1200 – 3300

Analyses of DDT and derivatives in various tissues from Antarctica marine mammals provide the largest body of data, although there is considerable inter-species variability potentially masking temporal and spatial trends. The values shown in Table 3.6 correspond to seals collected in the Weddell Sea (Luckas et al., 1990).

DDTs were also determined in the tissues and organs of cetaceans (*Stenella coeruleoalba*, *Tursiops truncatus*, *Balaenoptera physalus*, *Steno bredanensis*, *Grampus griseus* and *Globicephala melaena*) stranded along the Italian coasts in the period 1988-1994 (Corsolini et al., 1995). DDT concentrations measured confirmed that in Mediterranean dolphins, the accumulation of contaminants is higher than in similar species living in the Atlantic (Marsili and Focardi, 1997).

DDTs were the dominant contaminants in blubber and liver of Caspian seals (*Phoca caspica*) found stranded on the coast of the Caspian Sea (Kajiwara et al., 2002). Although compositions of OC pesticides in seals suggested that the contamination status in the area is improving, the levels found in Caspian seals in 2000 were comparable to those in other marine mammals that have suffered from epizootics. This implies that the present status of contamination found in Caspian seals poses a risk of immunosuppression. Other DDT concentrations for mammalian samples collected in the Atlantic and Pacific Oceans are also shown in Table 3.6.

Chlordane

Like other odontocetes in the Canadian Arctic, the porpoises had higher concentrations of chlordane than animals from southern Norway. Chlordane was also determined in Arctic bears. The highest levels were found in young (3380 µg/kg) and sub-adult specimens (3440 µg/kg), which suggests an increased capacity with age to metabolise chlordane-related compounds. On the other hand, the lower levels in polar bears from Wrangel Island and the Alaskan Beaufort Sea indicate that chlordane loading is less in the Chukchi and Bering Seas than in the rest of the Arctic. This is consistent with results in seawater, for which high chlordane levels are found in the Canadian Archipelago and Barents Sea compared with the Chukchi Sea (AMAP, 2000).

Chlordane was also found in marine mammals from the Pacific China and Russia coasts at levels between 14-840 µg/kg and 1500-1700 µg/kg, respectively. A group from Australia also reported chlordane levels in whales (20-100 µg/kg), dolphins (60-140 µg/kg) and seals (340 µg/kg).

Toxaphene

High levels of toxaphene were found in blubber of Weddell seals from the Weddell Sea by Luckas et al. (1990). The presence of toxaphene in animals which typically had low levels of other PTS (such as HCB, HCH and DDT) may indicate that toxaphene contamination in the Antarctic marine ecosystem is widespread.

Slightly higher toxaphene levels are observed in the Baffin Bay and southeast Baffin beluga compared to those from the Chukchi/Bering Seas and from the western Canadian Arctic (southern Beaufort Sea). No other references of toxaphene in marine mammals exist in the literature except one from the Pacific Russia coast at levels between 930-1300 µg/kg.

HCB

HCB has been detected in marine mammals but tissue loadings are highly variable. HCB in polar bears were more uniformly distributed over the study area. This result is consistent with the finding of lower geographical variation of HCB in air and seawater in the northern latitudes than in tropical areas (Iwata et al., 1993).

Luckas et al. (1990) determined HCB concentration in blubber samples from seals collected in the Weddell Sea. Mean level was 4 ng/g ww. HCB was also found in marine mammals from Australian coasts. Beaked and pilot whales and bottlenose dolphins exhibited levels ranging from 80-220 ng/g and 80-160 ng/g, respectively.

HCHs

Few studies report HCH concentrations in marine mammals. Data for the Antarctica date back to the 80's. Schneider et al. (1985) analysed adipose tissue from seals collected along the ice shelf in the Weddell Sea and found an overall range of lindane (γ-HCH) concentrations of 17-103 µg/kg fat. Karolewski et al. (1987) sampled adipose tissue from five Antarctic seal species collected at King George Island. The highest levels were in leopard seal, with 24-26 ng/g ww of total HCHs. For other species, total HCH varied from 8 ng/g ww in elephant seal to 18 ng/g ww in fur seal. Contrasts between species reflect feeding ecology and dispersal. HCHs were also found in marine mammals from the Pacific China and Russia coasts at levels between 5.4-2200 µg/kg and 200-220 µg/kg fat, respectively.

PCBs

PCBs, together with DDT, are the most prevalent PTS in marine mammals (Table 3.6). Both exhibit a similar geographical pattern in the Arctic ringed seals and bears, a west to east increase from North America to western Russia with highest levels in samples from the Yenisey Gulf. This trend may be due to the combined influence of long-range atmospheric transport from North America and Europe. Another possible factor is transport of contaminants in sea ice and overlying snow or associated with sediment particles embedded in sea ice derived from the Russian continental shelf (AMAP, 2000).

The large number of ringed seal populations studied has revealed the large degree of complexity of geographic trends for this species. Ringed seals from Hudson Bay had higher concentrations of PCBs than those in the central Canadian Archipelago and western Greenland. The high levels in seals from Russian waters, compared with other Arctic locations, are consistent with observations of higher PCB levels in seabirds, marine fish, freshwaters, and some near-shore marine sediments in the western and central Russian Arctic.

Female adult ringed seals from the Baltic Sea have about 40-100 times higher levels of PCBs than ringed seals from western Greenland. Female fur seals from the northwest Pacific coast of Japan have similar ΣPCB levels to harp seals in the southern Barents Sea (Tanabe et al., 1994).

North-south comparisons can also be made with beluga because of the presence of isolated populations in the St. Lawrence estuary and Cook Inlet (Alaska). Concentrations of total PCBs in beluga blubber from the eastern Canadian Arctic (about 4-6 µg/g fat) were about 12-times lower (in males) than in blubber of dead belugas from the St. Lawrence estuary. Levels of PCBs in belugas from Cook Inlet on the Pacific coast of Alaska were about two-fold lower than in the Beaufort Sea population.

There is also a comparatively large body of data on PCB concentrations in tissues of marine mammals in the Antarctic, are the blubber of dolphin species (e.g. *Tursiops truncatus, Stenella coeruleoalba, Grampus griseus*), whales (*Globicephala macrorhynchus*), porpoises (*Phocoena spinipinnis*), etc. from other marine regions (Table 3.6).

PCDD/PCDFs

Oehme et al. (1995) measured these compounds in blubber from fur seals sampled at Bird Island in 1987. PCDD/PCDFs were present at levels around 2 pg TEQ/g blubber. These are significantly lower levels than Arctic pinnipeds, and PCDD/PCDF congener patterns were also different. PCDD/PCDFs levels in Canadian polar bear fat sampled in 1983-1984 ranged from 2-23 pg TEQ/g ww (Norstrom et al., 1990). More recent Canadian data from 1992-1994 gave PCDD/PCDF levels in liver of 27 pg TEQ/g ww (Letcher et al., 1996).

Concentrations in two whales species from the Japan Sea have also been reported (0.71- 13 pg TEQ/g ww, 17 – 360 pg TEQ/g fat. Levels of dioxins and furans in beaked whales and bottlenose dolphins from the Australian coasts were in the range of 1-3 pg/g and 0.1-2.6 ng/g ww (UNEP, 2002i).

PBBs and PBDEs

Brominated biphenyls and brominated diphenyl ethers have already been identified in ringed seal blubber from Svalbard (Arctic) with concentrations doubling every five years (Ikonomou et al., 2002) and in beaked whale and bottlenose dolphin from Australia.

PFOS

The presence of perfluorooctanesulfonic acid (PFOS) in liver samples of top predators, such as seals and polar bears, has recently been reported. Some current representative concentrations are shown in Table 3.4 (Giesy and Kannan, 2001; Kannan et al., 2001).

3.2.2.4 Food

Food intake is one of the most important pathways of continuous entry of PTS to the human body. In recognition of this, many countries and international organizations have established several health risk criteria such as the Tolerable Daily Intake (TDI), which is the maximum daily amount of the pollutant intake into the human body without risks of injury. Relevant data is currently obtained and gathered by public health authorities but this information is not easily available. The one given below are intended for a general perspective of the area and basically refer to the Regional Reports.

DDT and other polychlorinated pesticides

The analysis of pesticides in human food has been adopted all over the world. Practically, all regions reported information regarding pesticide levels in foods, with significant declining trends and still some unexpected occurrences of banned products. In Egypt, for example, organochlorine pesticide residues were not detected in 70-80% of the fruit and vegetable samples collected from local markets in Cairo but DDT and HCHs above the MRL were found in 4 and 14% of the potatoes from Kafr El Zayat Governorate. This indicates an illegal use of both pesticides during the storage period (Dogheim et al., 1999). In Turkey, residue analysis has been conducted on milk, butter and wheat with 60-90% of positive results but all values below the MDL (Kara et al., 1999; Yentur et al., 2001).

In the FR Yugoslavia, measurements were carried out in 1662 meat samples during a 5-year period (Spiric and Saicic, 1998). Among lamb samples, 2.5% contained lindane residues exceeding the RL, with a mean of

4.7 ng/g, suggesting improper use of lindane. In Croatia, raw cows' milk from 19 dairy locations (174 samples) was monitored for organochlorine pesticides from 1994 to 1998 with results below the DL except for DDT (7 ng/g) (Cerkvenik et al., 2000). Monitoring of pesticide residues in agricultural products in Slovenia was performed over the past twenty years. For over more than 1000 samples, the permitted level was exceeded in 3.3% of these. The analyses showed that DDT values were reduced by a factor of ten in seven years.

Data on pesticide residues in fruit, cereals and vegetables provided by the Laboratories of the Italian National Health Service (1993-1994) have shown no detectable residues of the pesticides analysed (aldrin, chlordane, DDT, dieldrin, endrin, HCB and HCHs) (Ministry of Health, 1995). However, a recent study carried out by Camoni et al. (2001) has estimated DDT and γ-HCH intakes of 2.01 and 1.75 µg/person/day based on the residue analysis of 152 types of food (agricultural products, products of animal origin, processed food, etc.).

Food items have been extensively examined for pesticide residues in India and widespread contamination was evident. Under a nationwide programme, vegetables were analysed for aldrin and 34.2% were found contaminated at 0.03µg/g level, 42.3% contained DDT at 0.10 µg/g, 96.3% contained lindane (av. 0.15 µg/g), and 78.9% contained endosulphan (av. 0.82 µg/g). The proportion of samples containing pesticides above MRL was 14% for endosulphan and 9.2% for lindane. In a more recent survey of 796 vegetable samples, 485 were found to contain pesticide residues, with endosulphan and γ-HCH above MRL values in 18 and 3 samples, respectively. In fruits, 183 out of 378 samples were contaminated mainly with DDT, HCHs and endosulphan but only 3 contained HCHs above the MRL value. Spices and various herbal medicines produced and used in India have also been analysed but levels were below MRL values (ICAR, 2002).

In a latest ICAR survey, baby milk powder of five named brands was analysed for DDT and HCHs (Agnihotri, 1999). HCHs were present at levels of 0.01-3.73 µg/g, and DDT ranged from 0.02-1.47 µg/g. Among the isomers of HCH, the β–isomer was the highest followed by α-, γ-, and δ-HCH. A fear has been expressed that feeding on contaminated infant milk will exert increasing burden on growing children. Similar studies were carried out in Pakistan revealing the widespread occurrence of DDT and γ-HCH in vegetables and fruits. The DDT levels in vegetables ranged from ND-8.6 µg/g, whereas γ-HCH ranged from 0.12-4.3 µg/g (Hayat et al., 2001).

In a recent study, total diet of Kuwait residents was assessed for the residues of OC pesticides (Saeed et al., 2001). Samples (230) collected during 1995-96 were analysed. No residues of DDT, HCHs, heptachlor, heptachlor epoxide, aldrin, endrin and dieldrin for vegetables, fruits and wheat flours samples were detected (ICAR, 2002). A total of 243 non-vegetarian and 264 vegetarian diet samples were analysed and 176 of non-vegetarian (72.6%) and 197 vegetarian diet samples (74.6%) exhibited the presence of DDT, HCHs or endosulphan. In some samples, aldrin and other pesticides were also present. In 29 vegetarian diet samples (11%) and 36 non-vegetarian diets sample (14.8%), the residue levels were above ADI value.

Kannan et al. (1992) reported the levels of several PTS in foodstuffs collected from several locations in Viet Nam. HCHs were generally low except in caviar samples reaching up to 290 ng/g. DDT was also found in high-fat products especially animal fat. Other PTS were in the sub- ng/g levels. In Guatemala, the diet of the lower socio-economic strata was examined. Data on total diets is available from 1981 to 1997. The levels detected of DDT were well below the ADI indicating that the high levels found in human milk and adipose tissue stemmed mostly from direct exposure. As can be seen in Figure 3.14, the levels are now a low detection limits, a clear effect of the ban on DDT in 1979.

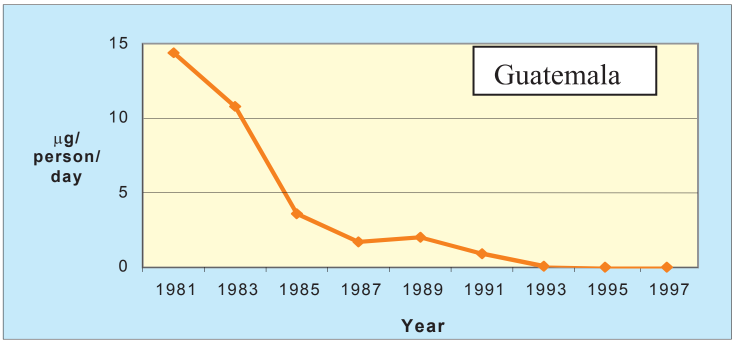

Figure 3.14. DDT in total diet µg ingested/person/day: mean of 10 values 1981 – 1996 (UNEP, 2002k)

In Colombia, of all organochlorines analysed in fish, only DDT metabolites were present at levels below those acceptable (0.6 – 1.6 μg/kg for the wet season and 1.4 - 30.9 μg/kg for the dry season). In a study regarding the contamination of tomatoes by pesticides (Palmira, SW Colombia) done in 1997, residues (HCHs, heptachlor, aldrin, dieldrin, endrin, DDTs and endosulphan) were well below the acceptable levels. The highest concentrations were found for endosulphan (65.1 μg/kg) (Nivia, 2001).

Probably, the most complete database of PTS substances in Chile is that related to food levels. The National Institute of Health (ISP) has been collecting, at least for 7 years, samples of butter, milk, powder milk and cheese in different regions of the country. The most interesting results are shown in Figure 3.15, where the trends in total DDT concentrations clearly show a decrease during a 10 year period (1983 - 1993) following the banning of DDT in 1984. Levels were always below risk values (i.e. 1.25 mg/kg fat basis for total DDT).

In Uruguay, between 1978-87, 34856 samples of meat were analysed for HCHs, HCB and endrin. The results showed a very low percentage of samples (< 1%) exceeding action levels and a decreasing trend throughout the period (Boroukhovitch, 1999).

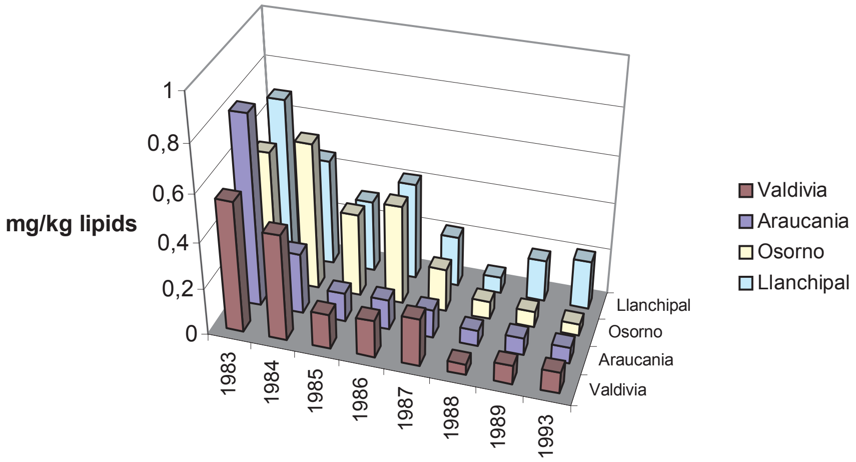

Figure 3.15. Temporal trends of DDT in Butter (data from ISP, Chile, South America)

In Argentina, the most frequently reported PTS in food are HCHs and DDT followed by heptachlors, chlordane, aldrin and endosulphan. High detection frequencies and relative abundance are reported for HCHs and DDT (in meat and vegetables) supporting the results of other environmental compartments and confirming widespread distribution. More recent data show concentrations well below action levels (HCHs: 12–51 vs. action level of 200-300 μg/kg; DDT: 12–24 and up to 990 vs. 1250 μg/kg), probably reflecting pesticide restrictions in the 80's and 90's.

PCBs and PCDD/PCDFs

PCBs and PCDD/PCDFs have been increasingly determined in food since the last decade. This is to assess chronic exposure in part due to the concern originated by noted incidents of severe contamination in different parts of the world such as those occurred in Europe.

Reported data from the Arctic residents consuming large amounts of traditional foods from the aquatic and marine environment show high intakes. Two surveys of Canadian Inuit women have shown that 16% and 4% of the women's daily intakes exceeded the TDI for PCBs (UNEP, 2002e).

Monitoring programmes on food products have been implemented in Europe. Evidence from market basket surveys of principal food groups suggest that exposure to many of the classical PTS compounds via food is very similar throughout the Region. In France and Spain, for instance, samples were collected in markets, covering the period 1992-2001. Virtually no food sample was found to be over the maximum levels recommended by the EU council regulation (November 2001), except for some wild marine fish (mean 3.47 pg WHO-TEQ/g fat) and molluscs (8.67 pg WHO-TEQ/g fat in Spain and 50.3 pg WHO-TEQ/g fat in France). When the concentration of dioxin-like PCBs is added to the contribution of PCDD/PCDFs, the total WHO-TEQs increase significantly and almost all food types investigated were over the mentioned maximum levels.

Data on food levels of PCBs and PCDD/PCDFs is lacking in other regions, for example Sub-Saharan Africa, South America, Central America, Indian Ocean, and the Pacific Islands. Thus, the data base for these chemicals is biased to the developed world.

Recently, the Codex Alimentarius Comission (FAO/WHO, 2003) has released a report where data for PCDD/PCDFs are presented from several regions. Table 3.7 presents some of the reported data for milk and dairy products. The highest levels are related to the South American samples; however the report does not specify the country where samples were taken.

Table 3.7. Ranges of PCDD/PCDFs levels (pg TEQ/g fat) in milk and dairy products from several regions of the world

Region	PCDD/PCDFs (pg TEQ/g fat)
Europe	0.3-2.5
North America	0.3-0.9
South America	0.01-2.8
Asia	0.3-1.8

PAHs

Sources of PAHs in food are due to natural constituents, contaminants from food chain and environmental exposure (air particles deposits, sediments, water column) but mainly from food processing. A national food monitoring program was initiated in France in 2000. From 6 to 16 PAHs were measured in routine analysis and a BaP toxic equivalent was used to express the carcinogenic potency of the PAHs mixture, which was officially adopted by the AFSSA in 2001. Apparently, the main contributor for food intake is meat and especially grilled and fried meat indicating the main importance of food heating processes. Those cooking practices using coal, wood or other source of energy seem to be related to PAHs intake by food.

Organomercury compounds

In areas contaminated to differing degrees total mercury and methyl-mercury concentrations from long-term monitoring of the terrestrial soil-vegetation-herbivore-carnivore food chain were studied in Slovenia, the second larger producer of mercury in the world, (Gnamus et al., 2000). Assessment of the inhaled and ingested mercury from the environment in roe deer (*Capreolus capreolus*) indicated that vegetation mediates significant transfer of Me-Hg to herbivores and this becomes subject to further accumulation in the higher trophic levels of the food chain.

A large monitoring of food contamination and intake of mercury and methyl-mercury was carried out in France by the AFSSA, in 2002. The main food contributors were fish (47%) and fruits and vegetables (19%). For a mean value of 206 µg/kg ww in pelagic fish, an average weekly intake of 3.3 µg/kg body wt has been calculated. The importance of fish as a vector of Me-Hg exposure focused the interest of risk managers to the high predator species, mainly pelagic carnivores (e.i. tuna, swordfish…). According to the mean annual per capita fish consumption, the mean weekly mercury intake is of 49.8 µg in Spain and 19.0 µg in Croatia (UNEP, 2002e).

In Colombia, organomercury derivatives were analysed in La Mojana region in samples of superficial waters, sediments, plants and fish in the dry and wet seasons. Fish samples, analysed only in the wet season, exhibited methyl-mercury in the range of 49 – 109 µg/kg dw (Ramos et al., 2001).

A general conclusion can be drawn from the preceeding information. PTS in food have been detected everywhere, however environmental levels for those pesticides included in the POPs list are clearly declining in such areas where effective regulatory measures have been taken. The exception to this rule is related to the recent use of pesticides, such as lindane and endosulphan, although the data base is scarce and more evidence is needed for verifying this fact. Monitoring programmes tend to show fewer analysis exceeding residue limits in recent years than was the case previously. The situation contrasts with the information available for industrial chemicals and unintentional released products, where levels are of concern although the available information for several regions is very limited.

3.2.2.5 Humans

As omnivores, humans occupy a top position in terrestrial and aquatic foodchains and as a result consume a high proportion of food in which persistent lipophilic compounds can be effectively biomagnified. Once ingested, PTS sequester in body lipids, where they equilibrate at roughly similar levels on a fat-weight basis between adipose tissue, serum, and breast milk. Compounds are most often monitored in these tissues, although milk monitoring is far more widely practised due to the relatively easy sample collection.

The available studies on levels of PTS in humans are mainly related to chlorinated pesticides (e.g. dieldrin, endrin, heptachlor, DDT, HCHs and HCB), PCBs and PCDD/PCDFs, with a lack of data for the others. However, they do not use consistent protocols, rendering comparisons difficult.

It is possible to document three distinct types of human exposure to PTS compounds:

a) High-dose acute exposure: typically resulting from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment or high dose food contamination.

b) Mid-level chronic exposure: predominantly due to the occupational exposure and, in some cases, also due to the proximity of environmental storage sites or high consumption of a PTS-contaminated dietary source such as fish or other marine animals.

c) Chronic, low-dose exposure: characteristic for the general population as a consequence of the existing global background levels of PTS with variations due to diet, geography, and level of industrial pollution. People are exposed to multiple PTS during their lifetime and all individuals today carry detectable levels of a range of PTS in their body lipids.

The following sections summarise significant features regarding levels and trends of PTS in the three main studied human tissues, namely human milk, blood and adipose tissue.

3.2.2.5.1 Human milk

A considerable number of studies have been produced on breast milk mainly aimed to characterise breast-fed infant exposure and the associated risk. Although studies on PTS in human milk have produced a considerable amount of information, caution is needed when trying to compare data from different countries and different times.

Mothers' age, number of breast-fed infants and dietary habits are in fact crucial parameters in determining PTS body burden and hence milk contamination. In particular, having additional breast-fed infants has been shown to progressively decrease the body burden of PTS (in the case of PCDD/PCDFs and PCBs the decrease can be up to 50%) while mothers' age may be responsible of a body-burden increase (up to 20-30% increase among different age classes for the same compounds).

DDT

A general overview of the levels found during the last decade in the different regions of the world (UNEP, 2002), is presented in Table 3.8. The large predominance of the pp'-DDE in almost all samples suggests the general absence of recent DDT sources.

Although it is difficult to assess the differences observed among regions, it appears that concentrations of DDE are four to five-fold higher in human breast milk from Inuit in northern Quebec than populations from southern Canada, probably related to the high consumption of marine food.

The relatively high levels found in the Sub-Saharan Africa Region are also of concern in view of WHO's vigorous campaign that mothers breast milk is best for children. DDT and DDE were also found in all samples of human milk analysed in several countries of Central and South America. The levels of residues were up to ten times higher in regions with intensive agriculture and vector control programs than in provinces with less agricultural use.

Levels increased significantly with maternal age. Total DDT concentrations exceeded the allowed daily intake set by the WHO in around 6% of the samples (Lacayo et al., 2000, Brunetto et al., 1996).

Table 3.8. Concentrations (mean or ranges) of chlorinated compounds in human milk samples (in µg/kg lipid basis)

Country	Year	pp'-DDT	pp'-DDE	**PCBs**	**HCB**	**HCHs**
Finland	84-85	660		930	80	200
Island	93	360		830	47	
Norway	92-93			534		
Russia	93			484-847		
Slovakia	92				5.4	
France	90-91	79	2183	411	147	
Italy	93	170	2200	290	217	
Spain	91	12	604	458		
Croatia	91-95	5	264	219	13	
Jordan	93-97	450	1060		290	710
Turkey	95-96	141-410	2260-2390		44-58	
Egypt	93	84	611			
Kuwait		12.4	833			0-84.4
Saudi-Arabia		64.5	183			0-440
Australia	91-94	225-800			100-411	108
N. America					238-271	
Guatemala	01	3-557				
Panama	87	10-4300	70-2400			
S. America		9-230			8-205	5.0-150
Zimbabwe	89	6000				910
Madagascar	96					49
Iran	90-92	302	1701		61	603
Pakistan		760-5230				93- 3430
China		390-700	2280-2850			95-1110

An interesting study was performed in Honduras after the Hurricane Mitch in October 1998. Breast milk samples from 138 women were tested for pesticides. DDE was the most common pesticide detected found in 130 of the 138 samples at concentrations ranging from 1 to 160 µg/L. These levels were surprising. Although DDT was banned in Honduras 15 years before the study it appeared that it is still used in the country (Balluz et al., 2001).

Cyclodiene pesticides, toxaphene and chlordane

Cyclodiene pesticides were determined in human milk samples in the 80's. However, levels have decreased significantly and determinations have been much less frequent during the last decade. Recent data on human milk contamination in Jordan report levels of about 860, 1400 and 3300 µg/kg fat of aldrin, dieldrin and endrin, respectively, and of 500 and 190 µg/kg fat of heptachlor and heptachlor epoxide (Nasir et al., 1998). In Turkey, heptachlor and heptachlor epoxide were found in human milk samples of 51 mothers working in agriculture at levels of 198 and 11 µg/kg fat, respectively (Üstünbaş et al., 1994).

In samples from Saudi Arabia, the levels found were for heptachlor in 20.9% of samples, 4.7 µg/kg fat (0-53.3 µg/kg fat), heptachlor epoxide in 36.5% of samples, 20.3 µg/kg fat (0-151 µg/kg fat), dieldrin in 48.7% of sample, 31.6 µg/kg fat (0-119 µg/kg fat), and endrin in 32.2% of samples 14.0 µg/kg fat (0-192 µg/kg fat) (Al-Saleh et al., 1998). In Kuwait, breast milk samples contained heptachlor epoxide (0-9.7 µg/kg fat), aldrin (0-45.0 µg/kg fat), dieldrin (0-53.5 µg/kg fat) and endrin (0-28.0 µg/kg fat) (Saeed et al., 2000). In South America, the levels of dieldrin in human milk samples were in the range of 3-48 µg/kg fat (av. 30.3 µg/kg).

Very few data is available on toxaphene and chlordane. In the Arctic region, the concentrations reported for chlorinated organic compounds in breast milk from Finland are intermediate in magnitude to those found in samples from Norway (lower levels) and Russia (higher levels), except for total chlordanes (410 µg/kg lipid), which appear to exceed the Russian values.

Chlordane and mirex are not currently registered for use in Canada and enters the Arctic ecosystem primarily via long-range atmospheric transport. The breast milk of Inuit mothers from Northern Quebec had chlordane and mirex levels ten times higher than those seen in southern Canadian residents. Toxaphene was reported at levels of 221 µg/kg lipid (Stern et al., 1992). A study carried out in France in 1990 reported human milk levels of 78 µg/kg fat α-chlordane and of 6 µg/kg fat γ-chlordane (Bordet et al., 1993); and a study carried out in Jordan in 1996 reported levels of 460 µg/kg fat α-chlordane and of 590 µg/kg fat γ-chlordane (Nasir et al., 1998).

HCB

In general, concentrations of HCB in breast milk in various countries or regions range widely and appear to be related to the degree of industrialisation and/or urbanisation within the survey area (Table 3.8). Results of most studies on the levels of HCB in food and human tissues over time indicate that exposure of the general population to HCB declined from the 70's to the mid-90's in many locations. Based on representative levels of HCB in air, water and food, the total intake of HCB by adults in the general population is estimated to be between 0.0004 and 0.003 µg/kg body weight per day. This intake is predominantly from the diet. Owing to the presence of HCB in breast milk, mean intakes by nursing infants have been estimated to range from < 0.018 to 5.1 µg/kg body weight per day in various countries.

PCBs

Available data is mainly restricted to industrialised countries where levels vary between 219-930 µg/kg lipid (Table 3.8). Several studies suggest that PCB levels in breast milk fat are significantly elevated in Arctic mothers. In breast milk samples collected from Inuit women residing in the Arctic Quebec (Hudson Bay, Hudson Strait and Ungava Bay), total PCB levels were elevated 5.6-fold in 1989/90 when compared to a southern Quebec non-indigenous population in the same sampling years. The 1992 southern Canada PCBs level in breast milk was of 238 µg/kg lipid.

Since the mid-80's, the WHO Regional Office for Europe, in collaboration with other international organisations and national institutions, has co-ordinated a comprehensive programme on possible health risks of PCBs and PCDD/PCDFs. The programme targets infants due to exposure through contaminated breast milk and aims to prevent and control environmental exposure to these chemicals (Van Leeuwen and Malish, 2002). The first exposure study took place in 1987-1988, the second round in 1992-1993 and the most recent in 2001-2002. This was organised in order to collect data on more countries including those beyond the European region.

Levels of indicator PCBs in human milk vary widely between the countries with lowest levels in Ireland and Bulgaria (median values 34 and 42 µg/kg fat, respectively), and highest levels in Slovak and Czech Republic (median values 443 and 502 µg/kg fat, respectively). Norway, Sweden, The Netherlands and Ukraine were in the range of 106-210 µg/kg fat.

PCDD/PCDFs

The monitoring programmes periodically carried out by WHO on a number of countries are a very valuable source of high quality data with mothers selected based on strict criteria allowing the highest degree of comparability among different countries and years. The results of the 2001-2002 co-ordinated exposure study (Table 3.9) show that, in general, variation between countries is much higher that within countries.

Table 3.9. Levels of PCDD/PCDFs and dioxin-like PCBs in human milk (2001-2002) [pg WHO-TEQ/g fat]

Country	PCDDs/Fs		Dioxin-like PCBs		Number of pools
	median	range	median	range	
Bulgaria	6.14	5.08-7.11	4.21	3.74-4.70	3
Czech Republic	7.78	7.44-10.73	15.24	14.32-28.48	3
Finland	9.44	9.35-9.52	5.85	5.66-6.03	2
Hungary	6.79	5.26-7.46	2.87	2.38-4.24	3
Ireland	6.91	6.19-8.54	4.66	2.72-5.19	3
Norway	7.30	7.16-7.43	8.08	6.56-9.61	2
Romania	8.86	8.37-12.00	8.06	8.05-8.11	3
Russia	8.88	7.46-12.93	15.68	13.38-22.99	4
Slovak Republic	9.07	7.84-9.87	12.60	10.72-19.49	4
The Netherlands	18.27	17.09-21.29	11.57	10.90-13.08	3
Ukraine	10.04	8.38-10.16	19.95	14.10-22.00	3

In some countries, specific sites of contamination could be identified. Industrialised countries like The Netherlands show relatively high levels of PCDD/PCDFs, whereas low levels have been found in Bulgaria, Hungary and Ireland. Elevated levels of dioxin-like PCBs were found in human milk from Ukraine, Russia and the Czech Republic whereas low levels were found in pooled samples from Hungary.

The average contamination levels in pooled milk samples in the period 1996-98 for France and Spain were of 19.6 and 13.7 pg-TEQ/g fat, respectively (EU-SCOOP Task 3.2.5, 2000). Breast milk in South Africa showed the presence of dioxins (318 μg/kg) and furans (21 μg/kg). In a very recent report (Dwernychuk et al., 2002), measurements of PCDD/PCDFs were reported in breast milk collected in villages in Aluoi Valley of central Viet Nam. The study attempted to correlate the effect of "Agent Orange" aerially sprayed in the valley to the apparent food chain transfer of dioxin from contaminated soil to cultured fish pond sediments, to fish and duck tissues and finally to humans. The report indicates values of 6.15-21.9 pg-TEQ/g fat in the affected area and 2.99-13.2 pg-TEQ/g fat in a reference site and described southern Viet Nam as dioxin reservoirs which should be seriously treated as hot spots for dioxin/furan contamination.

HCHs

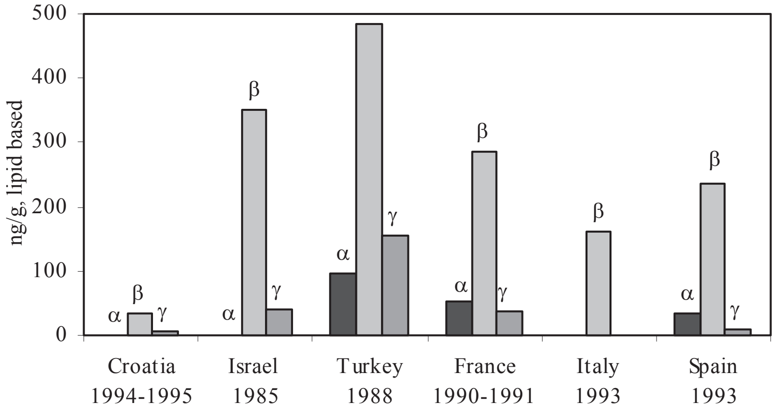

Figure 3.16. Levels of HCHs in human milk (1985-1995)

Because of its persistence, β-HCH is usually the HCH isomer found at the highest level in human milk. An overview of levels in different European countries is shown in Figure 3.16 (UNEP, 2002e). Other total HCH levels are also indicated in Table 3.8, the β-HCH isomer being always the predominant component.

A large survey on the levels of HCHs in breast milk samples was carried out in India in the 80's. In a subsequent study of 61 samples from donors of 20-30 years of age from Delhi (India) were found α-HCH at 1.83 (ND-17.8) mg/kg fat; β-HCH at 8.83 (ND-62.1) mg/kg fat and γ-HCH at 2.31 (ND-14.6) mg/kg fat (Banerjee et al., 1997). These were possibly related to the continued use of HCH in India and their ultimate translocation to human beings through the food chain. The highest level of β-HCH also indicated the use of technical HCHs.

In Pakistan, β-HCH from traces to 0.90 mg/kg were detected in breast milk of cotton pickers (Masud and Parveen, 1998). All HCH isomers were detected in breast milk in Iran with β-isomer in 92.5% of the samples, the α-isomer in 30% and the γ- in 42.5%. Total HCHs ranged from 0.093-3.43 mg/kg fat (Table 3.8).

PBBs and PBDEs

A recent Swedish study of human breast milk shows PBDEs exponentially increasing with a doubling time of 5 years (Meironyte et al., 1999). Recent studies in the U.S. also indicate that PBDEs levels in North Americans appear to be doubling every two to five years. Breast milk of North American women contains the highest level of PBDEs in the world, some 40 times greater than the highest levels reported for women in Sweden. (UNEP, 2002c). Data concerning levels of PBDEs in human breast milk may indicate that PBDEs will replace PCBs/DDT as the major environmental PTS over the next 15-30 years, especially since PBDEs continue to be manufactured within the North American region.

3.2.2.5.2 Blood, serum and plasma

A major concern for the occurrence of PTS in blood is the exposure of the foetus to maternal contaminants through the placenta during the critical stages of development. An extensive study has been performed in the Arctic region (AMAP, 2000). The patterns of PTSs found in Arctic maternal blood samples are consistent with the relative amounts of traditional food consumed, especially where marine mammals make up a larger amount of the diet. Thus, the greater reliance of indigenous people on marine species and the highest concentrations of contaminants in the species consumed are found in Greenland followed by Canada. Mothers sampled in Sweden, Iceland and Norway consumed marine fish species and terrestrial mammals such as reindeer, sheep and cattle but very few marine mammals. Hence, levels in these countries are very similar and virtually indistinguishable from values found at lower latitudes.

Based on geometric means, the contaminants present in the highest concentrations in newborn cord blood are HCB, DDE and PCBs. Levels of PCBs and DDE are twice as high in residents of northern Quebec as in the other population groups of southern Quebec. However, any comparison of maternal and newborn cord blood concentrations of contaminants needs to consider that the important determinants of contaminants levels are age of the mother, number of previous children, number of children breast fed, as well as the amount and type of country food consumption.

Other studies performed in the Great Lakes region indicate that persons who eat sport fish for more than 15 years have two to four times more pollutants in their serum than non-fish eaters, although levels decreased by 65% during the period 1982-89. Fishermen on the east coast of Sweden who have eaten fatty Baltic fish (herring and salmon) almost daily were found to have roughly twice the blood levels of DDT, PCBs and dioxins than people with an average fish intake.

DDT

DDT has been determined in human blood in many parts of the world in the 70's and 80's. More recent data is reported here for comparison among regions. Levels of DDE in Greenlandic and Russian Arctic samples were similar and three to five times higher than levels in the other four Arctic countries. However, the DDE/DDT ratio for Russian samples was markedly lower than that for samples from all other countries, suggesting current continuing use of DDT. On the other hand, the mean concentrations of pp'-DDE in maternal plasma of delivering women in Norilsk and Salekhard (Russia) were found to be rather low -0.67 and 0.38 µg/L, respectively- compared to 11.3 µg/L in the Inuit population of Quebec, Canada (Dewailly et al., 1994).

Serum levels of 3.4, 0.2 and 0.6 µg/L of DDE, DDD and DDT, respectively, have been reported for the Croatian general population in 1994-1995 (Krauthacker, 1996). In Spain, serum levels of 0.53 µg/L of DDT and 9.41 µg/L of DDE have been found in specimens from the general population sampled in 1992-1995 (Porta, 1999).

In India, the DDT residues measured in the general population of rural and urban areas averaged 48 µg/L and 32 µg/L, respectively. A study performed in Pakistan showed concentrations of DDT and DDE of 0.61-4083 and 8.88-32.61 µg/L (UNEP, 2002g).

In a study carried out in 1996-97, a total of 1834 blood samples were taken from New Zealanders aged 15 years and over from across New Zealand (Ministry for Environment, NZ, 2001). The average concentration of DDE increased from 646 µg/kg fat for the 15-24 years age group to 1780 µg/kg fat in the over 65 years old population, with an average of 1080 µg/kg fat across all age group.

In the Caribbean area (Belize), a survey on the use of DDT for the control and prevention of malaria showed that DDT was present in all blood samples tested, with average levels of 80 µg/L. Similar values were found previously in cotton growing areas of El Salvador. In Guatemala, DDT levels averaged 31 µg/L in people living in the southern coast, whilst in the northern coast these levels were below 10 µg/L. In South America (Brasil, Argentina and Chile), DDT levels were in the range of 0.4-97 µg/L (mean: 25.0) (UNEP, 2002k,m).

An interesting study was conducted in Honduras after Hurricane Mitch (October, 1998), which included assaying water and soil samples for contaminants, taking blood and urine samples from 45 adolescents aged 15-18 years and making a subjective evaluation of 155 households. Serum specimens showed that 51% of samples had pp'-DDE levels in the range of 1.16-96.9 µg/L (US reference mean in adults = 3.5 µg/L). These levels were surprising and led to the conclusion that even though these substances were banned in Honduras 15 years before the study, it appeared that they were still being used in the country (Balluz et al., 2001).

HCHs

Besides DDT, HCHs have been the most abundant pesticide found in human blood. Interestingly, β-HCH levels in Russian blood were 8-28 times higher than those in the other Arctic countries. These findings appear to suggest either that there are significant uses of HCHs in the area, or that there are significant amounts of these pesticides in the food products consumed. Serum levels of 1.2 µg/L β-HCH and 0.3 µg/L γ-HCH have been found in the general population in Zagreb (Croatia) in 1994-1995 (Krauthacker et al., 1996).

In India, the HCH residues found in rural and urban populations averaged 148 µg/L and 39 µg/L, respectively (NIOH, 1997). A study from Multan, in Pakistan showed that blood was contaminated mostly with HCH isomers from traces to 1440 µg/L (Naqvi and Jehan, 1996), whereas much lower values were found in Quetta (0.08-1.88, 1.39-6.05 and 0.29-0.56 µg/L for the α-, β- and γ-isomers, respectively) (Massud and Perveen, 1998). In South America (Brasil, Argentina and Chile), HCHs ranged from 1.1-50 µg/L (av. 15.0 µg/L).

PCBs

Few studies of PCBs in human blood have been carried out. In the Russian AMAP human health monitoring study, PCB levels were analysed in plasma from women 18-24 years old in Salekhard and Norilsk. The arithmetic mean concentrations were 6.8 µg/L and 7.5 µg/L. A mean concentration of 9.9 µglL has been reported in a comparable age group of an Inuit population in Canada (Dewailly et al., 1994). By comparison, the mean plasma PCBs concentration in a group of women 25-44 years old was 13.8 µg/L in Norilsk and 16.1 µg/L in Salekhard (19.5 µg/L in the Inuit population in Canada). The mean concentration of PCBs in cord blood samples was 2.1 µg/L in Norilsk and 1.6 µg/L in Salekhard (2.8 µg/L in the Inuit population in Canada).

Studies conducted from 1973 to 1996 in North America report current mean serum PCB levels ranging from 0.9 to 1.5 µg/L in individuals that do not have a diet high in fish. Analysis of serum samples collected from adult (>50 years old) recreational fishermen in Michigan in 1993-1995 showed significant PCBs exposure (mean: 14.26 µg/L) (UNEP, 2002c).

Data on blood contamination of the general population are available for the period 1994-1996 for Israel and Palestine, indicating levels of coplanar congeners in the range of 7-12 pgTEQ/g fat. For Croatia, levels of approximately 160 ng/g fat have been reported as the sum of the marker congeners (Krauthacker et al., 1996). Data from 13 main towns in France ranged from 3.79 to 6.14 µg/L (mean value of 4.9 µg/L) as the sum of the seven marker congeners. Values of about 3.7 µg/L as the sum of the three most abundant congeners (#138, 153 and 180) have been reported for Spain. PCB levels in samples of follicular fluid from healthy women from Rome were of about 900 pg/g fat as the sum of #138, 153 and 180 (UNEP, 2002e).

New Zealand undertook a nation-wide study on the levels of some PTS in human blood (Ministry for Environment, NZ, 2001). In the 1996-97 study, a total of 1834 blood samples were taken from New Zealanders aged 15 years and over from across the country. PCB concentrations increased with population age posting an average concentration of 79 µg/kg of fat.

PCDD/PCDFs

In some areas, high fish consumption correlates with elevated serum PCDD/PCDFs (Anderson et a1., 1998); the overall mean concentration of 2,3,7,8-TCCD and TEQs in the serum of recreational fishers from the Great Lakes region were 6.6 and 27.5 ng/L, respectively. In an unexposed comparison group from Arkansas, the serum levels were 2.8 and 15.5 ng/L. Levels were statistically different for different lakes (Huron>Michigan>Erie). In 20 pooled samples of plasma from Inuit blood in northern Quebec the average concentration of 2,3,7,8,-TCDD was 8.4 ng/L (range 2.5 to 81.8) compared to <2 ng/L in a comparison group from southern Quebec.

Data on blood contamination in Israel and Palestine in 1996 have been published (Schecter et al., 1997), showing levels of PCDD/PCDF in the range of 26.6-32 ngTEQ/kg fat and of 8.44-16.9 ng TEQ/kg fat, respectively. A study carried out on blood samples from the general population in Spain has shown an increase in PCDD/PCDFs body-burden as a function of age, as already highlighted in a number of studies (Schuhmacher et al., 1999). On the other hand, data from Germany shows a decrease of around 64% in mean PCDD/PCDF levels in blood lipid from 1988-1996.

New Zealand undertook a nation-wide study on the levels of some PTS in human blood (Ministry for Environment, NZ, 2001). In the 1996-97 study, a total of 1834 blood samples were taken from New Zealanders aged 15 years and average PCDD/PCDF concentrations of 12.8 ng TEQ/kg of serum fat were found with levels increasing with age.

As in the case of human milk, the exposure of the population of central Viet Nam to the “Agent Orange”, aerially sprayed during the Viet Nam War in the 60’s and 70’s is continuing to be assessed through the analysis of blood samples. The study revealed high levels of PCDD/PCDFs in the human blood samples from the A So population (16.6 – 45.9 pg I-TEQ/g lipid) and subsequent lower levels in blood samples from least affected areas (3.53-7.67 pg/g lipid wt) (Dwernychuk et al., 2002).

3.2.2.5.3 Adipose tissue

DDT

Levels of DDT and its metabolites in human tissue in the Arctic are considerably higher than those in southern Canadians reflecting the greater consumption of high trophic level species for food. Even higher concentrations of DDE are seen in abdominal fat tissue from Greenland Inuit. The levels of DDTs in adipose tissue from 15 postmortem samples from the Faeroe Islands in 1994 were found to be similar or higher than those reported elsewhere (1.1 mg/kg lipid) (Luotamo et al., 1991).

Available data from Spain indicate that in the years 1989-1993 levels of DDT and DDE in the adipose tissue of the general population have remained in the range of 0.7-1.5 mg/kg fat and of 3.7-6.3 mg/kg fat, respectively (Catalan et al., 1993). Mean concentrations of pp’-DDE in adipose tissue collected in 1991-1992 in Central Italy was 2.52 mg/kg wet wt (Corsolini et al., 1995). Data from Turkey and Jordan were similar (Alawi et al., 1999).

Jani et al. (1988) did a nation-wide assessment of DDT in India and established a national mean level of 11.1 mg/kg. The levels in East, West, North, South and Central India were for DDT: 6.5 (1.4-37.1 mg/kg); 17.2 (1.3-176 mg/kg); 15.4 (1.9-131.6 mg/kg); 7.8 (0.2-80.7 mg/kg) and 0.2 (1.0-37.1 mg/kg), respectively. The wide variation of pesticide in human fat in India was probably due to the geographical variation in consumption and use of pesticides and food habits (Bhatnagar, 2001). In Iran, the DDT residues reported in human adipose tissue were of 2.45 mg/kg pp’-DDE and 0.19 mg/kg pp’-DDT (Burgaz et al., 1995).

In Guatemala, for a study of 24 samples obtained during surgery of persons from rural areas the maximum concentration of DDT was 15 mg/kg (de Campos, 2002). In a study of adipose tissue of 93 Nicaraguan mothers living in the basin of the Atoya River, DDT residues were present in all samples. The mean concentrations found for pp’-DDE and pp’-DDT were 1.66 mg/kg of fat and 0.08 mg/kg of fat, respectively (Cruz-Granja et al., 1997).

HCHs

Data available for adipose tissue from the general population in Spain indicate levels of β-HCH in the range of 1160-3060 ng/g fat and levels of γ-HCH of 50-80 ng/g fat in the years 1989-1993 (Catalan et al., 1993). Available data for Turkey in 1995-96 indicate a contamination from β- and γ-HCH of 374 and 43 ng/g fat. In Jordan, levels were reported of β- and γ-HCH of 857-1332 ng/g and 90-330 ng/g, respectively (Alawi et al., 1999).

A nation-wide assessment of HCHs in India calculated national mean levels of 3.5 mg/kg. The levels in East, West, North, South and Central India were for HCHs: 1.6 (0.1-4.84 mg/kg); 3.2 (0.2-20.6 mg/kg); 2.2 (0.2-

11.0 mg/kg); 5.1 (0.02-94.5 mg/kg; and 1.1 (0.25-1.9 mg/kg), respectively. In South America, the range of HCHs in human adipose tissue was 0.3 -19 µg/kg.

HCB

In 1997-2000, concentrations of HCB in Central Italy averaged 335 ng/g ww and were positively correlated to age. Data available for Spain indicate that levels in adipose tissue of the general population have remained in the range of 2500-4000 ng/g lipids in the years 1989-1993. In the same period, available data for Turkey indicate contamination of about 170 ng/g lipids and, more recently (1995-96), levels of 33 ng/g fat have been reported for Manisa residents. Data on adult population in Jordan indicate levels of about 400-660 ng/g fat in early 90's, while recent data indicate values in the range of 120-220 ng/g fat (UNEP, 2002e).

In Iran, the human adipose tissue contained 160 µg/kg HCB (Burgaz et al., 1995) and in South America the range was 0.4-13 µg/kg. The mean level of HCB in adipose tissue from 15 postmortem samples from the Faeroe Islands was 100 µg/kg lipid.

PCBs and PCDD/PCDFs

Very few studies have been reported on human adipose tissue. The mean levels of PCBs reported by Chile are 54 µg/kg. These levels are almost one order of magnitude lower than the values reported for relatively non industrialised areas in Italy (400 ng/g lipids) (Mariottini et al., 2002). The levels of PCBs in adipose tissue from 15 postmortem samples from the Faeroe Islands were determined in 1994 and found to be similar to those reported elsewhere (Luotamo et al., 1991).

The NHATS detected 2,3,7,8-TCDD in about three-quarters of the samples in the 1982 survey for the U.S. population (6.2±3.3 pg/g fat). In the 1987 survey, the average concentration was 5.38 pg/g. The concentration of PCDD/PCDFs in 18 adipose fat samples of humans from southern India averaged 520 pg/g fat of dioxins and 30 pg/g fat of furans (Kumar et al., 2001). In the analysis of archived human adipose tissues from several regions of Japan, PCDD/PCDFs and co-PCBs were reported to be 31.6 and 35.4 pg-TEQ/g lipid basis in 1970-71, and 11.9 and 15.3 pg-TEQ/g wet in 2000 (Choi et al., 2002).

PBBs and PBDEs

Studies reporting the occurrence of these chemicals in human adipose tissue have been conducted in Europe. Tetra-, penta- and hexabrominated diphenyl ethers were found in samples from Spain, at average concentrations of 1.36, 0.93 and 1.83 ng/g lipid, respectively (Meneses et al., 1999). Values in other countries are similar.

3.2.3 Temporal trends

The data presented in this Chapter illustrate world-wide monitoring of PTS. However, these data are primarily produced by academic (research) institutions as a result of a scientific interest or in response to certain pollution incidents (e.g. spills) rather than for environmental, long-term monitoring purposes. This leads to a rather sparse geographical and temporal data coverage which makes difficult to discern statistically significant trends in many regions. However, on the whole, the concentrations of most pesticide PTS appear to be significantly decreasing over time. Levels of PCBs may be increasing in some areas and there is insufficient data for PCDD/PCDFs in many regions. Some illustrative examples of such trends are given below.

3.2.3.1 Abiotic compartments

Abiotic compartments, namely air, soil, sediment and water (continental and marine) reflect the temporal variability of environmental inputs of PTS. However, in assessing trends it should be taken into account that their responses differ in time as illustrated in Figure 3.17. Here the long-term trends of PCB contamination levels in various environmental media have been calculated from emission expert estimates for Spain (Dutchak et al., 2002). From the figure it is apparent that there is a downward trend in concentration levels following emission reduction but soil concentrations decrease at much slower rates.

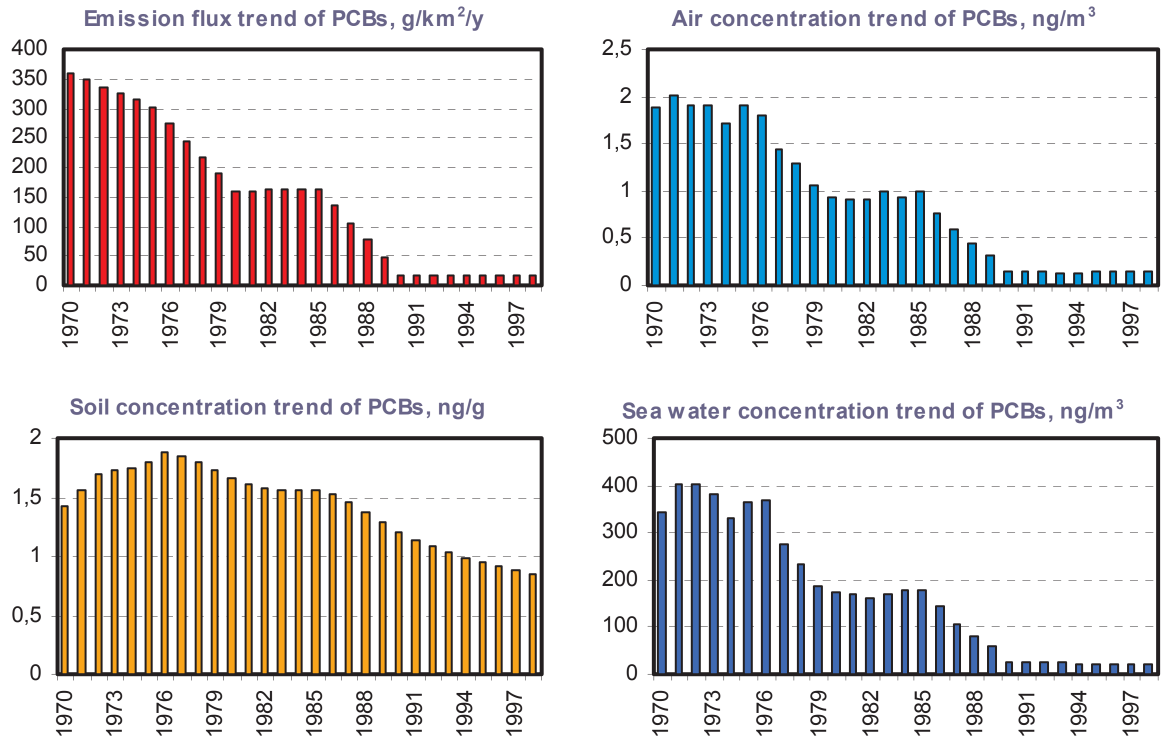

Figure 3.17. Long-term trends in PCBs emission and media contamination for Spain

A number of field studies also indicate a general decline of PTS concentrations although with some exceptions. The consistent data set of DDTs (DDT+DDE) and PCBs concentrations in sediments from the Eastern Adriatic Sea shown in Figure 3.18 allow identification of a different temporal trend for both pollutants according to the present use of these compounds in the area (Picer and Picer, 1991).

Sediment cores can be used as excellent tracers of past pollution; therefore they have been widely used in the northern hemisphere for reconstructing the historical trends in the concentrations of several PTS. Among them, the individual toxaphene congeners were determined in a dated sediment core from a mountain lake, Lochnagar (Scotland, U.K.) representing the first of such profiles in Europe (Rose et al., 2001). Toxaphene has been neither used nor produced in the U.K. and while some production was undertaken in France and Germany (1955 – 1990), much of this was exported to Eastern Europe and Cuba. Therefore, Lochnagar and its sediment record are ideally placed to monitor the long-range transport and historical deposition of this pollutant to an area of Europe remote from any direct treatment.

The profile of total toxaphene showed a bimodal distribution with maxima in the mid-70’s and early 90’s. The earlier toxaphene peak shows agreement with the U.S. source curve and therefore may correspond to modelled global patterns. The later peak may be due to long-range transport from eastern and southern Europe or from still lower latitudes.

The sediment record of total PCBs was also studied in this core, showing an increase from the mid-30’s and a large increase during the 60’s. This trend coincides very well with the known production of PCBs in the UK (Gevao et al., 1998). PCB profiles in dated sediment cores collected in remote lakes in Northern Finland (68 - 69° N) also show post-1950 deposition of PCBs with maximum in the 70’s.

A peat core from an ombrotropic bog in Northwest England also showed maximum PCBs in slices dated to the late 60’s and an approximately 50% decline in concentrations between 1970 and 1990 (UNEP, 2002d). Temporal trends of chlorinated pesticides have also been assessed in the Mediterranean using dated sediment cores collected in the mouths of the rivers (e.g. Rhône, Ebro, Nile, etc.). These show increasing discharges until mid 80’s and further decrease although HCHs are still currently increasing in the Nile (UNEP, 2002e).

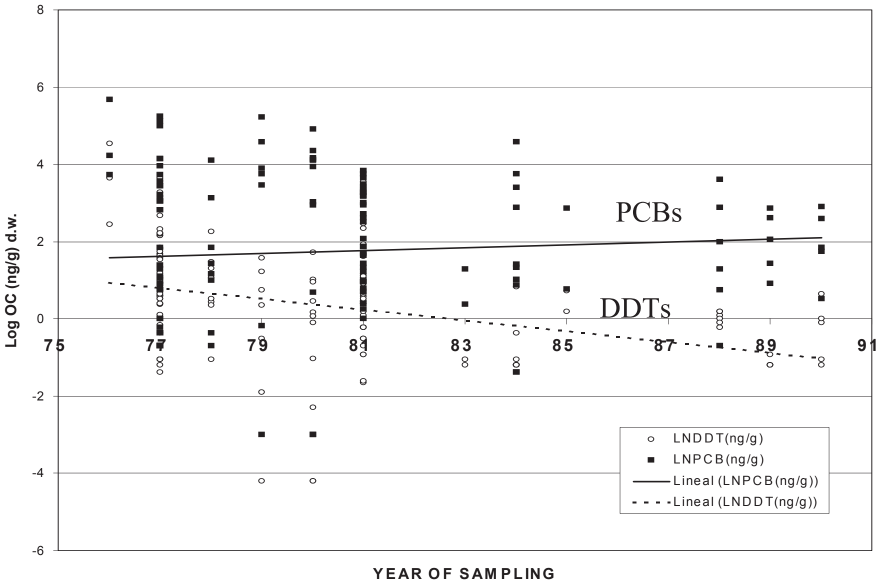

Figure 3.18. Temporal trend of DDTs and PCBs levels in Eastern Adriatic coastal sediments

In the North America Region based on analysis of a core sample from the central basin in the lake Ontario in Canada, accumulation of PCDD/PCDFs increased during the 30's and 40's; the greatest contamination occurred in the early 50's to the late 60's. Levels declined from the late 60's to the early 80's; further decline since the 80's is not apparent. Assessment of homologue profiles, on-going bottom sediment and biomonitoring have implicated point source discharges within the Niagara River as primary contributors to PCDD/PCDFs contamination in Lake Ontario.

PCDD/PCDFs were measured in 16 sections of sediment core from a freshwater lake in rural England (Green et al., 2001). Local industries such as mining, quarrying, charcoal burning, and iron smelting appear to have had a minor impact on the PCDD/PCDFs deposition in the lake. Since 1900, two major peaks in PCDD/PCDFs input to the lake were evident. The first, reaching a maximum in the 30's, had an unusual homologue pattern dominated by high molecular weight PCDFs and the source of this input is unknown. The second, with a maximum in the 70's, is in keeping with previously reported time trends for Europe and North America. Pre-1900, the PCDD/PCDFs isomer pattern was dominated by dimerization products of 2,4-dichlorophenol. Despite detailed knowledge of the catchment and of industry in the surrounding area, the identity of some sources and the contribution of other known sources remain unclear for each era.

3.2.3.2 Biotic compartments

The results of a number of temporal trend studies of Arctic biota indicate that PCBs and DDT levels in the Arctic have declined over the past 20-25 years since the first controls on DDT and on the open use of PCBs began. Less is known about the temporal trends of many other persistent OCs including HCHs, HCB, chlordane, toxaphene, dieldrin and PCDD/PCDFs (AMAP, 2000).

Evidence for the decline of airborne PCBs in the European Arctic comes from a study of mosses in northern Norway. This study showed a consistent three-fold decline of PCB concentrations in mosses from both coastal and inland areas over the period 1977-1990. Over the same time period, PCBs in southern Norway declined about four-fold. The decline of PCBs in Arctic mosses is consistent with observations in the nearby Swedish Arctic of declining PCB levels (about a three- to four-fold decrease over 26 years) in pike and char muscle.

The time trend study of Swedish reindeer from Abisko, based on annual samples, showed a significant change in α-HCH over the time period 1983-1994. A ten-fold decline was found which is quite close to the decline observed in air over the Bering/Chukchi Seas. Other OC's studied, such as PCBs, DDT, and β-HCH, did not change significantly in reindeer but the year to year variation was substantial implying that the time period was probably too short to allow a proper evaluation. Pike and char from Swedish Arctic lakes show α-HCH concentration decreases similar to those found in reindeer.

Declining concentrations of PCBs and DDT and increases in chlordane-related compounds in eggs of peregrine falcons and other birds of prey have been observed in both the European and North American Arctic, consistent with changes in the use of these OCs. Dieldrin, oxychlordane, and HCB also showed no change in concentration over the period 1977-1990. Levels of heptachlor epoxide actually increased over the period 1966 to 1987 but may have declined significantly during the late 80's. A problem with utilising contaminant levels in eggs of migratory birds of prey to assess temporal trends in the Arctic is that the levels in eggs may also reflect exposure at wintering areas.

The best evidence for declining OC concentrations in Arctic birds of prey comes from the study of Lindberg's group (1985 and 1995), who compared eggs collected during 1972-1981 and in 1991-1994, and found declines in concentrations of about two-fold for PCBs and five-fold for pp'-DDE. Levels of PCBs and DDTs in the eggs of black-legged kittiwake, northern fulmar, and thick-billed murre from the High Arctic colony on Prince Leopold Island (Canada) have also declined during the period between 1975 and 1993. Most of the decline was observed in the 70's and early 80's. These are migratory species and declines may reflect an overall reduction in the OC levels of the North Atlantic where many of these birds over-winter. In one of the few examples of increasing concentrations, there was a 50% increase in PCB levels and a two-fold increase in chlordane-related compounds in ivory gull eggs.

Monitoring of fish in lakes Storvindeln and Abiskojaure in northern Sweden has provided some of the strongest evidence for declining inputs of persistent OCs to the aquatic environment in northern Scandinavia. For DDT and PCBs, a sudden decline occurred immediately after European measures to reduce the discharges of DDT in the beginning of the 70's and PCBs in the middle of the 70's. After the initial decline, the annual change in concentration continued and there is still an annual decline of DDT and PCBs of 3-8% a year. While these recent changes in PCBs and DDT have been small, there is no indication that concentrations are leveling off. Levels of PCBs in pike in sub-arctic Finnish lakes also decreased 5- to 10-fold from the early 70's to the early 90's. Toxaphene, HCHs and chlordane levels underwent significant declines in burbot liver from the lower Mackenzie River in Canada over the period 1986-94 (UNEP, 2002a).

In the eastern Canadian Arctic and Greenland, temporal trends in marine mammals can only be examined over a 10-12 year period. No significant declines have been observed in concentrations of DDT, PCBs, chlordane, and toxaphene in female ringed seals at three locations or in male narwhal blubber from Lancaster Sound from the mid-80's to early 90's. These results are reasonably consistent with those for PCBs and DDT in ringed seals at Holman Island. There is insufficient information at present to discern temporal trends in marine mammals from Svalbard, northern Norway, and Russia (AMAP, 2000).

In Antarctica, data for birds and mammals endemic to the region suggest that levels of DDT and derivatives increased over the period from the early 60's to the early 80's. Since the mid-80's, levels appear to have fallen slightly, but less so than might be expected from regional and global environmental data (Bidleman et al., 1993, and Tatsukawa et al., 1990). It is difficult to assess whether the ratio of DDE to DDT concentrations has changed significantly over the same period against a background of inter-species and other sources of variability. The 60's data of Tatton and Ruzicka (1967) suggest that DDE:DDT ratio was about 10, even taking into account species ranging outside the region. Data from most recent samples of endemic penguins suggests that DDE:DDT ratio may have risen to 20 (Van den Brink 1997). Taken together, these data are indicative of the persistence of DDE in the biota and environment despite a significant fall in the input of 'new' DDT and DDE from outside the region.

The declining concentrations of persistent OCs in the Arctic parallel observations at lower latitudes for biota from the Great Lakes region or the Baltic Sea. Thus, the decline in concentrations of DDTs and PCBs in Lake Ontario trout was greater during the 70's immediately following ban on use of DDT and open use of PCBs, than during the 80's (Borgmann and Whittle 1991). These declines are not consistent with other observations in fish. For example, concentrations of 2,3,7,8-TCDD in Lakes Ontario and Huron trout did not decline significantly over the period 1980-1992 (DeVault et al., 1995). The many sources of PCDD/PCDFs to the environment may mean that declines in PCDD/PCDFs TEQs may be very site specific in comparison to trends for PCBs and semi-volatile OC pesticides.

In the Great Lakes sub-region, levels of PCBs and DDT have declined significantly in top predators. For example, continued decline in PCBs in Herring Gull eggs reflects lower emissions following controls on open uses. Declines in Great Lakes lake trout and walleye have not been as dramatic especially since the mid-80's reflecting continued emissions from urban areas and recycling of contaminants within the lakes.

In stark contrast to the declines observed in other OC contaminants, levels of dieldrin in Herring Gull eggs from all areas on the Great Lakes remained relatively unchanged. Nevertheless, a few significant decreases in levels of dieldrin and heptachlor epoxide have been noted during this period. Since the mid-80's, dioxin levels in Herring Gull eggs from all areas on the Great Lakes have also remained fairly constant.

In the Baltic Sea, the long term monitoring of DDTs, PCBs, HCB and HCHs in biota samples that has been carried out since the 70's show a similar decrease in the warmer south as in the colder north. (Bignert et al., 1998). Many authors consider the Baltic herring (*Clupea harengus*) to be a good indicator of the Baltic Sea ecosystem pollution by PTS (Roots, 1996; Falandysz et al., 1997). Its role as a bioindicator is currently increasing.

The longest time series, going back to the late 60's-early 70's, show decreasing concentrations of DDTs by about 7% per year in herring from southern Bothnian Sea and by 11-12% per year in both herring and guillemot egg from the Baltic Proper. Figures 3.19 shows the trends observed for cod and perch (Bignert et al., 1998).

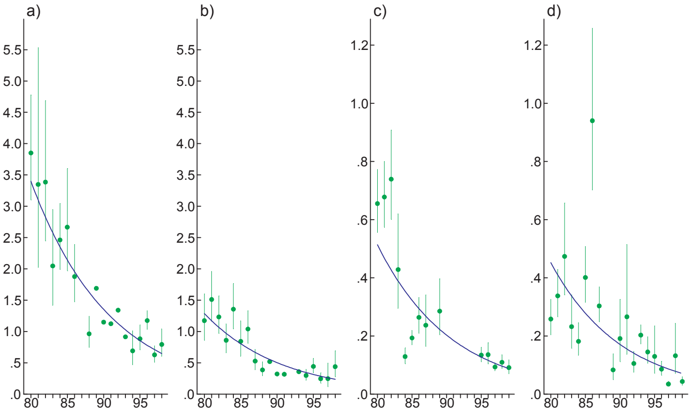

Figure 3.19. Concentrations of ∑DDTs (ng.g-1 l.w.) in fish samples (1980-98); cod liver in a) the Baltic Proper, b) the Kattegat; perch muscle in c) Gulf of Bothnia and d) the Baltic Proper. The 95% confidence interval for the annual geometric mean is given. The significant log linear regression line for the trend is indicated.

Further South in the Mediterranean Sea, two surveys conducted along the coast of France and Italy, in 1973/1974 and in 1988/1989 (Villeneuve et al., 1999) showed that PCBs and DDT levels in mussels decreased by a factor of approximately 5 in 15 years. A similar trend was observed in the Ebro Delta where a decrease by a factor of 3 was observed from 1980 to 1990 (Solé et al., 1994). However, it is interesting to notice that levels detected in the benthic red mullet were similar to those found 10 years earlier, which may well reflect the high persistence of OC residues associated with sediments in the region.

The Adriatic Sea has also been extensively monitored from this perspective. Decreasing trends of HCB and pp'-DDE concentrations have been observed in the eggs of little and common terns and black-headed gull collected at the River Po Delta over the past 20 years. In Figure 3.20 are shown the annual trends of DDTs in benthic and epibenthic fish from 1974 until 1991 (Picer and Picer, 1995).

However, the trends for PCBs were not so evident. Similar trends were observed in the French monitoring network of coastal pollution using bivalves as sentinel organisms (RNO, 2000). In general it can be seen that during the period 1979-1998 the decreasing trends were in the order: DDTs > HCHs > PCBs > PAHs. Corsolini et al. (1995) measured similar levels in tuna and sharks of the Mediterranean Sea collected in 1980 and in 1992, indicating a steady source of these contaminants in the Mediterranean ecosystem.

Cows' milk has been used by several countries as a biomonitor for ambient air contamination around potential dioxin point sources. When comparing the PCDD/PCDFs TEQs of the Irish cows' milk samples from two studies carried out in 1995 and 2000, it can be seen that the values that were at the lower end within European countries (e.g. France, Germany, Spain) exhibited a slight decrease (10%) in this period.

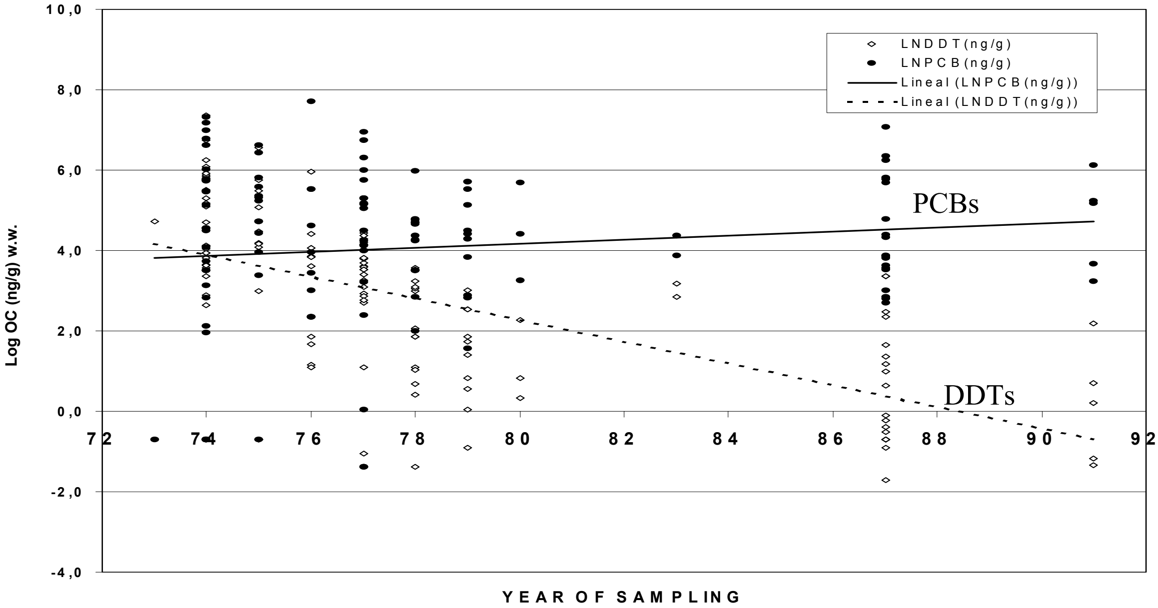

Fig. 3.20. Yearly trend of DDTs and PCBs levels in the eastern Adriatic coastal epibenthic and benthic fish.

Japan has been conducting environmental monitoring of major organochlorines for nearly three decades and of organotins for more than a decade (Chemicals in the Environment, Ministry of the Environment, Japan). Frequencies of detection (ratios between the number of detected samples and the total samples) have been decreasing in many of the compounds including PCBs, HCB, dieldrin, pp'-DDT, γ-HCH and TBT in fishes and bivalves. This suggests that their levels in Japan have generally been decreasing in recent decades.

Among the above samples, sea bass collected in the most populated areas of Tokyo and Osaka Bays in Japan, almost always showed the highest detection frequencies for all the chemicals and may deserve further discussion. In both cases, the average levels of PCBs seemed to decrease in late 70's but no clear decreasing trends were observed in the past two decades. DDT seemed to decrease in late 70's ~ early 80's and then stabilised. Chlordanes have been decreasing slowly in both places in the two decades.

A decrease in concentration levels of PTS such as DDT and HCHs in the green mussels over time was observed in most areas of the Southeast Asian region, with the 80's data significantly higher that the more recent findings. In Australia, the trends in the data seem to indicate a maximum level of DDT and dieldrin in fish occurring generally in the 70's and 80's with a decline since that period. Somewhat similar data have been produced for other aquatic biota. However, the data are limited and this trend is not always apparent. Although the concentrations of pesticides are lower in recent years, the range of pesticides is greatest during the 90's. This probably reflects the frequency of monitoring, analytical chemistry capability and other factors.

In all other regions, most of the data available on the levels of PTS are temporally scattered and it is difficult to see trends in various media. On the other hand, there is a real lack of time trend and general concentration data on less well studied PTS such as chlorinated phenols, chlorinated paraffins, phthalates, etc.

3.2.3.2.1 Humans

Levels of chlorinated compounds in human tissues have declined in the different regions during the last 20-30 years. For example, a ten-fold decline in total DDTs in human tissues over the last 20 years has been observed in the population in southern Canada (Conacher and Mes 1993, Mes 1994), due to the decrease of the dietary intake of total DDTs (including metabolites) since the 60's. From 13 studies in Canada and the United States, it has been calculated that average DDT levels in breast milk have steadily declined since 1975 with a half life of about 4.2 – 5.6 years. Endrin, dieldrin, heptachlor and heptachlor epoxide in human milk samples from Canadian women have also exhibited similar decreasing trends between 1967 and 1982.

Temporal trends in levels of PCDD/PCDFs in human milk for European countries participating in the WHO studies confirmed that on average, the decline between the levels found 1993 and those found in 2001-02 was about 40%. Breast-fed infants represent a distinct sub-group of the population whose exposure to

PCDD/PCDFs and dioxin-like PCBs will exceed current guideline values based on body weight for the first few months of life. Despite elevated levels of PCDD/PCDFs, WHO strongly recommend that breast feeding is encouraged and promoted for the clear benefits to the child.

Many of the PTS chemicals have been monitored in human breast milk obtained in Japan (Osaka Prefecture) for 27 years (Konishi et al., 2001). Total PCB levels, α-HCH, DDT and DDE showed decreasing trends with a couple of small peaks in late 70's and early 80's. Dieldrin also showed a decreasing trend in the first decade while HCB levels showed a slight increase at the beginning of 80's and then decreased steadily. Chlordane levels varied considerably but did not show a clear decreasing trend in the last decade.

Levels in humans are also following the downward trends in the northern areas, close to or above the Arctic Circle (Noren 1993). In breast milk sampled in Stockholm between 1967 and 1989, a decrease in the levels of certain pesticides and PCBs was found. The changes were related to the prohibitions and restrictions applied to the use of these compounds. Downward time-trends were also seen for PCDD/PCDFs and specific congeners of PCBs, including non-ortho and mono-ortho coplanar PCBs. Between 1972 and 1989, average levels of CB 153 in breast milk decreased from 220 to <150 ng/g lipid, CB 138 decreased from 190 to 120 ng/g lipid, CB 180 decreased from 90 to 70 ng/g lipid, and CB 118 decreased from 60 to <30 ng/g lipid. Levels of oxychlordane and trans-nonachlor also dropped from 20 to 12 ng/g lipid.

For some PTS compounds of emerging concern such as PBDEs, there is some evidence of increasing trends in human breast milk during the last 20 years.

Regarding adipose tissue, concentrations of well characterised compounds such as PCBs and PCDD/PCDFs have been declining significantly in recent years throughout Europe at a rate of approximately 5% per year since the early 90's. This decline coincides with European restrictions on the manufacture and use of PCBs and controls to reduce releases of PCDD/PCDFs.

In Japan, compared with the levels in middle 70's, γ-HCH decreased to 3.1% total DDT (DDT+DDE) to 7.1 % and PCBs to 13.2 %, respectively. Dioxins were analysed in archived samples, which were preserved as extracted lipids (Ministry of Health and Welfare, 2000). The total levels (including co-PCBs) were around 65 pg-TEQ/g lipid basis in mid 70's and decreased to 24 pg-TEQ/g lipid basis in 1999. The decrease of co-PCBs was most significant followed by PCDFs. PCDD levels, on the other hand, were nearly flat from early 70's until late 80's, and then started to decrease slowly.

PCDD/PCDF levels were also analysed in archived diet samples obtained in Kansai region (Ministry of Health and Welfare, 1999) and in Kobe and Nagano cities (Sakurai et al., 2001). PCDD and co-PCB levels were higher in mid-70's and showed decreases until late 90's. On the other hand, PCDF levels seemed constant from mid-70's to mid-80's and then decreased.

3.3 OVERVIEW OF OBSERVED HARMFUL EFFECTS

Many laboratory experiments have been conducted to test the relationship between PTS exposure and a range of adverse outcomes in animals. Table 3.10 shows some possible effects that can be produced by some of the principal chemicals assessed (PANNA, 2002). However, the scientific confirmation of these effects in field studies has been limited.

Biological effects can be measured in the field at different levels of organisation, from the molecular to the ecosystem. Biomarkers measurable at a molecular level respond early but are not readily interpreted ecologically, while measures with established ecological relevance, such as population declines or reduced reproductive rates, respond too late to have diagnostic or preventive value. In any case, at the present time it is very difficult to link contaminant levels or biochemical indicators of effects to effects on animals at the individual or population level. Such assessments are also complicated by the fact that the thresholds for effects of many contaminants are not well known and very little is known about effects of contaminant mixtures.

The interactions that have been seen indicate that the relative amounts and the composition of various contaminants in animals may partly be the result of selective effects on the organism's uptake, metabolism, and excretion of OCs, and not solely a result of the specific pollution burdens of contaminants in the area. In summary, while the concentration of a toxicant in a specific environmental compartment may be relatively easy to quantify, its potential biological/ecological effect on the population and assemblage would be more difficult to measure or predict.

Table 3.10. Potential effects of individual PTSs

Types of Effects	Aldrin and dieldrin	Chlordane	DDT	Toxaphene	Mirex	HCB	PCDDs, PCDFs, and PCBs	HCH	Endosulphan	PBDEs	Tributyltin
Reproduction and/or development	X	X	X	X	X	X	X	X	X	X	X
Cytochrome P450 system	X	X		X	X	X	X	X	X	X	
Porphyria						X	X				
Immune system	X	X	X	X	X	X	X	X	X	X	X
Adrenal effects			X	X				X			
Thyroid and retinol effects			X	X		X	X	X		X	
Carcinogenic effects	X	X		X	X	X	X	X			
Skeletal changes				X			X				

Since the results of manipulated toxicity tests can significantly differ from the ecological reality, we will discuss only results based preferentially on reported field studies and observations. In doing so, we will bear in mind that in some cases adverse (or non-physiological/irregular) effects are observed in the field. However the links/correlations between these effects and chemical contamination are complicated and are hard to be evaluated as a causal/specific/selective result of contamination (especially with respect to particular single chemicals or group of chemicals). In many situations, no particular chemical is often identified as responsible for the observed effect. We will also distinguish between acute effects resulting in mortality (poisoning) and sublethal effects more difficult to assess but probably more relevant over the long term.

Growing evidence of the occurrence and potential impacts of new chemicals suggest that detailed assessments should be conducted on flame retardants (PBDEs, PBBS and TBBPA), short chain chlorinated paraffins, perfluorooctane sulfonate (PFOS), polychlorinated naphthalenes (PCNs) and alkylphenol ethoxylates (APEs). Detailed studies of environmental concentrations and associated observed effects are rare. In the case of emerging PTS, basic ecotoxicological data are often not available.

3.3.1 Ecotoxicological effects

3.3.1.1 Observed lethal effects in the environment

Pesticide poisoning of domestic animals is prevalent especially in the rural sector. A common source of animal poisoning is feeding fodder mixed with straw. Farmers with meagre land resources heavily rely on weeds from standing crops for fodder. In India, examples of consequences of poisoning on animal health include loss in milk productivity (40%), loss in vigor (36%) and mortality (18%). Similar losses were reported for household poultry (32%) and sheep and goats (23%) kept as domesticated animals. As small farmers live in the close vicinity of sprayed fields and orchards, the continuing effects on humans and livestock take place and the health risk becomes cumulative in addition to financial losses.

The direct toxic effects of pesticides on wildlife and birds have not been studied in detail through field surveys. Studies carried out in Pakistan have shown that 10% of all birds on arable lands are killed annually by pesticides (UNEP, 2002g).

During the Viet Nam war (1961-1971), a large quantity of defoliants, 2,4-D and 2,4,5-T containing dioxin and furan impurities, was distributed into the Viet Namese environment. Hoang Dinh Cau (2002) has reported that large areas of forest were destroyed and have not recovered up to the present time. In addition, there have been losses of the flora and fauna associated with the forest. The composition of the wildlife is reduced by 30% of the total number of species with important animals such as elephant (*Elephas maximus*), banteng (*Bos gaurus*), samba deer (*Cervus unicolour*) and Elds deer (*Cervus eldi*) being particularly reduced.

A large number of poisoning or accidents related to PTS (mainly toxaphene) in wildlife have been reported in the 70's in Sub-Saharan Africa. According to Osibanjo et al. (1994) the accidental release of OCs in large quantities had caused massive fish kills in many countries, such as Senegal, Nigeria and Kenya. Frequent occurrences of fish kills have also been reported in Australia (New South Wales) in cotton growing areas during the season when endosulphan is used (Leonard et al., 1999). Endosulphan has replaced many of the organochlorine pesticides in the region as it is less persistent in the environment and residues are relatively much lower.

3.3.1.2 Observed sublethal effects

Terrestrial biota: birds and mammals

The association between DDT usage and declining populations of carnivorous birds is well known. This has been attributed to an adverse effect on the endocrine system leading to a residue induced imbalance in calcium metabolism resulting in shell thinning and loss of eggs as well as behavioural abnormalities. In Australia, the peregrine falcon (*Falco peregrinus*) has been intensively examined to determine if shell thinning was occurring as a result of DDT usage (Olsen and Olsen, 1979) having an adverse effect on the endocrine system. The CSIRO examined eggs of known age from museums, private collections, etc, from many different parts of the country (Connell, 1981). The results shown in Figure 3.21 indicate a decline in egg shell thickness during the period of introduction and usage of DDT (starting around 1947) and an adverse effect on breeding success would be expected as a result.

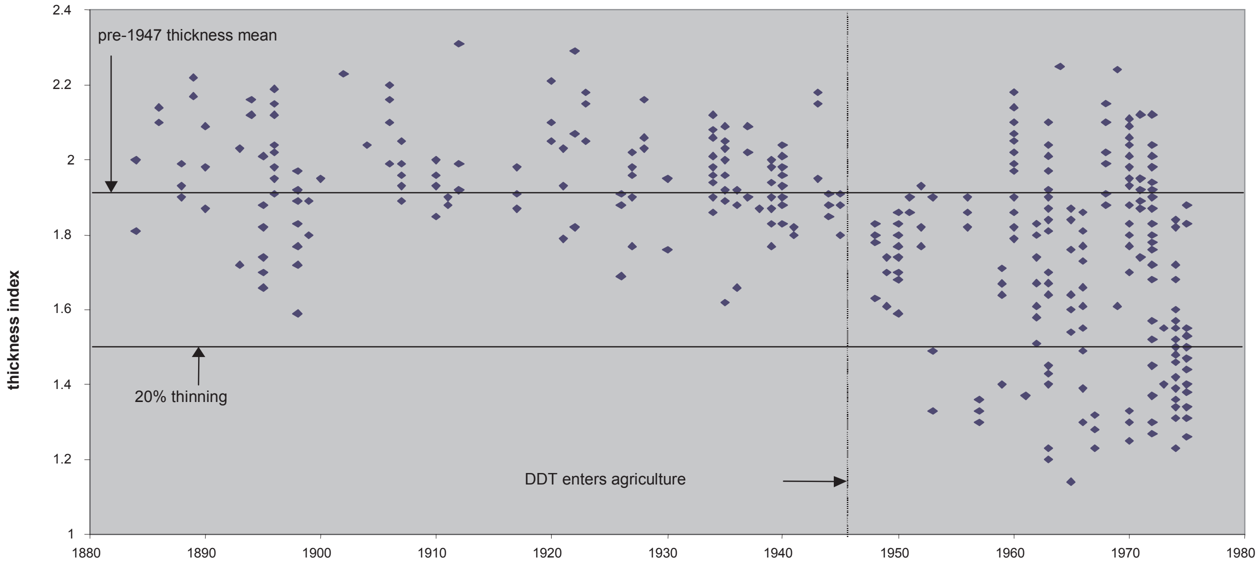

Figure 3.21. This figure indicates how the thickness of peregrine falcon (Falco peregrinus) egg shells has changed. Each spot represents the thickness of an egg shell. Before 1947 no shells were 20% thinner than the pre-pesticide mean but after 1947 a substantial proportion of the eggs, collected from all over the continent, were more than 20% thinner.

Studies in Canadian, Swedish, and Russian peregrine falcon still indicate that eggshell thinning also occurs due to high DDT levels in the eggs. For Canadian peregrines, these levels are high enough to still be causing reproductive failure in some cases. For Norwegian white-tailed sea eagle, correlations were found between eggshell thinning and concentrations of DDE, PCB, and HCB but the degree of thinning was below that affecting reproduction. The clear relation between decreased egg-shell thickness, as determined in bird of prey, and DDE has also been obtained in some of the European regions.

Intensive field studies have been performed in the Rhine, Meuse and Schelde estuaries (Murk et al., 1994; Bosveld et al., 1995) with colonies of common terns and cormorants in Belgium and Netherlands. The principal conclusions made on the basis of these field studies are that the Rhine and Meuse sedimentation areas are among the most highly contaminated in the world and, consequently, the ecotoxicological effects of PTS are substantial particularly in cormorants. Effects are most significant in sedimentation areas where the population of fish is the highest.

On the other hand, it has been observed that male sea gulls may ignore nesting colonies, and females may pair and nest together as a consequence of modified behaviour possibly caused by estrogenic chemicals such as DDT, DDE, dioxins, PCBs, and alkylphenols (Luoma, 1992). It has been found by Kelce et al. (1995) that some of these toxicants can also block androgen receptor-mediated processes, and in doing so, act as androgen receptor antagonists. There are also many well known examples of bird populations that have been affected by PTS exposure with decreased or retarded egg production, increased embryo mortality, egg-shell thinning, embryonic deformities, growth retardation and reduced hatchling success being among the effects reported.

Mammals were the organisms for which most of the effects of PTS were first researched, particularly in laboratory rats and mice. In this respect, immunosuppression may be one of the most sensitive and relevant environmental threats posed by PTS, as it has been shown in numerous studies that various ecotoxicants can suppress immune system function. PCB mixtures were shown to alter several morphologic and functional aspects of the immune systems, such as loss of thymic cortical lymphocytes, reduction of germinal centre size, reduction of leucocyte and T-limphocyte counts, altered reactivity of immune system, reduced antibody production against pathogens and reduced skin reactivity. Defects in the macrophage and natural-killer cell activities resulted in increased susceptibility to normally tolerated bacterial, viral and parasitic infections. These effects have been reproduced in birds, fishes, rodents and non-human primates (Dunier, 1994; Tryphonas et al., 1995).

The application of the laboratory findings to wild populations in field studies is not easy because the variation in genotypes in such species gives important variability in the toxicokinetics and toxicodynamics of these compounds and, thus, a large range in dose/effect relationships. For these reasons, it is difficult to predict adverse effects in wildlife from PTS levels measured in wild animal tissues. In this respect, the dramatic decline of some European otter (*Lutra lutra*) populations since the 50's was explaned by several reasons: e.g habitat destruction and direct or indirect influences of eutrophication, acidification and toxic chemicals. However, in the beginning of the 1980's, PCBs were suggested to be an important reason for the otter population decline (Olsson and Sandegren, 1991).

3.3.1.2.1 Freshwater environment: fish and aquatic birds

There are several studies in Europe of ecotoxicological effects on fish. In particular, researchers have seen extreme disturbances of reproduction in different regions and among several fish species including perch, burbot, cod and salmon. Although the mechanisms for these disturbances are unproven, it is thought probable that one or more PTS are involved (Alsberg et al., 1993). It is important to mention the results of semi-field Dutch studies (Besselink et al., 1998) showing the reduced vitamin A levels in flounder due to ecotoxicological effects of PAHs. Also the observation of the decreased fecundity for the Baltic Sea cod which has been explained by the authors (Petersen et al., 1997) as being due to the effects of lipophilic xenobiotics.

The biological significance of these pesticide residues in aquatic biota is difficult to interpret. However, growth reduction has been reported by Mortimer and Connell (1995) for Australian crab species when sub-lethal levels of chlorohydrocarbon residues were present in lipid tissues. This and other sublethal effects, such as lack of breeding success which has been observed with birds, have probably occurred and may be still occurring in the region.

Among sublethal effects affecting river fish, endocrine disruption may be the one more directly related to PTS. For example, barbels (*Barbus plebejus*, a benthic cyprinid) captured from the middle Po River showed profound intersexual alterations (50% of the individuals). These effects can be related to the high levels of NP and ethoxylates measured in Po river sediments, although the contribution of natural and synthetic estrogens cannot be excluded (Viganò et al., 2001). In France, in the Seine-Maritime region, cyprinids of the species *Rutilus rutilus* (roach) showed also intersex gonads, with an incidence of intersexuality of up to 21% in the different sampling areas. The same kind of effect was observed in 7% of the males of flounder (*Plathychthys flesus*), a flat fish captured in the Seine Bay.

It has also been shown in Great Britain (Jobling et al., 1998; Routledge et al., 1998; Mattiesen et al., 1998; Allen et al., 1999), Sweden (Andersson et al., 1998), Netherlands (Janssen et al., 1997) and Spain (Solé et al., 2000) that various fish species – rainbow trout, roach, flounder and perch have elevated blood vitellogenin. In some cases testicular abnormalities, intersex (up to 100%), ovotestis (up to 20%) and decreased turnover of steroids have been observed. The authors have concluded that sewage effluents, containing xenoestrogens, are responsible for the effects.

Inhibition of spawning in female species of sand goby has been observed in UK and the authors (Waring et al., 1996) believe that diluted sewage sludge is the main reason to explain this observation. Andersson et al. (1998) and Sandstrom et al. (1997) have concluded in their studies that reduced plasma sex hormone levels, reduced gonad growth and delayed sexual maturity for various fish species in Sweden are due to chlorinated organic chemicals, particularly from the bleached kraft pulp mill effluents.

Due to the widespread occurrence of PTS sources and the relatively high concentrations of NPE metabolites, it can be expected that the number of observations of endocrine disruption will rapidly increase. A much greater effort should be devoted to increasing our knowledge of the dimensions and consequences of this problem both in freshwater and marine environments.

3.3.1.2.2 Marine environment: fish and marine mammals

The use of biomarkers as tools for assessing sublethal effects on marine organisms has been introduced in a series of international coastal monitoring programs. In the Mediterranean, bivalves (mussels) and benthic fish (*Mullus barbatus*, *Serranus cabrilla* and *Dicentrachus labrax*) have been studied in areas exhibiting significant pollution gradients (e.g. harbours, urban and industrial waste oufalls, etc.) in comparison with cleaner areas (e.g. Corsica and Sardinia) (MEDPOL 1995-now, BEEP 2000-2003).

The biomarkers most commonly used have been the cytochrome P450 1A monooxygenase (CYP1A), the 7-ethoxyresorufin-O-deethylase (EROD) activity, the measurement of DNA damage, the benzo(a)pyrene oxydation (BPH), the inhibition of acetylcholinesterase and the determination of lysosomal membrane stability. CYP1A expression in the benthic species *Mullus barbatus* has been related to PAH levels in sediments (Burgeot et al., 1996). Likewise, studies examining residue levels of bioaccumulated PCBs in muscle tissue have shown a direct correlation with CYP1A activity along the NW Mediterranean coast (Porte et al., 2002), the higher response being observed in specimens collected near urban and industrial areas. Other fish species, such as *Serranus crabilla* and *Dicentrarchus labrax*, have also been successfully used in biomonitoring programs, particularly along the western coast.

Liver enzyme induction (EROD) seems to be correlated with concentrations of PCBs in burbot from the Canadian Arctic. A clear relationship has been seen between non- and mono-ortho PCB levels and liver enzyme induction (EROD, AHH) in starved beluga whales from the western Canadian Arctic. A relationship has also been seen between EROD and AHH activities and PCB and dieldrin concentrations in ringed seals from Arviat and between EROD activity and PCB concentrations in hooded seal from the West Ice. Cytochrome P450 1A activities in polar bear seem to be elevated and are correlated with concentrations of non-ortho and mono-ortho PCBs. Cytochrome P450 2B activities in polar bear liver seem to be correlated with chlordane levels.

Lysosomal alterations are accepted as a marker of general stress and it has been related to levels of PAHs and PCBs accumulated by mussels along the Spanish coast (Porte et al., 2001), the Adriatic Sea (Petrovic et al., 2001), and Venice Lagoon (Lowe and Fossato, 2000) among other areas. DNA damage in molluscs inhabiting contaminated areas has been reported in the Venice Lagoon (Frenzilli et al., 2001).

In addition to biochemical and cellular effects, several studies indicate disruption of normal endocrine function. A wide variety of compounds considered here (e.g. DDT, PCBs, nonylphenols and phthalates) have been associated with potential reproductive anomalies in fish, and there has been a growing awareness of the need to detect and assess the adverse effects. One of the most evident is the superimposition of male sex organs on female species (imposex). There are a number of examples in all regions of the development of imposex with gastropods as a result of exposure to TBT compounds used in the boating industry.

Studies performed in Europe include the experimental observations of imposex in dogwhelk (*Nucella lappilus*) from British and French coastal waters (Bryan and Gibbs, 1991; Huet et al., 1996) and common whelk (*Buccinum undatum*) from Danish waters (Strand, 1998) and Eastern Scheldt-North Sea (Mensink et al., 1998). This phenomenon is held responsible for global declines in populations of several species. TBT ecotoxicants are considered to inhibit cytochrom P450 dependent aromatase (CYP19) responsible for conversion of testosterone to estradiol. Apart from the imposex in marine snails, effects in other invertebrates are poorly documented.

In the Mediterranean area, the monitoring of a gastropod (*Bolinus brandaris*) along the Catalan coast (NW Mediterranean) showed that imposex was a widespread phenomenon. Imposex has also been described in the whelks *Stramonita haemastoma* and *Hexaplex trunculus* in Israel and Italy. Five neogastropod species (*Hexaplex trunculus*, *Ocenebra erinacea*, *Ocinebrina aciculata, Hinia reticulata* and *Nassarius reticulatus*) collected in TBT-polluted sites, near the port of Faro and on the south part of the Tagus River (Portugal) were examined in 1996 for imposex with positive results (UNEP, 2002e). The use of TBT in antifouling paints has also been associated with imposex in whelks and other gastropod molluscs throughout the Indian Ocean and Southeast Asia Regions (UNEP, 2002g,i).

Recently, new evidence based on monitoring hormone and vitellogenin levels together with gonad histology indicates that the central Mediterranean male swordfish (*Xiphias gladius*) is undergoing sex inversion (14%) (Fossi et al., 2001). There is no evidence, however, of reproduction impairment. The effect on other large pelagic predators or on marine mammals is also unknown. However, reproductive failure in the common seal population inhabiting the western part of Dutch Wadden Sea was attributed to PCBs after feeding experiments demonstrated that a diet of naturally PCB-contaminated fish had a detrimental effect on the seals reproduction (Reijnders, 1986).

In recent years, several species of marine mammals and birds have been affected by uncommon diseases and unusual mortalities. While several factors have been attributed for these events, a prominent suspect is exposure to PTS. Investigation of toxic effect of PTS in higher tropic level wildlife showed that PTS such as organochlorine pesticides, PCBs, organotins, etc. are found in tissues of a wide variety of wildlife.

PCB levels determined in the blubber and liver of striped dolphins affected by the 1990 morbillivirus epizootic in the Mediterranean Sea and in the blubber of striped dolphins from the same area in 1987-1989 and 1991 (see section 3.2.3), raised the question of the possible relation with the event. Three hypotheses were put forward as possible answers: (i) depressed immunocompetence caused by PCBs leading to an increase in individual susceptibility to the morbillivirus infection (ii) mobilisation of fat reserves leading to increased PCB levels in blood which, in turn, may produce a liver lesion capable of increasing the individual's susceptibility to the morbillivirus infection (iii) previous existence of an unspecific hepatic lesion producing impairment of the liver function which, in turn, could lead to an increase both in tissue PCB levels and in individual susceptibility to the morbillivirus infection.

Although extremely high PTS concentrations have been found in animals inflicted with diseases and/or victims of mass mortalities, toxic effects in wild animals at the current levels of exposure are difficult to assess.

3.3.2 Human health effects

Many environmental epidemiological studies indicate that correlations do exist between chemical contamination and observed human health effects. To evaluate critically the adverse effects of individual PTS, it is necessary to compare data derived from experiments with the laboratory animals, the results of epidemiological studies due to accidental or occupational exposure, as well as the effects observed for the “average“ population.

Although the measurable residues of PCBs, PCDD/PCDFs and various organochlorine pesticides present in human tissues and contamination of food including breast milk is a worldwide phenomenon, it is very difficult to elucidate cause-effect relationships between human exposure to low levels of a certain PTS in the environment and the particular adverse health effects. Among the reasons is the broad range of chemicals to which humans are exposed at any time.

Evidence for low-level effects of PTS on humans are more limited than those for wildlife but are consistent with effects reported both in exposed wildlife populations and in laboratory experiments on animals (UN-ECE, 1994). This is why data from accidental events or occupational exposures can help to formulate safety values for PTS. While trying to elucidate toxicological effects of PTS, one has always to remember the many concurrent factors affecting human health (life style, dietary habits), which are often very poorly evaluated.

3.3.2.1 DDT and metabolites

Very high levels of DDT have been reported during 1970-1980 in human blood samples from the southern regions of the former Soviet Union. The reason for this might be the huge quantities of pesticides used in agriculture practices. In certain regions of Moldavia, this has been suggested to be a reason for a high incidence of miscarriages and congenital malformations. It is proposed that the lack of adequate use and storage of PTS, including DDT, PCBs, and HCB, in agricultural districts of the Kemerovo area (Western Siberia) have also resulted in cytogenetic damages within the children's and adult population. The level of chromosomal aberrations was twice as high as in comparable groups in ecologically clear areas and corresponded to the level of genetic damage of the population of Kemerovo' industrial areas.

Breast cancer in women appears to be rising in many countries and pathogenesis of breast cancer has been linked with exposure to hormone disrupting chemicals (Davis et al., 1993). There were several studies (Falck et al., 1992; Wolff et al., 1993; Dewailly et al., 1994) supporting this hypothesis with observations of higher levels of DDE and PCBs both in mammary adipose tissue and plasma (see section 3.2.2.5). However, the situation became controversial when Krieger et al. (1994), Key and Reeves (1994), and Safe (1997) performed much larger studies and, after producing a statistical summary of results from these studies, concluded that it is unlikely that DDT in the environment is increasing the risk of breast cancer. They also concluded that for PCBs there is no evidence of such an association.

In Sub-Saharan Africa even though pesticide residue levels have been measured at relatively high concentrations, no data on effects has been reported.

The relationship between serum levels of DDE and bone mineral density in 68 sedentary women from northern New South Wales was investigated by Beard et al. (2000). These women reported an adequate dietary intake of calcium. However, reduced bone mineral density was correlated significantly with age as well as with increases in the log of DDE levels in serum. Hormone replacement therapy was also identified as another predictor variable. The authors suggested that past community exposures to DDT may be associated with reduced bone mineral density in women. Women in this study were selected because DDT was extensively used in cattle dips and significant residues remain.

An epidemiological study was carried out in Bogota (Colombia) with a total of 306 women enrolled including 153 incident breast cancer cases and 153 age-matched controls. The objective of this study was to evaluate the association between breast cancer risk and serum DDE levels. Socio-demographic and reproductive data, diet, and past exposure to pesticides were obtained through a structured questionnaire. Likelihood of developing breast cancer by exposure to these substances was evaluated through odds ratios (OR) adjusted for: first-child breast-feeding, family breast cancer history, body mass index (BMI), parity, and menopausal status. Data analysis was performed by conditional logistic regression techniques. Adjusted OR for exposure to serum DDE and breast cancer suggests an increase risk of breast cancer in the higher category of DDE exposure. The test for trend was not statistically significant ($p = 0.09$). The authors found that serum DDE levels are positively associated to risk of breast cancer and could support the association between risk of breast cancer and burden of DDE exposure (Olaya-Contreras et al., 1998).

3.3.2.2 HCHs

Bhatnagar et al. (2002) in a survey of 30 pesticides formulators (who handle a wide variety of pesticides including HCHs) found immunological alterations, along with HCH residues in serum (230 µg/L, as compared to 40 in controls). No correlation with other toxic effects was attempted in this study.

In India, HCHs in blood serum of workers in a manufacturing unit for this chemical were detected by Nigam et al. (1993). The highest exposure group (mean 600 µg/L, range 190 – 1150) also showed early symptoms of toxicity such as paresthesia of face and extremities, headache, giddiness and many showed tremors, loss of sleep, impaired memory and other neurological symptoms. The levels and effects were enhanced with the period of exposure.

The same authors, in a subsequent study involving 365 workers from all the 4 HCHs manufacturing units in India confirmed exposure-related blood levels and neurological symptoms. Evidence for hepatic toxicity, immunological disturbances and ECG abnormal were also pronounced in the high residue level group (600 µg/L and above). Over 80% of the residues were found to be β-HCH which was considered a reliable indicator for exposure. Simultaneous exposure to other pesticides also could lead to more complicated symptoms.

3.3.2.3 Toxaphene and chlordane

Elevated levels of toxaphene and chlordane coupled with current intake scenarios suggest some Inuit groups are exposed to levels of these three contaminants significantly above the Tolerable Daily Intake (TDI). The Dene of the western NWT has smaller exceedances of the TDI for toxaphene and chlordane (CACAR, 1997). Also, there is as yet little conclusive scientific information directly linking harmful human effects to these levels of exposure.

In one of the earlier studies, Balash et al. (1987) demonstrated that chlordane disturbed spermatogenesis and damaged the testes of mice. It has been shown (Broughton et al., 1990) that patients chronically exposed to chlordane demonstrated clinical and immunological symptoms highly suggestive of immune pathology and probably the chlordane/heptachlor-induced autoimmune disorder. Nearly identical immunological results were found in the patients exposed to pentachlorophenol as fungicide (McConnachie and Zahalsky, 1991).

3.3.2.4 PCDD/PCDFs

A large Netherlands study of breast milk and child development found levels of PCDD/PCDFs/coplanar PCBs in breast milk of 46.2 pg/g lipid. Subtle clinical, immunologic and neurodevelopmental alterations associated with breast-feeding have been reported in the infants/children of the Netherlands cohort (Koopman-Esseboom et al., 1994, Huisman et al., 1995, Weisglas-Kuperus et al., 1995). However, the dominant finding was that breast feeding was beneficial compared to no breast feeding.

Brouwer et al. (1995) demonstrated the wide range of neurobehavioral, reproductive and endocrine alterations observed in experimental animals following in utero and lactational exposure to PCBs and PCDD/PCDFs. There were also subtle changes observed in neurodevelopmental and thyroid hormone parameters in human infants at background human body burdens. Consequently, in assessing effects linked to the presence of PTS in the environment, the full range of toxic endpoints should be considered including the more subtle and complex chronic effects.

In one of the recent monographs of IARC (1997), it was concluded that TCDD should be considered as a definite human carcinogen. The Committee on Carcinogenicity (Department of Health, 1998) agreed that TCDD is a potent carcinogen in laboratory animals but suggested that the information from the most heavily occupationally exposed cohorts was showing, at most, only a weak carcinogenic effect in these individuals. It therefore concluded there were insufficient epidemiological and toxicological data on TCDD to propose a casual link with cancer in humans but it would be prudent to consider TCDD as a “probable weak human carcinogen”.

Swedish investigations have reported that dietary intake of PCDD/PCDFs and PCBs may be linked to reductions in the population of natural killer cells (Svensson et al., 1993). These cells are believed to play a role in the body’s defence against viruses and tumors. However, none of the subjects in this study displayed any signs of health impairment attributable to lowered number of natural killer cells.

Immune modulating effects have been detected in the Netherlands in people exposed to low-level environmental concentrations of PTS. In particular, it has been shown that certain immunologic aberrations were associated with pre- and post-natal exposure of Dutch infants to PCDDs and PCBs (Weisglas-Kupertus et al., 1995). Although their data did not indicate that these aberrations caused any more illness among the infants, they could persist and predict later difficulties such as immune suppression, allergy and autoimmune disease.

Another example of the long-term effects of high-level accidental releases of dioxins has been described recently by Mocarelli et al. (1996). The sadly famous accident in Seveso (Italy) had as one of the endpoints the female-skewed sex ratio in births about eight years after, which can be directly related to the dioxin exposure.

Reproductive and carcinogenic effects such as liver cancer have been associated with large scale spraying of 2,4,5-T herbicide, together with contaminating dioxins, by the US military during the Second Indochina war period from 1962 to 1971. About 10 percent of the land area of Viet Nam was sprayed mainly between the years 1965 to 1970. Since this period, 2,4,5-T would disappear due to degradation while the dioxins would persist (eg. see Schecter et al., 2002).

Phuong et al. (1989) compared reproductive anomalies in women living in a herbicide sprayed area (Thanh Phong Village) and non-herbicide sprayed area (Ho Chi Minh City), from 1952 to 1981. The pooled data indicate that the incidence of hydatidform mole and congenital malformations was significantly higher for the herbicide-exposed group than the unexposed one.

3.3.2.5 Organomercury compounds

Organic mercury is much more easily absorbed into the body than inorganic mercury. In pregnant women, it can pass from mother to foetus. Human exposures to high levels of methylmercury result in neurotoxic effects that have been well documented in a number of incidents globally (ATSDR, 1999).

Patterns of neurobehavioral damage produced by exposure to methyl mercury during development include mental retardation, cerebral palsy, deafness, blindness and dysarthria in those exposed in utero. Sensory system effects, motor or sensory-motor system effects, and cognitive effects occur in exposed adults. In humans, there is evidence of effects on the cardiovascular system even at doses below those associated with neurodevelopmental effects.

Considerable efforts have been devoted to establish dose-response relationships for fetal exposure with apparently contradictory results. Debate about acceptable exposure involves issues in balancing human nutrition and needs to be resolved in the light of the dietary importance of fish. Chronic (i.e. life-time) effects of adult exposure to methylmercury are not well understood; particularly the consequences of repeated but short term (‘bolus’) exposure characteristic of subsistence (e.g. aboriginal) and recreational fisheries. Limited guidance is available for dose-response relationships for adults.

Organomercury compounds (particularly, methyl and ethyl derivatives), unlike inorganic mercury salts and mercury vapor, have characteristic features of neurointoxication (Sarafian and Verity, 1991). The characteristic features of poisoning with organomercury toxicants are the persistence of neurological symptoms (the so- called “Minamata desease”).

The study in Russia of the dynamics (over 1.5 years and 3 years) of latent pathological effects to the nervous system caused by small doses of organomercury compounds (25 persons were fed meat and diary foodstuffs containing 1-10 ng/g of EtHgX for 2-3 months) showed an increase in complaints. This indicates pathology of hypothalamic structures in brain, and a reduction in complaints concerned with the pathology of peripheral nervous system.

3.3.2.6 Organolead Compounds

Organic lead compounds were formerly used as a gasoline additive. However, these compounds are largely destroyed in the combustion process or by atmospheric oxidation to inorganic lead (ATSDR, 1999).

While the most evident manifestation of chronic exposure to lead is anaemia, exposure has also been linked to impaired mental function, visual-motor performance, neurological damage in children and reduced memory and attention span (ATSDR, 1999). Exposure is also associated with lack of appetite, abdominal pain and constipation, fatigue, sleeplessness, irritability and headache. Continued excessive exposure to lead (such as may occur in an industrial setting) may affect kidney function.

Children are particularly at risk. They absorb lead more easily than adults do. Children also absorb a higher proportion of lead from all sources (air, food, water and dust for example) than adults. Contaminated dust is a particularly important source of exposure for babies and young children. During pregnancy, lead may cross the placenta and reach the tissue of the unborn child. The last trimester of pregnancy may be the most critical time for this to occur. In the past, increased spontaneous abortions and stillbirth rates were noted in female industrial workers exposed to high levels of lead.

Over the past decade, some researchers have found that exposure to even low levels of lead prior to birth or during infancy and early childhood may cause impairment to intellectual development, behavioural disturbances, decreased childhood size and hearing impairment.

3.3.2.7 Other PTS of emerging concern

Practically no information regarding observed human health effects were retrieved regarding other PTS, even though some relationships could be established with homologue groups of chemicals. This lack of information is widely recognised and precludes any attempt to perform a human health risk assessment with the available information. Currently, the U.S. EPA, the OECD, the European Union and Canada have all independently been carrying out hazard or risk assessments on PFOS. These initiatives will assist in providing information on a chemical for which very little is known in most countries of the world.

In summary, occupational exposure to various PTS – in manufacturing, formulation and application of pesticides – has been clearly linked to adverse effects and an appropriate suite of controls to address this are needed. The second issue are accidents and accidental exposure – often related to poor storage and poor use practices- and several cases of poisoning again probably related to over use and careless handling/disposal. For other long-term lower level exposure there are many examples most linked to diet, which lead to elevated exposures. Demonstrating effects in these circumstances is difficult although subtle effects on development have been reported for general population exposure to some PTS.

In general, reported problems are related to high exposure scenarios. Very little is known of chronic effects related to low-level exposure that results through environmental food chains. This is particularly critical since detecting effects at low levels in populations exposed to multiple chemicals is difficult and in part could also reflect a lack of effects.

3.3.3 Risk assessment

The assessment of the environmental or human health hazards associated with the presence of a chemical or chemicals in the environment is a challenging issue. The risk is determined by the combined relationship between exposure and toxicity; in determining whether there are adequate benchmarks to compare environmental levels against levels of concern which should prompt action, it should be stressed that there is a paucity of data on both fields. In the introduction to this section, the shortcomings of the approach have been pointed out. As shown, the direct observation of harmful effects of PTS is almost limited to hot spots and accidental episodes. Moreover, the effects are expected to be in most cases the outcome of a multifactorial stressor where toxic chemicals are just one of the elements.

In practice, threshold levels indicating predicted no effect concentrations (PNEC) have been or must be estimated for specific compounds and environments. Guidelines (environmental quality standards) for the PTS are described as ‘trigger values’ and have been developed to evaluate sustained exposure to toxicants or chronic toxicity. These standards, however, cannot be used worldwide; they need to be adapted to the different regional conditions.

On the other hand, except for professionally exposed workers, diet is the main route of human exposure to PTS (up to 90 %). Therefore, the risk assessment in this case may be carried out by comparing PTS dietary intakes with their pertinent Tolerable Daily Intakes (TDIs) established at national and international (e.g. FAO/WHO) levels.

Despite the application of the precautionary principle, the limitation of this approach is that only for a very limited number of compounds has it been possible to set critical levels and it does not take into account species differences, nor chemical mixtures. Where the comparison is made to environmental quality standards reference or tolerable daily intakes, there is a need to include the caveat that it is difficult to predict the accumulative effects of long-term low-level exposure to PTS. The improvement of this knowledge is a priority issue.

3.4 DATA GAPS

The lack of appropriate research and monitoring programmes is the main barrier to the advancement of our common understanding of the occurrence and consequences of PTS in the environment. A major step towards the filling of the existing data gaps will be the activation of monitoring programmes at three levels:

Monitoring activities should be established in the corresponding countries to fill the geographical and chemical data gaps and ensuring the continuation of existing time trend series. Regional surveys of emerging PTS and compounds currently on the market (e.g., PBDE, PFOS) or those difficult to analyse (e.g., PCDD/PCDFs) should be implemented.

Analyses of food to evaluate the general exposure of the population and to detect abnormal increases due to different cases of contamination are to be initiated. Monitoring design should allow the assessment of any correlation of PTS body-burden with factors such as age and gender groups, dietary habits, occupation and education. In this context, total diet studies taking into account regional habits are of primary interest.

Analysis of human tissues (blood, milk) for human body burdens estimation and risk evaluation. Human tissues are also exposure sources for developing organisms. Although this kind of assessment poses a series of technical and ethical problems, monitoring of human tissues provides the best information on human exposure to PTS. The data obtained should allow the validation of exposure models.

A closer relationship between monitoring and modelling should be encouraged for improving the estimates of the fate and effects of emissions and pools of existing PTS.

Also, there is as yet little conclusive scientific information directly linking ecotoxicological and harmful human health effects to low levels of exposure to these contaminants. In this respect, it is necessary to develop:

Environmental quality regional guidelines to evaluate the significance of the occurrence of PTS in air, soils, wastes, sediments, food and drinking water, so that management guidelines can be established.

A better understanding of physiological and toxicological effects of contaminants on humans and species identified as most at risk, especially on development of offspring, and/or immunosuppression and endocrine disrupting properties

Detailed information on the diet and food consumption patterns of specific populations, including necessary information on other factors (e.g., smoking), which can influence contaminant exposures to allow better estimates of dietary intakes of contaminants and permit more reliable estimates of associated risks.

Knowledge about combined effects of contaminants on biota and humans both at the individual and ecosystem level is to be increased.

Integration of physical and biological models with information on environmental measurements of sources and pathways are required to aid the design and implementation of monitoring, research, and management including mitigation.

3.5 SUMMARY AND CONCLUSIONS

A considerable amount of data is available on the occurrence of PTS in the different regions of the world, although with a very uneven distribution in terms of compartmental, geographical and temporal coverages, as well as analytical quality particularly for the older data.

In general, these data are mainly the result of one-off or sporadic and un-coordinated research campaigns using incompatible protocols and addressing narrow, local objectives rather than the existence of monitoring networks. In general, data available address local studies or hot spot situations. Consequently, there is a lack of comparable, high quality data and this poses a limitation for a global assessment of PTS. However, from the Regional Reports the following picture of regional concerns can be obtained.

3.5.1 Regional assessment

In comparison with most other areas of the world, the **Arctic** and the **Antarctic** regions remain relatively clean environments. However, for some pollutants, combinations of different factors give rise to significant concern in certain ecosystems and, particularly, for some human populations in the Arctic. Some indigenous groups are exposed to concentrations that exceed established TDI levels. Transfer to infants can result in newborn levels that are 2 to10 times higher than in regions further south. These circumstances sometimes occur on a local scale but in some cases may be regional or circumpolar in extent.

Apart from areas of intense local contamination, the major concern at present is focused on PCBs and pesticides, mainly because of the sensitivity of species to these contaminants and the biological processes which enhance levels and effects.

In contrast to the apparent global declines in environmental concentrations of PTS, in these regions there are increases in biological loadings for some compounds. This is probably the case for dieldrin and most likely for DDT. Concentrations of DDT and derivatives in endemic birds and mammals increased in the Antarctica over the period from the early 60’s to the early 80’s. The ratio DDE:DDT has increased more rapidly in biotic samples than in the environment suggesting that DDE is accumulating in the ecosystem.

The Regional Report for **North America** provides an extensive coverage of data on the Great Lakes Basin. Three decades ago, elevated levels of a wide range of PTS were associated with an array of impacts on wildlife and risks to human health in this region. As a result of extensive remedial activities since the 70’s, there has been significant environmental improvement as demonstrated by recoveries in reproductive success and increases in population for most of the affected fish-eating bird species. In 1991, concentrations of toxic chemicals in the open waters of the Great Lakes are well below Canadian and international drinking water standards. However, despite the declining levels, the interim guideline for PCB designed to protect Canadian wildlife that consume fish and shellfish is routinely exceeded by both predator and forage fish in many areas.

On the other hand, although the temporal trend in annual flow of pesticides into the five Great Lakes is generally decreasing, the presence of emerging toxic substances continues to be of significant concern for both wildlife and human health. Current use OCs, endosulphan and lindane and high volume herbicides, such as atrazine are reaching remote lakes. Decabromobiphenyl ether (a PBDE) and perfluorooactane sulfonic acid (PFOS), a product recently recently removed from the market, are also of concern.

In contrast, in Mexico, the occurrence of PTS and their levels in all environmental compartments are practically unknown. Large parts of Mexico are unstudied including the mountainous sub-region bounding the western edge of the region, coastal and riverine areas.

The **European Region** has produced a lot of information concerning the environmental levels of PTS. Monitoring systems for some PTS have existed in some countries at national (e.g. German rivers, food studies in many countries) and regional (e.g. air and deposition (EMEP), seas (OSPAR, HELCOM), etc.) levels. Some new programmes are ongoing (Caspian Sea and Black Sea, increased analysis of PCDD/PCDFs in foodstuffs). Human exposure is currently measured and studied in Europe at national level and through WHO activities.

As a result of former production and widespread use, OC pesticides, PCBs, PCDD/PCDFs, PAHs and also some new PTS are found in all environmental compartments, although monitoring indicates that the loads have been reduced by at least 50 % since the late 80’s, especially in the Baltic Sea. However, problems still persist. The Black and Caspian Seas still have many heavily contaminated sites and various obsolete pesticides still remain in temporary storage awaiting suitable disposal. Some “hot spots” also deserve consideration in the former eastern communist countries.

Several studies reported that air PCDD/PCDF levels are declining in urban/industrialised centres. These trends are observed in Western Europe and are believed to be largely due to emission abatement actions taken in the early nineties. Moreover, the human dietary intake of dioxins and furans dropped by almost a factor of 2 within the past 7 years. This reflects changes in diet, reductions in air emissions and controls on chemicals as well as changes in industrial and domestic behaviour. There is no reason to assume that the same pattern will be observed in all regions.

A substantial amount of information exists on the distribution of PTS in the different environmental compartments of the **Mediterranean Region**. However, data is often missing for some compartments, particularly atmosphere, ground and drinking water, soil and sewage sludge, etc.

The existence of the Mediterranean Action Plan (UNEP) has contributed significantly to monitoring activities of the marine environment. PTS comparison between Western and Eastern Mediterranean basins has been approached using the Audouin’s Gull eggs. Levels are significantly and consistently higher in the Western than in the Eastern basin, and, in general, significantly higher than in samples from the North Atlantic or the Arctic. Mediterranean marine mammals (dolphins) also exhibit values higher than those found in similar species living in the Atlantic.

During the period 1979-1998, the French monitoring network of coastal pollution shows general decreasing trends in the order: DDT>HCHs>>PCBs>PAHs, although they are not so evident for the latter two, indicating a steady source of these contaminants in the Mediterranean ecosystem. Results also suggest that atmospheric concentrations of PCBs have remained approximately constant during the past decade.

Localised “hot spots”, near sewage outfalls of big cities (e.g. NW Mediterranean and Northern Adriatic), the mouths of large rivers (e.g. Rhone, Seine, Po and Nile), coastal enclosures (e.g. Izmit and Iskenderun Bays, Venice Lagoon, etc.) and dumpsites (e.g. Durres, Skopje, Alger, Mustaganem, etc.) have been identified.

Apart from areas of intense local contamination, compounds of regional concern are PCBs, DDT, HCHs, PAHs, HCB and TBT. Other compounds e.g., phthalates, alkylphenols, PBDE/PBBs and PFOS are suspected to be ubiquitous but data are lacking.

Sub-Saharan Africa is mainly an agricultural continent and it has been using pesticides for pest and disease control for more than 30 years. Except for South Africa and Zimbabwe, no systematic pesticide monitoring/analysis was found in other country of the region. A big data gap therefore exists in the region as far as levels of PTS in the environment are concerned.

From the data gathered through filled questionnaires, the trend of concentration observed in Sub-Saharan Africa for PTS is DDT> PCBs> toxaphene. Open burning and the subsequent atmospheric release of PTS, particularly PAHs, is of major concern in the region. Data apparently indicate that humans were less exposed than animals and vegetation to PTS during the period 1970 - 2002. However, accidental or occupational exposure and food contamination still remain as the major risks.

In this respect, the occurrence of relatively high levels of DDT, PCBs and dioxins in adipose tissues and blood of occupationally exposed persons is of high concern. Equally disturbing is the high levels of HCB, lindane and endosulphan in human breast milk for the region in view of WHO's vigorous campaign that mothers breast milk is best for children.

In the **Indian Ocean Region**, considerable information is available on PTS levels in various environmental compartments and matrices, especially in India and Pakistan. The levels of the organochlorine pesticides in surface and ground water of various countries, especially those of agrarian and rural background could cause concern for long term low exposure effects on man and livestock as well as ecotoxicity.

PCDD/PCDFs and PCBs were rated of highest concern in regard to their levels in the environment. Among the PTS pesticides, DDT was of highest concern followed by the “drins”, atrazine, lindane and endosulphan. A similar pattern of response was obtained for data gaps, PCDD/PCDFs, PCBs and DDT were the chemicals that the experts considered of highest priority.

In the **Central and North-east Asia Region**, the results of the scoring exercise revealed that PCDD/PCDFs, PCBs, DDT and PAHs are chemicals of regional concern in terms of environmental levels and ecotoxicological effects, and these plus HCHs are of regional concern for human health. With regards to data gaps, there are insufficient reliable data on 7 of the 18 chemicals. These chemicals are mainly industrial chemicals (PCBs, HCHs and PBDE) and unintentional by-products (PCDD/PCDFs and PAHs). There is also insufficient data related to DDT and toxaphene. More information is needed concerning the temporal and spatial distributions of PTS in different ecological compartments, especially in developing countries and countries with economy transition.

In the **South-east Asia and South Pacific Region**, the levels of several PTS in air have been reported to be high in the Southeast Asian countries. In particular, DDT, chlordanes, HCHs, and PCBs were found to be relatively high in the air above coastal areas. Biomass burning (e.g. Indonesia) has produced episodic events of smoke haze and associated PAHs emissions. High levels of DDT and PCBs were found in soil across the region but some sites in Australia and Viet Nam were reported to be the most contaminated. However, studies of temporal trends revealed that DDT and several other chlorohydrocarbon pesticides are decreasing exponentially. Endosulphan and lindane were found at high levels in sediments and river waters in the region, particularly Malaysia and Thailand, suggesting the recent use of these chemicals.

The PTS levels in marine organisms such as fishes and mussels have been extensively studied in the region in the context of the Mussel Watch program. The spectrum of PTS in the collected samples has been reported, although there were indications that the levels of PTS for DDTs, HCHs and PCBs were declining.

PTS levels in humans have not been widely determined although Australia, New Zealand, and Singapore have undertaken population monitoring studies. New Zealanders have been found to have very low levels of PTS in blood and breast milk and could provide baseline values to compare with the rest of the region’s human population.

The amount of available data on environmental levels of PTS in the **Pacific Islands Region** is extremely limited. Many Pacific Island countries appear to have had no PTS analyses performed.

Where data exist, a large number of samples had detectable levels of PTS owing both to local usage and global transport especially by wind currents. PTS were recorded in some samples for which there is no knowledge that particular chemical was ever imported into the country. This could indicate either illegal entry or environmental transport.

In general, concentrations are relatively low for most samples. Overall the highest concentrations were found for DDT and its derivatives, especially in Papua New Guinea and Solomon Islands where DDT is used to control malarial mosquitoes. Also PCBs, which have been used as electrical oil insulating material and often disposed of in a haphazard manner were detected. A few urban contaminated sites are the result of past military activities in the region.

Data on PTS is highly scattered in the **Central America and the Caribbean Region** and difficult to assess because of the lack of monitoring networks and the variability of analytical methods used. OC residues, and particularly DDT, have been reported in agricultural areas (e.g. cotton, coffee and rice fields) of all countries, although most information dates back from the 80's. DDT, aldrin, lindane and endosulphan have been the most widely reported pesticides in different compartments. Combustion of leaded gasoline, diesel, other fuels and wastes, along with aerial spraying of pesticides release contaminants directly to the atmosphere. No regional data are available on groundwater transport of PTS.

The Caribbean coast is a critical sub-region. Dense tanker traffic and offshore oil exploration contribute to hydrocarbon contamination. Rivers transport high quantities of pesticides to the seawater. A Mussel Watch survey was conducted in 1995 in the region to assess coastal pollution. Massive coral mortalities and egg shell thinning cases have been reported in the past. Acute human poisoning by pesticides has also been frequently reported in the region (e.g. in Colombia, Guatemala, Nicaragua and El salvador), the causal agents varying according to use patterns and toxicity. Regional data suggest neurobehavioral deterioration following exposure to DDT and an association between breast cancer and DDE concentrations.

In the **Eastern and Western South America Region** information about environmental concentrations is heterogeneous, strongly biased towards some compartments and with scarce evaluation of temporal or spatial trends.

Very few data were retrieved for air samples, some of them related to PAHs levels in atmospheric particulate from urban areas (Santiago de Chile, Sao Paulo, Buenos Aires, La Plata). High levels in urban settings could represent a serious threat to human health considering that more than 75% of the total population within the region lives in these densely populated urban centres.

Some hot spots were reported from Brazil mainly related to contaminated industrial sites where HCHs and aldrin were produced. In Chile, a national survey performed by INIA in early 90's reported low levels of chlorinated pesticides in agricultural soils, concluding that the banning of pesticides during the 80's was effective. The industrialised and urban areas of Rio de la Plata (Argentina and Uruguay), Rio de Janeiro (Brazil) and Biobio River (Chile), present critical PTS values far exceeding international regulations.

The results of the Mussel Watch program indicate some critical coastal areas in Argentina (Río de la Plata), Brazil (Recife) and Chile (Punta Arenas). Available fish data also support the higher degree of PTS contamination in urban-industrial centres.

DDTs, HCHs, drins, heptachlor and endosulphan are the most frequently detected pesticides in food, mainly dairy products. In general, data shows a decreasing trend especially for DDT, and in the last few years, pesticides are being detected below accepted threshold levels.

3.5.2 General conclusions

From the presented information, it could be stated that in the industrialised world, levels of older or obsolete chlorinated pesticides are declining, since recent reported levels are much lower than those reported in late 80's or the early 90's. This decline could be explained by the reduction of the inputs into the environment from the recognised sources. The PTS pesticides may still be a problem in those regions highly dependent on agricultural goods, such as the Sub-Saharan Africa, Indian Ocean and Central and South American Regions, and those regions where these chemicals were produced, such as in the east Asian regions. Even though there is evidence of reduction in environmental levels of PTS pesticides occurring in temperate countries, this is not true for remote areas such as the Arctic, where an increase in some environmental levels has been detected. This is of concern because environmental conditions favour a higher persistence and hence a higher probability for PTS entering into the aquatic food web.

Concern regarding pesticides is heightened especially with the continued use of chemicals such as lindane and endosulphan as these are widely found in the different environmental compartments and in some cases in very high levels in the abiotic environment.

Industrial chemicals such as PCBs are of great concern in several regions of the world. Some regions report declining concentrations in the abiotic environment but there is concern that this is not always true for the developing world where very few data were retrieved and in some case very high levels were reported. In the case of dioxins and furans, it is clear from the data available from the Europe, North America, East Asia and Mediterranean Regions, that levels are always higher in urban and industrialised areas. In addition, it is clear that current waste management practices are a major source of these releases. Too few data are reported from other regions. Therefore, no firm conclusions can be advanced. Obviously, concern exists in several regions because the absence of data is characteristic for the developing world. Given the knowledge and experience in the industrialized regions of the world, it would be prudent to develop and advance sound waste management policies as a major global priority.

Incidentally, several war episodes have left the sad heritage of contaminated sites and subsequent human health effects (e.g. dioxins in Viet Nam, PCBs in Kosovo, oil in Kuwait, etc.).

Growing evidence of the occurrence and potential impacts of new chemicals suggest that detailed assessments should be conducted on flame retardants (PBDEs, PBBS and TBBPA), short chain chlorinated paraffins, perfluorooctane sulfonate (PFOS), polychlorinated naphthalenes (PCNs) and alkylphenol ethoxylates (APEs). Detailed studies of environmental concentration and associated observed effects are rare. In the case of emerging PTS, neither basic physical properties and toxicology information is not available nor as information on analytical methods.

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4 ASSESSMENT OF MAJOR TRANSPORT PATHWAYS

4.1 MOTIVATION FOR INTEREST IN THE TRANSPORT PATHWAYS OF PTS

PTS are a global issue due in part to their widespread use and emission but in particular because of their extraordinary mobility. A variety of transport processes are dispersing PTS throughout the global environment. An understanding of these environmental transport pathways of PTS is necessary because it provides a link, preferably quantitative, between sources of PTS and exposure to PTS within a region, and information on the potential of transport of PTS from one region to another (long range transport, LRT).

Such information is a necessary part of a control or amelioration strategy to reduce or eliminate harmful effects in the receiving environment. Regional and trans-regional PTS transport pathways can be investigated based on knowledge of both the physical characteristics of the regions and the fate-relevant properties of a particular PTS. Often a quantitative understanding is sought through the use of numerical models that integrate the multitude of transport and transformation processes in a comprehensive and quantitative picture of a contaminant's environmental fate. Such models can also provide a predictive capability through their application to PTS different from those they were originally developed and evaluated for, and by allowing forecasts about the future environmental fate of a PTS given alternative release scenarios. Some of the aspects of the environmental transport behaviour of PTS are common to all PTS and to all regions, but there are substantial differences in the transport and distribution behaviour between different PTS and also between different regions.

4.2 COMPARISON OF PTS FOR TRANSPORT PATHWAYS

Obviously a common feature of PTS is their high persistence. This characteristic increases the relative importance of transport relative to transformation in controlling a contaminant's fate. It is also a necessary, though not sufficient, condition for LRT in atmosphere, rivers and oceans. Another commonality is that most PTS have distribution characteristics that allow them to be in different environmental media (air, water, soils) in notable quantities. They are neither very polar substances, which would make them very water soluble and thus primarily water pollutants, nor are they very volatile, which would imply that they are mostly found in the atmosphere. PTS are typically sparingly soluble in water and are of intermediate to low volatility. They are therefore not exclusively air or water pollutants, but typically affect the environment as a whole and are sometimes referred to as multimedia pollutants.

Long range transport of PTS can thus occur by different modes (Figure 4.1):

- As a vapour, sorbed to suspended particles or dissolved in cloud water in the atmosphere.
- Dissolved in water or sorbed to suspended particles in oceans.
- Dissolved in water and sorbed to sediment particles in rivers.
- In tissues of migratory animals.
- Anthropogenic transport in the form of products and waste.

The relative importance of these transport pathways depends on the specific partitioning characteristics of a PTS substance. Four major groups of substances can be distinguished according to their volatility and water solubility (Table 4.1 and Figure 4.2).

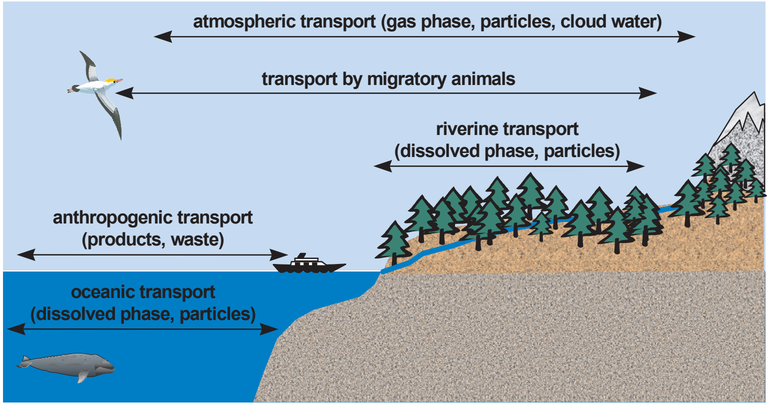

Fig. 4.1 Illustration of the various mechanisms by which a PTS can be transported over long distances.

Table 4.1 Categorisation of organic chemicals in terms of their LRT behaviour.

Category		Characterisation	Examples
A	no hop	Chemicals that are so volatile that they do not deposit substantially to the Earth's surface and therefore remain in the atmosphere	Chlorofluorocarbons
B	multi-hop	Chemicals that readily shift their distribution between gas phase and condensed phase (soil, vegetation, water) in response to changes in environmental temperature and phase composition, and therefore can travel long distances in repeated cycles of evaporation and deposition	PCBs,lighter PCDD/PCDF, HCB, toxaphene, dieldrin, chlordane, endosulphan
C	single-hop	Chemicals that are so involatile and so water-insoluble that they can undergo LRT only by piggy-backing on suspended solids in air and water	Heavier PCDD/PCDF, five ring PAHs such as benzo-a-pyrene, heavy PBDEs, mirex, decachlorobiphenyl
D	no hop required	Chemicals that are sufficiently water soluble to undergo LRT by being dissolved in the water phase	HCHs, PCP, atrazine, phthalates, PFOS

To which category a particular PTS belongs can be assessed from its distribution properties. Figure 4.2 uses a space defined by the octanol-air and air-water partition coefficients log K_{OA} and log K_{AW} to characterise a chemical's distribution properties (octanol serves as a surrogate for organic matter in the environment). Increasing K_{OA} implies decreasing volatility, and increasing K_{AW}-decreasing water solubility (Fig. 4.2A). Each organic chemical occupies a location in this map. Model simulations can identify, which sections of this map (and therefore which chemicals) share similar distribution properties and thus similar transport behaviour (Fig. 4.2B). Chemicals with high K_{AW}, but low K_{OA} fall into category A ("no hop"), those with high K_{OA} to category C ("single hop"). Chemicals with low K_{AW} and K_{OA} are category D ("no hop required"), whereas category B ("multi-hop") includes chemicals with intermediate volatility and water solubility.

None of the PTS assessed in this report is so volatile to belong to category A. Instead, most PTS chemicals fall into that part of the map, where categories B, C and D intersect (Fig. 4.2C). Most PTS are mixtures of chemicals, consisting of constituents with widely variable distribution characteristics. As a result, the areas that correspond to various PTS in Fig. 4.2C straddle often two or more transport categories. This implies that different constituents of these mixtures can undergo different transport pathways. Whereas e.g. the lighter congeners of the PCBs and PCDD/PCDF are "multi-hop" chemicals (cat. B), the heavier congeners of the same PTS undergo "single hop" transport behaviour (cat. C). The boundaries between the various categories are not sharp, and a single chemical can belong to more than one group. Category D, for example, overlaps with C, ie some substances undergoing aqueous LRT are also capable of undergoing multi-hop atmospheric transport. An example is hexachlorocyclohexane (HCH). As both K_{OA} and K_{AW} are temperature dependent, the boundaries between the categories shift to the upper left with increasing temperature. This means that the categorisation of a PTS may change depending on the temperature of the environment in which they find themselves.

The transport behaviour of "single hop" compounds (category C), such as a benzo-a-pyrene (a PAH) or octachlorodibenzo-p-dioxin (a PCDD/PCDF), is mainly controlled by the location of atmospheric PTS sources relative to the major atmospheric flow patterns. Atmospheric conditions at the time of release will have a strong impact on their transport behaviour and areas close to the sources are generally affected more strongly than those further away. Efficient LRT is restricted to episodes that are characterised by conditions that favour rapid horizontal air movement, limited vertical air movement and lack of precipitation. Once deposited, these chemicals will only move if the particles to which they sorb are remobilised, eg as a result of storm run-off or dust storms.

On the other hand, the LRT behaviour of "multi-hop" substances (category B), such as hexachlorobenzene or tetrachlorobiphenyl, is controlled by the ease of transfer between the atmosphere and the Earth's surface.

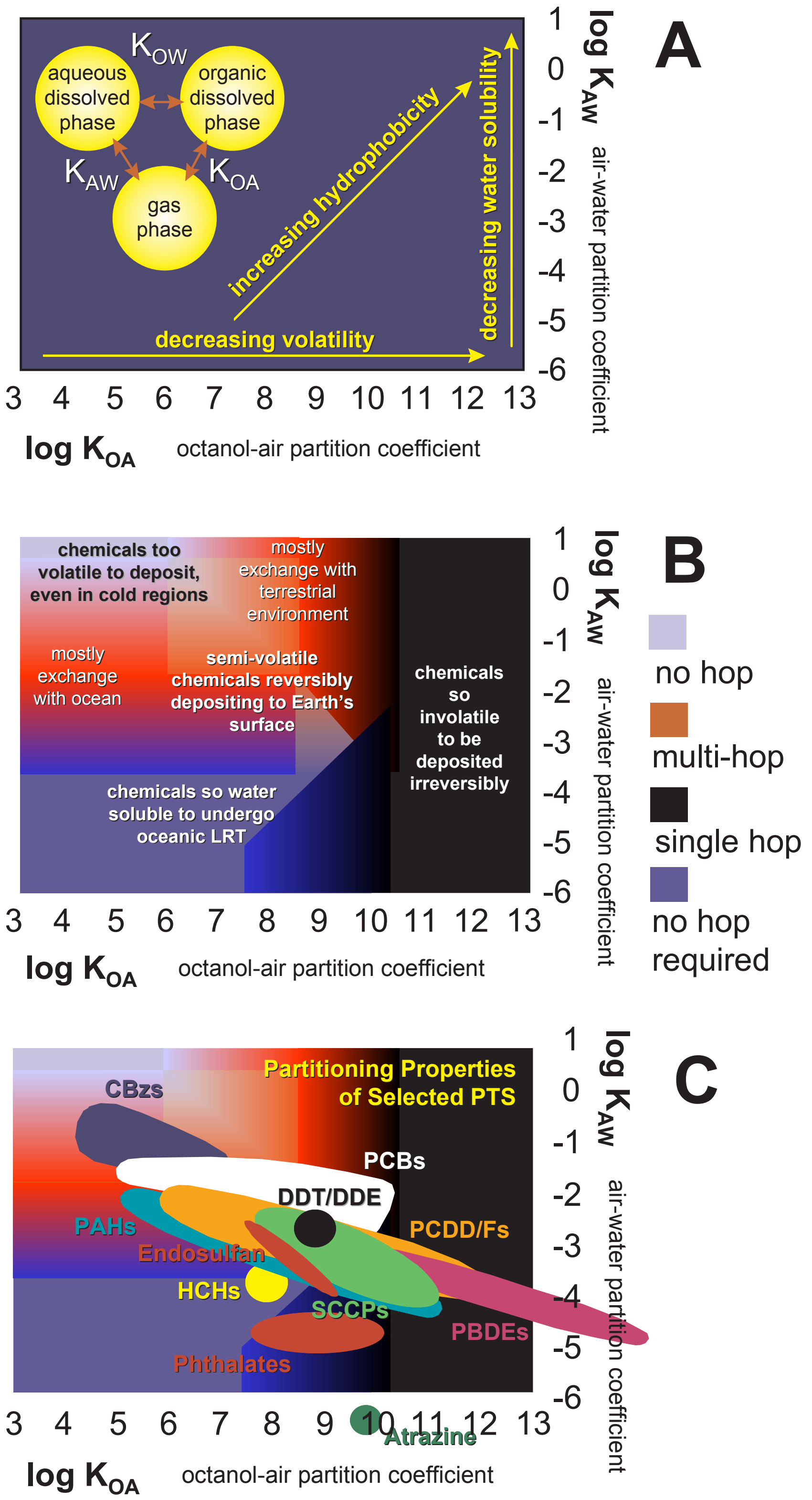

Figure 4.2 Categorisation of the transport behaviour of organic substances as a function of their distribution characteristics, defined by the air-water and octanol-air partition coefficients log KAW and log KOA (A). Four different categories of transport behaviour are identified and assigned distinct sections of the two dimensional partitioning space (B). Selected PTS mixtures are placed on this space to allow their easy categorisation (C).

Persistent chemicals which change from a gaseous state to a condensed state within the environmentally relevant temperature range, will undergo air-surface exchange (ie hop) more often and are most likely to travel far. Because cold temperatures favour deposition over evaporation and warm temperatures favour evaporation over deposition, hopping is enhanced by diurnal (Hornbuckle and Eisenreich, 1996, Lee et al., 1998) and seasonal temperature changes (Hoff et al., 1992, Wania et al., 1998).

Temperature gradients in space in combination with atmospheric mixing will favour gradual transfer from warm to cold regions (Wania and Mackay, 1993). This is observed both on a global scale (Iwata et al., 1993, Wania and Mackay, 1996) and on a regional scale, eg along altitudinal temperature gradients (Blais et al., 1998, Grimalt et al., 2002). Efficient retention in soils, vegetation and sediments as well as slow degradation will prevent the bulk of the global chemical inventory to be displaced to cold regions (Ockenden et al., 2002). Because of the relatively small size of the Earth's cold regions even a relatively small fraction of that inventory can result in elevated concentration levels in polar and high altitude regions ("cold condensation") (Wania and Mackay, 1993, 1996).

Since different PTS undergo air-surface exchange to a different extent, PTS mixtures tend to experience shifts in their relative composition with distance from source or along latitudinal and altitudinal gradients. The less volatile constituents of a mixture are being retained more efficiently close to the source, whereas the more volatile constituents are travelling further. PTS mixtures, such as the PCBs, will thus become relatively enriched in the more volatile components with increasing distance and decreasing temperature (Fig. 4.3). This phenomenon, called "global fractionation" (Wania and Mackay, 1993, 1996), has been confirmed by measurements of compositional shifts of PCBs in sediments and soils (Muir et al., 1996, Meijer et al., 2002).

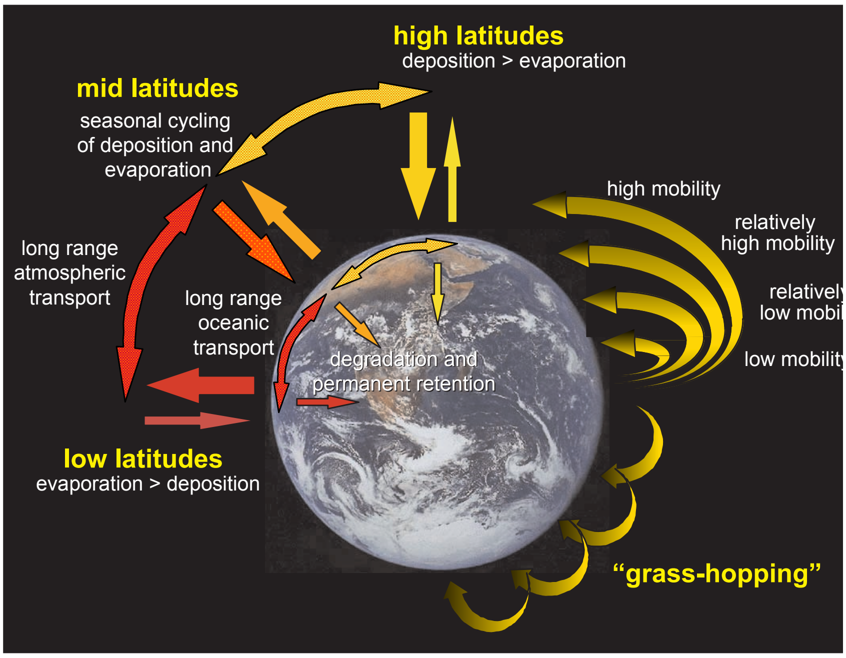

Fig. 4.3 Illustration of the principles governing the LRT behaviour of PTS, that can reversibly exchange between the atmosphere and the Earth's surface.

"No hop required" chemicals (Category D), such as atrazine, PFOS, or many phthalates, are so water soluble that they remain dissolved in the aqueous phase, ie volatilisation is not required for long range transport to occur. Such transport can take place in major rivers and oceans. Efficient LRT in water requires also high persistence in water. Because the same functional groups that impart water solubility often also increase the rate of degradation, such chemicals typically do not have a high potential for long range transport.

To some extent the categorisation of Table 4.1 and Figure 4.2C can assist in identifying the more mobile substances among the PTS. Chemicals undergoing multi-hop transport have a higher potential for LRT than single hop chemicals, if they are sufficiently persistent to survive for the time period it takes to undergo multiple deposition and evaporation cycles. This suggests that PTS with the partitioning properties of the lighter to intermediate PCBs, the DDT-related substances, endosulphan, the lighter short-chain chlorinated paraffins, the lighter PCDD/PCDF and the highly chlorinated chlorobenzenes have substantial atmospheric LRT capabilities, if the environmental conditions are such that their degradation is slow. PTS substances with the distribution characteristics of the heavy PBDEs and PCDD/PCDF have comparatively small potential for atmospheric LRT.

Even though the different modes of transport influence the extent of potential LRT, they do not necessarily make a chemical more or less of a threat. The potential for LRT (or the mode of transport as defined in Table

4.1) has in itself no direct relation to a chemical's potential for doing damage. One could even argue that a chemical with a small LRT is likely to achieve higher concentrations close to sources (because of the lack of dilution by transport) and thus is more likely to cause effects. However, there are several reasons why a high potential for LRT is nevertheless cause for concern:

- A chemical that has a high LRT, will potentially affect a large area. This implies that if there were effects/threats, these would not be contained, but potentially affect a huge human population or many ecosystems, ie, the effects might be widespread, even ubiquitous.
- A chemical with a high LRT potential may cause exposure, and therefore some risk to humans and their environment, in areas where such exposure would not occur normally, ie, without LRT.
- This is related to the issue of environmental justice. High potential for LRT increases the likelihood that the beneficiaries of the use of a chemical have a lower risk than those persons far removed from such benefits and who are passively exposed.
- Finally, LRT is the justification to deal with a chemical on an international level. A chemical with low LRT is a national concern and one may argue should be regulated at the national level.

4.3 COMPARISON OF PTS TRANSPORT BEHAVIOUR IN THE REGIONS

Despite the huge diversity of the various regions, there are some common features to PTS transport:

- **The *multimedia nature* of most PTS**: the need to take into account the multimedia nature of most PTS and the region-specific dynamics of exchange between these media. Whereas the relative importance of various transport pathways may differ between regions, the basic mechanisms and principles of LRT (Figs. 4.1. through 4.3) are valid throughout the global environment.
- **Interest in *land to ocean/lake transfer* of PTS by atmospheric and riverine pathways:** The sources of PTS are mostly land-based, whereas many receptors are aquatic (fish/marine mammals). Human exposure to PTS is also often mediated through the aquatic food chain. Populations relying heavily on aquatic organisms for nutrition tend to be most at risk with respect to PTS. Examples of land to water transfer pathways of regional importance are the transport of PCDD/PCDF and other PTS from Japan to the Northern Pacific Ocean (Region VII Report), input of land-based PTS to the Mediterranean Sea (Region IV Report), and the transfer of organochlorine pesticides from agricultural use areas to the North American Great Lakes (Region II Report) or the Baltic Sea (Region III Report).
- **Interest in *transoceanic or transcontinental atmospheric transport between region:*** In the Arctic and Antarctic, local sources of PTS are minor and quantifying trans-regional transport becomes imperative for understanding the origin of PTS in these regions (Region I Report, Region XII Report). The same applies for particular PTS that were not used in a Region and whose occurrence in the environment thus signifies transport from other world Regions. Examples are transoceanic transport of DDT and other pesticides across the Pacific Ocean (Bailey et al., 2000), or the exchange between Europe and Africa (Region IV Report).
- **Interest in *pollutant convergence zones*:** As effects of PTS tend to be associated with elevated contamination levels, the convergence of PTS in particular parts of the environment is a common concern across the Regions. Various mechanisms operate to focus PTS in estuaries, lakes, and mountain regions. Recently, attempts to conceptually categorise the phenomena leading to contaminant amplification have been presented (Wania, 1999, MacDonald et al., 2002).

The various regions differ immensely in terms of:

- ***Climate***, including temperature, precipitation and wind speed, and its seasonal and diurnal variability.
- ***air flow patterns*** and ***ocean currents***.
- ***Surface coverage*** including land/ocean distribution, land surface cover (vegetation type/lakes/land use/snow cover), and topography.
- **Characteristics of the *hydrological cycle:*** Includes type, frequency, seasonality and intensity of precipitation, evaporation and run-off.

How such regional characteristics can affect the transport behaviour of PTS will be discussed in the following sections.

4.3.1 Region-Specific Influences on Atmospheric Transport of PTS

4.3.1.1 Influence of Air Flow Patterns on Atmospheric Transport of PTS

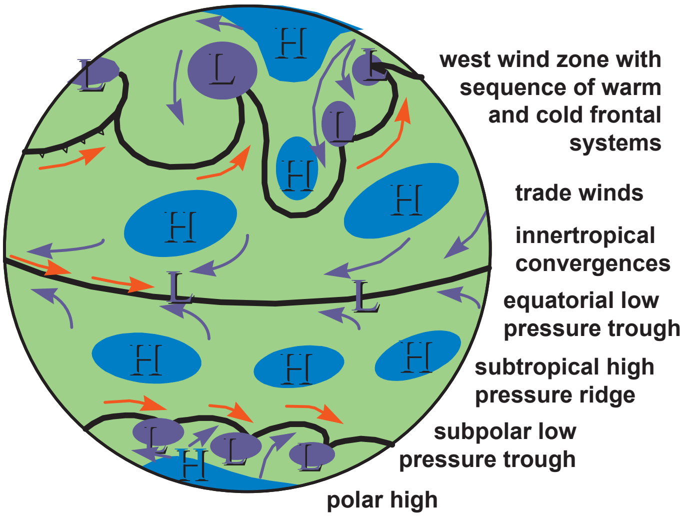

Fig 4.4 Illustration of the planetary pressure and wind belts in the atmospheric boundary layer. Blue and red arrows depict cold and warm winds, respectively.

The direction of atmospheric transport is influenced by air flow patterns, which in turn are the result of the general atmospheric circulation. Fig. 4.4 shows a simplistic diagram of the major global pressure and wind systems. There are several key features relevant for the atmospheric LRT of PTS:

In the mid-latitudinal west wind zone, there is a preferential direction of mass flow year round resulting in clear upwind/downwind patterns. The Northern Atlantic Ocean receives much of its PTS load from North America, whereas the Northern Pacific is the recipient of PTS originating in Asia. Trans-oceanic PTS transport in this zone occurs from Asia to North America and from there to Europe. Also on a smaller scale, ie within the regions, the westerly wind leads to pollutant transfer that is usually unidirectional, eg from Western to Eastern Europe. We may also suspect that the sequential passage of warm and cold frontal systems within the mid-latitudes encourages hopping in response to changing temperatures.

The uneven continent/ocean distribution in the Northern hemisphere assures that the location of high and low pressure system is not statistically random, but that preferential air mass movements occur. For example, the pronounced high pressure system over winter-time Siberia directs European air masses preferentially northward, which is the basis for effective atmospheric transport of PTS originating in Europe to the Arctic environment. Also because of these differences in land/ocean distribution, the extent of meridional exchange is much stronger in the Northern than in the Southern hemisphere. Antarctica is therefore much more isolated from the rest of the global atmosphere than is the Arctic.

Regions exist within the influence of the inner-tropical convergences with pronounced seasonal changes in air flow, ie the monsoons. These wind systems are particularly pronounced in the Indian Ocean region. PTS may be transported in one direction in one season and in the opposite direction during another. For example, the Arabian Sea is influenced by PTS transport from the Indian subcontinent during the NE monsoon (see also Fig. 4.S), but air flow from Arabia and Western Africa during the SE monsoon. Such influence of different air masses is evidenced by the occurrence of higher concentrations of DDT, PCB, and pyrolytic PAHs during the NE monsoon and of fossil hydrocarbons during the SW monsoon (Dachs et al., 1999). The seasonal changes in wind direction is often combined with variable precipitation patterns, suggesting distinct seasonal differences in the direction and extent of atmospheric PTS transport.

Another feature of the general circulation pattern with importance for PTS transport is the very limited exchange of air masses between the hemispheres, resulting from the inner-tropical convergence. For example, there is no evidence of PTS transport between SE Asia and Australia and vice versa (Region VIII Report), and many PTS show distinct concentration gradients at the equator.

Air flow patterns can be strongly influenced by topography. The Western Cordillera obviously has a strong influence on air and contaminant flow patterns in the Americas, and the Himalayas greatly restrict contaminant exchange between Regions VI and VII, although it is possible (Hindman and Upadhyay, 2002).

4.3.1.2 Influence of Air-Surface Exchange and Degradation on Atmospheric Transport of PTS

The extent to which a chemical can undergo atmospheric LRT is influenced by its residence time in the atmosphere, which in turn is dependent on the kinetics of its *atmospheric degradation* and *deposition*. Chemicals that neither degrade rapidly in the atmosphere, nor deposit to the Earth's surface effectively, will have the greatest potential for atmospheric LRT. If a chemical is emitted into media other than the atmosphere (eg discharge to water/application of a pesticide to soil, vegetation or human residences), its potential for atmospheric LRT is further influenced by the rate of *evaporation*, ie by how quickly it can enter the atmosphere.

4.3.1.2.1 Atmospheric degradation

The most likely reaction of most PTS chemicals in the atmosphere is with the hydroxyl radical (OH). The concentration of OH radicals, and therefore the rate of atmospheric reaction, varies greatly with season, time of day, latitude and altitude. Highest OH radical concentrations, ie fastest degradation and thus reduced atmospheric LRT, occur in low latitudes, at high altitudes, during day time and in summer. The reaction with the OH radical is also temperature-dependent with reaction occurring faster at higher temperatures. In the sub-tropical atmosphere, daytime depletions of PCB concentrations could be explained by efficient reaction with simultaneously measured OH radicals (Mandalakis et al., 2003). The potential for chemical *evaporation* increases with higher temperature, higher wind speed, and reduced retention capability of surface material. For example, evaporation potential would be very high from a hot desert sand but very limited under a snow-covered organic-matter-rich soil under a dense forest canopy.

4.3.1.2.2 Atmospheric deposition

Involves multiple pathways, such as dry and wet deposition of both gaseous and particle-associated PTS. Influence of regional climatic characteristics on the potential for deposition is thus quite complex, but PTS deposition processes tend to increase with higher precipitation rate, lower temperature, higher atmospheric particle load, higher wind speed and atmospheric turbulence, and high retention capacity and roughness of the surface.

Whether certain climatic regional circumstances enhance the potential for atmospheric LRT is thus quite complex and ultimately dependent on the specific chemical characteristics of a PTS. For example, a higher temperature may decrease the potential for atmospheric LRT by enhancing degradation, but it also decrease deposition rates thus potentially promoting atmospheric LRT (Beyer et al., 2003). Different chemicals thus may see an increase or a decrease in their potential for atmospheric transport with a change in temperature (Fig. 4.5). We may nevertheless attempt to draw some general conclusions concerning the potential of PTS for atmospheric LRT under different climatic circumstances.

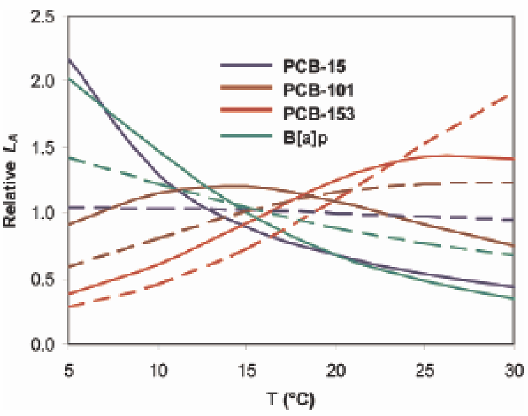

Fig. 4.5 Characteristic travel distance for four chemicals calculated as a function of temperature (Beyer et al., 2003).

4.3.1.2.3 Low latitudes

High temperatures at low latitudes should generally lead to a high potential for evaporation (Samuel and Pillai, 1989, 1990) but high OH radical concentrations would favour relatively fast degradation in the atmosphere. Deposition rates may also be high in areas of frequent and strong rain fall or if atmospheric particle concentrations are high, eg downwind of highly polluted urban areas (Ramanathan et al. 2001). For PTS that are reacting reasonably fast with OH, such as the PAHs, these considerations suggest that atmospheric LRT in low latitudes may be quite limited. Chemicals such as HCB survive long enough at the OH radical concentrations prevalent in the low latitude atmosphere. For these, there may be a high potential for rapid cycling of multi-hop PTS (category B) driven by diurnal temperature fluctuations and by cycles of wet deposition and evaporation. This may result in effective regional re-distribution from source areas to areas of high rain-fall and/or regional cold spots (eg mountains). Similarly, single-hop PTS (category C) from urban/industrial sources (PCDD/PCDF, PAH, etc.) may be focusing in regions of high rain fall downwind/ uphill from these sources. In areas affected by the monsoon, we would expect potentially large seasonal differences in the scope and direction of atmospheric LRT.

4.3.1.2.4 Mid-latitudes

Are characterized by a constant fluctuation of conditions favourable for evaporation/ degradation and deposition/persistence. These fluctuations occur on a diurnal and seasonal scale, and as a result of the frontal nature of mid-latitudinal circulation also on a time scale in between. For PTS whose LRT is limited by efficient degradation (relatively reactive, relatively volatile, examples are lighter PCB congeners or most of the PAHs) atmospheric LRT is higher in winter, whereas for chemicals whose LRT is limited by efficient deposition (relatively slow reaction, semi-volatile, examples are the heavier PCBs or the PCDD/PCDF) the opposite will be the case.

4.3.1.2.5 High latitudes

Generally have a low potential for evaporation (ice and snow cover) and degradation (dark and cold), although during polar summer there is considerable solar radiation and thus OH radical formation, especially at the higher altitudes of the Antarctic continent. During snow metamorphosis and melting, there is also a potential for substantial evaporation of PTS. Some polar characteristics such as low temperature and efficient snow scavenging may suggest efficient deposition under polar conditions but low precipitation rates, a low atmospheric particle content and a generally strong atmospheric stratification suggest otherwise.

4.3.2 Region-Specific Influences on Oceanic Transport

4.3.2.1 Influence of Currents on Oceanic Transport of PTS

For relatively water soluble compounds (category D, eg HCH or PFOS), the ocean is increasingly recognised as a slow, but nevertheless efficient medium for LRT. Analogously to the situation in the atmosphere, the direction of oceanic transport depends on the large scale oceanic circulation. The dominant feature of that oceanic circulation is the “conveyor belt” that transfers water masses between the world oceans and between the surface and deep ocean on the time scale of a 1000 years (Fig. 4.6). On a regional scale, currents in the surface ocean are driven by geostrophic winds (Fig. 4.7). In the equatorial region these currents are mostly in a zonal direction, easterly in the equatorial counter current and westerly to the North and South of the equator. Cold currents flowing towards lower latitudes, such as the California and Humboldt current in the Eastern Pacific and the Canary and Benguela currents in the Eastern Atlantic, occur on the western side of continents. Examples of warm currents flowing to higher latitudes along the Eastern rims of the continents are the Kuroshio and Eastern Australian currents in the Western Pacific, and the Brazil current and Gulf Stream in the Atlantic. Together these currents form gyres within the subtropics that flow clockwise in the Northern hemisphere and counter-clock wise in the South. An example is the subtropical gyre forming in the Southern Indian Ocean and including the Western Australian current and the Agulhas current off Southern Africa. These currents determine the potential direction of marine long range transport of PTS.

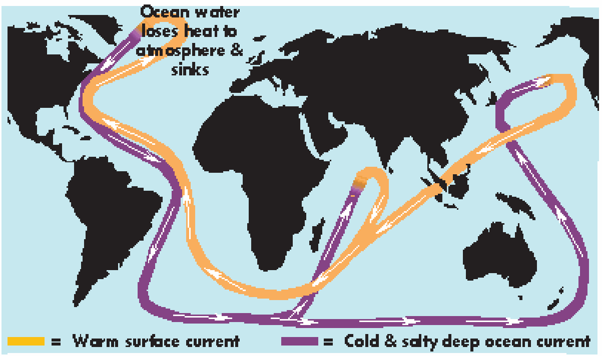

Fig. 4.6 Schematic of the global oceanic conveyor belt.

Several of the Regional Reports (eg Region VIII Report, Region X Report) highlight the role ocean currents potentially play in transporting PTS, although very little experimental evidence exists for marine transport of PTS in lower latitudes. PTS, delivered to the ocean by the great South American rivers (Amazon, Orinoco, St. Magdalena), may be transported to the Caribbean Islands (Region X Report). HCH may be exchanged between the various regional seas of South East Asia, and this exchange may be subject to similar seasonally variable flow conditions as for the atmosphere (Region VIII Report). The best evidence for marine LRT comes from the extensive study of the distribution of HCH in Northern waters. These investigations have revealed the large scale transport of PTS within and between ocean basins (MacDonald et al., 1997, 2000, Li et al., 2002). In analogy to the atmosphere, the Southern Ocean is relatively isolated from the rest of the world's ocean through the Antarctic convergence.

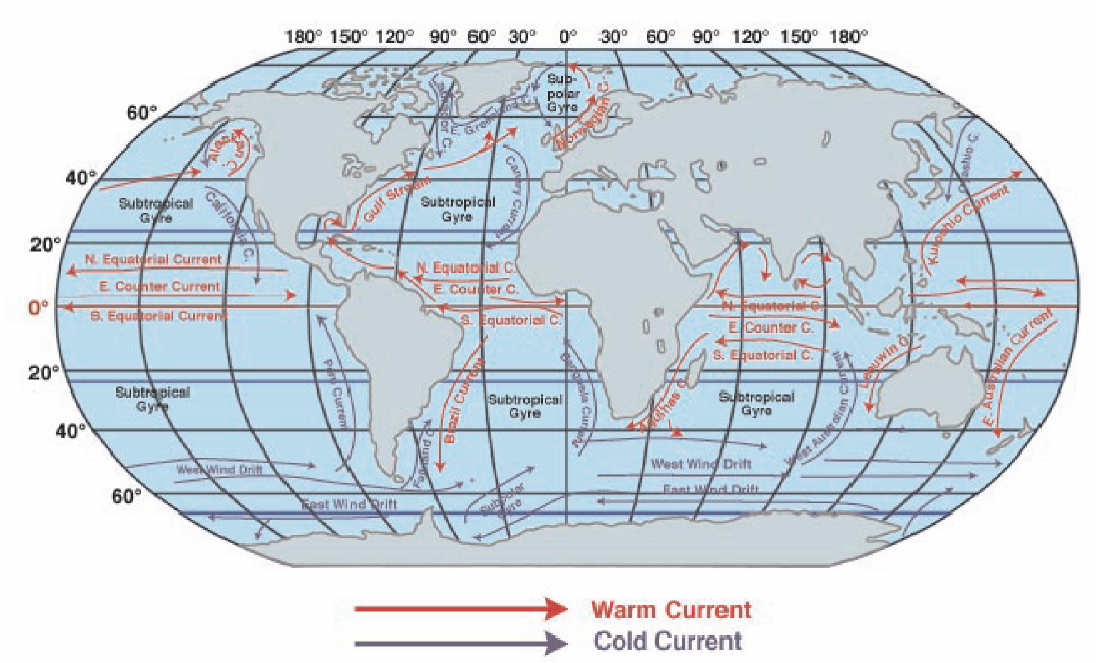

Fig 4.7 Global map of the wind-driven surface ocean current patterns (Source: NASA).

4.3.2.2 Influence of Particle Settling and Degradation on Oceanic Transport of PTS

Over longer distances, the oceanic transport of PTS is important only for fairly water soluble compounds that are extremely persistent in the aqueous phase. The persistence requirements for oceanic LRT are much higher than for atmospheric LRT, because of the slow pace of oceanic transport. Whereas degradation half lives in air on the order of a few days are clearly sufficient for atmospheric LRT to occur, oceanic LRT requires chemicals to survive in water for several months to years. Less water soluble compounds (log K_{OW} > 5) will sorb effectively to suspended organic solids and therefore have only a limited residence time in the surface ocean because of gravitational settling (Dachs et al., 1996, 1999, Gustafsson et al., 1997).

The two processes that may limit the oceanic LRT of PTS are thus clearly dependent on regional characteristics. The rate of *degradation* of PTS in ocean water is dependent on temperature in the case of hydrolytic reactions (Ngabe and Bidleman, 1993), the presence and activity of microorganisms capable of metabolising a chemical in the case of microbial reactions (Hühnerfuss et al., 1993; Harner et al., 2000), and the intensity of sunlight in the case of aqueous phase photo-oxidation. This suggests that degradation is slower in high latitudes (less light, colder temperatures, less microbial activity) and faster in warm, sunny and biologically highly active seas. The extent of *gravitational settling* of PTS will similarly be dependent on marine biological productivity and is thus likely highest in coastal and shelf areas, and marine regions of nutrient upwelling. Deposition from the surface ocean has been estimated to be highest in mid-high latitudes (Dachs et al., 2002). Vertical oceanic transport with settling particles is not only of relevance in limiting oceanic LRT, but may also constitute a major final sink for very persistent PTS on a global scale. Thus it will determine the rate of concentration decline after phasing-out the use of these PTS (Dachs et al. 2002, Axelman and Gustafsson, 2002, Wania and Daly, 2003). Overall, indications are that oceanic LRT is most important at high latitudes, because low evaporation from water, slow degradation rates and limited gravitational settling will increase the residence time of PTS in cold surface waters.

4.3.3 Region-Specific Influences on Riverine Transport

The water solubility of many PTS is too small for rivers to be an important conduit for transport in the dissolved phase. The exceptions are relatively water soluble PTS (category D), such as HCH. Riverine transport of sparingly soluble PTS is thus dependent on the transport of colloidal or suspended sediment matter to which the PTS sorb. The load of suspended solids and colloidal organic matter in rivers in turn depends on the hydrological regime and drainage basin characteristics. During normal flow conditions, the load of dissolved and suspended organic matter depends on the relief, geology, vegetation cover and climate of a drainage basin. Unusually high suspended solids load in rivers are associated with high flow conditions, in particular periods of intense, even catastrophic run-off or floods. These conditions, as occur during snow melt, unusually heavy rainfalls, or episodic rain events in arid regions. For example, periods with high flow conditions (>5000 m^3/s) only account for 10 % of the water flow in the Rhone, but contribute about 80 % of the suspended particle and thus PTS flux (Region IV Report). Hurricanes in the Central American Region bring heavy rainfalls that quickly saturate soils and lead to surface run-off and erosion (Region X Report).

Contaminant transport with rivers is thus very region specific and there may even be large differences between rivers of one region. It is likely most effective in regions with contaminated sediments and the seasonal or episodic occurrence of high flow regimes leading to a substantial, though temporary increase in the suspended sediment load.

PTS transported with rivers will eventually contaminate coastal sediments. However, beyond the zone of influence of these discharges, concentrations drop rapidly reflecting the enhanced sedimentation processes which take place at the fresh water/sea water interface. In fact, 80 % of the terrestrial sediments are trapped on the continental shelf and only the finest particles are transported by currents to deep sea sediments (Region IV Report). The continental shelf will thus likely constitute the final resting place of many PTS delivered by rivers to the oceans (Jönsson et al., 2003). An exception may be the entrapment of sediments in Arctic sea ice with subsequent transport during ice drift (Pfirman et al., 1995).

4.3.4 Region-Specific Influences on Transport of PTS by Migratory Animals

Some organisms, such as migratory birds and marine mammals, undergo regular long distance migrations. Because of the bioaccumulative properties of many PTS and the high trophic status of these organisms, they often contain substantial amounts of contaminants. As the organisms migrate, they transport PTS within and between regions. Some of the key features of the transport of PTS by migratory animals are:

- Animal migrations occur generally in a meridional (North-South) rather than a zonal direction, because they are often related to the avoidance of seasonally unfavourable living conditions.
- Animal migrations are cyclical, ie occur in either direction, which implies that PTS accumulated in the organisms move in either direction as well.
- In terms of absolute quantities of PTS being moved, migratory animals are likely not a major transport pathway relative to transport in air and water (Wania, 1998). However, that is of little relevance to the organism itself because it is not the origin of the contaminants in the physical environment that is of importance, but the origin of the contaminants accumulated in its tissues. That also applies to the organism’s predators, including humans, that may hunt and consume migratory animals. For example, the amount of a PTS transported by a migratory bird or marine mammal to the Arctic may be negligible compared to the amounts advected into the Arctic with air and water masses. However, the Northern hunter may take up more PTS by eating these organisms and their predators (and thus PTS delivered to the Arctic by organisms) than by consuming non-migratory animals that took up PTS from the Arctic environment into which it had been delivered by abiotic means. Migratory birds in the Arctic acquire often the bulk of their pollutant load in their wintering locations.
- Because of the use/depletion of lipid reserves during migration, migratory animals may be particularly vulnerable to PTS that bioaccumulate in lipid tissues and are released upon mobilisation of lipids during migration.

Even on a smaller scale, contaminant transport by migratory animals may occur. Birds commuting between Venezuela and Trinidad are reported to transfer mercury across the ocean (Region X Report).

4.4 MODELS OF PTS FATE AND TRANSPORT

Models of the fate and transport of chemicals have a variety of uses. One of which will be to assess whether a chemical is likely to have effects beyond the country or region where it is released.

The types of models being developed and used vary greatly in their scope and complexity (Fig. 4.8). Generic models do not aim to describe transport in one specific region, but rather to assess the general and relative capabilities of chemicals to undergo atmospheric and/or oceanic long range transport. More ambitious approaches try to quantify PTS transport processes in a specific regional environment, with the complexity ranging from fairly simple, spatially unresolved fate models to meteorology-based regional transport models with high demands in terms of input parameters and computing resources. It appears that so far only a few of the 12 Regions, in particular Europe (Region III Report), North America (Region II Report) and Central and North East Asia (Region VII Report), have developed the capacity to describe PTS fate and transport under the specific environmental conditions prevalent in their Regions. Finally, there are several efforts of variable complexity to describe the global scale fate and transport of PTS. The purpose of the models is to take into account the influence of a chemical's environmental phase distribution on its ability to be transported over long distances. The environmental phase distribution is influenced by a large number of factors related to both environmental and chemical characteristics and is not necessarily intuitive or easily comprehended. A multimedia model provides a tool to take most of these factors into account in a transparent, objective and reproducible manner (van de Meent et al. 2001). Accordingly, there has been intense scientific activity within the last few years aimed at developing model-based approaches to LRTP assessment (Scheringer et al., 2001).

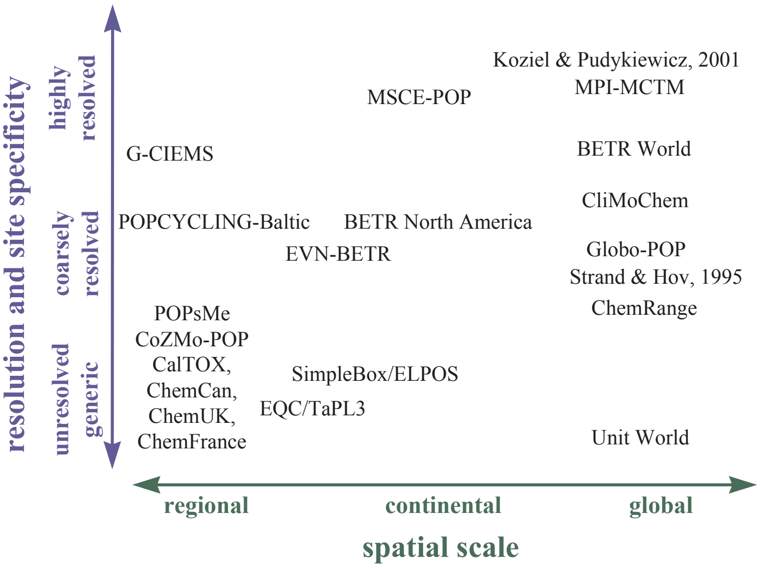

Fig. 4.8 Complexity and spatial scale of various transport models for PTS.

4.4.1 Generic Approaches to Long Range Transport Potential Assessment

Several approaches have been proposed to evaluate various chemicals in terms of their potential to undergo long range transport. These are exemplified by the models of Scheringer (1996), Beyer et al. (2000) and Wania (2003), who demonstrated that the LRT potential of a substance can be expressed either as a Spatial Range (SR), a Characteristic Travel Distance (CTD), or as an Arctic Contamination Potential (ACP). The absolute values of these numerical indicators have little real world significance because they depend on the specific model used and the input parameters. However, the relative size of such indicators allows one to discriminate, compare and rank different chemicals in terms of their LRT potential. Fig 4.9 shows the results of such calculations for a series of eight PCB congeners using four assessment models. Various models have been compared (Wania and Mackay, 2000, Bennett et al. 2001, Beyer et al. 2001, Wania and Dugani,

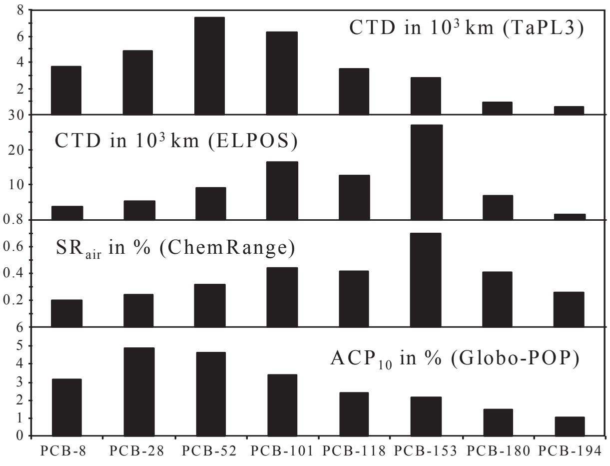

Fig. 4.9 Indicators of ALRT potential for eight PCB congeners as calculated by four generic assessment methods. All models indicate largest potential for ALRT for intermediate PCBs. The ALRT of the smaller PCBs is limited by efficient atmospheric degradation, whereas the ALRT of the higher chlorinated PCBs is limited by efficient deposition to the Earth's surface (Wania and Dugani, 2003).

2003), and differences in results can usually be explained by variable input parameters or differences in the specific nature of the LRTP indicators. For example, whereas the CTD quantifies the potential for atmospheric transport of airborne chemicals, the ACP expresses the extent to which an airborne chemical is accumulating in remote Arctic ecosystems (Wania and Dugani, 2003).

These generic calculations tend to highlight the characteristics of chemicals that can undergo efficient transport over long distances. The chemicals need to degrade slowly in the atmosphere, and atmospheric deposition should not be fast and irreversible. The latter is the case for chemicals with intermediate partitioning properties. Very involatile chemicals (log $K_{OA} < 11$) are effectively deposited through particle-associated dry and wet deposition processes, whereas very water soluble substances (log $K_{AW} < -4$) tend to be washed out effectively by precipitation. Very volatile chemicals (log $K_{AW} > 0.5$ and log $K_{OA} < 6$) tend to remain in the atmosphere and are thus not taken up effectively by organisms. Chemicals with intermediate water solubility and volatility (log K_{OA} 6 to 12 and log K_{AW} 0 to –4) have the highest likelihood to undergo atmospheric long range transport and accumulate in colder regions (Wania, 2003).

It must be recognised that although ostensibly generic, the regional input parameters and fate processes considered in most generic models tend to reflect the environmental conditions of cool-temperate Europe and North America. Whereas a recent study by Beyer et al. (2003) evaluated the influence of different temperatures and OH radical concentrations on the estimated characteristic travel distance of several chemicals (Fig. 4.4), the influence of other environmental parameters has not been investigated in detail. It is clear however, that other environmental characteristics, such as surface cover (forest vs. grassland vs. water) or the extent and frequency of precipitation, could also have a strong impact on the extent of atmospheric LRT (Hertwich, 2001). It is thus not necessarily appropriate to assume that the relative transport potential calculated with these generic models is applicable to the different world regions. Beyer et al. (2003) for example noted that the CTD can vary by a factor of six over a 25 K temperature range and the direction of the change is highly dependent on chemical characteristics (Fig. 4.5). Accordingly, chemical ranking with respect to CTD can change significantly if performed under different climatic and regional circumstances. Great care must be taken to ensure that conclusions drawn about the likelihood of LRT for a PTS is based on a sound analysis of the conditions in the Region being addressed.

4.4.2 Regional Approaches to Long Range Transport Assessment

It is desirable to have fate and transport models that characterise the transport behaviour of PTS in specific Regions. The various Regions of this RBA have widely divergent capacities in this respect. Europe and North America, in particular, have developed or are currently developing an array of models of varying complexity to describe the transport of PTS within their Regions. Three types of models are emerging: spatially unresolved regional box models; spatially resolved regional box models; and, highly resolved, meteorology-based regional transport models.

Box models, in particular those that are not spatially resolved, can be adapted relatively easily to different regional circumstances by adjusting the respective environmental input parameters. Within EUSES, for example, the SimpleBox model can be run with different environmental scenarios reflecting conditions typical for Northern, Central and Southern Europe (Berding and Matthies, 2002). Newer spatially resolved regional box models, such as the BETR modelling framework, are deliberately designed in a fashion to allow easy adaptability to different regions (MacLeod et al., 2001, Sofiev et al., 2003). The meteorology-based regional models are not as easily transferred between regions because the density of meteorological observations and the availability of meteorological data in many world regions is not as good as for say Europe and North America.

4.4.2.1 Spatially Unresolved Regional Box Models

There are many spatially unresolved regional box-models, often for use in chemical fate assessment within a national context (SimpleBox, ChemCan, ChemFrance, ChemUK, CalTOX, EQC, CoZMo-POP). Another example is the POPsMe model for S-Korea (Lee et al. 2002, Region VII Report). These simple models, many of which assume steady-state, are normally not developed and used with the explicit intention of understanding regional scale transport pathways, but some basic information may be derived. In particular, it is feasible to determine which transport processes are responsible for removing most of a chemical from a particular region. For example, a very simple version of such a model was used to reveal the potential importance of the oceanic pathway for the LRT of HCH in South East Asia (Region VIII Report).

In is noteworthy, that the CTD-based LRTP assessment models TaPL3 and ELPOS mentioned in section 4.4.1 are based on the spatially unresolved box models EQC and SimpleBox models, respectively. This suggests that it should be feasible to estimate region-specific CTDs by adjusting the environmental input parameters to those specific for a region. Initial efforts in this direction have been made by Beyer (UBA report, 2001).

4.4.2.2 Spatially Resolved Regional Box Models

By creating multiple instances of the regionally unresolved regional box models discussed in 4.2.2.1 and by then linking them through advective and macrodiffusive transport of chemical in atmosphere, ocean and/or river water, it is possible to create regional box models with a coarse spatial resolution (Wania and Mackay, 1999). Such models can be used to investigate the transport behaviour of PTS within and between regions, and are particularly suitable for understanding the regional transport behaviour of multi-hop chemicals (category B) over a long-term time scale.

Two models that have been used in that way are the POPCYCLING-Baltic (Wania et al. 1999) and the BETR North America (McLeod et al., 2001) models. Two examples illustrate the information that can be obtained from such models. Breivik and Wania (2002) used the POPCYCLING-Baltic, a multi-segment multi-media model of the Baltic Sea drainage basin to quantify the transport behaviour of α- and γ-HCH over the three decades from 1970 to 2000. Following a detailed evaluation of the model performance (Breivik and Wania 2002a), a budget analysis revealed that less than half of the amount of HCH entering the region is from usage of the chemical within the drainage basin, suggesting that atmospheric advection of HCH used elsewhere is at least as important a source (Fig. 4.10). As a result of the semi-enclosed nature of the Baltic Sea, oceanic advection plays only a minor role in the mass budget of HCH in the region. The same amount of HCH entering the region by atmospheric advection over three decades was also leaving the region through this process, highlighting the high mobility of HCH in the atmosphere.

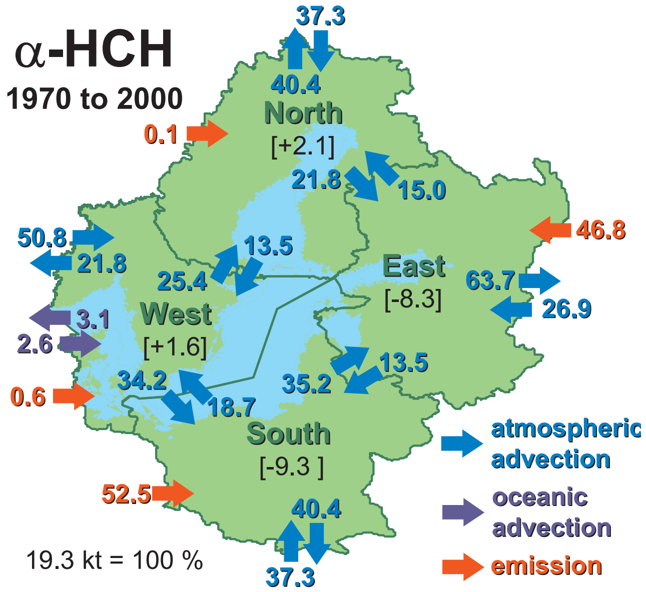

Fig. 4.10 Cumulative atmospheric and oceanic fluxes of α-HCH into and out of the Baltic Sea drainage basin from 1970 to 2000 in percent of the total cumulative emission to the basin during that time period. The numbers in brackets give the net atmospheric exchange in the atmosphere (based on data in Breivik and Wania, 2002b).

Using the BETR North America Model, MacLeod et al. (2002) derived a transfer matrix to examine the deposition of toxaphene in the Great Lakes region that results from usage in 24 regions of the North American continent. The values in that matrix are quantitative measures of the efficiency of transfer of toxaphene to fresh water bodies in that region (Fig. 4.11A). If regional emission data are available, such transfer efficiencies can be used as weight factors to attribute the chemical burden in a region to various source regions (Fig. 4.11B). These calculations are based on the assumption of steady state, ie there is no change in time.

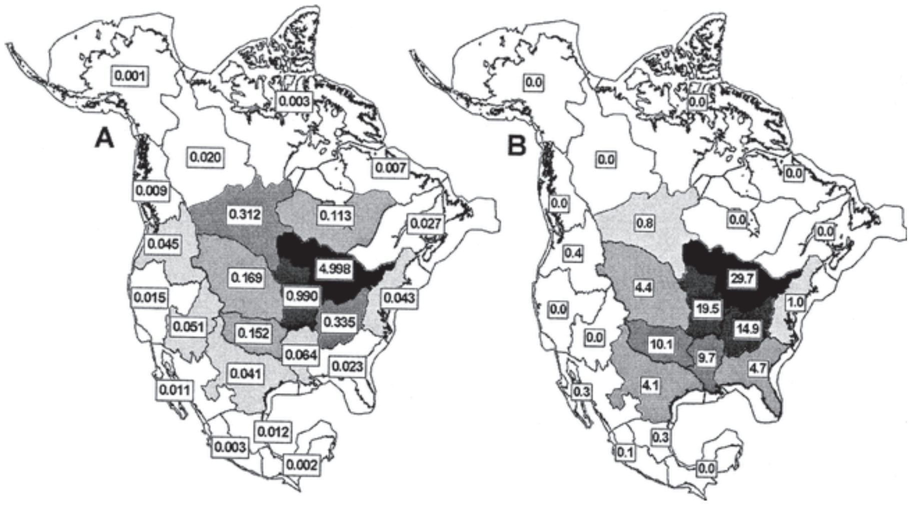

Fig. 4.11 Transfer efficiencies expressing quantitatively the potential of toxaphene used in various regions of North America to be deposited to fresh water compartments in the Great Lakes Region as calculated with the BETR North America model using a steady-state assumption (A). When combined with usage information in the various regions, relative loadings to the Great Lakes can be estimated (B). (taken from MacLeod et al. 2002).

A serious limitation to the use of these models is the availability of sufficiently detailed emission information. For a complete quantitative treatment they require historical emission data at the resolution of the model segments. It is however possible to derive useful information even with no or incomplete emission data. For example, the transfer efficiencies from one region to another (Fig. 4.11A) are a function of chemical properties and environmental characteristics, yet independent of the actual emitted amounts. To derive relative loadings to a receptor region, (such as in Fig. 4.11B) information is required on the relative amount of a chemical emitted in each region but not the absolute amount, which is often much more difficult to obtain.

Another complication arises from the need to properly parameterise the coefficients quantifying atmospheric transport between the segments of the model, which are among the most influential input parameters. This has been done using Eulerian (in POPCYCLING-Baltic) or Lagrangian (in BETR North America) atmospheric transport models. Another option is to segment the atmosphere into regular sized cells, as atmospheric transport coefficients are more easily obtained for a grid. The spatial resolution of the surface does not have to follow the atmospheric grid. Suzuki et al. (Region VII Report) are developing such a model for catchments in Japan and are using it to understand the transport behaviour of PCDD/PCDF. The adaptation of the BETR framework to Europe (EVN-BETR) involves a similar approach.

For water soluble PTS (category D) emitted primarily into the waste water stream, such as detergents and pharmaceuticals, the models described so far are inadequate because the main conduit for regional transport of such chemicals are rivers and lakes. Highly site-specific, drainage, basin models which use extensive geographically referenced environmental and emission data are being developed and used in Europe and North America to simulate transport of such chemicals in regional waterways (Schowanek et al., 2001). In contrast to the multimedia models discussed here, such drainage basin models focus primarily on the aqueous phase.

4.4.2.3 Highly Resolved, Meteorology-Based Regional Transport Models

If even higher spatial and temporal resolution is desired in the description of regional scale PTS transport, a highly resolved, meteorology-based regional transport model is required. High resolution is necessary if the objective is to resolve specific episodes or events of efficient atmospheric LRT on the time scale of days, or to identify the contribution of specific point sources or relatively small source areas to the contamination of a receptor. Such models are thus particularly suitable for type C PTS (single hop), because these tend to undergo atmospheric LRT in distinct, short-term episodes. Traditionally, meteorology-based regional transport models did not allow for reversible air-surface exchange and were thus not suitable to describe the atmospheric transport of category B PTS (multi-hop). Currently, the models are being modified to account for the multimedia nature of multi-hop substances. Again, two studies are highlighted to illustrate the information that can be obtained from such models.

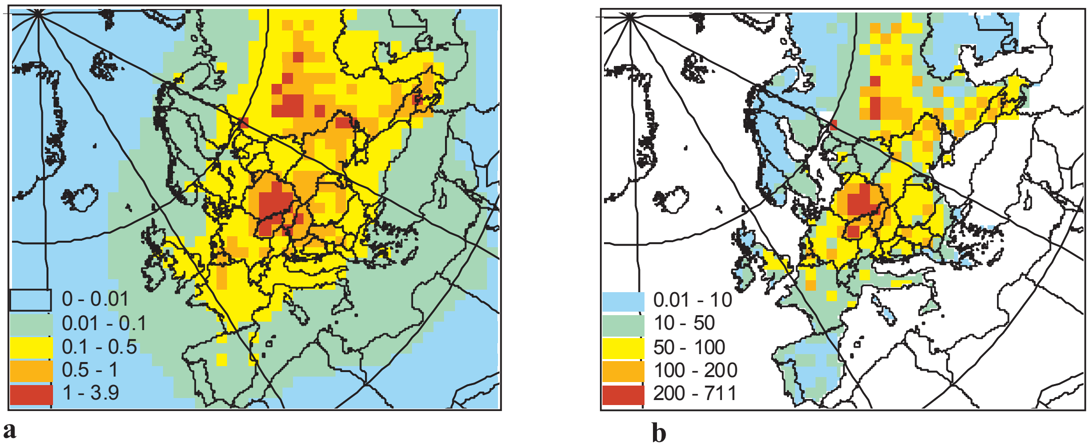

Fig. 4.12 **Atmospheric emissions of benzo-a-pyrene in Europe in 1997 [g.km-2·y-1] (b) and atmospheric concentrations of benzo-a-pyrene [ng·m-3] calculated with the MSCE-POP regional transport model (a).**

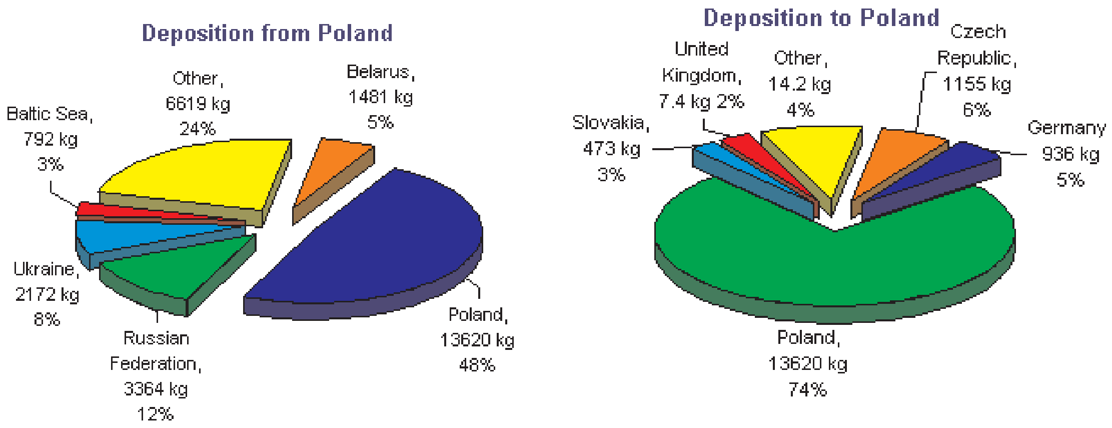

Fig. 4.13 **National export and import chart for benzo-a-pyrene in Poland calculated with the MSCE-POP regional transport model.**

The Meteorological Synthesising Centre-East of EMEP has developed a highly resolved, meteorology-based multimedia transport model, called MSCE-POP (Shatalov and Malanichev, 2000. Shatalov et al., 2001). The resolution is 50 km x 50 km and explicitly accounts for the exchange with vegetation, soil and sea water. Spatially resolved atmospheric emission estimates from national experts are used as input parameters (Fig. 4.12b). The model produces detailed concentration maps such as shown in Fig 4.12a for benzo-a-pyrene in the atmosphere. It can also be employed to derive national import and export charts, that account for the destination of emissions originating in a country (export charts) and the countries of origin of the deposition occurring in that country (import charts) (Figure 4.13).

Commoner et al. (2000) used a Lagrangian approach to quantifying the transport of PTS on a continental scale, specifically the transport of PTS from sources in Central North America to the North American Arctic. Using highly spatially resolved emission estimates for PCDD for North America in combination with air mass trajectories calculated with the HYSPLIT (Hybrid Single-particle Lagrangian Integrated Trajectory) air transport model, they derived source-receptor relationship for several communities in the Canadian High Arctic. The model estimated the amount of PCDD emitted by each of 44000 sources that is deposited at each of eight receptor sites in Nunavut over a one-year period, 1 July 1996-30 June 1997. A fairly limited number of North American sources outside of Nunavut were found to be responsible for almost all of the PCDD deposited on that territory.

The high uncertainty of spatially, highly resolved emission data and the small number evaluation data for PTS sources limit the credibility of the results of highly resolved, meteorology-based regional transport models (Wania, 1999). In many cases, the high resolution of dispersion models may not be required and model outputs such as shown in Fig. 4.12, 4.13 and 4.16 could actually create a false impression of the degree of quantitative understanding of regional and global PTS transport that is currently achievable.

4.4.3 Global Approaches to Long Range Transport Assessment

There is an increasing number of models that aim to study the transport and accumulation behaviour of PTS on a global scale. This topic has recently been reviewed by Scheringer and Wania (2003). Some PTS, especially the multiple hop chemicals (category B) can undergo global scale transport, ie may cross continents and oceans, and even continental scale models such as BETR North America or MSCE-POP may not capture the full picture of their large scale distribution patterns. Global scale models are particularly relevant to:

- study transoceanic and/or intercontinental transport of PTS,
- understand long term global re-distribution and convergence processes such as cold condensation and global fractionation (Wania and Mackay, 1993, 1996), and
- quantify global scale loss processes and clearance times for PTS achieving worldwide distribution.

In analogy to the regional models, there are coarsely resolved box models and highly resolved meteorology-driven dispersion models to describe PTS transport on a global scale. Both types of models are used in connection with global emission estimates. The box models, in particular have proven useful in the absence of quantitative emission information, as they can be used in an evaluative mode.

4.4.3.1 Spatially Resolved Global Box Models

Global box models tend be zonally averaged, assuming that mixing is much faster in the longitudinal than in the latitudinal direction. Examples of such models are the Globo-POP (Wania and Mackay, 2000) and CliMoChem (Scheringer et al., 2000) models, and the model by Strand and Hov (1995). Two examples are given for how these models can be employed.

The historical global distribution behaviour of α-HCH from 1947 to 1997 has been investigated with the Globo-POP model (Wania et al., 1999, Wania and Mackay, 1999). Figure 4.14 summarises an analysis of

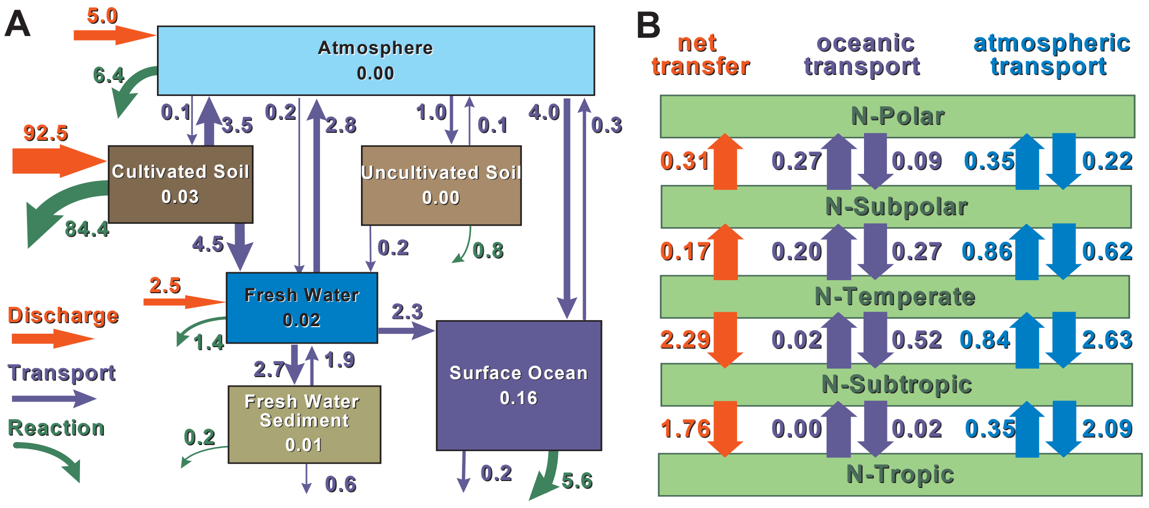

Fig. 4.14 Fluxes of □-hexachlorocyclohexane in units of percentage of total global usage from 1947 to 1997 as calculated by the Globo-POP model. The left figure A displays a zonally and temporally averaged global mass balance, whereby the number in each box is the percentage of total global usage present in an environmental compartment in 1997. The right figure B displays the meridional transport between climate zones in the northern hemisphere in both atmosphere and ocean (Wania and Mackay, 1999).

the major transport pathways of α-HCH globally. The global mass balance reveals that over the course of five decades, the bulk of the α-HCH has been degraded within the agricultural systems to which it had been emitted. Only a minor fraction has been dispersed more widely either by volatilisation from soils or through the hydrological cycle. However, the little α-HCH that still remains in the global environment in 1997 is mostly found in the oceans (Fig. 4.14A).

In terms of the transport of α-HCH in the meridional direction, both atmosphere and oceanic advection was found to be important (Fig. 4.14B) with the ocean increasing in relative importance with latitude. The mid-latitudes were found to be a net source of α-HCH to both tropical and polar regions. Whereas most of the α-HCH exported to lower latitudes was degraded fairly quickly, the amount transferred to the North could accumulate in the Arctic Ocean (Wania and Mackay, 1999).

Zonally averaged box models have also been used to investigate in an evaluative fashion, the combination of partitioning properties that make a persistent organic chemical susceptible to accumulation in cold remote regions (Scheringer et al., 2000, Wania, 2003). In this case, no emission information is required because a hypothetical generic emission scenario can be assumed to apply to all chemical property combinations. Specifically, an Arctic Contamination Potential has been defined that relates the amount in the Arctic environment to the total amount of a chemical in the global environment (Wania, 2003).

Figure 4.15 displays values of this Arctic Contamination Potential after 10 years of steady emissions of a perfectly persistent chemical with partitioning properties defined by its octanol-air and air-water partition coefficient, log K_{OA} and log K_{AW} (see also Fig. 4.2).

The calculations clearly show the potential of reversibly deposited multi-hop chemicals (category B) to accumulate in remote polar environments if they are sufficiently persistent. It is also possible to derive upper and lower volatility thresholds: chemicals with a log K_{AW} greater than 0 and a log K_{OA} smaller than 6 are too volatile to deposit even at the low temperature prevalent in polar regions (category A). On the other hand, chemicals with a log K_{OA} greater than 10 tend to be associated with particles in the atmosphere and their ALRT is determined by the ALRT of these particles, which is generally low (category C).

Fairly water soluble chemicals with a log K_{AW} less than -3 (category D) are likely to be subject to transport in the oceans if sufficiently persistent in water (Fig. 4.15). Additional calculation reveals the importance of the medium and the zone of emission on a chemical's potential to reach remote regions (Wania, 2003). Although model simulations may assist in categorising substances according to their potential to undergo long range transport, model results should always be confirmed by actual field measurements.

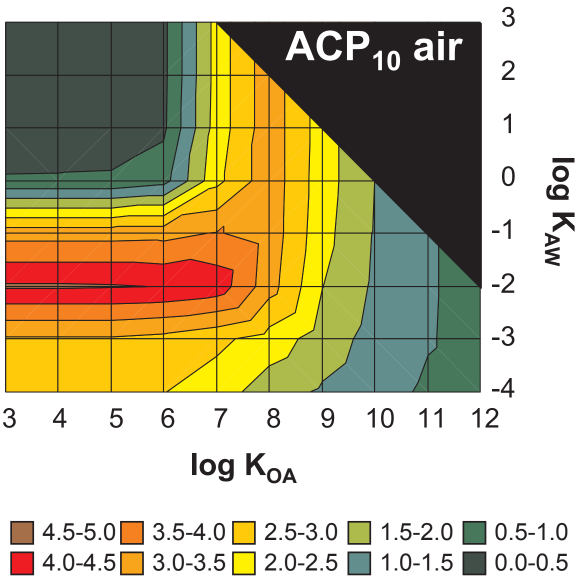

Fig. 4.15 Arctic Contamination Potential for perfectly persistent hypothetical chemicals defined by octanol-air and air-water partition coefficients log KOA and log KAW and calculated by the Globo-POP model using a generic emission scenario of 10 years steady emissions into air (Wania, 2003). Semivolatile multi-hop chemicals show the greatest potential for long term accumulation in the Arctic environment.

Although zonally averaged models may be appropriate to understand general pathways and distribution patterns on a global scale, they are of limited value in predicting actual concentration values at particular points in space and time. They can not resolve concentration differences between source regions and remote regions within the same zone. They also can not describe transoceanic or intercontinental pollutant transport. This is why the BETR framework is currently applied to the global scale to yield a global box model that distinguishes between major continental and marine regions (D. Mackay, Trent University, pers. comm.).

4.4.3.2 Highly Resolved, Meteorology-Based Global Transport Models

There are also efforts to describe the transport of PTS based on highly resolved atmospheric global circulation models. An example is the MPI-MCTM model (multi-compartment chemistry-transport model of the Max Planck Institute for Meteorology, Hamburg) (Region III Report). It aims to simulate the environmental fate of semi-volatile organic substances with consideration of the geospheric transport and transformation processes, including their geographic distribution and temporal variability. The model is fully dynamic and can be run either in a climatological mode (then generating its own but realistic climate) or simulating historic climate (then driven by weather and sea surface observations). Although these models can also be used in an evaluative sense, there strength lies in the simulation of the real historical behaviour of a contaminant and possibly the prediction of its future fate. The greatest limitation is the lack of PTS emission information that is sufficiently reliable at a high spatial resolution of the models. Another model of this type has been developed by Koziol and Pudykiewicz (2001) and used to model the global transport of α- and γ-HCHs in 1993 and 1994 on a 2° x 2° grid. Figure 4.16 is an example of the type of output generated by highly resolved, meteorology-based global transport models.

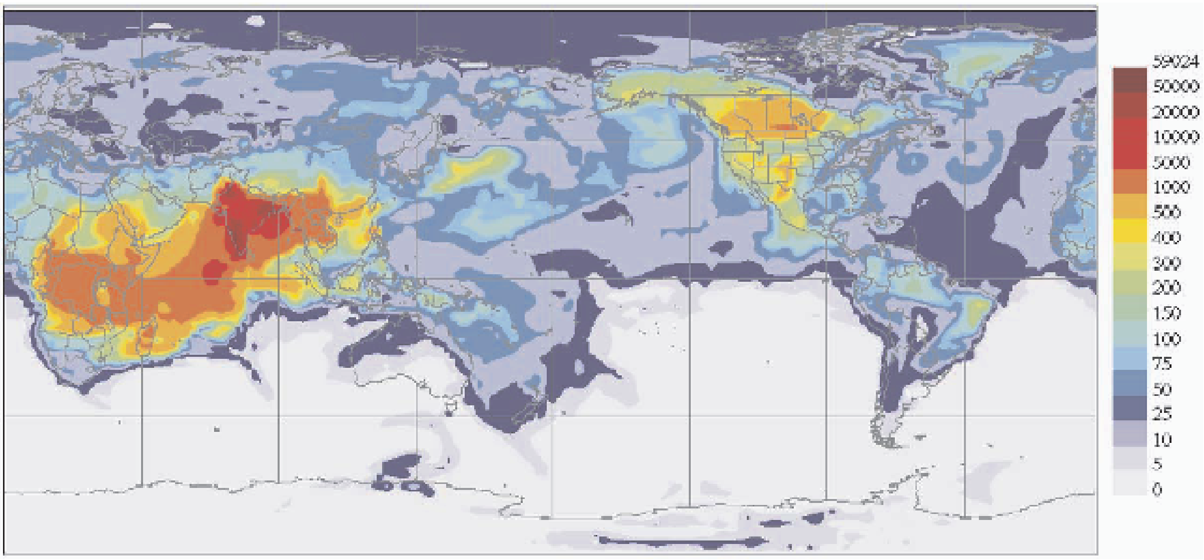

Fig. 4.16 Atmospheric concentrations of γ-HCH at ground level in pg·m-3 calculated for March 1, 1993 by the global dispersion model by Koziol and Pudykiewicz (2001).

4.5 KNOWLEDGE GAPS WITH RESPECT TO PTS TRANSPORT PATHWAYS

For most of the regions of the globe no quantitative region-specific tools for transport assessment exist. The three major reasons for that are:

Lack of region-specific process understanding. Existing models describe conditions in the Northern temperate zone. Simply adjusting the environmental input parameters (such as temperature and precipitation rate) of an existing model to those of another global region may not be sufficient, because contaminant fate processes may occur under different climatic circumstances that are not included or not appropriately described in the existing models. Examples for such insufficiently characterised fate processes are:

- The impact of a seasonal or even permanent snow and ice cover on the air-surface exchange of PTS in high latitude regions.
- The partitioning characteristics of the Earth's surface in arid ecosystems. The lack of organic matter and humidity in desert ecosystems may cause mineral surfaces to constitute an important storage medium for PTS. This partitioning process is not included in any existing PTS transport model.
- The dynamics of PTS in a tropical forest ecosystem is completely unknown. Eg, there is no reason to believe that deposition velocities derived for temperate forests are widely applicable.
- Many PTS transport models assume precipitation to occur continuously throughout the year, whereas precipitation in many regions is a strongly seasonal phenomenon.

- The nature and rate of degradation of PTS under tropical conditions is poorly characterised.
- The oceanic transport of PTS in low latitudes has not been investigated and even at higher latitudes is largely restricted to studies on HCH. This knowledge gap not only prevents a quantitative treatment of PTS fate, but may often impede even a conceptual qualitative understanding of PTS transport behaviour in regions other than the Northern temperate environment.
- There is a lack of suffcient and/or sufficiently good data for model input and model evaluation. Regional transport models such as the one by MSC-E for Europe requires meteorological and emission data at a resolution that is not available for most world regions. If an evaluation of a model is not possible, its usefulness is limited. One reason that many of the model examples given in this chapter are for □-HCH (Figs. 4.10, 4.14 and 4.16), is that historical emission estimates for this substance have been estimated, whereas for most other PTS, such information does not exist.
- There is a lack of capacity for developing and using transport models for PTS within the region.

4.6 CONCLUSIONS

PTS chemicals can undergo long range transport in the atmosphere, with ocean currents, rivers, and in the tissues of migratory animals. The effectiveness and relative importance of these processes is strongly dependent on the characteristics of the chemical and the characteristics of the region in which transport occurs.

The transport of PTS with very low volatility and very low water solubility (category C) is determined by the transport behaviour of the solids to which they sorb in atmosphere, surface ocean and rivers. Because solids tend to be deposited relatively fast, and often irreversibly, to the Earth surface, to the deep sea and to sediments, the transport of such substances is limited and often dominated by episodic events such as dust storms and floods. PTS with intermediate volatility and intermediate water solubility (category B) can reversibly exchange between the atmosphere and the Earth's aquatic and/or terrestrial surface, the direction of their air-surface flux being driven by fluctuations in temperature. They have the potential to be effectively transported over long distances by multiple "hops", if they survive sufficiently long in the atmosphere and surface media. The more volatile they are the less they are retained in surface media. PTS with relatively high water solubility (category D) can undergo efficient long range transport in oceans and rivers, if sufficiently persistent in the aqueous phase.

Chemicals undergoing multi-hop transport (category B) have a higher potential for LRT than single hop chemicals (Category C), if they are sufficiently persistent to survive for the time period it takes to undergo multiple deposition and evaporation cycles. This suggests that PTS with the partitioning properties of the lighter to intermediate PCBs, the DDT-related substances, endosulphan, SCCPs, the lighter PCDD/PCDF and the highly chlorinated chlorobenzenes have substantial atmospheric LRT capabilities, if the environmental conditions are such that their degradation is slow. PTS substances with the distribution characteristics of the heavy PBDEs and PCDD/PCDF have comparatively small potential for atmospheric LRT. Even though the different modes of transport influence the extent of potential LRT, this in itself has no direct relation to a chemical's likelihood for causing damage. However, a chemical with high potential for LRT will (1) potentially affect a large area which implies that effects, if they occur, might be widespread, even ubiquitous, (2) cause exposure, and therefore some risk to humans and their environment, in areas where such exposure would normally not occur, and (3) increases the likelihood that the beneficiaries of the use of a chemical have a lower risk than those persons far removed from such benefits and who are passively exposed. It further highlights the need for a chemicals regulation at the international level.

The direction of long range transport of PTS in air and ocean is governed by the general circulation of the atmosphere and the surface ocean. In the case of multiple hop compounds, there is a preference for moving from warm to cold regions. The extent of long range transport depends on climate and other geographic circumstances. Conditions that accelerate chemical degradation (such as intense sun light, high microbial activity, warm temperatures) and enhance settling and deposition processes (low temperatures, high precipitation rate, high particle content in atmosphere, high productivity in ocean, high roughness and uptake capacity of the surface) limit the potential for transport. How these various factors interact is complex and no general statements as to which regional circumstances favour efficient PTS transport is currently possible.

Several models with different scale, complexity and resolution are being used and developed to describe the atmospheric, oceanic and riverine transport of PTS within and between regions. At the simplest level these models assess the theoretical long range transport potential in a hypothetical environment, whereas the most complex models strive to reproduce the global transport of a PTS at high spatial and temporal resolution. Most regional scale models were developed in Europe, North America and East Asia and therefore tend to describe PTS transport and fate under temperate environmental conditions. Progress in quantitatively describing the regional and global scale transport of PTS with models is limited by an incomplete understanding of fate processes under non-temperate conditions, incomplete and/or highly uncertain emission information, and the lack of measured data required to evaluate the simulation results.

4.7 RECOMMENDATIONS

Major recommendations with respect to the transport pathways of PTS are to:

- Conduct studies aimed at a quantitative understanding of fate processes that are both unique and important for the transport behaviour of PTS under various regional circumstances. Specifically, identify PTS fate processes of importance in polar, arid and tropical ecosystems and investigate them with an aim to derive quantitative information suitable for inclusion into regional and global fate and transport models for PTS. Such fate processes may include phase partitioning, air-surface exchange, contaminant focusing and degradation processes.
- Ensure there are resources and capacity for monitoring PTS in remote environments. Models and a quantitative understanding of fate processes cannot substitute for field data, but are dependent on them.
- Support the development, improvement, evaluation and use of regional and global PTS transport models of variable complexity.
- Build capacity within the regions for studying and modelling PTS transport processes.

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5 ROOT CAUSES, NEEDS, BARRIERS AND ALTERNATIVES TO PTS

5.1 ROOT CAUSES OF PROBLEMS LINKED TO PTS

Problems with PTS arise both because of their inherent properties and because of inadequate chemical management and pollution control. For some PTS current problems have been caused by historical activities.

Many of the PTS considered share similar basic characteristics which have contributed to problems, it is important to recognise that these properties may also be beneficial in some circumstances:

- **Persistence** - Persistence may be a desirable property for chemical products. Persistence and resistance to thermal, environmental or chemical decay of the chemical ingredient/agent allows the functionality/efficacy of the product containing that chemical to be maintained over long periods of time. Replacement with non-persistent chemicals is not always a feasible option. Examples include:

    - **DDT and other organochlorine pesticides:** residual insecticidal functionality maintained over long time periods, reducing frequency of application and cost and increasing efficacy.

    - **PFOS:** stain repellency maintained over life-time of consumer products

    - **PBDEs:** flame retardancy maintained over life-time of consumer products

However, long-term environmental persistence can lead to problems with effects seen at a long distance from the point of release or use and problems that may be expressed over a timescale of decades. High chemical and thermal resistance can also make disposal problematic.

- **Low Water Solubility** – Many PTS are only poorly soluble in water but more soluble in fats and oils. This property can mean that PTS are liable to bioaccumulate in food chains. Low water solubility may be a valuable property and the use profile of chemicals may demand that the chemical is not water-soluble. An obvious example is the use of PFOS and similar chemicals for water proofing and stain repellency. Also, water-soluble flame retardants would be easily washed/leached out of consumer products, which would lose their fire protection. In other words, one of the root problems is that there is demand for chemical products that have the specific combination of properties (e.g. persistence and lipopilicity) that also render a chemical a potential environmental hazard.

- **High toxicity** – Some PTS show high toxicity. One consequence of this can be that we are concerned about low levels in the environment. At low levels these chemicals may be hard to detect leading to expensive and complex analytical requirements. Pollution caused by PTS at low concentrations is likely to be “invisible”. It can be problematic getting action taken relating to contaminants that are not visible to the public and politicians.

  Unintentionally produced PTS present problems in part because they may be formed by such a wide range of processes that include various chemical production processes, metal processing, and combustion processes whether industrial, domestic, agricultural or accidental. The wide range of processes that can release PTS and the complexity of the chemistry of formation and control of releases mean that identifying and addressing problems caused by this group of PTS can be difficult.

  In addition to the problems that arise from the particular properties of PTS there are a wide range of problems related to more general chemical management, industrial practice, waste management and patterns of development that can lead, or have contributed, to problems of PTS contamination.

Many PTS problems have their roots in previous or historical activities. Widespread and, at times, indiscriminate worldwide use of many PTS chemicals occurred during a period of ignorance of the environmental problems that could be caused by them. Production, distribution, use and disposal of chemicals developed with relatively little attention to releases to the environment and effects on the environment and users. Some examples of the issues are listed below:

- **Unsustainable production/Consumption** - A major cause of global environmental degradation lies in current unsustainable production and consumption patterns. The challenge is to reorient these unsustainable patterns by promoting a life-cycle economy that incorporates a cleaner production strategy including improvement of production processes and development of products with acceptable persistence, toxicity and potential for bioaccumulation. In addition, continued misuse and abuse of chemicals contributes to the pollution and contamination of the environment and the food chain. Despite the efforts of industry to provide instructions for use, pesticide PTS are still used outside of the approved use patterns resulting in residues in food and pollution of sediments in water bodies.

- **Cost of chemicals –** Given the increasing economic pressure on most developing States, States with economies in transition and even in the developed world, the pull toward the use of low-cost chemicals is strong.
- **Perceived effectiveness** – Certain PTS have a reputation for being efficacious and their use can result in apparent and easy success in solving a particular problem (although they may store up problems in the future or in other areas). Even where effective alternatives are available they may not be readily accepted. For sustained success alternatives must be found that are as cost effective and work with similar efficacy.
- **Ignorance** – 'Ignorance is bliss'. This phrase extends to over 75% of the world's population that are ignorant to what PTS are and how these chemicals can affect the environment and human health. This means that there is strong demand for certain PTS pesticides and particularly for inefficient industrial combustion processes undertaken in many countries with little or no knowledge of the dangers that ensue from emission of PTS from such combustion processes.

5.2 ASSESSMENT OF THE GLOBAL CAPACITY AND NEEDS

5.2.1 Introduction

The capacity and needs to manage PTS across countries are varied and differ markedly depending on the overall level of development of the country in particular and the region on a whole. In order to make a meaningful assessment, the regions are categorised and addressed based on the relative levels of development. Three categories are presented: Category I includes North America and Europe and represent, in the main, only developed countries. Category II includes the Mediterranean, Central and North East Asia along with South East Asia and South Pacific. These regions have countries that are developed, developing and some with economies in transition. Category III includes Sub-Sahara Africa, the Indian Ocean, the Pacific Islands, Central America and the Caribbean and Eastern and Western South America. While the assessment will introduce sample situations from countries within these categories, emphasis will be placed on alternatives for technology development and transfer. The lack of resources among the developing countries poses a major hurdle toward having global competence in handling the monitoring, regulation and control of the chemicals under review. Most regulations broad-brush the environment with limited emphasis on the protection of water bodies, especially fresh water sources that continue to decline in quantity and quality.

5.2.2 Monitoring capacity

Monitoring capacity relates to the ability to measure:

- The releases of PTS to the environment from a variety of sources;
- The deposition of PTS into the environment from processes such as the long-range atmospheric transport of PTS;
- The concentrations of PTS in the ambient environment e.g. in air, water, biota; and
- The concentrations of PTS in humans (North America Report, 2002).

A measurement is normally designed to answer a specific question and often, the possibility of using the results for other purposes is not considered. Measurements are often labour and instrument intensive and the results are therefore expensive to obtain. It is therefore essential that they can be used as effectively and as broadly as possible. Measured data can be used for many purposes, e.g. to study:

- The emission strength of a specific source

- The distribution of such an emission
- The presence of a chemical in pristine or background areas
- The geographic distribution of a chemical
- Temporal trends of a chemical in the environment
- Specific exposure situations
- The fate of PTS
- The toxicology of the chemical

These are the most commonly expressed aims with monitoring programmes, but it should be kept in mind that the data may also be used for a number of other purposes e.g. to determine the bioaccumulation, biomagnification and other specific parameters of a chemical. The risk assessment of a chemical or chemicals is also heavily dependent on existing exposure data and there is normally no time and few resources to start new targeted measurements and so the assessor has to rely on existing data.

There is a clear need for increased harmonisation of measurements of chemicals in the environment. Ongoing monitoring programmes are to some extent harmonised and data from e.g. national activities are often fed into regional or global programmes an operation for which harmonisation is a prerequisite. Smaller programmes and surveys may be less well planned and thus the results are often difficult to compare with those from other, more systematic, investigations (Europe Regional Report, 2002).

On a global scale, there is not much monitoring of PTS being done on a consistent basis. Most analyses of PTS are done at the research level by academic institutions mainly for scientific interest and also to satisfy the study of particular environmental accidents that occur ad hoc. Currently, UNEP Chemicals is developing a project to implement a global monitoring programme for POPs. It is envisaged that this programme will categorise selected laboratories based on quality control and capability to undertake various levels of analytical work on POPs on a routine basis and to provide an avenue whereby scientists can exchange information on these chemicals. A global meeting to design the programme is earmarked for March 2003.

In order to provide a perspective of the monitoring programmes globally, examples are presented from the regions based on the categories outlined above.

5.2.2.1 Category I Regions

While the capacity to monitor PTS in North America and Europe is advanced compared to other regions, there is still a strain to provide the necessary resources to analyse the ever-increasing number of chemicals being produced and used.

5.2.2.1.1 North America

Canada, the USA and Mexico provide a good example of regional cooperation in establishing inventories of releases of substances from facilities and other sources to the environment. To name a few, Canada maintains its National Pollutant Release Inventory (NPRI), and the United States its Toxics Release Inventory (TRI). These programmes mandate by law that all facilities and industries report data annually on releases and transfers of selected chemicals to the environment. The NPRI reports on some 300 chemicals while the TRI includes over 700 chemicals. Both programmes contain chemicals that are being assessed in this report.

Along with Mexico, Canada and the United States have joined to establish the tri-national Sound Management of Chemicals (SMOC) programme. This programme collects through Pollutant Release and Transfer Registers (PRTRs), information on chemicals including PTS in order to establish North American Regional Action Plans (NARAPs). This regional effort has allowed the update of inventory for releases of dioxin and dioxin-like compounds across all three countries. Much success achieved from these programmes in North America is attributable to the cooperation between industry and government regulatory institutions. Transparency is agreed where information may affect the public at large but other sensitive data considered confidential for other competitors is kept as such.

In terms of environmental monitoring, both Canada and the United States have established extensive programmes for checking certain key environment areas. Canada has a broad based scientific partnership among stakeholders from all sectors. The Ecological Monitoring and Assessment Network (EMAN) brings together individual monitoring activities to prioritise the contaminants that are affecting various ecosystems. The International Joint Commission have been monitoring cross-border areas such as the Great lakes ecosystem and the U.S. EPA is carrying out a study on Fish Tissue to research the levels of persistent bio accumulative toxic chemicals in fish (North America Regional Report, 2002). These and other initiatives in monitoring long range transport of selected PTS allows Canada and the United States to keep abreast of certain chemicals that have shown to represent possible danger to the environment of these countries. Even so, the programmes are usually a response to particular problems and are not necessarily ongoing programmes on a general basis. Also, despite the economic links created between Canada, the United States and Mexico, there are still only limited monitoring capabilities and exercises being undertaken in Mexico. The efforts of the SMOC initiative in developing NARAPs go a long way in ensuring monitoring of selected substances in this region and demonstrate the usefulness of regional collaboration in tackling the problem of PTS especially considering the transboundary movement of these chemicals. However, even in this more developed region of the globe, funding is still inadequate particularly in Mexico where resources are far less than in Canada and the United States.

5.2.2.1.2 Europe

Within the Europe Region, there are many monitoring programmes that have been used successfully to maintain control of the releases and deposition of PTS especially in major water bodies. A list of these is captured in Table 5.1.

Table 5.1 Ongoing monitoring programmes for PTS in the Europe region

Global Environment Monitoring System – Food Contamination Monitoring and Assessment Programme EURO (GEMS/Food-EURO)	Monitoring of contaminants in food and assessment of contribution to total human exposure and significance to public health and trade
The Co-operative Programme for Monitoring and Evaluation of the Long range Transmission of Air Pollutants in Europe	Monitors the movement of pollutants in the atmosphere across State boundaries and the movement of these substances in and out of the region
The Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM)	Monitors the level of pollutants in the Baltic marine environment and publishes a periodic assessment every five years
The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR)	Persistent pollutants are measured in the Arctic Waters, the Great North Sea, the Celtic Seas, the Bay of Biscay and the Iberian Coast and the Wider Atlantic
The Caspian Environment Programme (CEP)	To monitor the environmental conditions of the Caspian Sea

Besides these elaborate regional programmes, many countries in Europe conduct extensive national monitoring programmes within various scope and intentions. However, similar to the case of Mexico in the North America region, many countries in Eastern Europe including Moldova, Belarus and the Ukraine have no ambient air measurements and limited information concerning other environmental compartments (Europe Report 2002).

5.2.2.2 Category II Regions

In these regions, the disparity in monitoring exercises is wide between countries and the conditions for collaboration are not as easy given the differences in language, culture and capacities that exist. International waters have played however, a catalytic role in bringing together countries of varying development that have a water body as a common border. More and more, this pathway to collaboration is being used to create conventions, agreements and bonding between countries as it is in the interest of all to ensure the protection of bordering water bodies. This is even more critical when considering fresh water, as this is a dwindling resource worldwide.

5.2.2.2.1 The Mediterranean

The three more developed countries of the Mediterranean – France, Italy and Spain – combined have established over 10 distinct monitoring programmes covering all compartments of the environment. This is in sharp contrast to the countries south of the Mediterranean. Most have just limited monitoring activities with Lebanon, FYR Macedonia, FR Yugoslavia showing no programmes for monitoring persistent toxic organic pollutants.

Still, in response to the increasing pollution of the Mediterranean Sea, the Mediterranean Pollution Monitoring and Research Programme (MEDPOL) was formed in 1975. Its main aim then was the establishment of a network of institutions undertaking marine pollution work and the collection of information regarding the level of pollution in the Mediterranean Sea. The monitoring activities covered heavy metals in marine biota (mainly mercury and cadmium), halogenated hydrocarbons in marine biota (mainly PCB and DDT), and petroleum hydrocarbons in seawater. The MEDPOL programme underwent a massive capacity building exercise during the first 15 years. Many scientists were trained, laboratories equipped with suitable up-to-date equipment, consultants were hired to provide advice, workshops were organised, analytical methods were corroborated and intercalibration exercises carried out between laboratories. The development and maintenance of these national monitoring programmes was the aim of the second phase (1981), whereas more recently (1996), the emphasis shifted from pollution assessment to pollution control (Mediterranean Regional Report, 2002).

In this latter phase, the introduction of quality control and common reference methods for the analysis of contaminants in the various matrices has definitely been the most important achievement of the MEDPOL Programme. The use of certified reference materials and common analytical methods provided a good approach to the collection of meaningful data and allowed their comparison on a Mediterranean-wide scale. In total, 17 laboratories across countries of the Mediterranean take part in delivering comparable data on selected substances. The revised programme has allowed for considerable improvement with time in the number of analytes measured and the reduction in technical errors being made.

Even though mistakes have been made and there are some areas that still need to be improved, the MEDPOL initiative represents an example of achievement among countries with a common desire to protect a valuable resource from chemical pollution.

5.2.2.2.2 Central and North East Asia

In this region, there are four countries that undertake national monitoring programmes on PTS. These include: Japan, China, South Korea and the Russian Federation. There are no monitoring exercises done in the other eight countries. Even within the top four countries, only Japan has established a comprehensive programme that covers most PTS selected in this assessment. There, the Ministry of Environment has an elaborate structure of scientists and other personnel dedicated to carrying out monitoring of differing compartments of the environment. Environmental monitoring started from 1974 and Japan has been reporting monitoring data annually in *Chemicals in the Environment* (or kurohon—"black book" in Japanese). The monitoring includes several categories: **1)** a survey of prioritised chemicals (c.a. 20 compounds each year) in air and water; **2)** yearly monitoring by GC/MS of Class I and frequently detected chemicals in water and sediments; **3)** yearly GC/ECD and GC/FPD monitoring of Class I organochlorines and organotins in mussels and other organisms respectively; **4)** monitoring of residue levels of some of the designated/registered chemicals in ambient air, indoor air, foods, water and sediments; **5)** monitoring of unintentionally produced chemicals (until 1997 - PCDD/PCDF and coplanar-PCB; 1998 - PBDD and PBDF).

An extensive nationwide survey for unintentionally produced chemicals has been conducted and the data reported. Legislation has been passed concerning special measures against PCDD/PCDF in 1999. Furthermore, another nationwide survey in Japan on endocrine disruptive chemicals started in 1998 (SPEED'98) (http://www.env.go.jp), and the analytical data on some PTS are also reported.

Even though effort has been made to set up systems in the other advanced countries, there is still a major void for monitoring PTS specifically. A link has been made between Japan and South Korea to carry out a joint research program to study Endocrine Disrupting Chemicals (EDC) such as PCDD/PCDF and PCB. Research includes methods to monitor and techniques to test EDC. Organisations taking part in the program include NIES of Japan and NIER of South Korea (Central and North East Asia Regional Report, 2002).

Given its position of strength technically, Japan offers a good opportunity for collaborative work to monitor the Sea of Okhotsk (Russian Federation), the Sea of Japan (South Korea/Russian Federation), the Yellow Sea (China/South Korea) as well as initiating pre-emptively, monitoring of riverine flows into these major marine water bodies from the Amur, the Huang He (Yellow River) and the Chang Jiang (Yangtze River).

Most of the other countries in this region are landlocked and so do not offer much incentive for collaboration in terms of water bodies. However, Mongolia and the Russian Federation share the Celenge River that empties into the Baikal Lake and the Kerulen River transects both Mongolia and China. As rivers pose a major opportunity for the transboundary pathway for pollutants attached to sediments, the monitoring of other smaller rivers that course between States can also be included in joint control exercises for pollutants.

5.2.2.2.3 South East Asia and South Pacific

Even though Australia and New Zealand have superior monitoring capabilities, some of the other countries in this region are making great strides in instituting programmes to check on releases to air, water and land for some of the PTS being assessed. New Zealand and Australia have now established the capability to analyse for PCDD/PCDF and this capability is being instituted in Malaysia, Thailand and Singapore (Region 8 Report, 2002). All these countries are already doing some monitoring of organochlorines but there is still no regional coordinated programme to look at these substances.

5.2.2.3 Category III Regions

With the exception of India, all the countries within these regions lack comprehensive monitoring programmes. Most do ad hoc testing of pesticide organochlorines based on research, perceived hotspots or for filling legal requirements. Industrial facilities in these countries may undertake routine analyses of effluents and emissions but such data is considered confidential and rarely is presented for public scrutiny.

There is little doubt that the lack of financial resources is the key disincentive for creating monitoring programmes for PTS. Unless controlled, with regional programmes being developed with full long term support from the developed countries, it is unlikely that data will be available over extended periods from these countries. Given the movement of these persistent chemicals through air and possibly attached to sediment in reverine flow, it is to the benefit of all that such collaborative programmes are instituted in these developing regions.

5.2.3 Existing regulation and management structures

The level of monitoring of PTS is concomitant with the degree of regulations and infrastructure established in the various regions. Financial wealth invariably dictates the magnitude of the regulatory structures being employed to control chemical contamination of the environment. Even though the focus is on PTS, usually the discussion on existing infrastructure concerns general chemicals management in each region. Also, the examples given below do not reflect the complete assessment of the existing capabilities for chemical management around the globe.

5.2.3.1 Category I Regions

Between North America and Europe, there are many sophisticated regulatory systems and structures for controlling chemicals. These systems underscore the financial wealth available from the development of the private industry but also the subsequent need to provide a controlling balance to the ever-increasing levels of input and output of chemicals from these industries. The study of the Great lakes under the Integrated Atmospheric Deposition Network - a cooperative link between Canada and the United States – to study the complex pathways of PTS (PCB, atrazine, trans-nonachlor and mercury) provides a successful example of this regulatory function.

The complex web of regulatory systems for this region is approached either in a diverse or central direction from country to country. Canada has nine different pieces of federal legislation covering the control of PTS. The approaches include the intent for **i)** virtual elimination, **ii)** management of substances during their life cycle, **iii)** voluntary regulation.

The United States has a more centralised system where the Environment Protection Agency (EPA) oversees all matters pertaining to protection of human health and the integrity of the environment. EPA also uses a broad range of approaches to manage PTS including regulatory, compliance assistance, enforcement, research, voluntary actions and international negotiations. In so doing, the United States has the widest experience in regulation of PTS and along with other developed systems, presents the best opportunity for providing assistance in the development of regulatory mechanisms in developing countries (North America Regional Report, 2002).

On the other hand, Mexico, like Canada, has several pieces of legislation through which PTS are regulated. However, the difference is that there is multi-overlap between these legislation and eventually much confusion as to who is doing what. Still, with the assistance from its NAFTA partners, Mexico has been improving its regulatory system and is steadily bringing itself in line with the elaborate processes established to the North.

5.2.3.2 Category II Regions

Again, the disparity in regulatory mechanisms between countries in these regions is obvious. Countries such as Japan, Australia, France and Italy have extensive regulatory organisations that control all aspects of PTS including registration of the chemical, monitoring of emissions, standards for environmental levels, management of accidents, voluntary and mandatory reduction programmes and regulatory framework for storage and disposal of these chemicals.

In Central and North East Asia, Japan has specific laws pertaining to PTS (see Table 5.3). This provides a clear message on the importance placed on the concern given to PTS by the Japanese government and allows for control of the release of these chemicals to the environment.

Table 5.3 Major laws concerning regulation of PTS in Japan

Japan	Law Concerning the Examination and Regulation of Manufactures, etc. of Chemical Substances (1973) Agriculture Chemicals Regulation Law (1948) Law Concerning Special Measures against Dioxins (1999) Law for the Promotion of Environmentally Sound Destruction of PCB Waste (2001) Law Concerning Reporting, etc. of Release to the Environment of Specific Chemical Substances and Promoting Improvements in their Management (2001)

Source: Taken from the Central and North East Asia Regional Report, 2002)

Many of the PTS under scrutiny have been banned in Japan. The ones still present are controlled by environmental standards as outlined in Table 5.4.

Table 5.4 Environmental Standards on PTS in Japan

PCBs	Water: not detected (detection limit of the analytical method is set to 0.5 µg/L)
Dioxins	(Dioxins = PCDD + PCDF + co-PCB) Air: yearly average <0.6 pg TEQ/m3 Water: yearly average <1 pg TEQ/L Sediments: <150 pg TEQ/g Soils: <1000 pg TEQ/g Refer to Table 5.4, Table 5.5

Source: Taken from the Central and North East Asia Regional Report, 2002)

Where many other countries also have enacted laws and have environmental standards, Japan ensures that there is compliance and these laws and standards are enforced.

A similar picture is gleaned from the Mediterranean region for France and Italy. Here, these countries like others in Europe, are covered by their association to the European Community (EC). There are many EC directives pertaining to PTS and countries within this regional economic integration organisation are obliged to enforce these measures. The general strategy of the EC to address environmental issues of chemicals is part of the general objective of the Sustainable Development taking place while considering the potential responsibilities of the chemical industry in relation to the precautionary principle. At the same time, it takes into consideration the rules of the common market as well as the competitiveness of the European industry. In this respect, over the past two decades the Community has proposed wide ranging legislation aimed at directly or indirectly reducing the release of PTS with the objective of reducing human exposure and protecting human health and the environment. Emission and source related data for most PTS in the European countries indicate a decrease on the release of these chemicals since the legal instruments have been put in place (Mediterranean Regional Report, 2002).

Directives pertaining to PTS include control of plant protection products and on the marketing and use of certain substances (PCP, PAH, TBT and lindane). Additionally, emission of particles (PAH, PCDD/PCDF and mercury) and total organic matter from all types of waste incineration have defined limit values. Control of water has a high priority. There are directives to eliminate certain substances from inland and coastal waters. DDT, aldrin, endrin, dieldrin, PCP and HCB all fall into this category. Within these directives are instructions for monitoring of the particular compartment of the environment. These are only a sample of the many directives for the EC States to comply to control certain PTS.

After a revision of the current legislation, the Council of Ministers adopted, in 1999, a *White Paper* on a new Chemicals Policy for the Community. The guiding principles of this new strategy are: precaution and prevention; replacement of dangerous chemicals by safer ones; a greater responsibility of industry to generate and deliver information on risk assessment of chemicals prior to going on the market. The REACH system (Registration, Evaluation and Authorisation of Chemicals), run by an expanded European Chemicals Bureau, is a key element in the process (Mediterranean Regional Report, 2002).

In South East Asia and South Pacific, Australia has established regulatory schemes to manage PTS. In 1975, Australia established the National Environment Protection Council (NEPC) to enable the development and implementation of a consistent and national environmental protection policy through the development of national environment protection measures. As at June 1998, NEPC had made measures for the National Pollutant Inventory (a Pollutant Release Register), the Movement of Controlled Waste across State and Territory borders and Air Quality Standards (National Chemicals Profiles, 2000).

In marked contrast, the developing countries in all three regions have limited legislation to deal with PTS. Where legislation does exist, the full complement of personnel and adequate equipment and infrastructure to implement and enforce are not in place. A typical example is the status of Mongolia in Central and North East Asia. In outlining their chemical management programmes, Mongolia refers only to ‘expectations’, as currently there is little management being implemented. The goals of Mongolia include:

- Assessment and Classification of Dangers Entailed by the Use of Chemical Substances and Products
- Creation of a risk assessment system for chemical substances consistent with international standards;
- Development of a classification of chemical substances risk assessment system;
- Establishment of a chemical labelling system compatible with world standards.
- Reduction of Dangers from Toxic Chemicals and Creation of an Information Exchange System
- Substantial reduction of chemical hazards in all aspects of its "life cycle";
- Creation of systems that promote information exchange with other countries and international organizations on chemical security, hazards and waste.
- Strengthening the Chemical Management Capacity

- Creation of a national system for proper utilization and reduction of toxic chemicals ensuring the ecologically safe system, developing and implementing essential norms and standards.
- Prevention of Illegal International Toxic and Hazardous Chemical
- Strengthening of the national capacity to inspect and search for illegal transportation of toxic chemicals or hazardous products through the country's border.

These are worthwhile objectives for any country. Unfortunately, it is doubtful that without financial and technical assistance, Mongolia will be able to achieve its goals for chemical management. A similar situation exists for the other developing countries in that region.

In the Mediterranean, pesticide control is mainly carried out by a system of national registration, which limits the manufacture and/or sale of pesticide products to those that have been approved. Most developing countries have limited capability to carry out their own tests on pesticides and tend to adopt regulatory criteria from the developed world. Some of these countries, like Egypt, Morocco, Tunisia, Syria, Cyprus and Turkey have their own Pesticide Registration offices that handle the management of pesticides.

For the other PTS considered that are mainly of industrial use, effort has been put in managing their spread and subsequent destruction. Most of the countries of the Region, for example, have performed inventories of PCB with varying degrees of comprehensiveness. Although many of them have developed regulation for industrial PTS, they do not have the management capability in place to enforce such control.

Some of the developing countries of South East Asia and South Pacific have been making strides in instituting regulatory mechanisms to deal with PTS.

Besides having a wide array of laws to manage PTS, Thailand has obtained assistance in carrying out PCDD/PCDF emission level inventories and is establishing a laboratory to undertake these analyses. Most developing countries within this region have legislated laws to regulate chemical substances. The major drawback is the state of enforcement of these laws given the inadequate number of qualified personnel and the poorly equipped laboratories assigned to implement enforcement.

5.2.3.3 Category III Regions

The countries in Sub-Saharan Africa, the Indian Ocean, the Pacific Islands, Central America and the Caribbean and Eastern and Western South America all undertake limited monitoring of PTS. Most carry out analytical surveys designed to answer a specific question for research or to investigate a particular problem that has been found pertaining to a specific chemical. It is evident from available data that most of the countries of these regions have developed, and others are in the process of developing, policies and regulations in the management of chemicals including PTS. It is possible that the limited financial resources, a low level of awareness among the stakeholders and the poor dissemination of available information of the adverse effects of PTS on humans and the environment, are responsible for the slow pace in enforcing regulations and policies on PTS. Even then, some of the existing national policies need to be reviewed in response to new challenges and international obligations within existing Conventions (e.g. Stockholm Convention on POPs).

It is regrettable that most of the national legislations are either too general or too fragmentary in nature and non-specific to PTS. It will be important that national legislations are enacted and/or harmonised to deal with hazardous chemicals in general and PTS in particular.

A major constraint towards sustainable chemical management is the lack of and/or weak enforcement of regulations. For these regions to contribute effectively in the global effort to reduce PTS, there is need to establish and/or strengthen existing institutions and the legal framework.

The monitoring of PTS in the environment varies from country to country depending on the level of development and financial resources available. The few established organizations and research institutions that exist, lack adequate trained scientists and proper equipment to monitor and assess PTS in various media. Data that might have been generated by research is rarely published and disseminated to relevant authorities that might use such data to establish control measures or perform enforcement. It must also be noted that most generated data, if not all, are from individual studies, and not ongoing. This has resulted in fragmentary data and numerous data gaps. Despite these limitations, the increasing awareness about PTS is stimulating cooperation amongst the various research institutions and other stakeholders. This may be a good indication of proper future PTS management in these regions. It is also encouraging that international agencies are joining hands with most developing countries in addressing the potential effects of PTS.

5.2.3.3.1 Sub Saharan Africa

There are no regional programmes documented for the regulation and control of PTS. There are individual country programmes including the inventory of pesticides being carried out by the World Bank and FAO and the DDT elimination initiative for certain countries. However, the general awareness of these substances is weak and given the perceived greater needs of these countries, such regulatory development is low in priority.

5.2.3.3.2 Indian Ocean

The Regional Network on Pesticide Production in Asia and Pacific (RENPAP) is mainly focusing on pesticides production and safe use-related issues in order to reduce associated adverse effects. The organisation works regionally within both the Indian Ocean and South East Asia Regions. The member countries of the RENPAP include China, Pakistan, India, Bangladesh, Nepal, Myanmar, Bhutan, Thailand, North and South Korea, Sri Lanka and Maldives.

Other regional organisations such as the UNEP: Regional Organisation of the West Asia (ROWA) and the Regional Organization for the Protection of the Marine Environmental (ROPME) have been assisting countries within this region to improve capacity, implement environmental monitoring and management and control marine pollution (Indian Ocean Regional Report, 2002).

While most of the countries in this region have laws pertaining to pesticides, there is little control of the industrial chemicals being assessed in this report. No country has regulations governing the emissions of dioxins and furans nor the capability to analyse such emissions.

5.2.3.3.3 The Pacific Islands

Most countries in the Region have regulations covering imports and use of pesticides including POPs. However, all other chemicals including PTS are mostly not controlled or in many cases partly covered by regulations for other related areas such as Public health and Environment Acts. In addition, the existing regulations are mostly outdated and do not cover aspects such as the proper disposal of containers or excess and obsolete stocks. Throughout the region, there is lack of control on use of PTS chemicals in consumer and industrial products. Also there is a general lack of the management and administrative structures needed for proper control and enforcement of existing regulations. The French and US territories are generally better off through the regulations, support and controls provided by the "parent" states (Pacific Islands regional Report, 2002).

5.2.3.3.4 Central America and the Caribbean

It is evident that basic legislation exists for the implementation and adequate control of pesticide management in the Region, but there is room for improvement and for harmonisation, as has already been done by some Central American countries.

For the second group of PTS, the industrial and involuntarily produced toxic substances, the situation is quite different. In the majority of countries there is no registration office for these compounds and for that reason, no registration is required for the import and use of industrial PTS.

In some countries such as Barbados, Cuba, Jamaica and Colombia, there are specific regulations for a reduced number of industrial PTS. The regulations are general, and few allow an effective management of PTS and adequate enforcement. The situation is worse in relation with emission of dioxin and furans and solid waste disposal. Only Jamaica reports national regulation of dioxin and furan emissions, to be implemented in 2004. Costa Rica is developing sample procedures and analytical methods for PTS emissions (dioxins and furans), however, at the moment there is no regulation of these compounds.

For solid waste disposal, the situation in the Region is no better than with the industrial emissions, in spite of the fact that it is a common problem in the countries of the Region and a known source of PTS (dioxins, furans, PAH). Only Barbados reports that open burning for garbage disposal is illegal, but does not quote the particular law or regulation (Central America and the Caribbean Regional Report, 2002).

5.2.3.3.5 Eastern and Western South America

In these countries of South America, there are regulations for the registration of pesticides. Consequently, most of the POPs are banned from these countries. Lindane is used in most countries and even where pesticide PTS are banned, there may be use continuing because the regulatory mechanisms are not in place to enforce the ban. Brasil is the only country with capability to analyse PCDD/PCDF. However, the control of industrial chemicals in general is ad hoc and dependent on the area of the country being considered. All countries within this region have regulations to control pesticides and chemicals in general. The infrastructure to carry out these laws is not competent enough to ensure full compliance of the laws.

5.2.3.3.6 Polar Regions

Inclusive of the main areas of the Antarctic Region, environmental protection within the Antarctic Treaty area is governed by a protocol to the treaty. This protocol states that ‘activities in the Antarctic Treaty area shall be planned and conducted so as to limit adverse impacts on the Antarctic environment and dependent and associated ecosystems’. Any wastes containing PTS are required to be removed from the Antarctic. Some classes of material, including PCB, are specifically prohibited under the protocol. Discharges of ‘noxious substances’ to the marine environment are prohibited, although no specific categorisation of these noxious substances is provided within the annex of the Treaty (Antarctica Regional Report, 2002).

In the Arctic, regulations are covered within the countries responsible for the respective sections of the region. The Nordic Council of Ministers has proposed guidelines for PTS concentrations in food. Although covering only a restricted segment of the circumpolar Arctic (between longitudes 44° W and 51° E), the 1992 Convention for the Protection of the Marine Environment of the North East Atlantic (OSPAR), is currently one of the most applicable international agreements addressing Arctic marine pollution from various sources. On both monitoring and source-related assessment issues, therefore, OSPAR 1992 represents a relevant agreement to be taken into account (Arctic Regional Report, 2002).

5.2.3.4 International Agreements

PTS pollution issues are covered by several Multilateral Environmental Agreements (MEAs) or arrangements that form an important focus for political efforts aimed at reducing their environmental impacts. The following have particular relevance to the present assessment.

5.2.3.4.1 Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal

The Basel Convention strictly regulates the transboundary movements of hazardous wastes and provides obligations to its Parties to ensure that such wastes are managed and disposed of in an environmentally sound manner when moved across national boundaries.

The so-called Ban Amendment to the Basel Convention bans the export of hazardous wastes for final disposal and recycling from Annex VII countries (Basel Convention Parties that are members of the EU, OECD, Liechtenstein) to non-Annex VII countries (all other Parties to the Convention). The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted in 1989 and entered into force on 5 May 1992.

5.2.3.4.2 The Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade

The Rotterdam Convention on the Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals and Pesticides in International Trade was adopted at a Conference of Plenipotentiaries in Rotterdam on 10 September 1998. The Convention enables the world to monitor and control the trade in very dangerous substances and, according to the Convention, export of a chemical can only take place with the prior informed consent of the importing party. The Convention covers a list of five industrial chemicals and 22 pesticides, including aldrin, chlordane, DDT, dieldrin, heptachlor, HCB and PCB.

5.2.3.4.3 International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978, (MARPOL 73/78)

The MARPOL Convention is a combination of two treaties adopted in 1973 and 1978. It covers all technical aspects of pollution from ships, except the disposal of waste into the sea by dumping, and applies to ships of all types. The Convention has five annexes covering oil, chemicals, sewage, garbage, and harmful substances carried in packages, portable tanks, freight containers, etc.

5.2.3.4.4 Stockholm Convention on Persistent Organic Pollutants

This is the most relevant in the context of the current assessment. The convention was adopted at the meeting of the Intergovernmental Negotiating Committee for an international legally binding instrument for implementing international action on certain persistent organic pollutants in Johannesburg (December 2000). The objective of this Convention is to protect human health and the environment from persistent organic pollutants. The selected list of POPs is of direct relevance to the UNEP assessment of PTS. The Convention was opened for ratification signatures on 23 May 2001 in the Intergovernmental Conference held in Stockholm. The protocol will enter into force as soon as it is ratified by 50 countries (30 ratifications registered as of March, 2003).

Besides these, there are many regional agreements that speak specifically to the control of certain conditions of the environment against PTS (UNEP, 1997). These and all other MEAs do play a key role in the development of chemical management in general across respective member States. All carry out training and capacity building exercises under their given mandates and being binding agreements, a good measure of sustainability is attained. MEAs are internationally accepted standards and the basis and reference for development assistance. If a developing country seeks assistance for management of obsolete pesticides and to have final disposal undertaken in an industrialised country, the transport of this toxic waste must be carried out according to the Basel Convention. To facilitate these kind of projects, both the exporting and the recipient country must be parties to the Convention.

5.2.4 Status of enforcement

The status of enforcement takes a similar line to the pattern of regulations and laws in the various regions. In North America, the United States of America has a set of regulations covering over 900 pages. All of these regulations are enforced in some way, resulting in a comprehensive programme ranging from the control of the chemical industry, the analysis of emissions and releases, the monitoring of environmental compartments, to the handling of hazardous chemical waste. Along with this set of programmes, there is a constant promotion of awareness of the dangers of PTS, especially through an array of non-governmental organisations that provide public involvement and a non-tolerant approach to matters concerning human health and the integrity of the environment. Even so, the vast number of production sites that have chemicals as inputs or outputs, make it difficult to maintain control of the possible emissions that can occur.

On the other hand, many developing countries in Sub-Saharan Africa, the Mediterranean, the Indian Ocean, Central America and the Caribbean, Central and North East Asia and South East Asia and South Pacific have laws and regulations but cannot enforce them. States facing low levels of organisational capacity and weak economies have serious difficulties in increasing environmental protection and fulfilling international commitments. In this respect, investigations have shown that old stocks of chlorinated pesticides (eg lindane) continue to be used in practice under no control of the authorities and that even banned products such as DDT are still being illegally imported in some of these countries. In Sub-Saharan Africa, no country has policies to address PTS specifically and only approximately one half have the proper institutional framework to implement any such policies.

Still, there are examples where developing countries, with some assistance have made strides in controlling the emission or release of pesticide PTS to the environment. In Jamaica, the German aid agency GTZ provided financial assistance for developing the Pesticides Control Authority (PCA). This institution is legislated to regulate the pesticides industry in Jamaica but no implementation of the legislation was undertaken for eighteen years after enactment. The key feature that caused extended success of the creation of the PCA was that the legislation allowed the PCA to collect and spend its revenue stream solely on areas for controlling pesticides. Revenue was gained from charging a percentage of value of chemicals imported into the country along with other fees for registration etc. Besides instituting and enforcing regulatory mechanisms without strain on the central purse, the PCA was able to do an inventory of obsolete pesticides, repackage where necessary and arrange to export eight tonnes including DDT for disposal (Hyacinth Chin Sue, 2003).

There are no satisfactory regulatory or management strategies in place for PTS of industrial uses such as organo-lead compounds and phthalates in the Indian Ocean region countries. Even enforcement of the regulations in existence has been poor. In enforcement of any regulation, especially in relation to an industry, it is vital that viable alternatives according to the prevailing situation are made available. Lack of availability of alternative technologies adoptable under local conditions and economic factors have retarded the industry in taking measures to reduce the use of PTS in this region.

In the case of PTS of unintended by-products, no regulatory or management control measures are in place except the establishment of standards for levels in environmental compartments by few countries in these regions. The control measures adopted according to the standards are limited to incineration of certain solid wastes. Efficient and successful implementation of such limited regulations in respective countries must be carefully assessed.

It is difficult to see extensive improvement in enforcement of PTS in most of the developing countries in the short term. There are implementation plans being developed for countries that have signed the Stockholm Convention. However, the prioritisation necessary to implement those plans is not yet established.

5.2.5 Technology transfer

The transfer of technology to facilitate reduction in sources, environmental concentrations and eventually the effects of PTS, requires the involvement of all stakeholders between countries and a willingness for the donor and receiving parties to understand the limitations to be addressed. Technology is not always appropriate. Introduction of improved technology has, on many occasions, failed because the culture, climate, laws and inadequate infrastructure to support viability have not been considered during transfer. Some of the avenues of transfer are discussed below.

⇒ **Trade Shows** – These events although limited in exposure, provide a useful means of interacting potential users to the latest technology especially in the industrial sector for reducing and eliminating environmental pollution. Such events should be promoted by countries especially within a regional context and should involve both developed and developing countries.

⇒ **Scientific Workshops** – This tried and tested method of information exchange continues to create a medium for participants to meet and exchange views and ideas. Besides showcasing innovative concepts, such fora initiate contacts and create friendships that go a long way toward generating collaborative efforts for technology transfer.

⇒ **The Internet** – Now an accepted form of gaining information, the internet is increasingly becoming the primary source for all facets of the society to seek information. Especially among students, the internet is accepted as the place to display new technology to capture the largest audience possible. As more of the populace within developing countries tack on to the internet library, this means of data exchange will be a vital link to these countries in the quest to keep pace with environmental control methods for PTS and other pollutants. However, there is still need for structuring this vast network to ensure that quality can be a function within the search exercise. An excellent starting point is the Information Exchange Network on Capacity Building for the Sound management of Chemicals (INFOCAP) developed on behalf of the Intergovernmental Forum on Chemical Safety (IFCS). INFOCAP provides linkages and information on National Profiles, country priorities, sources of potential support, past, ongoing and planned projects and is a reference library of existing training and guidance documents in the field of chemical management.

⇒ **Multilateral Environmental Agreements (MEAs)** – Such agreements have served as a platform for technology to be transferred between parties to any given agreement. Good examples include the Montreal Protocol on protection of the Ozone layer and the Stockholm Convention on the reduction of POPs. On the regional scale, these MEAs have been even more influential and should be encouraged especially where a common bond is available. The linkage between countries that share a common water body is a suitable example. The

MEDPOL organisation in the Mediterranean, the CEC in North America and the EMEP research in Europe are typical examples.

- ⇒ **Adoption of Countries** – The adoption principle for growth and development has been used in other spheres of life. Cities and universities in different countries have used this link to great advantage over the years. In this instance, it requires the linkage between a developed country and one or more developing countries in a particular region to work together toward the improvement of technological practices in the developing country. In some instances, the developed countries can also benefit from exposure to the indigenous practices of the developing country that has potential on a wider scale. This alliance can allow the exchange of personnel for training in both directions, the increase in the understanding of the culture between countries and the timely improvement of the environment as the process is expected to continue over an extended period. Commitment from both sides is the key factor in such a process. In the development of linkages between countries of differing economic status, it is prudent to seek common factors for pairing. Such factors include:
- ⇒ **Language** – A vital means of communication that goes a long way toward having harmonious relations between countries. Developing countries would seek to form alliances with those countries sharing the same language to allow for easy transfer of technology, training and scientific workshops.
- ⇒ **Regional Pairings** – If both parties have a common environmental concern, it will be a useful incentive for collaboration. This represents the best opportunity for success globally and investigation should begin to review current collaboration and how best to foster new links on a similar basis where none now exist.
- ⇒ **Shared Responsibilities** – The collaboration that is to be developed must also intertwine between developing countries within a region. It is foolhardy for neighbouring developing countries to seek to create the expertise in the same expensive non-sustainable analytical technology. Therefore, there must be an overall strategy where countries that have signed on to the programme accept the responsibility to provide certain services for others in the region and for the reciprocal undertaking to be acceptable for other capabilities. Additionally, it must be understood that trained personnel should remain within his/her State for a given period to ensure development of a cadre of experts. Too often, persons trained leave for the developed countries having been lured by attractive offers.
- ⇒ **Use of Existing Collaborations** – There is no need to 're-invent the wheel'. There are many regional monitoring programmes that already exist and are productive. These should be logged and an analysis done to see how best to integrate these programmes into a global exercise. The developed countries of North America, Europe, East Asia and South East Asia should immediately seek to increase the pace toward compatibility of analytical methods, quality assurance and data presentation. Here is the key to future development of global monitoring. If the same analytical language is spoken at this level, the stage will be set for compatibility to trickle down to the other countries around the globe.

5.3 IDENTIFICATION OF BARRIERS TO SOLUTIONS

This section aims to identify and list barriers that have been encountered in the regions that are preventing or hindering the proper management and prevention of problems caused by PTS. In general the regional reports did not explicitly address barriers.

Needs and barriers, as they relate to effective management of PTS chemicals, will depend on the chemical or chemicals being addressed and also the circumstances in the country being considered. Solutions to problems must be developed to respond effectively with local issues and reflect local conditions to be useful. However, there are recurring themes and many of the barriers identified will be applicable to many countries and regions. Effective assessment and management of PTS requires the following steps:

- o Identify and quantify the problems (risk assessment);
- o Assess options;

- o Prioritise PTS issues and establish the rationale for acting to address PTS related problems;
- o Develop solutions;
- o Implement solutions.

There is concern for number of chemicals, some of which have been used for many years and consequently this process of assessment and implementation of solutions is more advanced for some chemicals than for others. For example, the problems linked to the 12 Stockholm POPs have led to a series of actions described in the Stockholm Convention. The Convention lays out minimum actions that will be taken by parties to mitigate and prevent problems occurring from these chemicals and for these chemicals the barriers relate mainly to implementation of defined actions within a country context. For emerging chemicals the focus may be more on identifying and quantifying the current and potential problems.

The following paragraphs list some of the barriers to effective assessment and management of PTS which have been identified during this project:

❖ **Lack of comprehensive scientific data:**

The development of a suitable and effective management framework for PTS assessment and action should be underpinned by adequate scientific information. The information gathered must adequately cover the sources, pathways, fate and transport, human and ecosystem exposure, toxicology and ecotoxicology. It must be complemented by a detailed understanding of the trade, the commercial environment, demand drivers and alternatives to the chemical or process in question to enable soundly based decisions to be made. Decision makers must take account of the threats posed, costs incurred by possible changes and identify realistic measures needed to ensure effective management of PTS.

This project has attempted to gather existing data on the issues above and has clearly identified barriers preventing the adequate assessment of all the PTS chemicals. Barriers identified have included:

- ⇒ An absence of comprehensive data on all compounds relating to sources, environmental concentrations, actual or potential effects on humans and ecosystems and long-range transport. In addition limited or absent data on the socio-economic aspects, demand drivers and availability of alternatives. This is reflected in the numerous data gaps identified in this work;
- ⇒ Technical deficiencies in terms of limited or absent capacity for analytical work, inconsistent or poorly harmonised systems for generating and collating data, a lack of inventory capacity and capacity to assess effects are found in many countries and regions;
- ⇒ High costs associated with detailed, long-term and wide-ranging studies form an important barrier and require careful targeting of future research to maximise the benefits by focusing on key areas of the production, source, exposure and control framework;
- ⇒ Limited technical resources and diverse demands on expertise and manpower can be a barrier in some countries and regions. Difficulty in training and then retaining expert staff;
- ⇒ Low awareness of the potential problems and complacency about the existence and severity of data gaps can be a barrier to generation of commitment to study the scientific basis for actions related to PTS;
- ⇒ A lack of tools enabling proper assessment of the socio-economic aspects of PTS use, inadvertent production and alternatives in particular in the less developed areas of the world restricts and hampers soundly based decision making on options and possible solutions;
- ⇒ Decision makers are lacking tools to help to prioritise PTS related issues. There is a need to identify priorities amongst different PTS issues and also to assign appropriate priority to PTS related issues in the wider context of environmental degradation and needs for development.
- ⇒ Except for the Category I regions, there is little knowledge on the pathways that these semi-volatile chemicals take across boundaries. In order to fully establish the threats to distant regions, appropriate models must be created to focus on particular regions with individual characteristics. Dynamic models such as the EMEP (MSC-East) multi-media POP transport

model from Europe should be revised and made to be used in regions devoid of such capabilities.

❖ Lack of monitoring and inventory capacity

Monitoring and the establishment and maintenance of inventories are essential elements of effective PTS management. The monitoring systems include surveillance of the legal requirements and practices as well as monitoring of the environment, human and ecosystem health and contamination levels in products. Monitoring programmes in the developed world are increasing rapidly and analytical capacity is being installed and upgraded. Analytical monitoring can be expensive, hard to sustain and needs a suitable environment and infrastructure in which to operate. Opportunities to collaborate across borders and between government and industry should be developed alongside a strengthening of the available capacity and skills. Barriers to effective monitoring include:

- ⇒ Poorly developed or absent standards for measuring and reporting data;
- ⇒ Poorly harmonised systems of establishing inventories;
- ⇒ A lack of resources to pay for high cost and complex analytical work;
- ⇒ A lack of available, lower cost, proven and reliable alternative analytical procedures;
- ⇒ Inadequate staff training and skills for fieldwork or inventory development, inadequate resources and infrastructure to maintain inventories and databases.

❖ Lack of suitable legislative framework

An integrated and coordinated approach is required to the development of effective international actions and national legislation that links the diverse aspects of PTS management from source/import through use to disposal and effects. A system or legislative framework that facilitates coordination between actions taken by key stakeholders within the country at the local level and beyond the country to regional and international legal frameworks and Conventions is crucial. Such systems are not yet in place in many of the countries and may have only recently been put in place in others. Barriers to the development and implementation of a suitable legislative framework at the international, regional and national level include:

- ⇒ The considerable resource and cost implications of generating the necessary data to identify chemicals for which international or regional action and to underpin the development of effective regulations and actions;
- ⇒ Difficulties in ensuring smooth and effective working between the different institutions involved with problems caused by poor coordination and cooperation between institutions. Actions to develop the Strategic Approach to International Chemicals Management (SAICM) should help to address this barrier at the international level;
- ⇒ A lack of capacity within some regions and countries to draw up and put in place suitable legislation.

❖ Ineffective enforcement of regulations and legislation

A comprehensive and appropriate legal system requires fully functioning enforcement and surveillance in order to make it effective. Enforcement has to take place at many levels and requires active participation of many stakeholders involved in the management of PTS. Designing an effective and sustainable system of enforcement and linking this to appropriate monitoring strategies is a complex task and requires on-going inputs in terms of training and resources. Barriers to effective enforcement of regulations and legislation include:

- ⇒ Providing suitable training and resources to achieve adequate numbers of staff with the necessary skills and equipment to enforce existing regulations;
- ⇒ Lack of resources within many national Governments for enforcement staff on chemicals issues in general including PTS;

- ⇒ Lack of technical and management capacity for monitoring to underpin enforcement.

❖ Illegal trade and use

The illicit trade in chemicals and products can be a major problem and circumvents national and international legislation. The problem may be particularly acute where obsolete stockpiles of PTS form an attractive source of chemicals for which there is a demand. Control of illegal trade is a complex issue and requires providing a mechanism for monitoring potentially significant trade which could move PTS chemicals, liaison between agencies and countries and active enforcement by informed and well equipped officers. Barriers to effective control of illegal trade and use include:

- ⇒ Lack of coordination between nations to control imports and exports of PTS;
- ⇒ Lack of information to assist customs and other inspectors in identification and dealing with potentially illegal PTS;
- ⇒ A need to address the demand drivers including effective enforcement of regulations, controls on end users and provision of economically attractive, legal, alternatives to illegal PTS;
- ⇒ Lack of resources to monitor all entry and exit points for PTS from many countries.

❖ Inappropriate use and abuse

Problems with PTS (as with other chemicals) can often arise from the way in which they are handled, used and disposed. Careless handling, poor health and safety practices and improper disposal can lead to contamination of the environment and poisoning of operators and others. Excess chemical use contributes to pollution and is costly and ineffective. Systems to control and monitor practices are needed and require cooperation between legislative and enforcement authorities. Good practice also depends crucially on the education and cooperation of the suppliers and users of the chemicals. The same logic applies to operators of processes that may produce PTS unintentionally where the way a facility or process is operated has a large impact on the potential releases. Barriers to addressing and controlling inappropriate use, abuse and disposal of PTS chemicals include:

- ⇒ Lack of resources to monitor and quantify the problem or to police such use;
- ⇒ Lack of information suitable to educate users about the potential dangers both to applicators as well as the wider environment of poor practice;
- ⇒ Lack of affordable and effective safety equipment that is user friendly in all environments where the PTS chemicals are used (there is a problem with unwieldy and uncomfortable protective gear in hot climates);
- ⇒ Lack of facilities and experience at dealing with wastes;
- ⇒ Problem of used containers having intrinsic value where containers are generally scarce or expensive creating a demand for empty chemical containers for a variety of potentially dangerous and inappropriate uses;
- ⇒ Lack of provision of affordable and effective alternatives;
- ⇒ Commercial pressure on elements of the supply chain to supply chemicals without ensuring suitable controls exist from supplier to end-user to ensure safe and appropriate use.

❖ Lack of awareness and information

Information is lacking in many parts of the world to stakeholders who may be able to influence the management of PTS. Provision of scientific information as well as decision-making materials for politicians and policy makers is inadequate. Education for stakeholders on the requirements and practices for effective PTS management needs to be increased and made more widespread.

Achieving the necessary levels of awareness amongst all stakeholders is hindered by the need to develop effective tools to communicate appropriate messages in a form that is easily understood and relevant to the target audience.

❖ Commercial pressures

It is crucial that commercial imperatives are recognised and addressed in developing controls for PTS. Where possible the commercial pressure should be harnessed to improve management. Economic effects on producers as well as distributors and users of PTS need to be considered. Solutions that do not adequately deal with the needs of commercial concerns as well as the economic reality of end users and affected populations will not be successful. Barriers to understanding and aligning commercial incentives with good practice include:

- ⇒ Incomplete data on the value chain and flows in the commercial market
- ⇒ Ineffective pricing to reflect external costs

❖ Lack of availability and acceptance of alternatives

The development of alternative chemicals and alternative processes or practices which reduce reliance on PTS needs to be stimulated and subject to proper assessment of the benefits, effectiveness and value in replacing PTS in the particular circumstances in a given country or region. Any process to replace one chemical or process with another type, needs to gain acceptance at all levels from the national and international down to the individual or enterprise actually having to work with each stage of the process. The process of developing suitable alternatives can be long and drawn out and ensuring that a net benefit results is a complex process. Failure of new processes and products to work in the regional setting contributes to reluctance to change and adherence to old practices which may be unsustainable. Barriers to development and application of alternatives include:

- ⇒ High costs and long lead times of developing and assessing alternatives;
- ⇒ Potential for unforeseen difficulties in application of an alternative in widely variable environments and with highly variable levels of infrastructure and resources in different countries;
- ⇒ Lack of demonstrations in appropriate situations of alternative solutions;
- ⇒ A reluctance to change old established and well understood ways of tackling a problem;
- ⇒ Potential problems with alternatives that are more costly.

❖ Lack of clear responsibilities and limited coordination

Implementing solutions to problems caused by PTS requires that many stakeholders work closely together. In some cases there can be difficulties related to ensuring effective coordination and assigning responsibilities between stakeholders. For example, this may have particular relevance to stockpiles of obsolete chemicals and historic problems caused by past actions and decisions related to PTS. The issue may also be an issue where enterprises may have ceased to trade. Assigning responsibilities appropriately along supply chains from producer through to end user and those faced with the consequences can be time consuming, sensitive and difficult. Barriers to assigning and agreeing responsibilities for aspects of PTS management include

- ⇒ Frequently complex relations between producers, suppliers, users
- ⇒ Potential distortions to commercial operations
- ⇒ Historical actions carried out in ignorance of potential for future problems
- ⇒ Absence of key players and potential problems with assumption of liability

❖ **Lack of financial resources**

The achievement of effective PTS management necessarily requires adequate resources to be available. Finding means to generate the necessary resources from all parts of the value chain in an effective and equitable manner is a major challenge. These resources will need to complement national Government, international and non-Governmental organisation resources. Barriers to provision of necessary resources include:

- ⇒ Limited funds available from Governments, aid programmes, multilateral aid programmes;
- ⇒ Competing demands for limited resources and a lack of a mechanism for evaluating comparative severity of problems;
- ⇒ Difficulty in ensuring that the ‘polluter pays’ principle is balanced with a need to secure improvement and action;
- ⇒ Difficulties in ensuring effective use of resources to address root causes of the problem

5.4 ALTERNATIVES OR MEASURES FOR REDUCTION

It is firmly established in the developed regions that pollution prevention and new technology to protect the environment is big business. Alternatives to the use of PTS and measures for the reduction of PTS to the environment will likely continue to be a focus of attention in these regions. This can be expedited by means of firmer government policy and action on PTS.

Industry in general has shown itself to be technologically capable of developing alternative processes or products to replace the uses of PTS where it has been shown that risk management is not an option. Removal at source and other pollution prevention techniques has been the preferred course of action, where feasible. Where PTS are present in waste streams as a consequence of industrial processes, treating and disposing of such toxic releases in an environmentally sound manner is required.

An important driver for new technology is the clear, stated intent of governments to legislate/regulate the product or release out of existence, either initially or as a backstop to voluntary initiatives by industry. Technology-forcing regulations have been used extensively to eliminate/reduce the release of toxic substances to the environment. While there are those who do not favour this approach, it has been generally successful in achieving environmental objectives.

While many alternatives to PTS have been researched, it is not necessarily to find suitable, workable systems to replace the desired qualities of these chemicals. The quality of persistence, low water solubility toxicity and the cost efficiency of processes that may release or emit PTS are difficult to replace. However, there are real examples that do exist where alternative measures have been instituted and have generated the desired result that was provided by the replaced PTS. It must be cautioned that any situation presented has been developed within the conditions of the particular environment and should be tested before blanket transferral of such technology is taken and applied elsewhere.

5.4.1 Precautionary Approach

Principle 15 of the Rio Declaration states *inter alia*: Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation. Given the little we know about PTS and their fate and potential toxicity, a precautionary approach to addressing these substances is warranted. The rationale for applying precaution rests on both what we know and what we do not know about these substances and the potential for impacts that are both global in nature and can last for generations. It can change our focus from trying to develop complete knowledge about the risks of each PTS to trying to developing solutions that would prevent exposures and result in a new generation of environmentally-friendly products and goods. Applying precaution to PTS is consistent with the Stockholm Convention and other international agreements, such as the North Sea Conferences and the U.S.-Canada International Joint Commission, that have called for precaution to be applied to these substances.

Implementing a precautionary approach to PTS does not necessarily mean an outright ban to each chemical that fits pre-defined characteristics for PTS. Rather precaution embodies an approach to rapid assessment, monitoring, risk reduction and development of safer substitutes. A framework for applying precaution to PTS would encompass the elements of Rapid Identification; Assessment and prioritization of PTS. Many of these elements are described in the Measures for Risk Reduction System.

A first step toward filling data gaps is to identify those substances that qualify as PTS. The burden for this rapid identification should fall on producers and users of these substances, though governments can also undertake such an assessment. To complete this rapid identification, all available information on the substance or similar substances, including informed judgment should be used.

For substances identified as potential PTS, a second step is the development of a rapid assessment of toxicity, production, potential routes of exposure, transport, fate and occurrence – a qualitative risk characterisation. The purpose of this step is to use all available information from multiple disciplines, constituencies, and regions as well as informed judgment to understand the risks that a substance might pose. This assessment should also consider the potential for high exposures and higher susceptibility to vulnerable subpopulations.

Prioritisation is the third step of a precautionary assessment process. Prioritisation should be based on both toxicity and persistence characteristics of substances. Chemicals of highest priority should be addressed through risk management first, though substances that are PTS of lesser concern should also be considered for exposure reduction or substitution.

Following the rapid assessment process, substances which have been identified as PTS or potential PTS should undergo an alternatives assessment process. The goal of the alternatives assessment process is to identify alternative substances, production process or product designs, or use controls (such as improvements in processing conditions or uses with less dispersal), which would reduce exposure and transport of PTS. The alternatives assessment should consider not only existing, easy and feasible options, but also those that can be developed – that are "on the horizon." Subsequently, a comparative analysis of alternatives is undertaken. The goal of comparative options analysis is to thoroughly examine and compare technical feasibility and economic, environmental, and health and safety impacts and benefits of the existing or proposed substance and identified alternatives.

A precautionary approach to PTS uses a variety of regulatory and market-based approaches to reduce exposure and stimulate the development of safer substitutes, process designs, and products. It is clear that the ability to use these approaches will differ by country and region and some financial and technical assistance to developing countries will be necessary (Cedillo Becerril, 2003). Some particular approaches include:

- Research and Technical Support
- Phase-outs
- Published lists of chemicals of concern
- Procurement controls
- Labelling
- Taxes
- Incentives
- Information flow to society
- Training and Monitoring

General presentations of alternative strategies for PTS are given below with particular situations of real, successful activities given to support these presentations.

5.4.2 Selected PTS Chlorinated Pesticides

The use of these chemicals is fostered due to their low cost and exceptional efficacy. The alternatives to their use are limited but well known. However, cost and poor resources for implementation hamper such introduction. Additionally, many of the alternatives discovered and implemented focused on short half lives (limited persistence) but carried high acute toxicity properties. Many of these pesticide alternatives are now being banned as the extreme acute toxicity has created new risks to users and the ecology. Other corrective strategies include:

⇒ **Legislative Control –** Introducing regulations and laws to ban the use of persistent chlorinated pesticides and actively enforcing such a ban, remains the first and foremost step for countries to use to control these chemicals. Given the political will to first enacting such legislation, countries in the developing world stand favourable to attracting assistance to build the necessary institutions and for training the personnel required to enforce the ban against the use of PTS pesticides.

⇒ **Integrated Pest Management (IPM) –** This technology has shown itself to effectively reduce the reliance on chemicals in general. However, an IPM programme advocates the use of chemicals as a last resort but does not necessarily suggest a complete ban. Major considerations include: cultural control; mechanical and physical control; biological control; genetic control and legislative control. This procedure has been instituted across the developing world with mixed results. The Sudan has been successful in implementing IPM procedures in its cotton production. The use of resistant varieties of cotton, the introduction of parasites to worms, the use of heat treatment of seeds to kill larvae and the use of pheromone traps have all allowed the reduction of chemical insecticidal spray cycles from 9 to <4 per season (Bashir, 2003). On larger farming estates, the inclusion of IPM procedures is usually entrenched but the use of chemicals forms a standard process of the control measures for pests. Given the cheap availability of mainly illegal chlorinated pesticides and the greater efficacy achieved, the success of IPM to reduce the use of PTS as pesticides will only be effective from strong regulatory control of the production, importation and use in each country.

⇒ **Integrated Vector Management (IVM) –** A programme similar to IPM in concept, IVM seeks to control vector borne diseases such as malaria. The historical use of DDT to control malaria and the current efforts being made to substitute this PTS with IPM initiatives that do not include DDT, stand as the hallmark of this programme. Even though DDT continues to be used in many malaria infected countries, efforts by the WHO in introducing IVM initiatives have reduced the amount of DDT being sprayed and has formulated an alternative strategy toward the control of the **Anopheles** mosquito that carries this deadly disease. In Mexico, in the past, the main consideration was to find an alternative pesticide to DDT for control of the Anopheles mosquito. This approach was abandoned in the Mexico initiative to include a more holistic approach that incorporated:

- ✓ Participation of the various communities under a public health programme
- ✓ Diagnosis of DDT use and malaria conditions
- ✓ Elimination of Anopheles breeding sites
- ✓ Promotion of basic sanitation measures to avoid mosquito contact
- ✓ Providing symptomatic treatments to malaria infected families
- ✓ Use of deltamethrin only in infected houses
- ✓ Encouragement of participation of local authorities
- ✓ Building institutional capacity for chemical analysis and malaria diagnosis.

This broad direction for control resulted in the reduction of malaria cases in the Oaxaca State of Mexico from 17 855 to 284 in three years (CEC, 2001). Spearheaded by the WHO, other regions have started to introduce IVM measures for reducing if not eliminating the reliance on DDT.

⇒ **Inventory and Destruction of Obsolete Stocks –** In many developing countries, there are large stocks of these chemicals. Such deposits are considered a source of income for the owners. The sale for use in agriculture and for vector control will continue to allow release of these chemicals to the environment. The Food and Agriculture Organisation has played a key role in establishing inventories of old stock in Africa. The continued assessment of these stocks and ultimate destruction will be an effective measure to reduce the release to the environment of pesticide PTS.

⇒ **Genetically Engineered Pest Resistant Plants –** The introduction of such varieties for cotton, wheat and maize production has reduced the reliance on insecticides considerably in certain developed countries. As expected, the cost of these new varieties plays a role in the slow introduction to crops grown in the developing countries. In addition, there is some reluctance to embrace these plants as there is uncertainty as to the deleterious effects that can be had from exposure of both plants and animals to these crops.

⇒ **Replacement of Selected PTS Chlorinated Pesticides –** First, substitutes have to be identified, so that the production or use of PTS can be prohibited. For example, DDT and HCH were major pesticides in China during the 1970's and early 1980's. In the middle of the 1980's China began to replace organochlorine pesticides with organophosphate pesticides. Since 1983 DDT and HCH have been banned as pesticides. In Kyrgyzstan, pyrethroid pesticides have replaced DDT and HCH. The annual consumption of pyrethroids is about 33 t, which represents a replacement rate of about 75% (C&NE Asia Regional Report, 2002). It would greatly enhance the process of replacement if industry introduced a differential costing programme for developing countries so that new less persistent chemicals are made available at comparative costs to the old chlorinated pesticides. Successful replacement for DDT in agriculture has been implemented in the Sudan. Since 1980, the use of toxaphene and DDT for controlling insect pests in cotton production has been banned. These Stockholm POPs pesticides have been replaced by pyrethoids, (deltmethrin, permethrin, cypermethrin, fenvalerate) organophosphates (chlorpyrifos, triazophos, dicrotophos) and the carbamate – carbaryl (Bashir, 2003). Similar replacements have taken place in Sri Lanka (**Dr. G.K. Manuweera**, 2003) and in many other countries across the globe.

⇒ **Organic Agriculture** – In many countries, organic farming is a distinct , ongoing alternative practice. Organic agriculture avoids chlorinated and other chemical pesticides and fertilizers on many crops by utilizing different management systems and the greater use of natural biological resources.

5.4.3 Industrial Chemicals and Unintended By-Products

Great strides have been made to reduce the environmental levels of industrial PTS in the developed countries where most are released. These are some of the strategies employed for reduction and even elimination where required:

⇒ **Sustainable Production –** With developed countries taking the lead, encourage and promote the development of programmes in support of regional and national initiatives to accelerate the shift towards sustainable consumption and production. To promote social and economic development within the carrying capacity of ecosystems. This is best done by delinking economic growth and environmental degradation through improving efficiency and sustainability in the use of resources and production processes, and reducing resource degradation, pollution and waste. Establish and support cleaner production programmes and centres and more efficient production methods. This initiative should be further considered within the framework of the Plan of Implementation from the World Summit on Sustainable Development regarding changing unsustainable patterns of consumption and production.

⇒ **Best Available Technology –** As mentioned earlier in the chapter, the industrialised countries have been innovative in implementing replacements for PTS producing processes. In pulp and paper production, emissions of 2,3,7,8-TCCD/TCDF in the United States and Canada have been virtually eliminated because of the shift from molecular chlorine, to chlorine dioxide. Significant reductions in the release of dioxins from incinerators that burn municipal and hospital medical wastes have been achieved through improved combustion technology and source separation. However, source separation appears to be considerably less effective when compared with the technological solution. In the USA, as part of the effort to protect the Great Lakes Basin, a workshop – "Burning Household Garbage: Impacts and Alternatives" was held to provide educational training to the public on trash and open burning in the Great Lakes region. A website (www.openburning.org) was also launched providing information on dealing with household waste. Thailand, with financial support from GTZ, UNEP Chemicals and EuroChlor, established an emission inventory for PCDD/PCDF. Seven typical facilities representing respective industries were selected for sampling of stack gas emission and liquid, sludge and solid waste residues. The results of this programme will serve as the basis for focusing on the most efficient risk reduction measures against PCDD/PCDF emissions in Thailand (Kern, 2003). The preferred options for PCBs management are the total replacement of PCBs fluids, either by retrofilling of the existing materials or by plain destruction. Retrofilling involves the selective recovery and decontamination of the PCBs fluids of transformers and capacitors and their replacement by non-PCBs fluids. This enables the conservation of the equipment in place and diminishes the volume of PCB waste to be handled. Avoidance of the use of additives (e.g. flame retardant in plastic) containing chlorine or bromine will contain the release of PBDEs and other flame retardants although this has to be weighted against the much higher risk involved in fires. In industrialised countries and elsewhere, there have been increasing efforts to collect and exchange mercury thermometers. Such programmes typically involve hospitals, schools, universities where relevant personnel have an opportunity to turn in old mercury thermometers and receive a free or reduced price non-mercury alternative. There are existing alternatives that provide an opportunity to reduce the use of mercury thermometers and help promote their proper disposal. Alternatives include digital electronic, glass alcohol and glass galinstan thermometers. All of these alternative thermometers provide comparable accuracy with reduced environmental impact than those presented by mercury thermometers. The button cell batteries in the electronic thermometers do contain mercury but far less than in regular mercury thermometers (~7mg vs 700mg).

⇒ **Destructive Technology -** The most diffused destructive technology used is incineration. There are some problems related to the difficulties in burning substances, which are high temperature resistant such as PCB/PCTs. The main problems that arise from thermal destruction are: a) Incomplete destruction of PCBs due to their thermal resistance which require the use of high temperature. b) The generation of dioxins as secondary product. Dioxins are generally formed as the re-combination of partially degraded organic fragments after the first PCBs burn up during the cooling process in the critical temperature range 200-400 C°. It has been discovered that the poor and incomplete combustion of PCBs and a low speed of effluent gases cooling, can generate significant levels of dioxins. As a consequence, certain alternative destruction technologies are used and others are being investigated. Dechlorination of PCB oils with sodium is a cost-effective alternative that has the added benefit of recovery of the oil for re-use (UNEP, 2000). However, any implementation of new destruction technology must ensure the same destruction efficiency as incineration and also show less emission of unwanted PTS.

5.4.4 Others

Greater attention being placed to prevention/control of forest fires will reduce considerably the emission of PAHs to the air. Open burning is widespread throughout many countries and little or no effort is made to rein in this practice. The enactment of legislation to prevent open burning would go a long way to increase awareness and stimulate alternative methods for removing waste.

The use of TBT-containing antifouling paints are now controlled or banned in many countries. In October 2001, several countries have signed at IMO level, a Convention for phasing out TBT from use on ships and boat and as antifouling agents in many other marine applications. This represents a concrete step towards the elimination of an uncontrollable and diffuse source of an important marine pollutant. Viable alternatives to the use of TBTs have been proposed, the most interesting ones are copper based self-polishing coatings, which are commercially available. TBT-free self-polishing coatings can now achieve control for 60 months whereas ablative and conventional paints reach a maximum of 36 months (WWF Toxics Programme, 2000). The International Boat Fair in Barcelona in November, 2002 has shown that the majority of the recreational boat constructors that operate in the Mediterranean region have replaced TBT antifouling paints by TBT-free self-polishing coats (Mediterranean Regional Report, 2002).

5.5 CONCLUSIONS

The desired qualities inherent in PTS make it difficult to achieve alternatives without the negative effects. Emphasis on public awareness, cleaner production, legislation, increased capacity and availability of financial resources will assist in alleviating some of the problems that exist. While alternatives do prevail for some of the chemicals under assessment, for many research is required to further assess the threat and to find other methods to reduce emissions to the environment. The differences in economic development, culture, agriculture, technology and climate present unique opportunities for countries to direct their attention to the control of any adverse effects of PTS. The protection of the environment and human health from the adverse effects of PTS chemicals requires significant capacity in a variety of areas which is effectively integrated and coordinated within a country but also between countries within a Region. Adequate capacity is required in:

Monitoring and testing of sources, environmental and product contamination, human exposure

National, Regional and International Legislation, including control of manufacturing, registration, use, disposal of PTS

Supervision of chemical production, use and disposal including production of wastes, operator health and safety, control and monitoring of releases

Identification and application of alternatives and controls

Within the developed countries, there are monitoring exercises ongoing for the PTS being assessed. Even so, the financial pressure to keep abreast of the required analyses for the ever-increasing number of chemicals is daunting.

For Europe, the EC has created policies that make it mandatory for member countries to have monitoring programmes for selected PTS. However, many countries outside of the EC in this region are still saddled with stockpiles of PCB, obsolete pesticides and relatively high emissions of PCDD/PCDF from inefficient industrial plants. These countries mainly from Eastern Europe will probably benefit upon accession to the EC where strict policies will have to be accepted and enforced.

The creation of the MEDPOL initiative in the Mediterranean can be argued as a success story for collaboration between developed countries and others sharing a common environment body open to pollution from poor protective directives. Much can be gleaned from this initiative and other regions should consider studying the programme with a view to possibly imitating at least the concept behind the programme.

In Central and North East Asia and South East Asia and South Pacific, there is limited regional collaboration taking place on the monitoring and control of PTS. It requires novel and innovative ways to transfer technology and information to the less developed countries in these regions as many of the high profile initiatives will not be sustainable there. In Sub-Saharan Africa, Central America and the Caribbean and Eastern and Western South America, greater links need to be forged with the more developed regions in order to establish sustainable capacity for monitoring and control of PTS.

The needs of the regions are varied in order to fully address the problems of environmental pollution from PTS. A major concern is the differing levels of priority placed on PTS control between countries. As the globe comes under increasing pressure from these travelling chemicals, more emphasis should be placed on creating linkages to strengthen the developing countries to allow precise assessment globally.

5.6 REFERENCES

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6 CONCLUSIONS

The Regionally Based Assessment of Persistent Toxic Substances (PTS) provides a snapshot of the sources, environmental concentrations, effects, environmental transboundary movement and the parameters surrounding the control of the selected substances globally. Besides the process of gathering data, there were over 600 scientists, government and industry representatives as well as persons from non-governmental organizations from countries around the globe that were directly involved in the assessment exercise. In total, twenty eight substances were considered but the actual number varied for each of the twelve regions in which the globe was divided.

It is important to recognise that there is a defined process contained in the Stockholm Convention to propose and assess chemicals as possible Persistent Organic Pollutants. This project is entirely separate from that process and no judgement, explicit or implicit, was made regarding whether the compounds addressed beyond the 12 Stockholm POPs are or may in future be classified as POPs under the Stockholm Convention.

This project was primarily concerned with data gathering and not with assessing which chemicals are or could be considered PTS and the inclusion of a chemical for assessment does not imply that it meets any particular criteria of toxicity, persistence or effect. It is crucial to recognise that the exclusion of chemicals from this assessment does not imply that there are not other potential PTS that may be important.

The findings of the project were summarised in 12 regional reports (see reference list). The overall findings, key themes and examples from the regional reports have been assembled into this report but for a full picture of the work carried out and data gathered, the regional reports should be used alongside this global report.

The project provides information on those chemicals that were considered and is based on the information and data provided during the project period. Supplementary data and further studies may change the relative priorities and may change the interpretation of the data available. The work is therefore to be seen as a step in the process of evaluating PTS and not as a definitive study and all conclusions are drawn with that in mind.

6.1 PRIORITY SOURCE ENVIRONMENTAL ISSUES

A lack of data was a serious constraint with the compilation of many of the regional reports, especially from regions with developing countries and countries with economies in transition.

Quantitative comparisons of production and releases by source type and chemical across regions was very difficult, as the lack of data, method of reporting, completeness, reported time trends in reductions and or increases, allowed mostly qualitative horizontal comparisons.

The general and comparative sensitivity of specific regions was not considered (i.e. would a small source of PAH in Region I be more important, than a relatively large source in a region just to the south?). Key observations, considerations, conclusions and suggestions that follow are outlined below:

- Obsolete stocks and reservoirs of released PTS (such as contaminated sediments and soils, and stocks of obsolete pesticides) are located in a number of regions and are major current sources. This aspect has been identified as a serious concern in developing as well as developed regions, thereby sharing a common environmental issue. This presents a potential of collaboration on remediation and other technologies between developed and developing nations, including nations with economies in transition.
- Even though much has been done to reduce emissions, industrial activity, (both in developed and developing regions as well as countries with economies in transition) must still be considered as a major source of PCDD/PCDF, and probably other related PTS. The characterisation and location of these activities on a global basis needs to be better understood, for a strategic application of interventions to be cost and time effective.
- Open burning and biomass burning are probable, but largely unknown sources of PAH and PCDD/PCDF in developing regions, or regions with a mixed economy. Open burning and biomass burning in many areas expose biota and human populations, due to their close proximity (land fills, domestic heating, close location to water etc), and needs to be much better understood. Large cities as such can also be considered as a concentration of both various PTS sources and exposure routes, specifically involving the

human population. Large cities are normally also located close to fresh water, and often with coastal areas, two areas of major concern due to pollution potential and sensitivity of the ecosystems.

- The developed regions can be considered as the major sources of intentionally produced industrial PTS (chlorinated paraffins, PBDE, PFOS and others). This is then transported via the environment, as well as through trade, to other regions. A better understanding is needed, as double counting (produced in one country, and used in another) could give the false impression about specific chemicals. The issue of secondary sources, such as e-waste, also needs to be better understood, as production, transport, primary use, and waste treatment (secondary use), will all be potential sources (to a greater or lesser extent).
- Very little is still known about the sources of organometalics in all the regions, although mercury is being addressed by the Global Mercury Assessment. Not enough information was available to make any qualitative statements about this issue, but concern is still obvious from the various regional reports.
- PCB remains a large problem in almost all the regions, although it should be recognised that PCB is one of the specific issues that will be addressed by the National Implementation Plans under the Stockholm Convention.
- DDT and the lack of a clear and effective alternative continue to hamper development, as well affecting the health of millions of people in many regions. Combined and continued efforts (such as with the WHO) is needed to address this insidious issue, as well as to raise the understanding of the problems in other regions.
- The source profile (Table 2.9) indicates that much more is known about most PTS sources in the developed regions, but in developing regions, major data gaps exist regarding the non-intentional and intentionally produced industrial PTS. Capacity and means to address the related issues remain a primary aspect that will need attention to assist developing regions in this regard.
- It must be recognised that the source profile is likely to change with more information from various activities, including the NIPs. Part of the lack of information can be ascribed to little capacity within developing regions to address source aspects. It will therefore by very useful if the source profile could be regularly updated, providing a clear means to understand the global issues, as well as to provide guidance on interventions, research and prioritisation.
- The source profile is also likely to change, as changes in sources within the various regions, through mitigation measures or through economic and social development,.
- Perhaps one of the most useful outcomes of the Global Source Characterisation was the beginning of the relative understanding of the contributions and problems faced by the various regions. If the enhancement of this understanding can be done through the maintenance and expansion of some of the momentum and networks that has been generated through this effort, much value will be derived on a number of levels, inter alia research, capacity building, intervention planning and public trust.

The majority of the issues identified above, are in most cases regional specific. This means that addressing these priorities within the identified regions, will contribute significantly towards reducing the releases on a global scale. Addressing the issues on a regional level, within the scope of a global strategy, will enable better application of resources on mitigation measures, sustainable development, environmental protection and human health improvement

Future developments however, could change the pattern. Increased industrialisation of developing regions could alter the global source profile, if appropriate technologies are not instituted.

6.2 PRIORITY ENVIRONMENTAL CONCENTRATION ISSUES

As expected, the situation is very different across the regions. There are regions with a tradition in gathering information on PTS since the 70’s, whereas in others there are important data gaps or even no information exists for some PTS. Therefore, priorities across regions may be based on facts (existing information and reported hot spots) or suspicions that environmental levels are high due to the existence of a variety of sources. From the regional reports the following picture of concerns can be obtained:

- The levels of PTS pesticide chemicals that were widely used across the regions in the past are now declining because of regulatory measures, such as banning, use restrictions, etc. This is the case of DDT, DRINs, heptachlor and chlordane. The use of mirex and toxaphene, which has been limited to certain regions, follow the same trends. These are in general PTS of secondary concern, except in the Polar Regions where there is evidence of still increasing levels.

- PTS pesticide chemicals that are still in use show detectable levels in practically all environmental compartments and, in some cases, quite high. Even when they are banned in some regions there are also examples of elevated environmental levels in recent records, demonstrating illegal use or transport between regions. Examples include lindane and endosulphan.
- Industrial PTS chemicals which have been banned or subject to control in some regions (and environmental levels shows a clear decline since regulatory measures were taken), may still continue to be used in developing countries, where levels are even increasing; for example, in the case of PCBs. Effective assessment, control of use and remediation will be a priority.
- Unintentionally produced PTS are of concern in the developed world, where levels reported are high, and obviously of great concern. Data are scarce in the developing world, representing a big data gap, although open burning may be of high concern. This is the case of PCDD/PCDFs and PAHs.
- New chemical candidates for global concern are insufficiently covered to draw a complete picture, while there are clear evidences of ecotoxicological effects for some of them. Gathering information becomes a priority. This is particularly the case with PCP, brominated compounds, alkylphenols, etc.

For a better assessment of the PTS levels and effects, two major gaps need to be adequately filled, and this becomes also a priority:

Data generation and gathering should be extended throughout the regions, particularly for some PTS and compartments, and more importantly, in a harmonised manner, to allow data to be compared over time and between studies, countries and regions.

Regionally adapted benchmarks, namely environmental quality guidelines and human tolerable daily intakes, should be defined and more widely used to compare measures of environmental levels with environmental or health effects.

Integration of information on environmental measurements of sources and pathways with physical and biological models is required to aid the design and implementation of monitoring, research, and management, including mitigation.

6.3 CAUSES, NEEDS, BARRIERS AND ALTERNATIVES

Problems with PTS arise both because of their inherent properties and as a result of inadequate chemical management and pollution control. For some PTS current problems have been caused by historical activities.

Many of the PTS considered share similar basic characteristics which have contributed to problems, it is important to recognise that these properties may also be beneficial in some circumstances. Such properties include:

Persistence

Low water solubility

High toxicity

Many PTS problems have their roots in previous or historical activities. Widespread and, at times, indiscriminate worldwide use of many PTS chemicals occurred during a period of ignorance of the environmental problems that could be caused by them. Production, distribution, use and disposal of chemicals are undertaken with relatively little attention to releases to the environment and effects on the environment and users. Some examples of the issues are listed below:

Unsustainable production/consumption

Cost of chemicals

Perceived effectiveness

Ignorance

The capacity to monitor PTS differs widely across regions. While undertaking sophisticated monitoring programmes and having adequate legislative action to enforce environmental protection, the developed regions still require further financial resources and increased monitoring facilities. However, the gap is wide with regards to the needs of the developing regions. In Sub-Saharan Africa, Central America and the Caribbean, the Indian Ocean and parts of Asia, the monitoring of PTS is mainly ad hoc and relies on analyses from research and on accidents. There is need for practical technology transfer and an increase in available financial resources to provide sustainable development of control mechanisms. Regional partnerships between developed and developing countries and among the latter should be encouraged.

Barriers that exist to implement meaningful solutions include:

- Lack of comprehensive scientific data
- Lack of monitoring and inventory capacity
- Lack of suitable legislative framework
- Ineffective enforcement of regulations
- Illegal trade and use
- Inappropriate use and abuse
- Lack of awareness and information
- Commercial pressures
- Lack of clear responsibilities and limited coordination
- Lack of financial resources
- Lack of availability and acceptance of alternatives

Industry in general has shown itself to be technologically capable of developing alternative processes or products to replace the uses of PTS where it has been shown that risk management is not an option. Removal at source and other pollution prevention techniques have been the preferred course of action, where feasible. Where PTS are present in waste streams as a consequence of industrial processes, treating and disposing of such toxic releases in an environmentally sound manner is required.

Principle 15 of the Rio Declaration states *inter alia*: Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation. Given the little we know about PTS and their fate and potential toxicity, a precautionary approach to addressing these substances is warranted. The rationale for applying precaution rests on both what we know and what we do not know about these substances and the potential for impacts that are both global in nature and can last for generations. It can change our focus from trying to develop complete knowledge about the risks of each PTS to trying to develop solutions that would prevent exposures and result in a new generation of environmentally-friendly products and goods. Applying precaution to PTS is consistent with the Stockholm Convention and other international agreements, such as the North Sea Conferences and the U.S.-Canada International Joint Commission, that have called for precaution to be applied to these substances.

While many alternatives to PTS have been researched, it is not necessarily to find suitable, workable systems to replace the desired qualities of these chemicals. The quality of persistence, low water solubility toxicity and the cost efficiency of processes that may release or emit PTS are difficult to replace. However, there are real examples that do exist where alternative measures have been instituted and have generated the desired result that was provided by the replaced PTS. Examples include:

For pesticides – Integrated Pest Management (IPM); Integrated Vector Management (IVM); Replacement of chlorinated pesticides; Organic farming.

For industrial chemicals and unintended by-products – Environmentally sustainable production; Best Available Technology (BAT); Best Environmental Practices (BEP); Destructive technology without unwanted emissions.

The desired qualities inherent in PTS make it difficult to achieve alternatives without the negative effects. Emphasis on public awareness, cleaner production, legislation, increased capacity and availability of financial resources will assist in alleviating some of the problems that exist. While alternatives do prevail for some of the chemicals under assessment, for many, research is required to further assess the threat and to find other methods to reduce emissions to the environment.

6.4 RECOMMENDATIONS FOR FUTURE ACTION

While many recommendations were made in reports at the regional level, an attempt has been made to extract considerations that can be translated to achieving a global strategy. It is expected that any future actions that would consider the data from these reports will ensure that only validated information is captured in the decision process. Some positive considerations which developed during the implementation of this project should be incorporated into any relevant post project exercise.

- **Network –** The use of the network established should be incorporated into any relevant post project enterprise. A good relationship exists among all the regional coordinators and teams that will provide synergy for any future project.
- **Regional Direction -** The use of a regional strategy to attain global results has proven successful for the implementation of this project. This pattern should be replicated for future initiatives.
- **Emerging Chemicals -** It will be appropriate for UNEP to concentrate on work associated with the twelve selected PTS under the Stockholm Convention. However, certain other emerging chemicals are a cause for concern globally and these should be considered in future programmes.

The Stockholm Convention has legally binding obligations for the Parties that ratify. These obligations consider the activities required to address the reduction and control of the selected twelve chemicals under the Convention. This report recognises the ultimate responsibility of the Parties to the Stockholm Convention, and presents certain recommendations on the Stockholm POPs for possible consideration at the Conference of the Parties. These include:

- **Ratification of Environmental International Conventions –** The three major International Conventions pertaining to chemical management (Stockholm, Rotterdam and Basel) present a unique opportunity for all countries to be involved regionally and internationally in chemical management exercises that can only enhance the reduction of the levels and effects of PTS in the environment. In particular, the ratification of the Stockholm Convention that directly considers the reduction and ultimate elimination of twelve POPs should be considered with priority. The programme for development of National Implementation Plans (NIPs) and the subsequent support envisioned for reducing the twelve POPs in the environment, must be seen as a major global initiative that will benefit all countries. These substances are a threat to all given the propensity for transboundary movement through the environment.
- **Global strategy for Implementation of NIPs –** All countries that have signed the Stockholm Convention that are considered 'GEF eligible' have access to funds to create National Implementation Plans under the Stockholm Convention. These Plans are being administered by several Executing International Agencies. Even though there are differencies between countries, it is recommended that a global strategy be crafted to ensure efficiency, foster synergy between Executing Agencies and to promote regional collaboration during both the development of NIPs and their actual implementation.
- **A global assessment of the strategies to eliminate the use of DDT for malaria control -** Many countries are now battling to reduce if not eliminate the use of DDT for malaria vector control. Only recently, the disease has returned to Malaysia even though this country has not asked for exemption for the use of DDT under the Stockholm Convention. Malaysia thought it had the problem solved. The success of the programme in Mexico has been documented but its expansion to other countries needs to be analysed as conditions may not be the same for all other regions and countries suffering from this malady. The UNEP programme now being implemented in certain African countries follows closely the Mexico experience. There is no known programme in Asia similar to the above-mentioned initiatives. A global assessment would include a close collaboration with industry and with the WHO recommending the best alternatives that now exist. The assessment would be used to promote the development of alternatives and to pursue the use of other less harmful chemicals and non-chemical solutions. The successes of local programmes and treatments to

combat the proliferation of the disease would be documented and the possibility of expanding these successes to other countries explored.

Below are post project initiatives suggested for future action based on the results of the assessment. These initiatives involve, in the main, chemicals outside of the twelve selected Stockholm POPs.

- **Update of the Regionally Based Assessment of PTS –** Many pieces of data and aggregated analyses were not captured under the current assessment. Additionally, new data will be generated with time. Consideration will also have to be given to the discovery of possibly new PTS that are being released or emitted to the environment. As such, it is considered prudent that the assessment be updated on a regular basis. This exercise could be carried out every 3-5 years resulting in a periodic assessment of the status of the selected chemicals with room for possible addition or subtraction.

- **Filling of data gaps –** Consistently throughout the regional reports, it was established that major data gaps existed that prevented the scientific acknowledgement of intuitive concerns for certain chemicals. These gaps varied from region to region and from chemical to chemical. The regional reports provide a useful measure of the areas prioritised for work to be undertaken to fill data gaps. With careful analysis, vital information could be obtained to make more informed decisions on the level of threats and effects that certain chemicals pose to the environment both regionally and globally. Unfortunately, it is difficult to prioritise the importance of these data gaps on a global scale given the differences between regions. The project has identified the wealth of measured data available in some regions and the large gaps that exist in many others. There is an urgent need to begin to develop systematic, representative monitoring on a global basis. A strategy for this needs to be developed that takes account *inter alia* of the need for representative samples both for interpretation of results and validation of models, for harmonization of reporting procedures to ease the burden on those reporting, and for the additional resources to help initiate the reporting of data from many areas.

- **Conduct of a global assessment of dioxins/furans/PAHs emissions from open burning**

It is being shown from the RBA PTS that open burning is a major concern in all habitable regions under the project. Even the Arctic report expresses concern for open burning being a major local source for dioxins/furans and PAHs in that region. However, there is limited knowledge of the extent of the problem. The NIPs being developed by each signatory to the Stockholm Convention includes an assessment of the needs associated with the reduction of emissions of dioxins and furans. However, this could be aided by a global programme to ascertain measurements for various open burning sites. The assessment is difficult given the wide variability involved in the combustion processes throughout the various climatic conditions and input material being used across the globe. Such an assessment would establish the relative input material for the major open burning sources and undertake analyses to further narrow the range for the estimated concentration of emissions. Finally, to develop a model or models for calculating with a fair degree of accuracy, the levels of global emissions of dioxins, furans and PAH based on representative measurements taken from major, established open burning sites. This would be undertaken in conjunction with an expansive public awareness programme to improve the poor understanding of the sources and of the danger posed by these emissions targeting administrators and the public at large. Consideration should be given for best practices to be identified and provided for short-term reduction of emissions of PTS from open burning.

- **A resource centre for new PTS chemicals**

In order to be at the cutting-edge of the emerging concerns from certain PTS, UNEP Chemicals will develop a resource centre for those chemicals for which limited information is available especially in the developing world. The centre would be interactive and developed as a network with a clearinghouse function. Included in the function would be the presentation of tools to address the chemicals under consideration. These substances will include all the emerging chemicals identified in this report outside of the Stockholm POPs. Such a centre would collate data from the developed and developing world, collaborate in ongoing work analysing these chemicals in terms of production, use and environmental concentrations and provide publications to share the emerging information in a wide circulation throughout all countries. Critical to this initiative is that the information would be available and presented in a format that could be useful for a wide cross section of stakeholders.

■ A global strategy for increasing public awareness on PTS issues

Consistently, the recurring message in the recommendations for all the regional reports is the need for broad public awareness programmes especially among civil society to increase the knowledge and sensitivity on the dangers of these chemicals. The increased awareness of what these chemicals are in the first instance and the danger involved from exposure will go a long way in ensuring reduced risk to public health and the environment. Working with SAICM and the IOMC, emphasis is placed on informing the public through audio-visual means and wherever possible, in the local language and using appropriate awareness strategies. Working with the widest stakeholder partnership, effort would be made to tailor the message to local conditions (culture, language, use patterns) to ensure maximum effect. Pre and post surveys would provide assessment of the effectiveness of the programme to change behaviour and attitude across the globe toward exposure to the selected chemicals. PTS related efforts should be coordinated and whenever possible, combined with public awareness raising activities on toxic chemicals and chemical safety in general as outlined in chapter 19 of Agenda 21 and promoted by IFCS.

■ A global source profile

Currently, the Stockholm Convention obliges Parties to the Convention to carry out source profiles for those substances under that Convention. In order to keep track of what is happening, a global profile of selected priority chemicals would be undertaken on a timely basis to provide useful information on the production, emissions and releases of certain PTSs. Such a programme would rely on relevant, existing, global and regional data centres as well as the global monitoring network being established. It would make use of the wide network already developed through the RBA PTS Project as a means of collecting vital country and regional information for assessment. The SAICM should consider this recommendation as part of its portfolio.

■ A global strategy for technology transfer

In the past the transfer of technology has on occasion not been appropriate given the differences in geography, development of supporting institutions, culture and language. In order to ensure maximum benefit from the transfer of technology to reduce the release and emissions of PTS and subsequent effects to the environment, an agreed strategy would be developed that has the acceptance of all stakeholders. It is recommended that the SAICM consider in its work the importance of technology transfer and the need for it to reflect national requirements and situations, and to consider developing guidance on this matter.

■ Development of capacities and predictive capability of the LRT of PTS

For most of the regions of the globe no quantitative region-specific tools for transport assessment exist. The three major reasons for that are: Lack of region-specific process and understanding; lack of sufficient/and or sufficiently good data for model input and a lack of capacity for developing and using transport models within the regions. This knowledge gap not only prevents a quantitative treatment of PTS fate, but may often impede even a conceptual qualitative understanding of PTS transport behaviour in regions other than the Northern temperate environment. Therefore, there is need to gain a quantitative understanding and predictive capability of the transport and accumulation behaviour of various PTS under a variety of geographic and climatic circumstances, that reflect the diversity of the entire global environment. To achieve this, the following should be undertaken: a) Conduct studies aimed at a quantitative understanding of fate processes that are both unique and important for the transport behaviour of PTS under various regional circumstances. Specifically, identify PTS fate processes of importance in polar, arid and tropical ecosystems and investigate them with the aim to derive quantitative information suitable for inclusion into regional and global fate and transport models for PTS. Such fate processes may include phase partitioning, air-surface exchange, contaminant focusing and degradation processes; b) Ensure there are resources and capacity for monitoring PTS in remote environments. Models and a quantitative understanding of fate processes cannot substitute for field data, but are dependent on them; c) Support the development, improvement, evaluation and use of regional and global PTS transport models of variable complexity; and d) Build capacity within the regions for studying and modelling PTS transport processes.

ANNEX I BASIC CHEMICAL DEFINITIONS

Stockholm POP Pesticides

Aldrin

Chemical Name: 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-imethanonaphthalene ($C_{12}H_8Cl_6$).

CAS Number: 309-00-2

Properties: Solubility in water: 27 µg/L at 25°C; vapour pressure: 2.3 x 10^{-5} mm Hg at 20°C; log K_{OW}: 5.17-7.4.

Discovery/Uses: It has been manufactured commercially since 1950, and used throughout the world up to the early 1970s to control soil pests such as corn rootworm, wireworms, rice water weevil, and grasshoppers. It has also been used to protect wooden structures from termites.

Persistence/Fate: Readily metabolised to dieldrin by both plants and animals. Biodegradation is expected to be slow and it binds strongly to soil particles, and is resistant to leaching into groundwater. Aldrin was classified as moderately persistent with half-life in soil and surface waters ranging from 20 days to 1.6 years.

Toxicity: Aldrin is toxic to humans; the lethal dose for an adult has been estimated to be about 80 mg/kg body weight. The acute oral LD_{50} in laboratory animals is in the range of 33 mg/kg body weight for guinea pigs to 320 mg/kg body weight for hamsters. The toxicity of aldrin to aquatic organisms is quite variable, with aquatic insects being the most sensitive group of invertebrates. The 96-h LC_{50} values range from 1-200 µg/L for insects, and from 2.2-53 µg/L for fish. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 mg/kg milk fat to 0.2 mg/kg meat fat. Water quality criteria between 0.1 to 180 µg/L have been published.

Dieldrin

Chemical Name: 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endo-5,8-dimethanonaphthalene ($C_{12}H_8Cl_6O$).

CAS Number: 60-57-1

Properties: Solubility in water: 140 µg/L at 20°C; vapour pressure: 1.78 x 10^{-7} mm Hg at 20°C; log K_{OW}: 3.69-6.2.**Discovery/Uses:** It appeared in 1948 after World War II and is used mainly for the control of soil insects such as corn rootworms, wireworms and catworms.

Persistence/Fate: It is highly persistent in soils, with a half-life of 3-4 years in temperate climates, and bioconcentrates in organisms. The persistence in air has been estimated in 4-40 hrs.

Toxicity: The acute toxicity for fish is high (LC_{50} between 1.1 and 41 mg/L) and moderate for mammals (LD_{50} in mouse and rat ranging from 40 to 70 mg/kg body weight). However, a daily administration of 0.6 mg/kg to rabbits adversely affected the survival rate. Aldrin and dieldrin mainly affect the central nervous system but there is no direct evidence that they cause cancer in humans. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 mg/kg milk fat and 0.2 mg/kg poultry fat. Water quality criteria between 0.1 to 18 µg/L have been published.

Endrin

Chemical Name: 3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth[2,3-b]oxirene ($C_{12}H_8Cl_6O$).

CAS Number: 72-20-8

Properties: Solubility in water: 220-260 µg/L at 25 °C; vapour pressure: 2.7 x 10^{-7} mm Hg at 25°C; log K_{OW}: 3.21-5.34.**Discovery/Uses:** It has been used since the 50s against a wide range of agricultural pests, mostly on cotton but also on rice, sugar cane, maize and other crops. It has also been used as a rodenticide.

Persistence/Fate: Is highly persistent in soils (half-lives of up to 12 years have been reported in some cases). Bioconcentration factors of 14 to 18,000 have been recorded in fish, after continuous exposure.

Toxicity: Endrin is very toxic to fish, aquatic invertebrates and phytoplankton; the LC_{50} values are mostly less than 1 µg/L. The acute toxicity is high in laboratory animals, with LD_{50} values of 3-43 mg/kg, and a dermal LD_{50} of 5-20 mg/kg in rats. Long term toxicity in the rat has been studied over two years and a NOEL of 0.05 mg/kg bw/day was found.

Chlordane

Chemical Name: 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene ($C_{10}H_6Cl_8$).

CAS Number: 57-74-9

Properties: Solubility in water: 56 µg/L at 25°C; vapour pressure: 0.98×10^{-5} mm Hg at 25 °C; log K_{OW}: 4.58-5.57.

Discovery/Uses: Chlordane appeared in 1945 and was used primarily as an insecticide for control of cockroaches, ants, termites, and other household pests. Technical chlordane is a mixture of at least 120 compounds. Of these, 60-75% are chlordane isomers, the remainder being related to endo-compounds including heptachlor, nonachlor, diels-alder adduct of cyclopentadiene and penta/hexa/octachlorocyclopentadienes.

Persistence/Fate: Chlordane is highly persistent in soils with a half-life of about 4 years. Its persistence and high partition coefficient promotes binding to aquatic sediments and bioconcentration in organisms.

Toxicity: LC_{50} from 0.4 mg/L (pink shrimp) to 90 mg/L (rainbow trout) have been reported for aquatic organisms. The acute toxicity for mammals is moderate with an LD_{50} in rat of 200-590 mg/kg body weight (19.1 mg/kg body weight for oxychlordane). The maximum residue limits for chlordane in food are, according to FAO/WHO between 0.002 mg/kg milk fat and 0.5 mg/kg poultry fat. Water quality criteria of 1.5 to 6 µg/L have been published. Chlordane has been classified as a substance for which there is evidence of endocrine disruption in an intact organism and possible carcinogenicity to humans.

Heptachlor

Chemical Name: 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene ($C_{10}H_5Cl_7$).

CAS Number: 76-44-8

Properties: Solubility in water: 180 µg/L at 25°C; vapour pressure: 0.3×10^{-5} mm Hg at 20°C; log K_{OW}: 4.4-5.5.**Production/Uses:** Heptachlor is used primarily against soil insects and termites, but also against cotton insects, grasshoppers, and malaria mosquitoes. Heptachlor epoxide is a more stable breakdown product of heptachlor.

Persistence/Fate: Heptachlor is metabolised in soils, plants and animals to heptachlor epoxide, which is more stable in biological systems and is carcinogenic. The half-life of heptachlor in soil is in temperate regions 0.75 – 2 years. Its high partition coefficient provides the necessary conditions for bioconcentrating in organisms.

Toxicity: The acute toxicity of heptachlor to mammals is moderate (LD_{50} values between 40 and 119 mg/kg have been published). The toxicity to aquatic organisms is higher and LC_{50} values down to 0.11 µg/L have been found for pink shrimp. Limited information is available on the effects in humans and studies are inconclusive regarding heptachlor and cancer. The maximum residue levels recommended by FAO/WHO are between 0.006 mg/kg milk fat and 0.2 mg/kg meat or poultry fat.

Dichlorodiphenyltrichloroethane (DDT)

Chemical Name: 1,1,1-Trichloro-2,2-bis-(4-chlorophenyl)-ethane ($C_{14}H_9Cl_5$).

CAS Number: 50-29-3.

Properties: Solubility in water: 1.2-5.5 µg/L at 25°C; vapour pressure: 0.2×10^{-6} mm Hg at 20°C; log K_{OW}: 6.19 for *pp*'-DDT, 5.5 for *pp'*-DDD and 5.7 for *pp'*-DDE.

Discovery/Use: DDT appeared for use during World War II to control insects that spread diseases like malaria, dengue fever and typhus. Following this, it was widely used on a variety of agricultural crops. The technical product is a mixture of about 85% *pp'*-DDT and 15% *op'*-DDT isomers.

Persistence/Fate: DDT is highly persistent in soils with a half-life of up to 15 years and of 7 days in air. It also exhibits high bioconcentration factors (in the order of 50000 for fish and 500000 for bivalves). In the environment, the product is metabolized mainly to DDD and DDE.

Toxicity: The lowest dietary concentration of DDT reported to cause egg shell thinning was 0.6 mg/kg for the black duck. LC_{50} of 1.5 mg/L for largemouth bass and 56 mg/L for guppy have been reported. The acute toxicity of DDT for mammals is moderate with an LD_{50} in rat of 113-118 mg/kg body weight. DDT has been shown to have an estrogen-like activity, and possible carcinogenic activity in humans. The maximum residue level in food recommended by WHO/FAO range from 0.02 mg/kg milk fat to 5 mg/kg meat fat. Maximum permissible DDT residue levels in drinking water (WHO) is 1.0 µg/L.

Toxaphene

Chemical Name: Polychlorinated bornanes and camphenes ($C_{10}H_{10}Cl_8$).

CAS Number: 8001-35-2

Properties: Solubility in water: 550 µg/L at 20°C; vapour pressure: 3.3×10^{-5} mm Hg at 25°C; log K_{OW}: 3.23-5.50.

Discovery/Uses: Toxaphene has been in use since 1949 as a nonsystemic insecticide with some acaricidal activity, primarily on cotton, cereal grains fruits, nuts and vegetables. It was also used to control livestock ectoparasites such as lice, flies, ticks, mange, and scab mites. The technical product is a complex mixture of over 300 congeners, containing 67-69% chlorine by weight.

Persistence/Fate: Toxaphene has a half life in soil from 100 days up to 12 years. It has been shown to bioconcentrate in aquatic organisms (BCF of 4247 in mosquito fish and 76000 in brook trout).

Toxicity: Toxaphene is highly toxic in fish, with 96-hour LC_{50} values in the range of 1.8 µg/L in rainbow trout to 22 µg/L in bluegill. Long term exposure to 0.5 µg/L reduced egg viability to zero. The acute oral toxicity is in the range of 49 mg/kg body weight in dogs to 365 mg/kg in guinea pigs. In long term studies NOEL in rats was 0.35 mg/kg bw/day, LD_{50} ranging from 60 to 293 mg/kg bw. For toxaphene there exists a strong evidence of the potential for endocrine disruption. Toxaphene is carcinogenic in mice and rats and is of carcinogenic risk to humans, with a cancer potency factor of 1.1 mg/kg/day for oral exposure.

Mirex

Chemical Name: 1,1a,2,2a,3,3a,4,5,5a,5b,6-Dodecachloroacta-hydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene ($C_{10}Cl_{12}$). **CAS Number:** 2385-85-5

Properties: Solubility in water: 0.07 µg/L at 25°C; vapour pressure: 3×10^{-7} mm Hg at 25°C; log K_{OW}: 5.28.

Discovery/Uses: The use in pesticide formulations started in the mid 1950s largely focused on the control of ants. It is also a fire retardant for plastics, rubber, paint, paper and electrical goods. Technical grade preparations of mirex contain 95.19% mirex and 2.58% chlordecone, the rest being unspecified. Mirex is also used to refer to bait comprising corncob grits, soya bean oil, and mirex.

Persistence/Fate: Mirex is considered to be one of the most stable and persistent pesticides, with a half-life in soils of up to 10 years. Bioconcentration factors of 2600 and 51400 have been observed in pink shrimp and fathead minnows, respectively. It is capable of undergoing long-range transport due to its relative volatility (VPL = 4.76 Pa; H = 52 Pa m^3/mol).

Toxicity: The acute toxicity of Mirex for mammals is moderate with an LD_{50} in rat of 235 mg/kg and dermal toxicity in rabbits of 80 mg/kg. Mirex is also toxic to fish and can affect their behaviour (LC_{50} (96 hr) from 0.2 to 30 mg/L for rainbow trout and bluegill, respectively). Delayed mortality of crustaceans occurred at 1 µg/L exposure levels. There is evidence of its potential for endocrine disruption and possibly carcinogenic risk to humans.

Hexachlorobenzene (HCB)

Chemical Name: Hexachlorobenzene (C_6Cl_6)

CAS Number: 118-74-1

Properties: Solubility in water: 50 µg/L at 20°C; vapour pressure: 1.09 x 10^{-5} mm Hg at 20°C; log K_{OW}: 3.93-6.42.

Discovery/Uses: It was first introduced in 1945 as a fungicide for seed treatments of grain crops, and used to make fireworks, ammunition, and synthetic rubber. Today it is mainly a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, solvents and several pesticides. HCB is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries.

Persistence/Fate: HCB has an estimated half-life in soils of 2.7-5.7 years and of 0.5-4.2 years in air. HCB has a relatively high bioaccumulation potential and long half-life in biota.

Toxicity: LC_{50} for fish varies between 50 and 200 µg/L. The acute toxicity of HCB is low with LD_{50} values of 3.5 mg/g for rats. Mild effects of the [rat] liver have been observed at a daily dose of 0.25 mg HCB/kg bw. HCB is known to cause liver disease in humans (porphyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.

Stockholm POP Industrial Compounds

Polychlorinated biphenyls (PCBs)

Chemical Name: Polychlorinated biphenyls ($C_{12}H_{(10-n)}Cl_n$, where n is within the range of 1-10).

CAS Number: Various (e.g. for Aroclor 1242, CAS No.: 53469-21-9; for Aroclor 1254, CAS No.: 11097-69-1);

Properties: Water solubility decreases with increasing chlorination: 0.01 to 0.0001 µg/L at 25°C; vapour pressure: 1.6-0.003 x 10^{-6} mm Hg at 20°C; log K_{OW}: 4.3-8.26.

Discovery/Uses: PCBs were introduced in 1929 and were manufactured in different countries under various trade names (e.g., Aroclor, Clophen, Phenoclor). They are chemically stable and heat resistant, and were used worldwide as transformer and capacitor oils, hydraulic and heat exchange fluids, and lubricating and cutting oils. Theoretically, a total of 209 possible chlorinated biphenyl congeners exist, but only about 130 of these are likely to occur in commercial products.

Persistence/Fate: Most PCB congeners, particularly those lacking adjacent unsubstituted positions on the biphenyl rings (e.g., 2,4,5-, 2,3,5- or 2,3,6-substituted on both rings) are extremely persistent in the environment. They are estimated to have half-lives ranging from three weeks to two years in air and, with the exception of mono- and di-chlorobiphenyls, more than six years in aerobic soils and sediments. PCBs also have extremely long half-lives in adult fish, for example, an eight-year study of eels found that the half-life of CB153 was more than ten years.

Toxicity: LC_{50} for the larval stages of rainbow trout is 0.32 µg/L with a NOEL of 0.01 µg/L. The acute toxicity of PCB in mammals is generally low and LD_{50} values in rat of 1 g/kg bw. IARC has concluded that PCBs are carcinogenic to laboratory animals and probably also for humans. They have also been classified as substances for which there is evidence of endocrine disruption in an intact organism.

Stockholm POP Unintentionally produced compounds

Polychlorinated dibenzo-p-dioxins (PCDD) and Polychlorinated dibenzofurans (PCDF)

Chemical Name: PCDD ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDF ($C_{12}H_{(8-n)}Cl_nO$) may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively.

CAS Number: Various (2,3,7,8-TetraCDD: 1746-01-6; 2,3,7,8-TetraCDF: 51207-31-9).

Properties: Solubility in water: in the range 0.43 – 0.0002 ng/L at 25°C; vapour pressure: 2 – 0.007 x 10^{-6} mm Hg at 20°C; log K_{OW}: in the range 6.60 – 8.20 for tetra- to octa-substituted congeners.

Discovery/Uses: They are by-products resulting from the production of other chemicals and from the low-temperature combustion and incineration processes. They have no known use.

Persistence/Fate: PCDD/Fs are characterized by their lipophilicity, semi-volatility and resistance to degradation (half life of TCDD in soil of 10-12 years) and to long-range transport. They are also known for their ability to bio-concentrate and biomagnify under typical environmental conditions.

Toxicity: The toxicological effects reported here are primarily based on studies of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). However, the term "dioxins" is often used to refer to all of the 2,3,7,8-substituted PCDD and PCDF compounds (17 congeners). Most of these compounds have not been assessed for the full range of biological responses that have been demonstarted for TCDD. When tested, the various compounds show variability in the relative degree of toxicity. The toxicity effects of TCDD observed in some species at varying doses include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption and carcinogenicity. At the present time, the only persistent effect associated with dioxin exposure in humans is chloracne.

Adverse endpoints identified in animal studies are effects on the developing male rat reproductive system after *in utero* exposure through dosing of pregnant dams resulting in maternal body burdens of about 30ng/kg.Other effects occuring at similar doses include neurobehavioral alterations in the offspring of the rhesus monkey and immune system effects in rats exposed *in utero*. Biochemical endpoint effects including enzyme induction have been seen in rats dosed as low as 0.1 ng/kg bw/day. In a re-evaluation of the TDI for dioxins, furans and coplanar PCBs, the WHO decided to recommend a range of 1-4 TEQ pg/kg bw. More recently, the tolerable intake value has been set to a monthly value of 70 TEQ pg/kg bw to protect against both cancer and non-cancer endpoints.

Other PTS considered by Regions

Hexachlorocyclohexanes (HCH)

Chemical Name: 1,2,3,4,5,6-Hexachlorocyclohexane (mixed isomers) ($C_6H_6Cl_6$).

CAS Number: 608-73-1 (γ-HCH, lindane: 58-89-9).

Properties: γ-HCH: solubility in water: 7 mg/L at 20°C; vapour pressure: 3.3 x 10^{-5} mm Hg at 20°C; log K_{OW}: 3.8.

Discovery/Uses: There are two principle formulations: "technical HCH", which is a mixture of various isomers, including α-HCH (55-80%), β-HCH (5-14%) and γ-HCH (8-15%), and "lindane", which is essentially pure γ-HCH. Historically, lindane was one of the most widely used insecticides in the world. Its insecticidal properties were discovered in the early 1940s. It controls a wide range of sucking and chewing insects and has been used for seed treatment and soil application, in household biocidal products, and as textile and wood preservatives.

Persistence/Fate: Lindane and other HCH isomers are relatively persistent in soils and water, with half lives generally greater than 1 and 2 years, respectively. HCH are much less bioaccumulative than other organochlorines because of their relatively low liphophilicity. On the contrary, their relatively high vapor pressures, particularly of the α-HCH isomer, determine their long-range transport in the atmosphere.

Toxicity: Lindane is moderately toxic for invertebrates and fish, with LC_{50} values of 20-90 µg/L. The acute toxicity for mice and rats is moderate with LD_{50} values in the range of 60-250 mg/kg. Lindane resulted to have no mutagenic potential in a number of studies but an endocrine disrupting activity.

Endosulphan

Chemical Name: 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide ($C_9H_6Cl_6O_3S$).

CAS Number: 115-29-7.

Properties: Solubility in water: 320 µg/L at 25°C; vapour pressure: 0.17×10^{-4} mm Hg at 25°C; log K_{OW}: 2.23-3.62.

Discovery/Uses: Endosulphan was first introduced in 1954. It is used as a contact and stomach insecticide and acaricide in a great number of food and nonfood crops (e.g. tea, vegetables, fruits, tobacco, cotton) and it controls over 100 different insect pests. Endosulphan formulations are used in commercial agriculture and home gardening and for wood preservation. The technical product contains at least 94% of two pure isomers, α- and β-endosulphan.

Persistence/Fate: It is moderately persistent in the soil environment with a reported average field half-life of 50 days. The two isomers have different degradation times in soil (half-lives of 35 and 150 days for α- and β-isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulphan is rapidly broken down to the corresponding sulfate, on most fruits and vegetables, 50% of the parent residue is lost within 3 to 7 days.

Toxicity: Endosulphan is highly to moderately toxic to bird species (Mallards: oral LD_{50} 31 - 243 mg/kg) and it is very toxic to aquatic organisms (96-hour LC_{50} rainbow trout 1.5 µg/L). It has also shown high toxicity in rats (oral LD_{50}: 18 - 160 mg/kg, and dermal: 78 - 359 mg/kg). Female rats appear to be 4–5 times more sensitive to the lethal effects of technical-grade endosulphan than male rats. The α-isomer is considered to be more toxic than the β-isomer. There is evidence that endosulphan acts as an endocrine disrupter. However, further investigation is necessary to determine the relevance and impact on human health.

Pentachlorophenol (PCP)

Chemical Name: Pentachlorophenol (C_6Cl_5OH).

CAS Number: 87-86-5

Properties: Solubility in water: 14 mg/L at 20°C; vapour pressure: 16×10^{-5} mm Hg at 20°C; log K_{OW}: 3.32 – 5.86.

Discovery/Uses: It is used as an insecticide (termiticide), fungicide, non-selective contact herbicide (defoliant) and, particularly as a wood preservative. It is also used in anti-fouling paints and other materials (e.g. textiles, inks, paints, disinfectants and cleaners) as inhibitor of fermentation. Technical PCP contains trace amounts of PCDDs and PCDFs.

Persistence/Fate: The rate of photodecomposition increases with pH ($t_{1/2}$ 100 hr at pH 3.3 and 3.5 hr at pH 7.3). Complete decomposition in soil suspensions takes >72 days, other authors reports half-life in soils of 23-178 days. Although enriched through the food chain, it is rapidly eliminated after discontinuing the exposure ($t_{1/2}$ = 10-24 h for fish).

Toxicity: It has been proved to be acutely toxic to aquatic organisms and have certain effects on human health, at the time that exhibits off-flavour effects at very low concentrations. The 24-h LC_{50} values for trout were reported as 0.2 mg/L, and chronic toxicity effects were observed at concentrations down to 3.2 µg/L. Mammalian acute toxicity of PCP is moderate-high. LD_{50} oral in rat ranging from 50 to 210 mg/kg bw have been reported. LC_{50} ranged from 0.093 mg/L in rainbow trout (48 h) to 0.77-0.97 mg/L for guppy (96 h) and 0.47 mg/L for fathead minnow (48 h).

Hexabromobiphenyl (HxBB)

Chemical Name: Hexabromobiphenyl ($C_{12}H_4Br_6$).

CAS Number: 59536-65-1

Properties: Solubility in water: 0.6 µg/L at 25°C; vapour pressure: 10^{-7} mm Hg at 20°C; log K_{OW}: 6.39.

Discovery/Uses: The production of polybrominated biphenyls (PBBs) began in 1970. HxBB was used as a fire retardant mainly in thermoplastics for constructing business machine housing and industrial (e.g. motor housing) and electrical (e.g. radio and TV parts) products. Smaller amounts were used as a fire retardant in coating and lacquers and in polyurethane foam for auto upholstery.

Persistence/Fate: HxBB is strongly adsorbed to soil and sediments and usually persists in the environment. HxBB resists both chemical and biological degradation. HxBB has been found in several sediment samples from the estuaries of large rivers and has been identified in edible fish.

Toxicity: Few toxicity data are available from short-term tests on aquatic organisms. The LD_{50} values of commercial mixtures show a relatively low order of acute toxicity (LD_{50} range from > 1 to 21.5 g/kg body weight in laboratory rodents). Oral exposure of laboratory animals to PBBs produced body weight loss, skin disorders, and nervous system effects, and birth defects. Humans exposed through contaminated food developed skin disorders, such as acne and hair loss. PBBs exhibit endocrine disrupting activity and possible carcinogenicity to humans.

Polybrominated diphenyl ethers (PBDEs)

Chemical Name: Polybrominated diphenyl ethers ($C_{12}H_{(10-n)}Br_nO$, where n = 1-10). As in the case of PCBs the total number of congeners is 209. In commercial mixtures the predominant congeners are the tetra-, penta- and octa-substituted isomers.

CAS Number: Various (PeBDE: 32534-81-9; OBDE: 32536-52-0; DeBDE: 1163-19-5).

Properties: Solubility in water: 0.9 ng/L at 25°C (PeBDE); vapour pressure: 3.85×10^{-3} to $<10^{-7}$ mmHg at 20-25 °C; log K_{OW}: 4.28 - 9.9.

Discovery/Uses: Since the 1960s, three commercial PBDE formulations are in production. The pentabrominated product is used principally to flame retard polyurethane foams in furniture, carpet underlay and bedding. Commercial octa is a mixture of hexa- (10-12%), hepta- (44-46%), octa- (33-35%) and nonabromodiphenyl (10-11%) ethers. It is used to flame retard a wide variety of thermoplastics and is recommended for injection moulding applications such as high impact polystyrene (HIPS). The deca product (a single congener) is used predominantly for textiles and denser plastics such as housings for a variety of electrical products in particular TVs and computers.

Persistence/Fate: Data on environmental fate, although limited, suggest that biodegradation is not an important degradation pathway, but that photodegradation may play a significant role. They have already been found in high concentrations in marine birds and mammals from remote areas. The half-lives of PBDE components in rat adipose tissue vary between 19 and 119 days, the higher values being for the higher brominated congeners.

Toxicity: The available data suggest that the lower (tetra- to hexa-) PBDE congeners are likely to be carcinogens, endocrine disruptors, and/or neurodevelopmental toxicants. Studies in rats with commercial PeBDE indicate a low acute toxicity via oral and dermal routes of exposure, with LD_{50} values > 2000 mg/kg bw. In a 30-day study with rats, effects on the liver could be seen at a dose of 2 mg/kg bw/day, with a NOEL at 1mg/kg bw/day. The toxicity to *Daphnia magna* has also been investigated and LC_{50} was found to be 14 µg/L with a NOEC of 4.9 µg/L. Although data on toxicology is limited, they have potential endocrine disrupting properties, and there are concerns over the health effects of exposure.

Polycyclic Aromatic Hydrocarbons (PAHs)

Chemical Name: PAHs is a group of compounds consisting of two or more fused aromatic rings.

CAS Number: Various numbers dependent on particular compound within the group that is under consideration.

Properties: Solubility in water: 0.00014 -2.1 mg/L at 25ºC; vapour pressure: from 0.0015×10^{-9} to 0.0051 mmHg at 25°C; log K_{OW}: 4.79-8.20.

Discovery/Use: Most of these are formed during incomplete combustion of organic material and the composition of PAHs mixture varies with the source(s) and also due to selective weathering effects in the environment.

Persistence/Fate: Persistence of the PAHs varies with their molecular weight. The low molecular weight PAHs are most easily degraded. The reported half-lives of naphthalene, anthracene and benzo(e)pyrene in sediment are 9, 43 and 83 hours, respectively, whereas for higher molecular weight PAHs, their half-lives are up to several years in soils/sediments. The BCFs in aquatic organisms frequently range between 100-2000 and it increases with increasing molecular size. Due to their wide distribution, the environmental pollution by PAHs has aroused global concern.

Toxicity: The acute toxicity of low PAHs is moderate with an LD_{50} of naphthalene and anthracene in rat of 490 and 18000 mg/kg body weight respectively, whereas the higher PAHs exhibit higher toxicity and LD_{50} of benzo(a)anthracene in mice is 10mg/kg body weight. In *Daphnia pulex*, LC_{50} for naphthalene is 1.0 mg/L, for phenanthrene 0.1 mg/L and for benzo(a)pyrene is 0.005 mg/L. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic action of these substances produces intermediates that bind covalently with cellular DNA. IARC has classified benz[*a*]anthracene, benzo[*a*]pyrene, and dibenzo[*ah*]anthracene as probable carcinogenic to humans. Benzo[*b*]fluoranthene and indeno-[123-*cd*]pyrene were classified as possible carcinogens to humans.

Phthalates

Chemical Name: They encompass a wide family of compounds. Dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), benzylbutylphthalate (BBP), di(2-ethylhexyl)phthalate (DEHP)($C_{24}H_{38}O_4$) and dioctylphthalate (DOP) are some of the most common.

CAS Nos.: 84-74-2 (DBP), 85-68-7 (BBP), 117-81-7 (DEHP).

Properties: The physico-chemical properties of phthalic acid esters vary greatly depending on the alcohol moieties. Solubility in water: 9.9 mg/L (DBP) and 0.3 mg/L (DEHP) at 25°C; vapour pressure: 3.5×10^{-5} (DBP) and 6.4×10^{-6} (DEHP) mm Hg at 25°C; log K_{OW}: 1.5 to 7.1.

Discovery/Uses: They are widely used as plasticisers, insect repellents, solvents for cellulose acetate in the manufacture of varnishes and dopes. Vinyl plastic may contain up to 40% DEHP.

Persistence/fate: They have become ubiquitous pollutants, in marine, estuarine and freshwater sediments, sewage sludges, soils and food. Degradation ($t^{1/2}$) values generally range from 1-30 days in soils and freshwaters.

Toxicity: The acute toxicity of phthalates is usually low: the oral LD_{50} for DEHP is about 25-34 g/kg, depending on the species; for DBP reported LD_{50} values following oral administration to rats range from 8 to 20 g/kg body weight; in mice, values are approximately 5 to 16 g/kg body weight. In general, DEHP is not toxic for aquatic communities at the low levels usually present. In animals, high levels of DEHP may damage the liver and kidney and affect the ability to reproduce. There is no evidence that DEHP causes cancer in humans but it has been reported as an endocrine disrupting chemical. The EPA proposed a Maximum Admissible Concentration (MAC) of 6 μg/L of DEHP in drinking water.

Nonyl- and Octyl-phenols

Chemical Name: NP $C_{15}H_{24}O_2$: Phenol, 4 nonyl, branched; Phenol, 4-nonyl; Phenoyl nony; OP $C_{14}H_{22}O$: 4-tert-Octylphenol; Phenol, octyl.

CAS Number: NP: 84852-15-3; 104-40-5; 25154-52-3. OP: 140-66-9; 27193-28-8.

Properties: Solubility in water: NP (CAS # 84852-15-3): 5.4mg/L; OP (CAS #140-66-9) 12.6mg/L; vapour pressure: 11.02 Pa m^3/mol; log K_{OW}: NP 4.48; OP 4.12.

Discovery/Uses: NP and OP are the starting material in the synthesis of alkylphenol ethoxylates (APEs), first used in the 60s. These compounds are highly effective cleaning agents or surfactants that have been widely used in a number of industrial sectors including textiles, pulp and paper, paints, adhesives, resins and protective coatings. Alkylphenols can also be used as plasticisers, stabilisers for rubbers, lube oil additives, and the alkylphenol phosphite derivatives can be used as UV stabilisers in plastics.

Persistence/Fate: NP and OP are the intermediates in the degradation of nonylphenol ethoxylates and octylphenol ethoxylates. The major releases occur to water and are concentrated in sewage sludges. NPs persistent in the environment with half-lives of 6-66 days in sediments, 14-30 days in water and >7 hours in the atmosphere. Measured half-life data is not available for OP. Due to their persistence they can bioaccumulate in aquatic species. However, excretion and metabolism is rapid.

Toxicity: NP and OP have acute toxicity values for fish, invertebrates and algae ranging from 17 to 3,000 μg/L. In chronic toxicity tests conducted on NP, the lowest NOECs were 6 μg/L in fish and 3.7 μg/L in invertebrates. The 96-h EC_{50} for OP in algae (S. *capricornutum*) was reported to be 1900 µg/L. Alkylphenols are endocrine disrupting chemicals in mammals but at high doses.

Organotin compounds

Chemical Name: Organotin compounds comprise mono-, di-, tri- and tetrabutyl and triphenyl tin compounds. They conform to the following general formula $(n\text{-}C_4H_9)_nSn\text{-}X$ and $(C_6H_5)_3Sn\text{-}X$, where X is an anion or a group linked covalently through a hetero-atom.

CAS Number: 56-35-9 (TBTO); 76-87-9 (TPTOH).

Properties: Solubility in water: 4 mg/L (TBTO) and 1 mg/L (TPTOH) at 25°C and pH 7; vapour pressure: 7.5×10^{-7} mm Hg at 20°C (TBTO) 3.5×10^{-8} mmHg at 50ºC (TPTOH); log K_{OW}: 3.19 - 3.84. In sea water and under normal conditions, TBT exists as three species in seawater (hydroxide, chloride, and carbonate).

Discovery/Uses: They are mainly used as antifouling paints (tributyl and triphenyl tin) for underwater structures and ships. Minor identified applications are as antiseptic or disinfecting agents in textiles and industrial water systems, such as cooling tower and refrigeration water systems, wood pulp and paper mill systems, and breweries. They are also used as stabilisers in plastics and as catalytic agents in soft foam production. It is also used to control the shistosomiasis in various parts of the world.

Persistence/Fate: Under aerobic conditions, TBT takes 1 to 3 months to degrade, but in anaerobic soils may persist for more than 2 years. Because of the low water solubility it binds strongly to suspended material and sediments. TBT is lipophilic and tends to accumulate in aquatic organisms. Oysters exposed to very low concentrations exhibit BCF values from 1000 to 6000.

Toxicity: TBT is moderately toxic and all breakdown products are even less toxic. Its impact on the environment was discovered in the early 1980s in France with harmful effects in aquatic organisms, such as shell malformations of oysters, imposex in marine snails and reduced resistance to infection (e.g. in flounder). Molluscs react adversely to very low levels of TBT (0.06-2.3 ug/L). Lobster larvae show a nearly complete cessation of growth at just 1.0 ug/L TBT. In laboratory tests, reproduction was inhibited when female snails exposed to 0.05-0.003 ug/L of TBT developed male characteristics. Large doses of TBT have been shown to damage the reproductive and central nervous systems, bone structure, and the liver bile duct of mammals.

Organomercury compounds

Chemical Name: The main compound of concern is methyl mercury ($HgCH_3$).

CAS Number: 22967-92-6.

Properties: Solubility in water: 0.1 g/L at 21°C ($HgCH_3Cl$) and 1.0 g/L at 25ºC ($Hg(CH_3)_2$); vapour pressure: 8.5×10^{-3} mm Hg at 25°C ($HgCH_3Cl$); log K_{OW}: 1.6 ($HgCH_3Cl$) and 2.28 ($Hg(CH_3)_2$).

Production/Uses: There are many sources of mercury release to the environment, both natural (volcanoes, mercury deposits, and volatilization from the ocean) and human-related (coal combustion, chlorine alkali processing, waste incineration, and metal processing). It is also used in thermometers, batteries, lamps, industrial processes, refining, lubrication oils, and dental amalgams. Methyl mercury has no industrial uses; it is formed in the environment by methylation of the inorganic mercurial ion mainly by microorganisms in the water and soil.

Persistence/Fate: Mercury released into the environment can either stay close to its source for long periods, or be widely dispersed on a regional or even world-wide basis. Not only are methylated mercury compounds toxic, but highly bioaccumulative as well. The increase in mercury as it rises in the aquatic food chain results in relatively high levels of mercury in fish consumed by humans. Ingested elemental mercury is only 0.01% absorbed, but methyl mercury is nearly 100% absorbed from the gastrointestinal tract. The biological half-life of mercury is 60 days.

Toxicity: Long-term exposure to either inorganic or organic mercury can permanently damage the brain, kidneys, and developing fetus. The most sensitive target of low level exposure to metallic and organic mercury following short or long term exposures appears to be the nervous system.

Short-chain chlorinated paraffins (SCCPs)

Chemical Name: Alkanes C_{10-13}, chloro, or short-chain chlorinated paraffins (SCCP) are represenetd by ($C_xH_{(2x-y+2)}Cl_y$) where X=10-13 and Y=1-13. They are manufactured by chlorination of liquid n-alkanes and contain from 30 to 70% chlorine. Medium (C_{14} – C_{17}) and long (C_{18} – C_{30}) chain lengths chlorinated paraffins are not assessed in this report.

CAS Number: SCCPs are usually associated with # 85535-84-8.

Properties: They are largely depending on the chlorine content. Based on the EU risk assessment, these are the values for SCCPs: water solubility: 150 to 470 $\mu g.l^{-1}$ at 20°C; vapour pressure: 1.6×10^{-4} mm Hg (0.021 Pa) at 40°C (with predicted range for C_{10}-30% chlorine to C_{13}-70% chlorine of 3.3×10^{-4} to 6.0×10^{-8} mm Hg at 20°C); log K_{OW}: in the range from 4.39 to 8.69.

Discovery/Uses: The main uses of SCCPs are as a flame retardant in textile and rubber, paints, and in metal working fluids. SCCPs impart a number of technical benefits, of which the most significant is the enhancement of flame retardant properties and extreme pressure lubrication.

Persistence/Fate: SCCPs may be released into the environment from improperly disposed metal-working fluids or other products containing SCCPs. Loss of SCCPs by leaching from paints and coatings may also contribute to environmental contamination. SCCPs with less than 50 % chlorine content are degraded under aerobic conditions more rapidly than SCCPs with greater chlorine content. SCCPs bioaccumulate in aquatic species; both uptake and elimination are faster for the substances with low chlorine content.

Toxicity: The acute toxicity of SCCPs in mammals is low with reported oral LD_{50} values ranging from 4 - 50 $g.kg^{-1}$ bw, although in repeated dose experiments, effects on the liver have been seen at doses of 10 – 100 $mg.kg^{-1}$ $bw.day^{-1}$. SCCPs have been shown, in laboratory tests, to show toxic effects on fish and other forms of aquatic life after long-term exposure. The NOEC identified in the EU risk assessment for the most sensitive aquatic species tested was 5 $\mu g\ l^{-1}$.

Organolead compounds

Chemical Name: Alkyllead compounds may be confined to tetramethyllead (TML, $Pb(CH_3)_4$) and tetraethyllead (TEL, $Pb(C_2H_5)_4$).

CAS Number: 75-74-1 (TML) and 78-00-2 (TEL).

Properties: Solubility in water: 17.9 $mg.l^{-1}$ (TML) and 0.29 $mg.l^{-1}$ (TEL) at 25°C; vapour pressure: 22.5 and 0.15 mm Hg at 20°C for TML and TEL, respectively; log K_{OW}.

Discovery/Uses: Tetramethyl and tetraethyllead are widely used as “anti-knocking” additives in gasoline. The release of TML and TEL are drastically reduced with the introduction of unleaded gasoline in late 70’s in USA and followed by other parts of the world. However, leaded gasoline is still available which contribute to the emission of TEL and to a less extent TML to the environment.

Persistence/Fate: Under environmental conditions such as in air or in aqueous solution, dealkylation occurs to produce the less alkylated forms and finally to inorganic lead. However, there is limited evidence that under some circumstances, natural methylation of lead salts may occur. Minimal bioaccumulations were observed for TEL in shrimps (650x), mussels (120x) and plaice (130x) and for TML in shrimps (20x), mussels (170x), and plaice (60x).

Toxicity: Lead and lead compounds has been found to cause cancer in the respiratory and digestive systems of workers in lead battery and smelter plants. However, tetra-alkyllead compounds have not been sufficiently tested for the evidence of carcinogenicity. Acute toxicity of TEL and TML are moderate in mammals and high for aquatic biota. LD_{50} (rat, oral) for TEL is 35 mg $Pb.kg^{-1}$ and 108 mg $Pb.kg^{-1}$ for TML. LC_{50} (fish, 96hrs) for TEL is 0.02 $mg.kg^{-1}$ and for TML is 0.11 $mg.kg^{-1}$.

Atrazine

Chemical Name: 2-Chloro-4-(ethlamino)-6-(isopropylamino)-s-triazine ($C_{10}H_6Cl_8$).

CAS Number: 19-12-24-9

Properties: Solubility in water: 28 mg/L at 20°C; vapour pressure: 3.0 x 10^{-7} mm Hg at 20°C; log K_{ow}Partition Coefficient: 2.3404.

Discovery/Uses: Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, christmas trees, and other crops, and in conifer reforestation plantings. It was discovered and introduced in the late 50's. Atrazine is still widely used today because it is economical and effectively reduces crop losses due to weed interference.

Persistence/Fate: The chemical does not adsorb strongly to soil particles and has a lengthy half-life (60 to >100 days)., Aatrazine has a high potential for groundwater contamination despite its moderate solubility in water.

Toxicity: The oral LD50 for atrazine is 3090 mg/kg in rats, 1750 mg/kg in mice, 750 mg/kg in rabbits, and 1000 mg/kg in hamsters. The dermal LD50 in rabbits is 7500 mg/kg and greater than 3000 mg/kg in rats. Atrazine is practically nontoxic to birds. The LD50 is greater than 2000 mg/kg in mallard ducks. Atrazine is slightly toxic to fish and other aquatic life. Atrazine has a low level of bioaccumulation in fish. Available data regarding atrazine's carcinogenic potential are inconclusive.

Perfluorooctane Sulfonate (PFOS)

Chemical Name: Perfluorooctane Sulfonate, C8F17SO3

CAS Number: The perfluorooctane sulfonate anion (PFOS) does not have a specific CAS number. The acid and salts have the following CAS numbers: acid (1763-23-1); ammonium (NH4+) salt (29081-56-9); diethanolamine (DEA) salt (70225-14-8); potassium (K+) salt (2795-39-3); lithium (Li+) salt (29457-72-5).

Properties: Solubility in water: 550 mg/l in pure water at 24-25°C; the potassium salt of PFOS has a low vapour pressure, 3.31 x 10-4 Pa at 20°C. Due to the surface-active properties of PFOS, the Log Kow cannot be measured.

Discovery/Uses: POSF-derived chemicals are used in a variety of fabric cleaner and protection products, including surface-treatments of fabric for soil/stain resistance, coating of paper as part of a sizing agent formulation and as a component in specialized applications such as fire fighting foams. Commercial production of PFOS started in 1948, with principal production reduced in 2000 with total elimination intended for 2002.

Persistence/Fate: PFOS does not hydrolyze, photolyze or biodegrade under environmental conditions. It is persistent in the environment and has been shown to bioconcentrate in fish. It has been detected in a number of species of wildlife, including marine mammals. Animal studies show that PFOS is well absorbed orally and distributes mainly in the serum and the liver. The half-life in serum is 7.5 days in adult rats and 200 days in Cynomolgus monkeys. The half-life in humans is, on average, 8.67 years (range 2.29 – 21.3 years, SD = 6.12).

Toxicity: The substance shows moderate acute toxicity to aquatic organisms, the lowest LC50 for fish is a 96-hour LC50 of 4.7 mg/l to the fathead minnow (*Pimephales promelas*) for the lithium salt. For aquatic invertebrates, the lowest EC50 for freshwater species is a 48-hour EC50 of 27 mg/l for *Daphnia magna* and for saltwater species, a 96-hour LC50 value of 3.6 mg/l for the Mysid shrimp (*Mysidopsis_bahia*). Both tests were conducted on the potassium salt. The toxicity profile of PFOS is similar among rats and monkeys. Repeated exposure results in hepatotoxicity and mortality; the dose-response curve is very steep for mortality. PFOS has shown moderate acute toxicity by the oral route with a rat LD50 of 251 mg/kg. Developmental effects were also reported in prenatal developmental toxicity studies in the rat and rabbit, although at slightly higher dose levels. Signs of developmental toxicity in the offspring were evident at doses of 5 mg/kg/day and above in rats administered PFOS during gestation. Significant decreases in fetal body weight and significant increases in external and visceral anomalies, delayed ossification, and skeletal variations were observed. A NOAEL of 1 mg/kg/day and a LOAEL of 5 mg/kg/day for developmental toxicity were indicated. Studies on employees conducted at PFOS manufacturing plants in the US and Belgium showed an increase in mortality resulting from bladder cancer and an increased risk of neoplasms of the male reproductive system, the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract.

Chlordecone

Chemical Name: 1,2,3,4,5,5,6,7,9,10,10-dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd)pentalen-2-one (C10Cl10O). Also known as Kepone.

CAS Number: 143-50-0

Properties: Solubility in water: 7.6 mg/L at 25°C; vapour pressure: less than 3*10-5 mm Hg at 25°C; log KOW: 4.50.

Discovery/Uses: Chlordecone is released to the atmosphere as a result of its manufacture and use as an insecticide. Chlordecone also occurs as a degradation product of the insecticide Mirex. As a fungicide against apple scab and powdery mildew former use and to control the colorado potato beetle, rust mite on non-bearing citrus, and potato and tobacco were worm on gladisli and other plants. Chlordecone was formerly registered for the control of rootborers on bananas Nonfood uses included wireworm control in tobacco fields and bait to control ants and other insects in indoor and outdoor areas.

Persistence/Fate: The estimated half-life in soils is between 1-2 years, whereas in air is much higher, up to 50 years. It will not be expected to hydrolyze, biodegrade in the environment. Also direct photodegradation is not significant similarly as evaporation from water. General population exposure to chlordecone is occurred mainly through the consumption of contaminated fish and seafood.

Toxicity: Workers who were exposed to high levels of chlordecone over a long period (more than one year) showed harmful effects on the nervous system, skin, liver, and male reproductive system. These workers were probably exposed mainly through touching chlordecone, although they may have inhaled or ingested some as well. Animal studies with chlordecone have shown effects similar to those seen in people, as well as harmful kidney effects, developmental effects, and effects on the ability of females to reproduce. There are no studies available on whether chlordecone is carcinogenic in people. However, studies in mice and rats have shown that ingesting chlordecone can cause liver, adrenal gland, and kidney tumors. Very highly toxic for some species such as Atlantic menhaden, sheepshead minnow or donaldson trout with LC50 between 21.4 – 56.9 $mg.l^{-1}$

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