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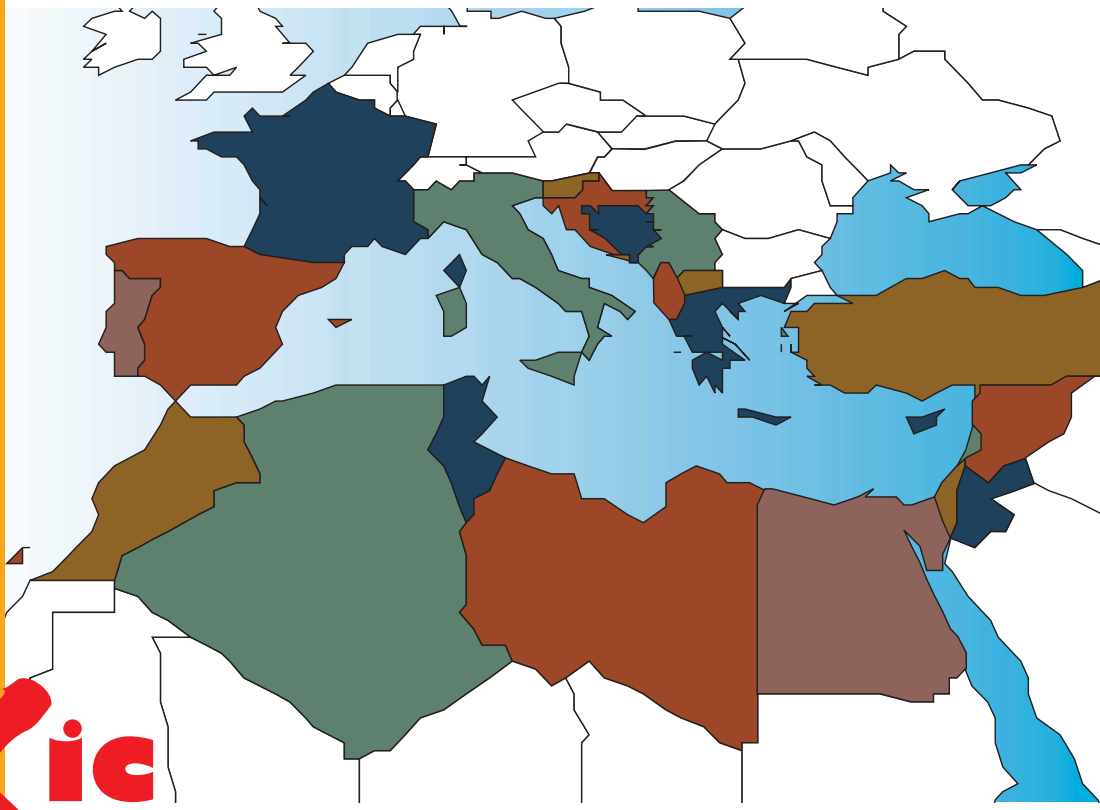
Mediterranean
REGIONAL REPORT



Regionally Based Assessment of Persistent Toxic Substances

December 2002

Global Environment Facility

UNITED NATIONS
ENVIRONMENT
PROGRAMME

UNEP

CHEMICALS

Regionally Based Assessment of Persistent Toxic Substances

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, Yugoslavia

MEDITERRANEAN REGIONAL REPORT

DECEMBER 2002

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The Inter-Organization Programme for the Sound Management of Chemicals (IOMC), was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and OECD (Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen cooperation and increase coordination in the field of chemical safety. In January 1998, UNITAR formally joined the IOMC as a Participating Organization. The purpose of the IOMC is to promote coordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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PREFACE

i. Overview of the project

The introduction of xenobiotic chemicals that are generally referred to as "persistent toxic substances" (PTS) into the environment and resulting effects is a major issue that gives rise to concerns at local, national, regional and global scales. Thus, and following the recommendations of the Intergovernmental Forum on Chemical Safety, the UNEP Governing Council decided in February 1997 (Decision 19/13 C) that immediate international action should be initiated to reduce and/or eliminate the emissions and discharges of an initial set of twelve persistent organic pollutants (POPs)[1], identified by the international community as the cause of serious environmental and health threats. Accordingly, an Intergovernmental Negotiating Committee (INC) was established with a mandate to prepare an international legally binding instrument for implementing international action on certain persistent organic pollutants. These series of negotiations have resulted in the adoption of the Stockholm Convention in 2001.

The UNEP Governing Council further identified the need to develop science-based criteria and a procedure for identifying additional POPs as candidates for future international action and recognised the need to develop an instrument that would take into account differing regional conditions. With funding from the Global Environment Facility (GEF) and support from several donor countries[2], the United Nations Environment Programme implemented a project to regionally assess PTS. The assessment should lead to the identification of priorities for future GEF intervention, and through application of a root cause analysis, should attempt to identify appropriate measures to control, reduce or eliminate releases of PTS, at national, regional or global levels and stimulate research through the identification of data gaps.

The activities to be undertaken in the project comprised an evaluation of the sources of persistent toxic substances, their levels in the environment and consequent impact on biota and humans, their modes of transport over a range of distances, the existing alternatives to their use and remedial options, as well as the barriers that prevent their good management. The outcome of this project will be a scientific assessment of the threats posed by persistent toxic substances to the environment and human health.

For the implementation of the project, the globe was divided into twelve regions[3], one of which being the ***Mediterranean,*** which is the object of the present Report. Under the direction of a project manager who is situated at UNEP Chemicals in Geneva (Switzerland), a Regional Co-ordinator and a Regional Team were appointed by UNEP to co-ordinate the collection and interpretation of existing data and to produce the Regional Report on the PTS selected for analysis. This Report should be drafted on the basis of:

- contributions from individuals through the completion of questionnaires previously prepared for collecting information on sources, levels, effects and transboundary movements of PTS, as well as on the barriers to their sustainable management;
- a series of regional Technical Workshops to review the regionally available data and information collected by experts from the region, including discussion papers setting the scene for these workshops; and
- a "Priority Setting" meeting which will bring together stakeholders from various sectors of academia, government, NGOs and the private sector to prioritise the issues and discuss their root causes.

A network of PTS experts and national focal points were part of the supporting structure for the regional assessment. At the end, consolidation of the results of the regional analyses will provide the basis for a global assessment, to highlight priority issues, suggest interventions to address the problems identified, and to provide guidance to the GEF for further actions.

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[1] Aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, dioxins and furans.

[2] The project costs approximately US$4.2 million funded mainly by GEF, with sponsorship from countries including Australia, France, Germany, Sweden, Switzerland and the USA.

[3] Arctic, North America, Europe (Northern part, including Baltic, Black Sea and Caspian Sea), Mediterranean (including Portugal and Jordan), Sub-Saharan Africa, Indian Ocean, Central and North East Asia (Western North Pacific), South-east Asia and South Pacific, Pacific Islands, Central America and the Caribbean, Eastern and Western South America, and Antarctica

ii. Structure of the Regional Team

The Regional Team included the Regional Co-ordinator, five Team Members and three Technical Advisors, whose names and addresses are listed below.

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iii. Acknowledgements

The Regional Team is highly indebted to those experts listed in Annex I, who attended the Technical Workshops and the Priority Setting Meeting and contributed with data and information.

A particular acknowledgement goes to the Institutions who provided support to the Team members as well as to those who hosted the Technical Workshops and the Priority Setting Meeting:

- The Mediterranean Information Office for Environment, Culture and Sustainable Development (MIO-ECSDE), Athens (Greece)
- Istituto Superiore di Sanità, Rome (Italy)
- Institut d'Estudis Catalans, Barcelona (Spain)

Finally, the enthusiastic co-operation of individuals who contributed in different ways to the project, either filling questionnaires, writing specific sections, or providing technical assistance during the meetings is greatly appreciated.

EXECUTIVE SUMMARY

The Mediterranean Region, embracing parts of two continents as diverse as Europe and Africa, is a complex geographic, ecological, cultural and socio-political set-up based around the Mediterranean Sea basin. The Mediterranean climate, with mild wet winters and hot dry summers, has been used as a model for many other regions around the world. Its landscape and monuments continues to be the greatest tourist destination in the entire world. As a consequence, urbanisation has been particularly growing along the coastal strip, to accommodate both permanent and temporal population, with the result of a substantial modification of the coast itself and adverse effects on the quality of the environment.

The highly developed industrial countries in the North stand in stark contrast to the countries in the South. These differences have significant implications when addressing environmental issues, and particularly those related with the management of persistent toxic substances (PTSs). The description of the main properties, uses, and environmental behaviour and toxicity of all these PTSs, are summarised in Annex II.

In addition to the problems originated by the controlled and uncontrolled chronic releases of these substances into the environment, the Region has been challenged by different accidental episodes, like the Seveso explosion in 1976 and the bombing of electric and industrial installations during the Kosovo war in 1999, apart from some of the largest oil spills in front of its coasts.

The Mediterranean Action Plan of UNEP and the traditional co-operation among countries in the region, in the framework of the Barcelona Convention, has contributed significantly to the progress of the project.

i. Sources of PTSs

For many Mediterranean countries no detailed information is available on the release of PTSs from point sources (industry and urban centres). In general, there is a lack of adequate data sets to perform a quantitative source assessment. This is because local and national authorities do not routinely monitor PTSs sources in the Region. However, an attempt has been made to collect the available information and to qualify and quantify the current status of PTSs sources.

The main findings of this assessment are as follows:

- For persistent pesticides, including lindane, the sources are multiple and diffuse. Although, there is a decreasing tendency in the use of these compounds in the Region as a result of the PIC procedures and associated conventions, there is a worrisome lack of control regarding the existing stockpiles of obsolete pesticides. 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 thousand tonnes.
- For industrial PTSs the situation in the Region is as follows. PCB containing equipment has been largely used. 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.
- For unintentional PTSs, dioxins and furans, the assessment indicates that main primary sources are thermal. Controls and optimisation in incineration plants have achieved a decrease of emissions from municipal waste incineration. Remaining sources are the metallurgical industry, the uncontrolled combustion of waste in landfills and the combustion of wood. There is a clear need for a comprehensive Regional Inventory that should include most of the primary thermal sources. Emission estimates indicate a decrease during the last decade in the MSC-E countries of the Region.
- For other PTSs of concern, the situation in the Region is as follows:
    - The main sources of PAHs in the Region are connected to oil shipping operations. They could be as large as 1000 tonnes per year, although continental emissions and runoff may represent a contribution of 40-700 range tonnes/year. River inputs contribute to some 40 tonnes/year.
    - Release from antifouling painting in commercial shipping is the source of TBTs in the Region. The present release rates estimates are in the order of some 240 tonnes/year. The harbours in the NW Mediterranean and in the Adriatic are potential hot spots for this type of PTSs.

- Emissions of brominated flame-retardants from the various countries of the Region are proportional to their consumption of electrical and electronic equipment. Hence, economic development patterns in the Region indicate an increasing trend in emissions, although the absolute levels are relatively low at present.
- The release of non-ionic surfactants is quite large, in the range of 167000 tonnes per year, due to the large consumption of detergents (6 million tonnes/year). The five EU countries of the region contribute to 50% of this release.

In terms of setting priorities to reduce PTSs sources, it would appear that a better control of remaining stockpiles of PCBs, PCB containing equipment and obsolete pesticides in the Region is highly needed. The development of sustainable destruction capacity is also required. A better control of oil shipping operations in the Mediterranean is also a top priority in order to reduce PAH releases in the Region. Commercial shipping is also responsible for the release of sizeable amounts of TBTs in the Region.

ii. Levels and effects in biotic and abiotic compartments

A substantial amount of information exists on the distribution of PTSs in the different environmental compartments of the Region. However, this is mainly the result of research campaigns rather than the existence of monitoring networks. In consequence, data available mainly deal with local studies, or hot spot situations. Data is often missing for some compartments, particularly atmosphere, ground and drinking waters, soils and sewage sludges, etc. Significant geographical data gaps also exist, particularly for the South and South-eastern basins, and for the PTSs of more recent concern (e.g. dioxins or alkylphenols). Moreover, the lack of standardised methodologies makes it difficult to compare and use data in a regional assessment, and draw definite conclusions on spatial and temporal trends.

In spite of these limitations, available data indicate that PTSs are widely, but not uniformly, distributed in the Region. For example, HCB and γ-HCH concentrations in air reach the higher values in northern France (2.4 ng/m^3 and 1.5 ng/m^3, respectively) and decrease to values below 0.1 ng/m^3 in remote areas. Total DDT concentrations in sediments vary from <0.25 to 885 ng/g at different locations, and PCBs from 1.3 to 7274 ng/g, the higher levels corresponding to localised "hot spots", near sewage outfalls of big cities or at the mouths of large rivers (e.g. Rhone and Seine). Similarly, freshwater and marine organisms, extensively used in biomonitoring, show PTSs concentrations closely associated to their habitats. Levels up to 400 μg/g ww of DDTs and 1400 μg/g ww of PCBs have been found in the blubber of Mediterranean marine mammals (dolphins), values which are higher than those found in similar species living in the Atlantic.

The marine environment is by large the compartment most widely studied, probably due to its regional importance but also to the incentive of the Barcelona and OSPAR Conventions. 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.

Few long-term temporal trend monitoring in fish, mussels and seabird eggs has been carried out in the Northern Mediterranean. A general decline of DDTs has been reported for marine biota along the Mediterranean coasts of France and Italy, and from the Adriatic Sea between 1960s and 1990s, which is consistent with the regulatory restrictions on production and use of this compound. The French monitoring network of coastal pollution shows, during the period 1979-1998, 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.

A number of reports have identified some geographical areas of concern. These include estuaries (e.g. Seine, Rhone, Ebro, Po and Nile), coastal enclosures (e.g. Izmit and Iskenderun Bays, Venice Lagoon, etc.) coastal areas (e.g. NW Mediterranean and Northern Adriatic), inland waters (e.g. Po, Ebro, Seine, Kupa and Lepenica rivers) and dumpsites (e.g. Durres, Skopje, Alger, Mustaganem, etc.). Apart from areas of intense local contamination, compounds of regional concern are PCBs, DDT, HCHs, PAHs, HCB and TBTs. Other compounds e.g., phthalates, alkylphenols, PBDE/PBBs are suspected to be ubiquitous but data are lacking.

Comprehensive studies have been conducted in a limited number of cases, e.g. in the NW Mediterranean, in the Adriatic coast, including the Venice Lagoon, or in the area affected by the Balkans war. Some of these case studies are described for illustrating the approaches followed to assess the sources and fate of PTSs.

Based on the limited data available, it is unlikely that present levels of chlorinated pesticides would adversely affect marine and continental higher organisms. Laboratory studies have shown bird species to be susceptible to exposure to PTSs displaying decreased egg production, embryotoxicity and thickness of the egg shell, but field evidence in the Region is very limited. However, the combination of chemical and biological methods has provided early identification and response to some emerging problems. For example, Imposex has been observed in gastropods from many coastal areas and attributed to the presence of TBT. A range of symptoms, e.g. endocrine disruption, is shown by fish exposed to PTSs in some Spanish and Italian rivers. Finally, exposure of marine mammals to certain PTSs has been demonstrated. The levels of organochlorine compounds were higher than those found in animals showing reproductive failure and physiological impairment following prolonged PCB exposure, suggesting that this contamination may be a major causative factor for the large-scale deaths of dolphins in the Mediterranean Sea, although this relationship is not conclusive.

The cases reported above, as an example of a presumably widespread and not yet fully characterised environmental contamination by PTSs, strongly indicate the need to activate monitoring programs of the general population. In fact, while the exposure of the population living in contaminated areas and in their surroundings has not been fully characterised, and data on levels in human tissues are not available, the ability of PTSs to enter the food chains and to biomagnify along them makes the hypothesis of a high human exposure to these compounds highly plausible, and the correlated damage for health worthwhile to be explored.

In spite of this “weight of evidence” data on human health effects in the Region show a substantial paucity. A common bias of most gathered data, basically including breast milk, adipose tissue and blood, is their lack of representativeness, since the generally small size of population sampled does not allow an extrapolation to the general population. Moreover, data comparability, even on a country basis, is in most cases affected by a number of variables inherent to the study design (individual vs/pooled samples, characteristics of the sampled groups) and to intrinsic factors (type oh human specimen, analytical procedure, time of the study).

Data on banned pesticides in human tissues mostly dates back to the 80’s, with the exception of DDT, which is largely found in the form of the DDE metabolite. Levels in adipose tissue were in the last decade, in Spanish and Italian populations, in the range of 3.7-6.3 μg/g fat. In general, in the case of DDT, PCBs and PCDD/Fs, for which quite large data sets are available, a temporal trend may be observed for the general population that shows a consistent decrease of the human body burden over the last two decades due to regulations applied in the eighties.

Since diet accounts for up to 95% of human exposure to PTSs, data on the presence of PTSs in various foodstuffs or in the "total diet" of a country are of primary importance to characterise the actual levels of exposure of the general population. "Estimated Daily Intake" (EDI) are available, at present, only for a small number of compounds/countries, representing a valuable indication of specific "local" situations rather than allowing an adequate risk assessment for the whole Region.

A major step towards the filling of the existing data gaps in the Region will be the activation of monitoring programs at three levels:

- Analysis of abiotic samples or sentinel species to identify hot spots and transport pathways. Monitoring activities should be established in the corresponding countries to fill the geographical data gaps, and ensuring the continuation of existing time trend series. Regional surveys of emerging PTSs and compounds actually on the market (e.g., PBDE, triclosan,...) or those difficult to analyse (e.g., PCDD/Fs) should be particularly envisaged.
- Analysis of food to evaluate the general exposure of the population and to detect abnormal increases due to different cases of contamination. Monitoring design should allow the assessment of any correlation of PTSs body-burden with factors 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 bodies. 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 PTSs. The data obtained should also allow the validation of exposure models.

A closer relationship between monitoring and modelling should, finally, be encouraged for improving the estimates of the fate and effects of emissions and pools of existing PTSs.

iii. Transport pathways

Presumably the atmospheric and the aquatic compartments play the major role in the transboundary transport of PTSs. Although the knowledge of the water circulation in the Mediterranean Sea and of the regional meteorology is well established, only recently a series of studies have been intended to document processes that connect the general circulation at the Basin level to pollution episodes. However, there is still a lack of broad scale information and baseline values of PTSs to be able to determine the significance of the major transport pathways. In general, it is difficult to assess what source(s) are controlling environmental levels and whether they can be further controlled or affected by long range transport processes.

The physiographic characteristics of the Mediterranean Region and the prevailing climatic conditions have as a result the development of a complicated atmospheric flow pattern. Its main features are the strong northern component, particularly pronounced during the warm period of the year. This is due to differential heating between the land of North Africa (almost bare soil), the Mediterranean waters and the land of South Europe (with mixed-type vegetation cover). On the other hand, a second path of transport has been identified from Western towards the Eastern Mediterranean with a stronger component during the cold period of the year.

Based on meteorological modelling, transcontinental scale transport of air pollutants between Europe, Asia and Africa is apparent, the Europe to Africa direction prevailing over the others, and the warm period of the year being the most effective. Air masses from Europe reach the mid-tropospheric layers of the Equatorial Zone within a time period of 3-4 days. These processes are further complicated by the appearance of desert dust particles, the role of which on the environmental fate of PTSs is unknown. Moreover, there are indications of a massive upward transport of various aged pollutants in the coastal zones which may also involve the cycling of PTSs, although this aspect has not yet been investigated. Some locations of the Mediterranean Region act as "temporal reservoirs" where air pollutants are "stored", and "aged enough" before they are re-advected again (e.g. Black Sea, Western Mediterranean).

Modelling of long range transport of PTSs (e.g. PCBs, HCB, lindane and B[*a*]P) has been developed by the MSC-East Centre, from EMEP data, and deposition values have been estimated. The Mediterranean Sea, particularly the Western basin and the Northern Adriatic, may be sinks for PTSs. However, the weak data coverage of the southern part of the Region does not allow a precise assessment of sources and receptors in the whole Region.

Several riverine and wastewater discharges from highly industrialised and populated cities have been identified as coastal "hot spots" and also potential PTSs sources for transboundary transport. However, beyond the zone of influence of these discharges, concentrations drop rapidly reflecting the enhanced sedimentation processes, which take place at the freshwater-seawater interface. In spite of this, currents may transport the finest particles and the dissolved species to long distances, and signatures are found in remote sediments and biota. Recent studies indicate that most PTSs coming from rivers are linked with flooding with suspended solids. The characteristic variations of the water regimes of Mediterranean rivers and the lack of long temporal series render it difficult to evaluate the impact of these discharges.

Finally, the assessment of long-range transport of PTSs using biological indicators deserves consideration. Accumulation of PTSs in biota is a well known process, and it will continue for a long time as a result of the environmental redistribution pathways after a substance has been banned. Indicator species can be identified and monitored for temporal trends assessment. In this respect, the following have been used tentatively in the Region: terrestrial vegetation, as an important receptor of long range transported PTSs, fish inhabiting remote places like alpine lakes and the deep sea, and eggs from sea birds, which constitute large colonies widely distributed in the Region.

iv. Management and capacity building

Monitoring of PTSs in the Region is heterogeneous at the National level, ranging from systematic monitoring networks in France to non-existing for many of the Southern and South-eastern countries. As a consequence, and with some exceptions, no comprehensive information exists on obsolete stocks of pesticides or on polluted or contaminated sites (hot spots). Capacity building plans are required to actively manage the generation of data for improving emission inventories and risk assessment studies.

Although the EU members and the associated countries have made an effort to harmonise the monitoring programs the degree of implementation is varying. MEDPOL is a good example of Regional collaboration in monitoring programmes, but its efficiency is weakened by the lack of commitment of some participant

countries. MEDPOL has also played a key role in developing quality criteria standards throughout the Region and it is a good example of a capacity building programme.

The regulatory status of the Region mimics the socio-economic and political structure. The European countries have more effective national environmental regulations and capabilities to undertake monitoring and enforcement activities for PTSs. These countries exhibit several positive signs of high compliance of substantive obligations through their commitments to EU directives. Other Mediterranean countries exhibit low commitments to relevant national and regional regulations even though they have developed a comprehensive national legal and institutional framework for the implementation of these regulations. Furthermore, as most of these countries have ratified only few of the Multilateral Environmental Agreements, they are not required to submit reports on several important parameters. As such, information about compliance of substantive obligations remains scarce and, where it exists, quite uneven in coverage and quality.

The control and management of PTSs at national level is quite dispersed among various authorities, depending on the PTSs type. Pesticides are usually regulated by the corresponding Agricultural Ministries, through a system of national registration. Industrial PTSs are usually left as a legacy to the new-born Environmental Ministries. The levels and effects of PTSs in biota are either the responsibility of the Environmental or Agricultural (Veterinary) Ministries. Finally, PTSs control and regulation in foodstuff is always the responsibility of the corresponding Health Authorities.

There are few examples of alternatives to the use of PTSs compounds in the Region, but since most of them have been gradually banned, there is a positive reduction of the cycling of these substances in the Mediterranean Region. The main alternatives to PTSs in the Region are connected to the replacement and reduction of the intensive use of pesticides. This requires quite a substantial educational effort to promote Sustainable Pest Control strategies.

There is a clear need to promote technology dissemination and transfer and one of the objectives should be to make information available in the languages of the Region, including the non-European. Measures for PTSs reduction in the industrial processes through cleaner production should be one of the targets. The Regional Activity Centres for Cleaner Production could play an important role in this context.

In terms of the specific needs for Regional Co-operation, the main requirements identified are the following: to develop institutional capacity building in individual countries; to introduce in national environmental regulations the obligation to declare possession and/or use of dangerous substances, which cause emissions and transfers; to control and reduce the wastes at source; to promote non-polluting technologies; and to develop containment facilities before disposal, in particular for pesticides and PCBs.

Mere formal State ratification of international agreements is not sufficient for effectively combating PTSs environmental and human health problems. For that to happen, countries need to go one step further and initiate actual domestic implementation and policy changes. Regarding the future actions, the most pressing ones are:

- The need for more comprehensive capacity building efforts in the Region, referred to all efforts and strategies to increase the ability to and effectiveness of government performance.
- The continued support and development of the on going national monitoring programmes and their co-ordination through the existing regional monitoring programmes.
- The improvement of the co-ordinated management efforts, technology transfer and international collaboration for handling stockpiles of PCBs and obsolete pesticides.
- The necessary integration of the diverse contamination issues at different educational levels in order to raise the general environmental and scientific literacy and promoting public awareness including the collective attitude towards municipal and industrial waste management.
- The development of national and international economic instruments to support the financial requirements for the proper management of PTSs. Strengthening existing regulations and implementation of international commitments invariably draw financial resources. Financing these activities constitutes continued challenges, particularly for the less developed countries.

In conclusion, it is necessary to develop an overall strategy for regional governance of PTSs. This should include explicit reporting procedures based on voluntary and binding agreements to report on a regular basis about emission estimates, levels, monitoring methods and activities, and control strategies planed and in force. Such a framework will provide the basis for improving the consistency and the coverage of available information and a possible mechanism to assess and improve compliance.

1 INTRODUCTION

1.1 DEFINITION OF THE MEDITERRANEAN REGION

1.1.1 Geographical and political boundaries

The Mediterranean Region is a complex geographic, climatic, hydrological, ecological, cultural and socio-political set-up based around the Mediterranean Sea basin. The Mediterranean Sea has been historically a means of spreading of a large variety of cultures. Phoenicians, Greeks, Carthaginians, Romans, Catalans, Turks and British, just to mention a few, have displayed the control of the trading and military activities and, to some extent, the political life around the Mediterranean Region. The three major monotheist religions, Christian, Muslim and Jewish, were born there. The sea has never been a difficulty for communications and, on the contrary, the Mediterranean Sea has allowed close ties to be laid down since remote times among the various nations and alternating periods of war and peace have configured present political divisions and alliances. As the cradle of many civilisations, the region has played during the last millennia a pre-eminent role in the development of human kind.

Located in the mid-latitudes half way between the subtropical and the temperate zones surrounded by large continents (Eurasia, Africa), it has climatic and ecological characteristics typical of these latitudes, partly maritime and partly continental. The countries included in this Region for the purpose of the present project are Albania, Algeria, Andorra, Bosnia-Herzegovina, Croatia, Cyprus, Egypt, France, Greece, Israel, Italy, Jordan, Lebanon, Libyan Arab Jamahiriya, Malta, Monaco, Morocco, Palestine, Portugal, San Marino, FR Yugoslavia (Serbia and Montenegro), Slovenia, Spain, Syrian Arab Republic, The Former Yugoslav Republic of Macedonia, Tunisia and Turkey (Figure 1.1).

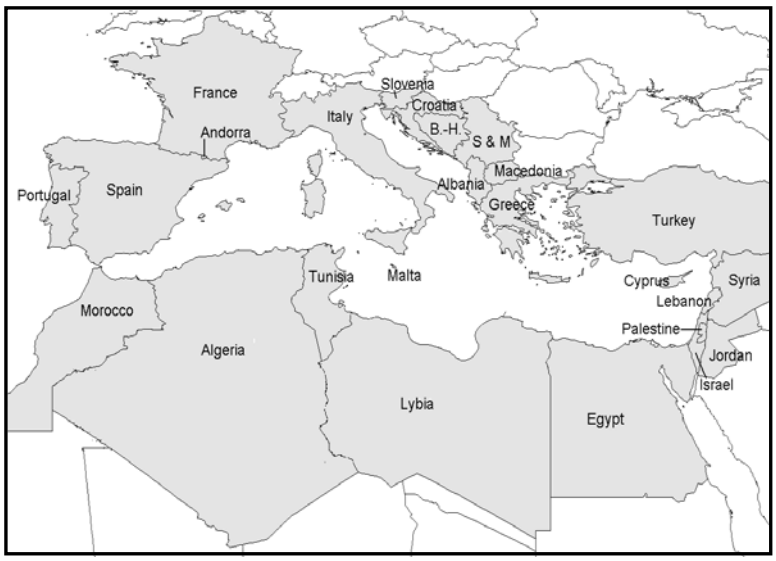

Figure 1.1. Map of the region

1.2 PHYSICAL SETTING

1.2.1 Climate and meteorology

The climate of the Mediterranean Region has been used as a model for many other regions around the world (California, South Africa, Australia, etc.). In simple terms, it may be characterised by mild wet winters and hot dry summers. Air temperature differences are generally limited to about 15ºC, although local meteorological factors can result in exceptional conditions. Winter rainfall accounts for more than 90% of the total precipitation. In much of the region summer rainfall is practically zero. This strong summer-winter rainfall contrast is associated with a pronounced seasonal cycle in almost all climate variables.

The seasonal cycle proceeds as follows: July, August and September are characterised by warm, dry conditions associated with a strong high-pressure ridge which pushes eastwards from the Azores over the Mediterranean the subtropical highs. The axis of this ridge is displaced southward over Egypt by a trough extending from the Persian Gulf area to the Northwest towards Greece, associated with the Indian summer monsoon depression. The rainy season begins in mid-October and is associated with a change in the mean-wave pattern of the upper westerlies characterised by a trough over Europe (whose position is highly variable). Winter is characterised by cyclonic disturbances and low mean pressure in the Mediterranean with higher pressure to the east associated with the Siberian High. In March, April and May, as the main features of the upper flow (jet streams, air mass discontinuities) begin to move northward from their southernmost winter positions, the rainy season continues. By May, the polar front and associated strong upper-air westerly flow is sufficiently far north that its influence is removed, and the subtropical highs and associated ridges once more exert their influence.

The rate of precipitation varies considerably from place to place and from year to year. There is a general decrease in yearly rainfall from west to east and from north to south. Rainfall varies from more than 1500 mm yr^{-1} along the western part of the Balkan peninsula and over mountain ranges in Europe to less than 100 mm yr^{-1} in the interior highlands of northern Africa and western Asia, as well as some islands of both the eastern and western basins. Precipitation, mainly associated with cyclonic disturbances, is strongly influenced by local mountain effects.

Mediterranean depressions originate in the western, central and eastern regions within the basin. Their formation is partly determined by transitory excursions of the polar front jet and the European trough modified by the land-sea temperature contrast which favours cyclogenesis over the warm Mediterranean Sea. Their movement is not well understood. In the western Mediterranean depressions are frequently “steered” by the temperature contrast which results from colder continental air moving over the warmer sea particularly strong in spring. Roughly half of the central basin depressions are routed over the Black Sea, and there is some evidence of steering by the upper flow along the axis of the subtropical jet. Eastern basin depressions are often associated with cold northerly airflow and lee cyclogenesis. These relationships provide a link between the local rain-producing pressure systems and larger-scale aspects of the general circulation over Europe. These depressions have also been a subject of major concern from the standpoint of their implication in the long range atmospheric transport of pollutants from central Europe to the region (see sect. 4.1).

Apart from the classic body of knowledge on meteorology in the Mediterranean Basin, a series of recent studies have documented previously unknown atmospheric processes that connect the atmospheric circulations at the Basin level to air pollution episodes (see sect. 1.4.2). These studies have shown the importance of feedback mechanisms in this region; for example, they have documented the relation between soil properties and atmospheric circulation patterns, and between sea temperatures and torrential rains in the area. However, because of the fact that much of this data is being processed at present and that research programmes adapted to the conditions of this region are still incomplete, it is not yet possible to substitute the long-accepted knowledge system with a new and consistent one.

1.2.2 Physiography

The region is formed by coastal and in-land areas draining into or connected with the Atlantic and the Mediterranean Seas, and limited by the existence of important mountain ranges:

- Coastal ranges in northern and eastern Iberian Peninsula,
- Massif Central and Alps in western and central Europe,
- Dinaric Alps and other mountain ranges on the western and southern Balkan Peninsula,
- Taurus Mountain range in the Anatolian peninsula,
- Lebanese mountains in the Middle East and
- Coastal ranges all along the North African continent

The broken geomorphology of the Basin ensures relatively rapid riverine run-off. Except for some of the rivers whose basins deeply penetrate in the European (e.g. Rhone and Po) and African (Nile) continents, most of the rivers of the region draining into the sea are relatively short and highly seasonal in discharge rates. These small drainage basins have defined a rather narrow littoral zone and, until relatively recently, a certain isolation ingrained in the culture of coastal populations. Very often one single cultivated species, the olive tree, may be sufficient to delimitate the Mediterranean climatic/ecological region.

1.2.2.1 The landscape

In recent years, efficient farming and growing urbanisation in the north has led to increased abandonment of farmland and rangeland and the corresponding advance of forests. This contrasts strongly in the south and east

where marginal areas, such as arid steppes and rangelands, are being cleared for grain production. Unfortunately, the lack of rain and continually flowing rivers has restricted the use of irrigation. Given the trends of the past 40 years, in the near future virtually all tillable land in the southern and eastern part of the Mediterranean basin will be cultivated for cereal production, even though the risk will be high and yields low.

Currently, forested areas in the Mediterranean countries cover 74 million ha (FAO, 2001). Over 2/3 of the total area and near 90% of the standing wood biomass are in the northern countries of the Basin, while about 10 million ha are in southern or eastern countries. Trends in forest conservation and use are very different in the Northern and in the Southern and Eastern borders, due mainly from different socio-economic dynamics. In the north, the countries with a larger proportion of forest areas are largely under temperate or Atlantic, non-Mediterranean climates. In the less productive, steepest or arid rural areas of these Northern Basin countries, a number of traditional activities have been abandoned, including crops and grasslands and many forests are mismanaged, due to low economic returns. Forests are invading old crops, and biomass increases within the forests, and so does fire propagation risk.

In Southern and Eastern areas, biomass is overexploited for fuel and wood, and overgrazing is frequent. Wild fires are rare, but forest area decreases at an annual rate of 1.1%, higher than the average in tropical countries (0.8%). These forests are also the most sensitive to climate change. In the slopes of degraded forest areas, there is a high erosion risk. Therefore, as a result of very different processes, for the entire Mediterranean countries, sensitive areas, mainly those that have less than 600 mm of average annual rainfall, are jeopardised by a serious desertification risk. Longer and deeper summer droughts, higher temperatures and the impairment in annual water balance (lowering soil moisture) may also favour changes in the dominant species and landscapes (Lavorel et al., 1998).

Wild fires may become a driver of future changes in landscape in the Mediterranean region. A fast increase in the number of days with a high meteorological fire-risk hazard has been observed due to the evolution of climate during the last decades. This has to be added to the increase of fire-risk human activities in the forest areas or in their neighbourhoods (traffic, industry, waste disposal, etc.). Not surprisingly, the records of the number of fires ignited show a continuous increase and the costs of current fire suppression policy increase as well. It is estimated that, on average, 500000 ha of the 35 million combustible hectares in Mediterranean Europe are burned each year, a figure that might well rise with the risks of climate change. These large fires are short catastrophic events, with serious socio-economic consequences and severe damage to living resources and to bio-diversity in the entire region. The forest fires are also considered as sources of a number of PTSs.

1.2.3 Marine environment

The Mediterranean Sea is a central compartment of the region and their characteristics and functioning are crucial for a proper description of the Region. It also plays a key role in the accumulation, diffusion and impact of pollutants in the region.

1.2.3.1 Geomorphology

The Mediterranean Sea is a semi-enclosed basin that extends for 3800 km in an East to West direction and for 800 km North to South in the widest sections, although almost half of its surface is within 100 Km far from a coast. It covers an area of 2.5 million km^2 and contains a volume of 3.7 million km^3 of water. The average depth of the basin is thus 1500 m. Depths over 4000 m are common and the maximum depth is 5121 m (Margalef, 1985).

The Mediterranean Sea is connected to:

- the Atlantic Ocean through the strait of Gibraltar (290 meters deep and 15 Km wide);
- the Black Sea through the straits of the Dardanelles (with a depth of 55 meters and a width from 450 meters to 7.4 Km), the Sea of Marmara and the Bosphorus;
- the Red Sea through the Suez Canal (12 meters deep and 1.2 Km wide).

The Mediterranean Sea is formed of various interconnecting but nearly autonomous basins. In the Western Mediterranean, the Alboran, Balearic, Tyrrhenian and Ligurian Seas can be identified though only bottom topography, hydrographic or even historical boundaries separate one from the other. In the Eastern Mediterranean, the Aegean and the Adriatic Seas are clearly separated from the rest of the basin while no real separations exist between the Ionian and Levantine Seas.

The Mediterranean sea-land interface, characterised by a relatively narrow continental shelf in most areas and a lack of tides, is very narrow but intensely utilised. The surface covered by the continental shelf is about 20% of the western basin and 22% of the eastern basin (80% of the Adriatic Sea can be classified as continental shelf).

Thus, the shelf usually extends for a few kilometres except in areas of the central and western basins and in the upper Adriatic Sea. The continental slope is steep dropping rapidly into submarine valleys and canyons that lead into deep basins. This is particularly true in the eastern basin where the continental shelf is not continuous but dissected by its complex topography.

The circulation and characteristics of the Mediterranean water masses are strongly affected by the complex physical feature of the Mediterranean Sea floor, originating from the existence of various tectonic entities to which the surrounding land masses and islands pertain. Knowledge of this complex topography is necessary for an understanding of the overall ecological view of the region (UNEP, 1977).

1.2.3.2 Hydrology

The Mediterranean Sea receives from rivers a contribution of about 15000 m^3 s^{-1} of which the 92% is coming from the northern bank. The total size of the catchment areas of the rivers draining into the Mediterranean Sea is about 4 million km^2. The continental runoff estimated in the framework of the MEDPOL project (UNEP 1984) gave a value for total runoff of about 14000 m^3/s. There is a large imbalance between runoff from the northern shore, draining 92 % of the water that flows into the Mediterranean Sea and the southern shore, draining only the remaining 8 %. This difference arises mainly from differences in yearly precipitation since the size of the areas drained is quite similar. The area of the Mediterranean that receives the largest input through river runoff is the Adriatic Sea, followed by the Northwest Mediterranean, receiving between nearly 70 % of all the river discharges. These two areas are followed by the Aegean, the Tyrrhenian and the Ionian Seas (20 %). The North African coast, including runoff from the Nile, receives less than 10 %.

The water budget for the entire Mediterranean basin is negative. The high evaporation rates caused by the strong heating of the surface water, and the dryness of the continental winds blowing across the basin from neighbouring continental masses outweigh the weak rates of precipitation and river runoff. The amount by which evaporation exceeds precipitation plus runoff is approximately 50000 to 70000 m^3/s. To account for the observed conditions of water and salt mass balance, approximately 20 times this amount of water must flow in from the North Atlantic Ocean through the Strait of Gibraltar, and consequently an almost equal amount of Mediterranean water has to flow out (Lacombe and Tchernia, 1974).

The most significant hydrological process occurring within the Mediterranean basin is the increase in salinity in the water as it follows a circuit from the incoming surface Atlantic Ocean to the outgoing intermediate and deep waters. During a mean residence time of approximately 75 to 100 years, almost all the substances dissolved in the former Atlantic water undergo an increase in concentration of about 4.7 % before they flow back at depth into the Atlantic Ocean at the Straits of Gibraltar. The relatively higher salinity allows the Mediterranean waters to be traced as far as the subequatorial Atlantic.

Incoming Atlantic surface water, with salinity only slightly above 36 psu is transformed into outgoing intermediate Mediterranean water, with salinity of 38.4 psu and above. The process by which the incoming surface North Atlantic water is transformed into the outgoing Mediterranean water requires large horizontal movements covering the entire basin and the general net gain in density generates unusual vertical movements seldom found in other regions of the world's oceans. The water circulation contains also strong vertical components determining the salinity distribution and proceeding to a vertical mixing up of dissolved nutritive and contaminating substances. Changes in salinity of subsurface and deep waters range from 38.35 psu to 39.10 psu (Miller and Stanley, 1965). The Mediterranean tides are of low interest, while the energy associated to such phenomena is sometimes meaningful.

The temperature of the surface Mediterranean water is subject to strong seasonal changes that affect the upper layers down to about 50 to 75 m deep. Sea surface temperatures range between 12 and 29ºC the lowest being in winter in the Northwest basin and in the North Adriatic Sea and the highest in summer in the Northeast Levant Sea. The temperature of the intermediate waters (below the warm surface layer), characterised by an outstanding homogeneity, is about 13ºC in the Western Mediterranean while a wider range of variation, between 13 and 16ºC, occurs in the Eastern Mediterranean. The deep waters of the Mediterranean Sea have an average temperature fluctuating between 12.5°C and 13.5°C in the western basin and between 13.5°C and 15°C in the eastern one, while the salinity varies from 38.4 psu to 39 psu. The water exchange time is of about 80 years and this parameter constitutes a very important value for the anthropogenic phenomena that condition its physical-chemical features on a local scale.

1.3 PATTERNS OF DEVELOPMENT

1.3.1 Urban and non-urban centres

The Mediterranean population has always been constrained in its physical settling by its mountainous physiography, except for a few major river basins. Therefore, urbanisation has been particularly growing along the coastal strip, to accommodate both permanent and temporal population, with the result of a substantial modification of the coast itself and adverse effects on the quality of the environment.

Mediterranean-rim countries presently hold 447 million people, mainly concentrated in the coastal areas and in the north-western part. In 1985, the 18 countries bordering the Mediterranean Sea had a combined population of 352 million people of which 37 % lived directly in the coastal zone, meaning that population densities range from greater than 1000/km^2 in the Nile Delta to less than 20/km^2 along coastal Libya. According to some projections, the population in the Mediterranean is expected to reach 545 million in 2025 (Grenon and Batisse, 1989). Increasingly, the population will urbanise: at present 63% of the population was urban, whereas by 2025 it is expected to be 75% urban. Countries like Israel, Lebanon and Libya are already much over this figure. Therefore, the economic and environmental burden on cities therefore will increase substantially, whichever type of development is pursued.

Population growth, however, shows major differences between north and south. The European countries have nearly stable populations, with annual growth rates often less than 1%. In contrast, population growth in southern countries ranges from 2 to 3% per year (UNDP, 2002). Thus, the population of the northern-rim nations will grow from 192 million in 2000 to 196 million in 2025, whereas the population of the southern- and eastern-rim nations will grow from 235 million to 327 million. As a result, the population in the coming years will increase and become younger in the south. With this shift, problems in education and job-creation will become critical in southern Mediterranean countries.

Finally, it should be pointed out that because of both climate and historical/archaeological significance, the Mediterranean continues to be the greatest tourist destination in the entire world. Concurrently, tourism is the greatest consumer/user of the Mediterranean coast. In 1984, for example, there were about 100 million tourists in coastal areas, whereas the number could rise to 200 – 340 million by the year 2025 (Grenon and Batisse, 1989). Such a growth will mean an increasing demand for coastal space as well as such commodities as electric power and water. Furthermore, the impact on certain habitats (particularly sandy beaches and dunes) will also increase. However, the economic importance of tourism for the Mediterranean is such that no riparian countries can do without this sector.

1.3.2 Industrial activity

The industrial structure in the region is likewise heterogeneous in terms of sectors and size of enterprises. The sector stretches from extraction activities, iron and steel, cement works and petrochemicals to agriculture activities, leather, paper and agribusiness. Taking into consideration the world's most important raw materials, the Mediterranean countries production of mercury (Spain), phosphates (Morocco, Tunisia and Jordan), chromite (Turkey), lead, salt, bauxite (Bosnia, Croatia, France, Greece, Slovenia and FR Yugoslavia) and zinc (Spain and Morocco) is higher than the world average. Steel manufacturing is concentrated in the north whereas oil and gas production is limited to the south, representing a production capacity of 4.55 million barrels/day.

The North-western part of the region is highly industrialised, receiving multiple sources of pollution through continental runoff, sewage sludge disposal, river inputs (Po, Rhone, Seine and Ebro) and atmospheric transport. However, as a result of oil-refining and transportation, the South Mediterranean countries are also highly polluting their coastal environments. In terms of added value in the manufacturing industries, which are much more important than the extractive industries, France and Italy together account for 72%, followed by Spain (15%), FR Yugoslavia and Turkey (3.6% each), and the rest (6%), out of a total of almost 600 billion dollars. At 7.3% of the world population, the region contributed 16% of the world production.

Looking at the industrial activities from the standpoint of the relative importance of export-import production, one can distinguish three groups of countries:

- Countries specialised in some export products, like oil and gas, the rest being imported, such as Algeria, Syria, Libya and Egypt, although the latter also produces some manufactured goods (e.g. textiles, shoes, etc.)

- Countries less specialised and with more diversified exports like Tunisia, Morocco, Turkey, FR Yugoslavia, Cyprus, Malta.
- Countries strongly diversified such as the EU Member States.

Industry frequently coexists with tourism along the coastal areas of the region, together with coastal overpopulation and proximity to large cities. Industry is even frequently located within the actual urban nuclei. All these factors, and this situation in general, mean that industrial activities are currently faced with environmental constraints.

The Mediterranean Sea, being part of the Atlantic Ocean, is also in the origin of ultramarine activity. Ports like Alexandria, Piraeus, Genoa, Marseille and Barcelona have been the bases of much of the transatlantic trade as some of the countries build their empires overseas. In modern times, the Straits of Gibraltar and the Sicilian Channel have become some of the more frequented passages for commercial, leisure and military navigation. The Dardanelle and the Bosphorous, joining the Black Sea to the rest of the world, are also an important passageway for all kinds of shipping. Around 200000 commercial vessels ply the Mediterranean annually, a large number visiting one of the 305 ports therein (approx. 1 port every 150 km of coastline).

1.3.3 Natural resources

Mediterranean countries mostly lack natural resources. Nevertheless, important mining and oil/gas producing activities exist. Libya, Algeria and Egypt are considered moderate-sized petroleum and gas producers. Morocco is the world's third-largest producer of phosphate ores, Albania the third-largest producer of chromium and Spain the second-largest producer of mercury.

Water resources are relatively plentiful in the north but scarce in the east and south. Forests have limited economic significance, but are important for the preservation of soil as for recreation and landscape. Though their surface is growing in the North due to abandonment of cropland, it is in clear regression in the South and East. Average wood biomass in the European countries is 84 m^3/ha, while in southern and eastern countries it is approximately 18 m^3/ha. A common problem existing all around the region is the high frequency of forest fires reaching great magnitude in relation to their extension (see section 1.2.3).

Mediterranean agriculture is characterised by long-term misuse and over exploitation. In part, this is due to generally poor soils, lack of rain and the increasing population pressure (particularly in the south). As a result, the agriculture in the region is characterised by multi-faceted crops, mainly aimed to meet the food demand of the resident population. In addition to more general crops such as cereals, typical Mediterranean products are olives, citrus fruits, grapes and hard grain. The main livestock is sheep. Increasingly, irrigation is needed in the south to maintain or increase crop production. While coastal regions tend to have little agricultural land, it often is of high quality, particularly around delta areas. The percentage of the agriculture in the GDP of the region is under 20%.

The Mediterranean Sea is highly oligotrophic, with primary productivity ranging from 50 to 150 mg C/m^2/y, with a net decrease towards the eastern basin. However, higher productivities are found both in shallow areas supported by fluvial nutrient inputs and by upwelling induced by very active water circulation processes. The Mediterranean Sea fish supply does not match the consumption of the local population. More than 50 % of fish consumed in the region is originated in long-distance fisheries from all over the world ocean. Most demersal fish stocks along the northern coasts of the Mediterranean are heavily fished and the introduction of regulatory measures is necessary to maintain high levels of yield and catch. Pelagic fish stocks are also endangered. Increasing coastal pollution may affect not only coastal fishing activities but also limit the extent to which aquaculture may be developed.

1.3.4 Socio-economic indicators

The wide variation in political and economic systems as well as historic differences have led to great discrepancies in the level of development between Mediterranean countries. The highly developed industrial countries in the North (e.g. France, Italy and Spain) and countries on the way to become industrialised (e.g. Greece and Turkey) stand in stark contrast to the countries in the south. For instance, in 2000, the Gross National Product per Capita ranged from around 24000 USD in France and Italy to around 3500 USD in Albania, Morocco or Egypt, although the annual growth rate during the 90's was in general slightly higher in the latter countries (UNDP, 2002).

The large spread between the northern-rim and the southern- and eastern-rim nations is also reflected in other indicators such as, for example, the public expenditure on health and education, the life expectancy at birth and the adult illiteracy rate. On the other hand, the northern countries are, in general, disbursing official development assistance to third countries, not necessarily in the region, whereas those in the south are primarily receivers.

These differences have significant implications for the establishment of environmental standards in the countries of the Region because there is a clear relationship between GDP, expenditure in education and the application of environmental control and environmental management. Countries that cannot satisfy the basic needs of their citizens cannot afford to digress into environmental management systems and these are only applied once a certain GDP threshold is attained.

This socio-economic context has also important consequences when addressing the potential technology transfer issues. Proper technology transfer opportunities can be created by making emphasis on education, social and environmental awareness and through the creation of long-term networks of scientific and technical collaboration among the countries of the Region. At the same time, the opportunities created by the increased internationalisation of the markets have to be monitored by the public administrations of the receiving countries, as well as by the stakeholders, so that the environmental standards are kept throughout the process. It is clear that the northern countries bear much of the responsibility of the actions taken, or not taken, today and over the past two centuries that shape the present state and delineate the future.

Finally, consumers from the more developed countries play an important role in defining the ethical and environmental standards for the goods they consume, which more and more are being grown and manufactured in the less developed countries of the Region. Hence, this could also be a driving factor for environmental progress.

1.4 SCOPE OF THE REGIONAL ASSESSMENT

1.4.1 Existing assessments

The Mediterranean region, embracing parts of two continents as diverse as Europe and Africa, has benefited of the adoption by the bordering countries, in 1975, of the Barcelona Convention for the Protection of the Mediterranean Sea. The initial focus of the Convention and of the associated Mediterranean Action Plan (MAP) was primarily on marine pollution. However, experience soon confirmed that poor management and planning of development were the roots of most environmental problems. Therefore, focus of the action plan gradually shifted from a sectorial approach to integrated coastal zone planning and management as the key tool through which solutions can be attained. Thus, during the last 20 years the Unit responsible in Athens (Greece) for the implementation of the Convention and its Protocols has carried out a series of activities aiming, on one hand, to the improvement of knowledge on the sources and fate of pollutants in the marine environment, and on the other, to the definition of strategic interventions under the provision of the Strategic Action Program (SAP) which address a list of priority substances, including PTSs. More than 100 Technical Reports have been produced to assess the state of the pollution by petroleum hydrocarbons, organohalogen, organotin and organomercury compounds, carcinogenic substances, etc. as well as the biological effects of pollutants and the identification of hot spots and sensitive areas, which constitute a valuable source of information and a diagnostic tool. Actually, the MEDPOL data bank includes a large inventory related to chemical contaminants in biota (over 15000 samples for 50000 analyses of heavy metals and halogenated hydrocarbons). Moreover, two overviews “The State of the Marine and Coastal Environment in the Mediterranean Region”, issued in 1989 and 1996, are of basic reference (UNEP, 1989 and 1996).

More recently, the European Environment Agency has published, with the co-operation of the UNEP/MAP Unit, the monograph “State and pressures of the marine and coastal Mediterranean environment” (EEA, 1999), following the DPSIR assessment framework (Driving forces/Pressures/State/Impacts/Response) developed by EEA, and describes the various interactions between human activities and the environment.

On the other hand, in 1973 the European Commission (EC) began supporting research into the physico-chemical processes which govern the dynamics of air pollutants in various regions of Europe, including the Mediterranean region. A driving and particularly important issue at that time was to make sure that the models affecting directives and important economic decisions were appropriate. Major aims of these projects (e.g. MECAPIP, RECAPMA, SECAP and T-TRAPEM) were the characterisation of pollutants dispersion in southern European regions and the issues of monitoring networks. Later, in early 90’s, started to launch within

their Framework R+D Programmes, targeted actions on the Mediterranean that besides a major emphasis on oceanographic research (e.g. MAST initiatives) also included the scientific assessment of environmental pollution. Projects on biogeochemical processes of pollutants in the coastal zones (EROS 2000), the assessment of antifouling agents (ACE), bioaccumulation of persistent organic pollutants in small cetaceans (BIOCET), biological effects of marine pollution (BIOMAR and BEEP), or atmospheric deposition and impact of pollutants on the open Mediterranean (ADIOS) are some examples of the initiatives funded, which have contributed to transfer up-to-date methodologies and to develop advanced studies in the region. As a result, environmental information on PTSs in the region has been significantly improved during the last 10 years, and can be found in the open literature.

Moreover, co-operation has been extended to southern bordering countries through the Avicenne Initiative (1993-97), INCO-DC (1997-2001), MATER (1996-2000) and FP5 (1999-2002), covering areas of action such as organic pollutants and their effects on the environment and the evaluation of risks to human health. The participation of North African countries has been, however, very limited.

Finally, there are a number of international initiatives which pay also attention to environmental problems of PTSs and concern some particular countries in the region. Among these are the Convention on Long-Range Transboundary Air Pollution (LRTAP) under the auspices of the UN Economic Commission for Europe (UNECE), the Basel Convention that regulates the transboundary movement of hazardous wastes, which may include PTSs, the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, and the recently adopted Stockholm Convention on persistent organic pollutants. On the other hand, a number of regional organisations have already conducted assessments of persistent toxic substances. Where they exist, the present project will rely on these assessments which include, for example, the work accomplished in the European Union through the Dangerous Substances Directive and the Quality Status of the North East Atlantic completed by the Oslo and Paris Commission (OSPAR).

In this respect, the countries also facing the Atlantic Ocean, namely Portugal, Spain and France, are members of OSPAR. The general objective of OSPAR is to prevent and eliminate pollution of the maritime area of the Convention and to ensure that the ecosystems of the maritime area are in a sustainable, sound and healthy condition and that human health is protected. In 1998 and 1999 the Commission adopted strategies for the purposes of directing its work in the medium to long term in several areas, including the area of hazardous substances. To this end, lists of priority pollutants including POPs have been compiled and updated from time to time. Monitoring activities and risk assessment studies have been implemented together with a constructive dialogue on the reduction of these substances with all parties concerned, including producers, manufacturers, user groups, authorities and environmental NGOs.

Within the framework of the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP), a number of workshops on persistent organic compounds have also been held, where series of measurements and atmospheric transport modelling of POPs over Europe were recommended. POPs contamination has been assessed for countries which are entirely covered by EMEP region: Albania, Bosnia-Herzegovina, Croatia, Cyprus, France, Malta, Greece, Italy, Portugal, FR Yugoslavia (Serbia and Montenegro), Slovenia, Spain, the FYR of Macedonia, Turkey, Lebanon, Palestine, Tunisia, Andorra, San Marino, Monaco, Mediterranean Sea. Information on POPs contamination includes distribution between environmental media, concentration and deposition fields, and contamination trends. Besides this, preliminary results on transboundary transport of some PTSs and their depositions to individual sub-basins of Mediterranean Sea have been obtained (see section 4.1).

All these activities have produced information relevant for the Project, which represents the higher effort carried out to date for a global assessment of PTSs.

1.4.2 Selection of PTSs of concern in the Region

The compounds of priority consideration were the twelve POPs included in the Stockholm convention. They are classified into three groups, pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene), industrial compounds (polychlorinated biphenyls) and unintended by-products (dioxins and furans), although one compound, hexachlorobenzene, belongs to all three.

The UNEP assessment allows as well for adjustments to the list of chemicals to be reported in the regional reports, based on regional priorities and data available. In the case of the Mediterranean region, other organohalogen compounds were also included, namely lindane, chlorophenols, and PBBs and PBDEs, as well

as organometallic compounds (organomercury and organotin), polycyclic aromatic hydrocarbons (PAHs), phthalates and alkylphenols.

The description of all these PTSs, regarding their main properties, uses, and environmental behaviour and toxicity, are summarised in Annex II.

1.4.3 Literature survey

As background material for the assessment a literature survey was used, performed for the candidate substances and the countries involved in the study, and covering the years 1980-2001. The survey provided 2331 references, which were organised in a database Manager programme for an easy retrieving. Among these references, 70 were reviews about different topics on PTSs in the region.

The analysis of the regional database (Table 1.1) showed that among the twelve POPs included in the Stockholm Convention, PCB, DDT and dioxins and furans were those PTSs accumulating the higher number of references. A preliminary search about other PTSs candidates seemed to indicate the interest of including in the assessment compounds such as PAHs, HCH (lindane), organomercury and organotins, phthalates, alkylphenols and brominated flame retardants.

Table 1.1. Literature survey (1980-2001)

	Aldrin	**Dieldrin**	**Endrin**	**Chlordane**	**Heptachlor**	**DDT**	**Toxaphene**	**Mirex**	**HCB**	**PCBs**	**PCDD/F**
Albania	0	1	0	0	0	2	0	0	0	0	0
Algeria	0	1	0	0	0	3	0	0	1	1	0
Andorra	0	0	0	0	0	0	0	0	0	0	0
Bosnia-H.	2	2	1	0	2	2	0	0	0	1	0
Croatia	5	9	3	0	7	34	0	0	12	35	7
Cyprus	0	0	0	0	0	1	0	0	0	1	0
Egypt	29	30	31	14	18	71	3	3	18	27	4
France	7	15	1	1	14	49	0	0	17	98	28
Greece	9	15	8	1	14	31	0	0	7	28	9
Israel	2	3	0	0	5	15	0	0	3	12	4
Italy	18	19	9	1	25	146	0	0	59	206	194
Jordan	6	6	5	1	6	8	0	0	4	3	0
Lebanon	0	0	0	0	0	2	0	0	0	0	0
Libyan A.J.	0	0	0	0	0	1	0	0	0	1	0
FYR Macedonia	1	3	2	0	3	4	0	0	0	0	0
Malta	1	0	0	0	0	0	0	0	0	0	0
Monaco	0	0	0	0	0	1	0	0	1	10	0
Morocco	3	3	2	0	2	2	0	0	3	1	0
Palestine	0	0	0	0	0	1	0	0	0	1	4
Portugal	4	4	2	0	2	10	0	0	2	13	10
San Marino	0	0	0	0	0	0	0	0	0	0	0
Slovenia	0	2	0	0	2	4	0	0	1	16	0
Spain	40	48	28	9	46	135	2	1	70	161	96
Syrian A.R.	1	0	0	0	0	0	0	0	0	1	0
Tunisia	0	1	0	0	1	6	0	0	4	1	0
Turkey	16	14	9	4	13	29	0	0	15	9	0
FR Yugoslavia	9	9	3	3	10	35	2	0	9	31	5
Total	**167**	**203**	**104**	**56**	**168**	**614**	**7**	**5**	**227**	**686**	**365**

Table 1.1. Literature survey (1980-2001) (cont.)

	Lindane	PCP	PBB/ PBDE	PAHs	Phthalates	Alkyl phenols	Organo-tin	Organo-mercury	Organo-lead	Total countries
Albania	0	0	0	1	0	0	0	0	0	**3**
Algeria	3	0	0	3	0	0	0	0	0	**9**
Andorra	0	0	0	0	0	0	0	0	0	**0**
Bosnia-H.	2	0	0	2	0	0	0	0	0	**6**
Croatia	24	2	0	15	1	4	0	1	2	**85**
Cyprus	0	0	0	1	0	0	0	0	0	**3**
Egypt	57	2	0	8	12	0	1	0	2	**137**
France	59	5	0	93	7	2	15	1	6	**320**
Greece	33	0	0	30	1	0	1	0	1	**122**
Israel	8	1	0	2	3	8	0	0	0	**43**
Italy	55	1	0	185	30	8	15	7	0	**771**
Jordan	6	0	0	2	0	0	0	0	0	**18**
Lebanon	0	0	0	0	0	0	0	0	0	**2**
Libyan A.J.	1	0	0	0	0	0	0	0	0	**1**
FYR Macedonia	3	0	0	2	0	0	0	0	0	**7**
Malta	0	0	0	0	0	0	0	0	0	**1**
Monaco	2	0	0	2	2	0	1	0	0	**16**
Morocco	3	0	0	1	1	0	0	0	0	**11**
Palestine	0	0	0	0	0	0	0	0	0	**6**
Portugal	3	0	0	4	0	0	0	0	0	**47**
San Marino	0	0	0	0	0	0	0	0	0	**0**
Slovenia	4	0	0	4	0	0	0	0	0	**26**
Spain	103	7	1	75	11	12	18	2	1	**516**
Syrian A.R.	0	0	0	3	0	0	0	0	0	**5**
Tunisia	3	0	0	1	0	0	0	0	0	**11**
Turkey	16	0	0	3	0	0	2	0	0	**43**
FR Yugoslavia	29	0	0	14	2	0	0	0	0	**83**
Total	**402**	**18**	**1**	**457**	**70**	**33**	**47**	**11**	**12**	**2331**

Some temporal and geographical trends were identified and a compartment (air, water, sediment, soil/sludge, human, animals, etc.) analysis was also completed.

The major outputs of the database were:

- The identification of regional experts on the different topics to be covered,
- Background information, complementary to that of the questionnaires, for the Regional Team about sources, levels, health effects, etc.

The whole literature database is available as a Report Annex, in the website of the project: www.chem.unep.ch/pts.

1.4.4 Other information sources

The materials presented in the Regional Workshops and the Priority Setting Meeting provided access to valuable unpublished data, which have been collected in the website of the project.

The following international organisations, among others which are cited along the report, may also provide information on several aspects dealt with in the report:

- Chemical Safety Information (http://www.inchem.org)
- Cleaner Production Centres (http://www.cipn.es)
- European Environment Agency (http://www.eea.eu.int)
- EU, Environment DG (http://www.europa.eu.int/comm/environment/index_en.htm)
- European Chemicals Bureau (http://ecb.ei.jrc.it)
- European Chemical Industry Council, CEFIC (http://www.cefic.org)
- Euro Chlor, representing the Chlor-Alkali industry (http://www.eurochlor.org)
- Food and Agriculture Organization, FAO (http://www.fao.org)
- MSC-E (EMEP) (http://www.msceast.org)
- OSPAR Convention (http://www.ospar.org)
- UNECE (http://www.unece.org)
- UNEP/MAP (http://www.unepmap.org)
- World Health Organization, WHO (http://www.who.int)

1.4.5 Overview of limitations and omissions

The activities undertaken in the project were not aimed to produce new data on PTSs but to assess the existing ones on sources, environmental levels, transport pathways and effects, on the alternatives to their use and remedial options, and to identify the barriers that prevent their good management. As a project of such broad scope has never been carried out in the region, a major difficulty encountered was the identification and active involvement of the different sectors. The responses were very different between members of the academic community, the administration and the private sector. A potential source of contributions such as that of the Focal points was also very irregular because some lack of members updating and the weakness of their commitment for such an exercise.

The definition of the region as Mediterranean and the inclusion of some countries which do not border the sea or also border other marine regions (e.g. the Atlantic) has introduced some difficulties in the treatment of the information. In this respect, information was sometimes unexpectedly biased, and the presentation of the regional pathways was not always coherent.

In spite these limitations and the short time available, the exercise was feasible on the basis of data and information published in the open literature and collected through the activities developed within the Project, particularly the Technical Workshops and the Priority Setting Meeting.

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2 SOURCE CHARACTERISATION

For many Mediterranean countries no detailed information exists on the releases of PTSs from point sources (industry and urban centres). In general, the local or national authorities do not routinely monitor most of the PTSs considered. Therefore, no data sets are available for an adequate assessment. On the other hand, larger, multinational companies often have information regarding the amount of PTSs used, produced and/or emitted by their plants in the Mediterranean region. However, the predominant small and medium enterprises in the area do not have either the means, or the required know-how to monitor PTSs.

The definition of sources for most PTSs has to take into consideration the fact that most of the concerned compounds have been banned in the majority of the countries of the Region. Hence, the main sources will consist on stockpiles and inventories due to former production and/or import, and more importantly the compounds present in the main environmental vectors and reservoirs due to previous chronicle usage and in accidental spills. The contribution from industrial production will only be important for those cases where some restricted usage of the PTSs is allowed (i.e. DDT as precursor of Dicofol) and for the PTSs that are generated as inadverted secondary products (i.e. PAHs and PCDDs from combustion).

2.1 PRODUCTION AND USE DATA FOR PERSISTENT PESTICIDES

An important effort was made in the first Regional Workshop on PTSs sources (Athens, 2002; Annex I.i), to identify the main PTSs sources. For the pesticide compounds the following Table 2.1 was agreed upon. The environmental vectors and reservoirs shown in bold are thought to be the main sources of pesticide PTSs in the region.

Table 2.1. Main sources of chlorinated pesticides to the various environmental vectors and compartments. Main vectors and reservoirs are shown in bold.

	Air sources	*Water sources*	*Soil sources*	*Sea*
Chlorinated pesticides	▪ **Agricultural usage** ▪ Spraying/Land application ▪ Production	▪ **Agricultural usage** ▪ **Run-off** ▪ Production	▪ **Stockpiles** ▪ Production waste ▪ **Misuse**	▪ Agricultural run-off ▪ **Major rivers and drains** ▪ **Atmospheric deposition**

This is in agreement with a previous overall study of the state of the Mediterranean Sea published by MEDPOL in 1996 (UNEP, 1996). In this study it was found out that pesticide pollution in the sea mainly comes from agricultural run-off and major rivers (see section 4.2.2). In particular, pesticide discharges are largely due to soil erosion in the Mediterranean watershed. However, it was assessed that the contribution from agricultural run-off within the coastal area was a fraction of the pollution loads carried by rivers into the sea. The air-borne load of pesticides could not be included in the study due to the lack of data. Therefore, it was concluded that rivers and drains carry most of the pesticide residues from agricultural areas in the Mediterranean watershed.

2.1.1 General situation in the Region

2.1.1.1 Production and use of chlorinated pesticides in the Region

Organochlorine pesticides have been largely used in the Region, but their production and usage is banned in the majority of the countries of the region as a consequence of the application of the PIC protocols, with some exceptions which will be discussed below. Aldrin, dieldrin, heptachlor, chlordane and HCHs are prohibited in the EU for plant protection whereas for other applications a written authorisation for import is needed. Endrin and mirex are not subjected to the PIC procedure although many countries have banned its use (PIC, 2002). Specific exemptions have also been requested by Algeria (chlordane, DDT and heptachlor) and Morocco (DDT) in the framework of the Stockholm Convention.

DDT is the only organochlorine pesticide that is still currently in production and use in the Region. In some Mediterranean countries both in the north and south side some specific uses are still in practice. DDT is also an intermediate in the production of dicofol and production for export still occurs for this purpose in Western

Europe. For example, Italy imported, in 1998, 1200 tonnes from Mexico to convert it totally in dicofol. At the same time, a decline has been noted for amounts of DDT used for agriculture in developing countries.

In European countries of the region, till middle nineties, EniChemi Synthesis produced DDT at Pieve-Vergonte, in Italy, at a 6000 tonnes per year rate, which was sold, among others in the region, to Rohm and Haas Italia Srl, Industrias Produtti Chimici SpA (Italy), and Lainco SA (Spain). The producer Elf-Atomchem had a 10000 tonnes per year plant at Jarrie (France) that was closed in 1988. DDT is at present being produced as a precursor of dicofol in the Montecinca factory, located close to Huesca (Spain) at a yearly rate of 1500 tonnes.

Hexachlorobenzene was also produced in the region up to the mid 80's, particularly by the Ercross factory located in Flix (Spain), some 200 km up from the Ebro delta. The annual production was in the order of 1000 tonnes/year. This has had as a consequence the presence of particularly high HCB levels in the area, as it will be discussed in chapter 3. HCB is included in the PIC procedure and banned in most countries of the Region.

The industrial and socio-economic structure of the Region implies that the Northern countries have been producers and users of chlorinated pesticides, while at present are mainly producers and exporters. On the other side, the Southern ones are mainly users of these substances. This was particularly critical when some of the pesticides were banned in the European countries of the region and their unwanted stocks were dumped in the Southern parts of the Region. These fluxes are largely unknown but some of their consequences are still apparent when looking into the environmental levels of some of the receptive countries.

Because of its intensive and extensive agricultural production Egypt is, through the Nile basin, a potentially large source of pesticides into the Mediterranean. In the period between 1952 and 1981 more than 13000 tonnes of DDT, 54000 tonnes of toxaphene, and 10500 tonnes of endrin (together with 11300 tonnes of lindane) were used (El-Sebae et al., 1993). Presently, the application of pesticides has decreased in the country, according to the data provided by the Ministry of Agriculture, from 20500 tonnes in 1980 to 16435 tonnes in 1995. As chlorinated pesticides are banned, the majority of these pesticides are presently organophosphorous compounds.

The same applies for Turkey where in 1978 up to 1700 tonnes of chlorinated pesticides were used (Kolankaya and Ayas, 2002), while now some 36 tonnes of pesticides are organohalides of the total 41000 being used in the country.

2.1.2 Hotspots, abandoned inventories and stockpiles in some countries of the Region

The available information concerning the remaining stockpiles of pesticides in some of the countries of the region is summarised in Table 2.2. It is clear that this Table is far from being complete, but it is expected that FAO database will be updated as new inventories are performed, so a key priority should be to establish a realistic inventory of abandoned pesticides in the Mediterranean region. As an example, there is information in Syria about a stock of obsolete pesticides of some 230 tonnes (although other data sources indicate a stock of 325 tonnes), which include some of the PTSs. Another example is found in Turkey, where since 1960 a considerable number of synthetic organochlorine pesticides have been produced for use against pests, including DDT. Of this last substance there is a reservoir in Kirikkale, with an amount of 10930 kg stored (Rejic Saydam Hygiene Institute).

In Tunisia, some preliminary studies revealed, in 1997, the existence of obsolete pesticides containing mostly HCHs, DDT and other organochlorines. These stocks were created mostly through massive provisions in order to fight against migratory pests such as locust and some date back more than 20 years. The stocks of obsolete or unwanted pesticides were estimated in 1997 to be approximately 882 tonnes. An additional problem to the existence of these old stocks is that, in some cases, banned pesticides continue to be used in practice under no control of the authorities.

Some accidents and spills have also been a source of pesticide hot spots. For instance, the large contamination that occurred in the area of Pieve Vergonte, a large industrial site in the Piemonte region, at north of Italy, had important consequences. The origin of DDT pollution was due to large spills from the factory EniChemi Synthesis, where 6000 tonnes per year were produced. It was estimated that 1000 tonnes was spilt, which for more than 40 years produced, among other substances, considerable quantities of organochlorine compounds, including DDT. Consequently, this episode of contamination extended over the River Foce that flows into Lago Maggiore. Due to the magnitude of the pollution, this has been considered a high priority area, and different actions of remediation and environmental restoration have been undertaken.

Table 2.2. Some referenced pesticides stocks in countries of the Mediterranean region (FAO, 2002).

Country	Location	PTSs	Container type	Container condition	Kg
Algeria	Tipaza	Aldrin	Metal	?	25
	Alger	Aldrin	Metal	?	320
Lybia	Tripoli-Bengazi-locust	Dieldrin	Cardboard	Bad	20 (1950)
Morocco	?	Dieldrin	?	?	880
	?	Endrin	?	?	122
	?	Heptachlor	?	?	2626
	?	DDT	?	?	2062
Syria	Hamah	DDT	Cardboard	Good	1500
Algeria	Ain Temouchent	DDT	Kraft	?	5000
	Alger	DDT	Plastic	?	1000
	Mustaganem	DDT	Kraft	?	180000
	Sidi bel Abbas	DDT	Kraft	?	2000
	Tizi Ouzou	DDT	Kraft	?	1075
	Mascara	DDT	Metal	?	1400
	Tipaza	DDT	Kraft	?	425

Other indications for accidental contamination from pesticides have arisen in Croatia where during the period 1976-1981, an intensive ecological investigation of the Rijeka Bay aquatic ecosystem was performed. A significant portion of the investigation concentrated on determining the extent of pollution from persistent chlorinated hydrocarbons, particularly on the distribution of DDT and its metabolites, as well as dieldrin and PCBs in various parts of the Bay ecosystem. The conclusion was that the investigated pollutants had been introduced into the Rijeka Bay from the atmosphere and through various local sources of pollution including urban and industrial wastewater, maritime activities, insecticides used on trees in recreational areas, etc. Ten years later the levels were significantly lower for DDTs but not for PCBs.

Another remarkable event occurred around the Black Sea and across Turkey because of the run-off of DDT coming from rivers from the nearby states and favoured with wind and rain, which caused serious problems to land, freshwaters and also to the Mediterranean Sea.

2.2 SOURCES OF INDUSTRIAL PERISTENT TOXIC CHEMICALS

2.2.1 General situation in the Region

PCB containing equipment has been largely used in the Region. The total production of PCBs in some European countries of the Region (e.g. France, Italy and Spain) has been estimated to be about 300000 tonnes for the period 1954-1984. This is some 15% of the total accumulated world-wide production (De Voogt and Brinkman, 1989). The production was stopped in 1985 in France, and in 1987 in Spain.

The first regulation on PCBs applied by the EEC was in 1976 when their usage was restricted to closed circuits; the second one, in 1985, when the use of PCB as a raw material or chemical intermediate was banned. Finally, in 1987, the usage of PCBs was completely banned in new closed circuits and a Directive issued in September 1996 (96/59) imposes the total elimination before December 2010. The UNEP Strategic Action Program for the Mediterranean has also included the phasing out of PCBs in 2010 (UNEP/MAP, 1999).

PCB are part of the PIC procedure followed by most countries of the Region. Details on the degree of commitment to the procedure by the various Mediterranean countries are given in Annex III. In spite of the legislation in force, there are still large amounts of PCB in use. This is because in many countries (e.g. Algeria, Croatia, FYR of Macedonia, Morocco and Slovenia), there are exemptions for restricted uses in devices in use for long duration. Moreover, there are stockpiled amounts waiting to be eliminated.

Studies performed in the last five years give substantial signs about the location of PCBs environmental pollution in the EU. Recent studies concerning the human intake of PCBs indicate that PCB exposition has increased (Draft report on implementation of Directive 96/59/EEC, 2000).

There is a general agreement that the disposal of equipment with PCB containing oils is the main source of PCBs in the Region. PCB production and usage has been linked to economical development before the use of the substance was banned. Hence, the main stockpiles of PCB equipment will reside in the northern parts of the region, where appropriate management of the PCB wastes has not been fully implemented. The less developed countries have their share of PCB stocks due to the import of PCB containing equipment without the appropriate environmental infrastructure to manage its disposal.

Only France has, at present, an installed capacity for incineration of PCB residues in the region, amounting 22000 t/y. Spain will have to get and provide, at least, an incineration capacity of 5000 t/y. Decontamination of materials and oils containing PCBs is ensured by national companies.

2.2.1.1 PCB situation in the various countries

There is not a uniform information regarding the statistics of actual uses and stocks of PCBs for the countries of the Region. The temporal trends of PCB uses are only available in a limited fashion for France and Italy, as a result of a EU study on the commercial transactions of PCBs in five European countries. In Table 2.3 the data collected in this study, which refers to the years 1973 and 1980, is presented.

Table 2.3. Development of PCB stockpiles in the northern countries of the Region.

Year	**1973**			**1980**	
Country	**France**	**Italy**	**Spain**	**France**	**Italy**
Production	9674	2519	1935	6577	1479
Import	525	1547	217	74	
Export	6136	1107	0	4848	1356

The data show a clear decreasing trend in all commercial operations related to PCB containing equipment in both France and Italy. A first inventory built up in France in 1987 reported that the number of installed transformers containing at least 100 kg of PCBs was at the time 100000 units, corresponding to 50000 tonnes of fluids with 60 % of PCBs (*Pyralène*) and to 50000 tonnes of carcasses with 5% of PCB residues. The 250000 medium voltage capacitors represented about 3000 - 5000 tonnes of pure PCBs. The low voltage capacitors appeared to represent 1500 - 2000 tonnes of hardly extractable PCBs. For Spain, the inventory made in 1997 by the Ministry of Environment indicated and existence of 6004 tonnes of PCBs, although the amount of materials containing or contaminated with PCBs may reach the 200000 tonnes.

From 1996 to 2001, France has eliminated on average 20000 tonnes per year of PCBs. The hazardous residues containing PCBs eliminated during the period 1992-99 in Spain was of 15334 tonnes. This is relevant information as it covers the main producers and users of PCBs in the Region.

A good example of international collaboration in the assessment of PTSs inventories is given by the Croatia case. A very thorough study concerning PCB containing equipment has been done (Table 2.4), which also gives a clear decreasing trend in the PCB use through the 70's, 80's and 90's.

Table 2.4. Inventory of electric devices containing PCBs in Croatia (UNEP, 2000)

Year of installation	**Industry and other sectors**		**Electricity plants**		**Total**	
	Number	Tonnes	Number	Tonnes	Number	Tonnes
Capacitors						
Until 1970	6630	150	1250	34	7880	184
1971-1975	6100	157	790	25	6890	182
1976-1980	4170	130	1900	47	6070	177
1981-1991	1800	70	740	14	2540	84
Total	18700	507	4680	120	23380	627
Transformers						
1970-1991	300	720	15	54	315	774
Subtotal	19000	1227	4692	174	23695	1401

In spite of the lack of homogenous data an attempt has been made to give a comparison of the main PCB stocks which reside in the various countries of the Region. These data should only be seen on the relative scale since it lacks the accuracy to make it valuable in the absolute sense.

Table 2.5 gives an indication about the main countries where the PCB stocks still reside and the percentage of the cumulative amounts by mid 90's. There is a clear need for a more systematic survey concerning the actual stocks of PCBs in the various countries of the Region.

Table 2.5. Relative country contributions to the cumulative stockpiles of PCBs in the Region at mid 90's.

Country	PCB inventories (tonnes)	% of Total PCB Stock in the Region
Spain	5972	24%
France	5846	23%
Italy	3872	12%
Algeria	3055	12%
Croatia	2082	11%
Greece	1768	7%
Tunisia	2000	8%
Portugal	657	3%
FR Yugoslavia (S & M)	197	1%

An additional source of PCBs is provided by their content in sewage sludge and the subsequent management of these sludges. The three major sewage sludge producing countries, France, Italy and Spain generate some 2350 tonnes of sludge per year. The three main lines of management of the sludge are: soil application, either for agricultural purposes or as plain landfilling (99% in Italy), incineration (15% in France) and sea dumping (24% in Spain). If we take into consideration the average PCB content in sewage sludge, some 0.4 tonnes/year of PCBs are inputted into the soil (either through land application or landfilling), some 0.03 tonnes/year are returned to the atmosphere and an additional 0.03 tonnes/year are dumped into the sea..

2.3 SOURCES OF UNINTENTIONAL PERSISTENT TOXIC BY-PRODUCTS

Polychlorinated dioxins and furans (PCDD/Fs) occur as trace contaminants in a variety of industrial and thermal processes. As a consequence, dioxins from so-called "primary sources" can be transferred to other matrices and enter the environment. Such "secondary" sources are sewage sludge/biosludge, compost, or contaminated areas. Enzymatic reactions can dimerize chlorophenols to PCDD/Fs. However, compared to chemical-industrial and combustion sources, biological formation seems to be negligible.

2.3.1 Primary Sources of Dioxins/Furans

2.3.1.1 Industrial-Chemical Processes

One main primary source of PCDD/Fs was, in the past, the production and use of chloro-organic chemicals, including use in the pulp and paper industry. Changes in the industrial processes have resulted in reduction of PCDD/Fs concentrations in the products. In addition, the interdiction of some of these products has decreased the emission of dioxins from this source. Wood treated with pentachlorophenol (PCP) or other chlorinated preservatives, as well as PCB-based electric fluids, are other actual sources.

2.3.1.2 Thermal Processes

The present inputs of dioxins are largely due to thermal processes. There is still a considerable focus on waste incineration but based on the requirements for dioxins reduction in stack gases set by several national authorities, the importance of this source category has declined during the last years in some countries.

An overview on combustion sources known to generate and to emit PCDD/Fs is shown in Table 2.6. It should be mentioned that PCDD/Fs are not only found in the stack gases but also in the solid residues from any combustion process, *e.g.* bottom ashes, slags, and fly ash. With advanced technology and better burn-out of the ashes and slags (characterised by a low content on organic carbon), the PCDD/Fs concentrations decline.

Table 2.6. Primary sources of dioxins

Stationary sources	
Waste incineration:	municipal solid waste, clinical, hazardous waste, sewage sludge
Steel industry:	steel mills, sintering plants
Recycling plants:	non-ferrous metals (foundry, Al, Cu, Pb, Zn, Sn)
Energy production:	fossil fuel power plants, wood combustion, landfill gas
Diffuse sources	
Traffic:	automobiles
Home heating:	coal, oil, gas, wood
Accidents:	PCB fires, fires in buildings

2.3.2 Secondary Sources of PCDD/Fs (Reservoirs)

Dioxin reservoirs are those matrices where PCDD/Fs are already present, either in the environment or as products. The PCDD/Fs found in these reservoirs are not newly generated but concentrated from other sources. A characteristic of the reservoir sources is that they have the potential to allow re-entrainment of PCDD/Fs into the environment. Product reservoirs include PCP-treated wood, PCB-containing transformers and sewage sludge, compost, and liquid manure, which can be used as fertilisers in agriculture and gardens. Reservoirs in the environment are for example landfills and waste dumps, contaminated soils (mainly from former chemical production or handling sites), and contaminated sediments (especially in harbours and rivers with industries discharging directly to the waterways). So far, hardly any country has done a reservoir inventory for PCDD/Fs.

2.3.3 Emission inventories of relevance for the Region

In the early 1990s, many industrialised countries initiated national emission inventories. As a consequence, countries commissioned national research institutes or agencies to identify and quantify PCDD/PCDFs emissions from known sources. In addition to national inventories, some regional inventories have been carried out, especially in Europe:

- The TNO Institute of Environmental Sciences, in Apeldoorn (The Netherlands), published an European emission inventory (38 countries) of heavy metals and POPs, including PCDD/PCDFs (UBA, 1997) on the basis of submissions of emission data from the Parties to OSPARCOM, HELCOM and the Convention on LRTAP. The inventory was based on official country submissions and supplementary default emission estimates by TNO. The default emission database was prepared for the base year 1990.
- The European General Directorate (DG) XI commissioned a research program to the State Environmental Agency North Rhine-Westphalia (LUA) to identify dioxin emitting sources and to quantify total releases of PCDD/Fs within the Member States. The program started in 1994 and the results were published in 1997 (Stage I) and at the end of 2000 (Stage II) (European Commission, 1977 and 2000a).
- In 1999, UNEP Chemicals reviewed the international situation on inventories and identified only 15 inventories, nearly all from developed northern countries (UNEP, 1999).

All these inventories have been used as information source to evaluate PCDD/Fs emissions in the countries of the Mediterranean region.

2.3.4 Present situation in the countries of the Region

Although data on levels of dioxins and furans in environmental compartments of the region start to increase (see chapter 3), no data is available about emissions in other countries of the Mediterranean region than those reported below. Besides the information given here, extended assessments of dioxin emissions in the EU countries until 2005 can be found as a Report Annex, in the website of the project: www.chem.unep.ch/pts.

2.3.4.1 Croatia

Croatia gave first estimates on emissions of PCDD/Fs in February 1998 (Table 2.7) (SDPNE, 1998). The methodology used is the same as the one described in the European CORINAIR project. Croatia estimates annual emissions of approximately 96 g TEQ per year from six major sectors. Of these, almost all emissions are due to the combustion of wood.

Table 2.7. Estimated PCDD/F releases into air in Croatia.

Sources	Emission flux (g I-TEQ/yr)
Coal combustion	0.036
Fuel combustion	0.97
Steel industry	1.7
Traffic emissions	0.21
Medical waste incineration	0.0016
Wood combustion	92.7
Total	95.5

2.3.4.2 France

Officially the atmospheric emissions of PCDD/Fs in France are estimated by CITEPA and made available to the public on the Internet site of the Ministry of Environment (www.environnement.gouv.fr/actua/cominfos/dosdir/DIRPPR/dosdppr.htm#dioxine). The site contains data on large MSWI (>6 tonnes waste per hour overall capacity) and facilities in the metal industry. The abatement measures as well as closures of plants have reduced the emissions to 25% from 1990 to 2000 and for 2005 it is assumed that the decreasing trend will continue with a further emission reduction by 50%. Regarding metal industry, iron ore sintering results showed that these processes constitute a considerable emission source. Besides sintering plants, also a number of electric arc steel works revealed to be rather strong dioxins emitting sources. The Recytech plant emission was estimated to be very high. After emission data became public, the company carried out a three-step abatement program and by mid 1999, an emission reduction of 90% was confirmed by concentration measurements.

The dioxins emission situation in France in 1995 reported by LUA (Table 2.8) was characterised by emissions from industrial sources (nearly two thirds) and non-industrial activities (ca. one third). According to the official informations (CITEPA), the atmospheric release of PCDD/Fs in year 2000 was 570 I-TEQ g/year, which is somewhat lower than the data reported by the EC, as seen in Table 2.8..

Table 2.8. Assessment of dioxin emissions in EU countries until 2005 (in g I-TEQ/year) (European Commission, 2000a)*

Country	Sources	Revised for 1995	Data 2000	Projection 2005
France	**Total of sources considered**	**1350-1529**	**804-949**	**692-813**
	Industrial sources	987-1027	461-461	340-340
	Non-industrial sources	363-502	343-488	352-473
Greece	**Total of sources considered**	**89-136**	**90-135**	**91-136**
	Industrial sources	55-58	56-56	58-58
	Non-industrial sources	34-79	34-79	34-78
Italy	**Total of sources considered**	**366-967**	**370-985**	**227-628**
	Industrial sources	271-620	281-648	153-303
	Non-industrial sources	95-348	89-336	74-325
Portugal	**Total of sources considered**	**90-136**	**88-133**	**82-123**
	Industrial sources	17-54	17-52	13-45
	Non-industrial sources	73-82	72-81	69-78
Spain	**Total of sources considered**	**131-388**	**117-327**	**122-323**
	Industrial sources	77-184	64-132	71-137
	Non-industrial sources	54-203	53-195	51-187

* Detailed data for the different countries are shown in the report website: www.chem.unep.ch/pts.

2.3.4.3 Greece

Data on PCDD/Fs emissions were scarce when the first inventories were set up in other European countries. Hence the estimation presented in the Stage I of LUA report and the assessment published by TNO was entirely based on the default emission factors chosen from other country's experiences and on statistical data reported in related statistical documents. During the Stage II of LUA inventory first PCDD/Fs emission measurements at industrial installations in Greece were performed (Table 2.8). Three facilities were investigated: a hospital waste incinerator, an electric arc steel plant and a drying kiln for residual materials from olive oil production. The electric arc furnace steel plant was the one with the highest annual emission, while the rotary kiln was

found to be negligible with regard to emissions of dioxins and furans. LUA inventory for 1995 also considered additional information obtained from Greenpeace about the PCDD/F releases to air caused by landfill fires. According to those data, the emissions from uncontrolled landfill fires seemed to be a considerable source of dioxins and furans to air and to land in this country.

2.3.4.4 Italy

A first national inventory, based on emission factors drawn from studies made in other countries and from activity rates taken from national statistics, and a detailed inventory of emissions from MSWI were presented in 1998 (Coutinho et al, 1998). Hence, those MSWI data were used by LUA for the revised 1995 inventory. Since no additional data had been obtained in the meantime, it was considered reasonable to assume, that the situation had not changed and the 1995 data could generally be assumed to be valid also for the year 2000. Similarly, future emissions for 2005 year were assessed (Table 2.8). According to the data presented by LUA, decreasing trends are likely for fossil fuel combustion sources. Further, it may be expected that PCDD/F emissions from road transport will decline due to cease of leaded fuel use. In the case of MSWI the min/max range of future emissions is determined by different scenarios with respect to the amount of waste being burned; emission factors are assumed to be the same and to reflect compliance to the upcoming European emission limit of 0.1 ng I-TEQ/m^3. A slight increase is assumed for emissions from crematoria on the basis of general European trend of annual cremation numbers.

2.3.4.5 Portugal

First national information on the dioxins emission situation in Portugal was restricted to the Oporto region and it was entirely based on emission factors (De Lauretis, 1999). The presented data indicated that the TNO values for 1990 most likely were incomplete. On the other hand, the LUA estimate presented in the Stage I report was considerably higher, mainly due to the estimate calculated for hospital waste incineration and non-industrial sources. In the Stage II of LUA inventory (Table 2.8) a number of emission measurements were performed: three hospital waste incinerators (two old ones and one new installation), and electric arc furnace steel plant, a secondary aluminium smelter and a secondary copper smelting facility. The 1995 inventory is dominated by the estimates of non-industrial sources, which make up around 90% of the annual emissions. This reflects, on one hand, the lower industrial capacity of Portugal and, on the other, that a better knowledge on the industrial structure should be gathered. Although future actions, such as the shut-down or upgrading of hospital waste incinerators with high emissions, will certainly decrease the emissions from industrial sources, it appears reasonable to assume that further industrial emission sources may be found which may make further revisions of the inventory necessary.

2.3.4.6 Spain

An inventory on dioxins emissions in Spain was first developed within the framework of CORINAIR in 1995 for the reference year 1990. It was based entirely on emission factors drawn from other countries or from a PARCOM-ATMOS report on emission factors. This inventory was set up in co-operation with TNO; hence the data presented in the TNO European Inventory on heavy metals and POPs are almost the same. It is apparent that a number of emission sources which are likely to exist in Spain have not been considered in both documents. For this reason, but also because higher default emission factors were used, the LUA estimates were nearly three times higher. The Spanish Ministry of Environment has become aware of these contradictory assessments and started to build up, more systematically, an inventory of the dioxins emission sources. A first output from these activities was a survey on the actual emissions from MSWI (Fabrellas et al, 1999). Regarding other emission sources not much additional information is available yet. Based on the available data, a revised 1995 inventory was set up by LUA as well as projections for the years 2000 and 2005 (Table 2.8).

2.4 OTHER PTS OF CONCERN IN THE REGION

2.4.1 General situation in the Region

2.4.1.1 Hexachlorocyclohexanes (HCHs)

HCHs and particularly lindane were extensively used against pests in many countries of the region. In France, 1600 t/y of lindane were used in the mid 90's (Bintein and Devillers, 1996) and, in Egypt, more than 11300 tonnes between 1952 and 1981 (El-Sebae et al., 1993). In Turkey, the usage of lindane amounted in 1976 to 96.6 tonnes that decreased to 21 in 1978 (Kolankaya and Ayas, 2002).

As described in Chapter 3, HCHs are ubiquitous in the region but this fact may only indicate the large environmental persistence of this compound because at present the use of the various HCH isomers is practically banned in the whole Region. HCHs are subjected to the PIC Procedure and the degree of compliance in the Region can be found in Annex III. Therefore, the main sources of lindane will be stockpiled inventories and contaminated land at hot spots, as a result of previous manufacturing and stockage (see section 3.5.2).

However, the situation in the Mediterranean region is not homogeneous. For example, Albania inherited several environmental impacts after the 90's war conflict, so it was required to assess their environmental "hot spots", including rundown industrial sites. The chemical plant of Durrës comprises a large area severely contaminated by hazardous chemicals and residues in Albania's biggest port. Until its closure in 1990 the plant produced sodium dichromate, for leather tanning, and pesticides such as lindane (γ-HCH) and thiram. The pollution from these processes heavily contaminated an area that includes the former plant, a nearby dumpsite and abandoned chemical storage facilities. Today, the area is one of the worst environmental hot spots in the Balkans. The chemical manufacturing complex of Vlorë, at the south of the country, closed in 1992, was substantially destroyed during civil disturbances in 1997. In the area, lindane and DDT were detected in soils.

Another remarkable event takes place in Skopje, FYR of Macedonia, where approximately 10000 tonnes of hazardous chlorinated organic chemicals (largely the technical mixture of HCH isomers) have been stored in several basins for the last 20 years. The condition of the barrels that contain the mixture is unknown today. Large stocks of lindane disposal were also identified in the Basque Country in Spain (around 80000 tonnes) while in Sabiñanigo (Huesca, Spain) it is supposed that there is a larger amount separated in two dumps.

2.4.1.2 Polycyclic Aromatic Hydrocarbons (PAHs) (including used lubricating oils)

The main sources of PAHs in the environment are natural and intentional combustion of organic matter (e.g. forest fires and fuel combustion) and petroleum manipulation (extraction, transport and refining). The contributions, therefore, range from diffused chronic inputs (e.g. atmospheric deposition and terrestrial run-off) to large point releases (i.e. tanker accidents or accidents at coastal installations). Present information concerning the sources and inputs of PAHs in the region is rather limited, but the Mediterranean Sea has been considered to be relatively more polluted by oil than any other sea from which data are available (US Nat. Acad. Sci., 1975 and UNEP/IOC, 1988).

2.4.1.2.1 Chronic sources of PAHs in the Region

Sea transportation appears to be one of the main sources of PAHs pollution into the Mediterranean. It has been estimated that about 220000 vessels of more than 100 tonnes each, cross the Mediterranean each year and about 250000 tonnes of petroleum hydrocarbons are discharged due to shipping operations such as deballasting, tank-washing, dry-docking, fuel and bilge oil, etc. This figure is less than the 500000 tonnes estimated by Le Lourd (1977) and which was not considered unreasonable by IMO (UNEP/IOC, 1988).

According to this, an annual input of PAHs ranging between 0.3 and 1000 tonnes, depending on the discharge figure and the type of oil being transported, can be estimated. This is assuming, tentatively, a concentration range of 3-5 ring PAHs in crude oils from 1.3 μg/g in light oils, up to 0.2% in heavy oils (as the ones spilled in the Eureka accident).

The land-based discharges are both industrial and urban. The number of major refineries located in the Mediterranean region is more than 40 with a combined capacity, in 2000, of about 438 million tonnes (Int. Petr. News, 2000). On the other hand, the weighted average oil content of European coastal refinery effluents, is approximately 1.9 g per tonne of crude oil processed (CONCAWE, 1998). Therefore, considering the total quantity of oil processed in Mediterranean countries, a total input of about 900 tonnes of oil, and an input of PAHs ranging from 1 kg up to 180 kg, depending on the kind of oil processed, can be estimated. These oil discharges seem to be constant since the last ten years (EEA, 2002).

There are no figures or estimates available regarding the amount of petroleum hydrocarbons carried directly through land run-off into the Mediterranean. Lipiatou et al. (1997) estimated that the total PAHs riverine inputs amount to about 5.3 to 33 tonnes per year from the Rhone river and 1.3 tonnes from the Ebro river. The difference in these riverine fluxes is due to differences in the annual water discharges and upstream land use.

An additional source of PAHs is the result of the sewage sludge management estrategies. The three major sludge producer countries, France, Italy and Spain generate an annual load of 2.9 tonnes of PAHs. Of those, some 1.2 tonnes are spread in the fields due to the use of sludge in agricultural applications, and additional 1.2 tonnes per year are input in the soil via landfilling while some 180 kg/year are returned to the atmosphere

mainly through sludge incineration in France. An additional 220 kg/year are dumped into the Mediterranean through sludge dumping in Spain.

As regards atmospheric inputs, Lipiatou et al. (1997) reported a total PAHs input ranging from 35 to 70 tonnes per year with a mean value of 47.5 tonnes (wet/dry mean ratio of ~2-3).

2.4.1.2.2 Hot spots and accidental sources of PAHs in the Region

Over the last 15 years, about 55000 tonnes of oil have been spilled at the Mediterranean Sea with 3 major accidents amounting to 75% of the quantity spilled. According to REMPEC statistics, 82 accidents involving oil spills were recorded during the period Jan. 1990 to Dec. 1999 while the quantity of spilt oil was 22150 tonnes (REMPEC, 2001). The Spanish and French Atlantic coasts have also been affected by several large oil spills (Table 2.9).

Incidents at oil terminals, together with routine discharges from land-based installations, contribute to elevated concentrations of petroleum hydrocarbons in their vicinity. MAP Technical Reports Series no. 19 estimates the overall input of oil from different industrial sources in the Mediterranean to be 110000 tonnes (UNEP/IOC, 1988). However, the total input in the selected hot spots exceeds 120000 tonnes. The oil loads in a number of priority pollution hot spots in the Mediterranean have also been assessed (UNEP/WHO, 1999). In some cases the volume of oil entering the sea exceeds 20000 tonnes per year while in others it is lower.

Table 2.9. The largest oil spill episodes in the Region

Tanker	Year	Location	Oil discharge
Urquiola	1976	La Coruña, Spain	100000 tonnes
Amoco Cadiz	1978	off Brittany, France	223000 tonnes
Sea Spirit	1990	West Gibraltar	12200 tonnes*
Haven	1991	Genoa, Italy	144000 tonnes
Aegean Sea	1992	La Coruña, Spain	74000 tonnes
Erika	1999	off Brittany, France	10000 tonnes*
Prestige	2002	La Coruña, Spain	10000 tonnes*

* amount of spilled oil

The estimates of the relative importance of the various sources of PAHs in the Region are summarised in Table 2.10. Riverine/urban inputs and atmospheric emissions appear to have a relatively high importance while the actual PAHs input from shipping activities remains uncertain. Another source, difficult to estimate, is the accidental fires which are rather current in the region (see section 1.2.2.1).

Table 2.10. Estimated PAH inputs from diverse sources,
assuming two different PAH contents in the case of oil discharges.

Type	Annual Oil Input Rate (tonnes)	PAH content (g/tonne)	PAH input (tonnes)
Shipping discharges	250000 (low estimation)	1.28	0.32
		2000	500
	500000 (high estimation)	1.28	0.64
		2000	1000
Accidents	3667	1.28	0.005
		2000	7.3
Refinery effluents	900	1.28	0.001
		2000	1.8
Urban and river discharges			30-40
Sludge sea dumping			0.2
Sludge applications in soils			1.2
Sludge landfilling			1.2
Atmospheric			48
Sludge incineration			0.2

2.4.1.3 Brominated Flame Retardants (BFRs)

These products, basically used as additives in different commercial applications, encompasses a variety of chemical species. The most used are polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), tetrabromobisphenol (TBBPA) and hexabromocyclododecane (HBCD) (see Annex II).

Information on sources in the region is basically restricted to EU countries, where are applied in the different sectors as shown in Table 2.11.

Table 2.11 Application of BFRs in various category products in Western Europe (BSEF, 2000)

Final use	Percentage
Electronics/electrical	56%
Building/construction	31%
Transportation	6%
Textile/other	7%

The general consumption of BFRs in Western Europe was quantified in 30860 tonnes in 1999, approximately the 15% of the world-wide production. The market volume of PBDEs in these countries indicate an increase of their usage from 1996 to 1998, from 11440 to 16250 tonnes. However, a market analysis of 1999 indicated a decrease in the use of PBDEs, mainly in Germany, the Netherlands and the Nordic Countries. PBBs are mostly used in the South European countries (some 2000 tonnes/year), with a clear impact in the Mediterranean region. TBBPA and derivatives accounted for 26% of the total market in 1998 in Western Europe. Table 2.12 shows data on consumption of plastics treated with brominated flame retardants for production of electronics and electrical equipment in Western Europe.

In the Mediterranean region there are two large facilities in France and one in Israel. However, none of these production plants is expected to contribute to a significant extent as sources of BFRs into the Mediterranean region, in comparison to the impact of electronics and electrical consumer goods and building materials.

At present, PBBs and PBDEs are not classified under the Council Directive 67/548/EEC on the classification and labelling of dangerous substances. However, the members of the German Association of Chemical Industries voluntarily stopped the production as early as 1986, while leading European companies in the electric and electronic industry have proclaimed an official policy of avoiding PBDEs and PBBs in their products. The last European manufacturer of PBBs stopped its production in the year 2000. In addition, member States will have to substitute PBBs and PBDEs by other substances in electrical and electronic equipment by 2008.

Table 2.12 Consumption of plastic materials treated with BFRs in Western Europe in 1995 (APME, 1998)

Sector	Plastic parts treated with FR	% of plastics treated with FR	Weight of FR treated plastics (tonnes)	% of plastics containing BFR
Brown products	For TV sets the majority of external parts are treated.	55%	128000	83%
Data processing	Apart from keyboards, the majority of monitors' external parts are treated. Epoxy internal parts are treated.	63%	71000	83%
Electrical equipment materials	Circuit breakers and carry fusible	20%	35000	54%

2.4.1.4 Alkylphenols

The main use of alkylphenols (normally octyl- and nonylphenols) is the production of non ionic surfactants by the detergent industry in the form of a complex mixture of oligomers and isomers of ethoxylated derivatives (see Annex II). Nonylphenol ethoxylates take some 80% of the market while octyphenols are responsible for the remaining 20%. The EU market for nonylphenol (NP) and nonylphenolethoxylates (NPE) was estimated to be, in 1997, of 78500 and 77600 tonnes, respectively. The main uses of the NPE in EU and their relative contribution to the risk for the aquatic environment are shown in Table 2.13

Table 2.13 Major NPE surfactant uses in the EU in 1997 (ENDS Report, 1999).

Sector	NPE use (tonnes)	% of aquatic burden
Cleaning	23000	44.7
Emulsion polymerisation	9000	--
Textile processing	8000	14.7
Chemical synthesis	7000	0.1
Leather processing	6000	6.1
Agriculture (pesticide)	5000	1.1
Paints	4000	0.2
Metal industry	2000	1.2
Pulp, paper and board	1000	1.7
Miscellaneous uses (electronics, oils, engineering, photography)	7000	0.2
Unknown	5600	23.7
NPE production		5.8
Product formulation		0.5
Total	77600	100

The major NPE sources in the region, both in terms of mass and also in terms of risk, would be connected to their use in cleaning activities, seconded by the miscellaneous usage and the textile and leather processing.

There are no specific data in the region concerning the use of octyl- and nonylphenol ethoxylates in detergents. However, the European detergent industry launched a few years ago the voluntary implementation of the AISE code of good environmental practice in Europe. AISE represents 90% of the detergent and cleaning industries of Europe and compliance with good environmental practices is audited by third parties. As a result of the implementation of the AISE code, the evolution of key production parameters has been monitored in the EU state members, and both detergent consumption per capita and PBO (poorly biodegradable products) generation per capita are being reported. Although, it is unclear what type of contaminants are lumped into the PBO definition, the detergent consumption and PBO generation indicators can give a suitable information about the key potential sources of NP and NPE in the European countries of the Region. Data indicate that per capita consumption of detergents in the European countries of the Region is quite constant around 11.2 ± 1.0 kg/year and PBO release per capita is even more constant, 0.29 ± 0.02 kg/year. Then, if we assume that most of the countries of the Region have similar water hardness (which largely controls detergent per capita consumption) and that the main detergent industries operate around the Region with similar makes and compositions, we may extrapolate the results from the EU countries to the rest of the countries in the Region. The results of these calculations are given in Table 2.14.

Table 2.14. Estimated detergent consumption and PBO generation in the countries of the Region in year 2000.

Country	Population (millions inh.)	tonnes detergent/ year	tonnes PBO/ year
Albania	3.1	34720	899
Algeria	30.3	339360	8787
Andorra	0.07	784	20.3
Bosnia Herzeg.	3.5	39200	1015
Croatia	4.7	52640	1363
Cyprus	0.8	8960	232
Egypt	67.9	760480	19691
France	59.2	663040	17168
Greece	10.6	118720	3074
Israel	6.0	67200	1740
Italy	57.5	644000	16675
Jordan	4.9	54880	1421
Lebanon	3.5	39200	1015
Lybia	5.3	59360	1537
FYR Macedonia	2.0	22400	580

Country	Population (millions inh.)	tonnes detergent/ year	tonnes PBO/ year
Malta	0.4	4480	116
Monaco	0.03	336	8.7
Morocco	29.9	334880	8671
Palestine	3.1	34720	899
Portugal	10.0	112000	2900
San Marino	0.02	224	5.8
Slovenia	2.0	22400	580
Spain	39.9	446880	11571
Syrian Arab	16.2	181440	4698
Tunisia	9.5	106400	2755
Turkey	66.7	747040	19343
FR Yugoslavia	10.6	118720	3074
Total	**447.72**	**5014464**	**129839**

2.4.1.5 Phthalates

Around one million tonnes of phthalates are produced and used in Western Europe each year. These include 674000 tonnes of di-2-ethylhexyl phthalate (DEHP), 18000-45000 tonnes of butylbenzyl phthalate (BBP), and 10000 to 50000 tonnes of di-butyl phthalate (DBP) (CEFIC). All these phthalates have been put, due to their potential risks to human health and the environment, on the first three priority lists for risk assessment in accordance with EU Regulation 793/93 on existing substances.

A large percentage of the production, approximately 900000 tonnes, are used to plasticise PVC (European Commission, 2000b). The remainder is used in rubber products, paints, printing inks, adhesives, lubricants and some cosmetics. The total market of flexible PVC in Western Europe was around 1.75 million tonnes in 1997, with the distribution among different products shown in Table 2.15.

Table 2.15. West European market for flexible PVC (Corden, 1998)

Application	Total flexible PVC (kt)	Percentage (%)
Cables	540	30.9
Flexible film/sheet	300	17.2
Flooring	250	14.3
Synthetic leather	120	6.9
Fabric coats	55	3.2
Flexible profiles	160	9.2
Wall coverings	80	4.6
Sealants	55	3.2
Others	185	10.6
Total	1745	100

The quantities of plasticisers added to the PVC polymer vary depending on the required properties. Depending on the final use, plasticisers contents vary between 15 and 60%, with typical ranges for most applications around 35 to 40%. Considering the former 40% as the typical percentage of phthalates in PVC flexible applications, an estimation has been done of the amount of phthalates used in each country of the region (Table 2.16).

The amount of PVC, and consequently of phthalates, is related to the GNP. Hence, it is expected that with time, some of the developing countries will see a growing consumption of PVC per capita. Average world growth rates of PVC production in recent years have been between 2 and 10%, with differences per region and per application (higher for rigid, lower for flexible). The consumption of phthalates is slightly increasing in the EU as a whole and stagnant in northern Europe (Hansen and Havelund, 2000).

Table 2.16. Estimation of phthalates use in countries of the Mediterranean Region

Country	PVC total (kt)	Phthalates (kt)
Albania	1.6	0.6
Algeria	31.6	12.7
Croatia	6.1	2.5
Cyprus	3.1	1.2
Egypt	39.1	15.6
France	274.2	109.7
Greece	33.3	13.3
Israel	24.2	9.7
Italy	261.7	104.7
Jordan	3.5	1.4
Lebanon	3.5	1.4
Lybian	9.7	3.9
FYR Macedonia	1.8	0.7
Malta	1.4	0.5
Morocco	19.0	7.6
Palestine	n.a.	n.a.
Portugal	33.0	13.2
Slovenia	6.2	2.5
Spain	145.1	58.1
Syrian Arab	9.7	3.9
Tunisia	10.8	4.3
Turkey	93.5	37.4
FR Yugoslavia	n.a.	n.a.
Total	1012.1	404.8

n.a. not available

In conclusion, the large quantities of phthalates used in PVC applications contribute to their ubiquitous presence in the environment. Transport in the air and leaching from certain applications seem to be major routes by which phthalates enter the environment. In 1998, the Scientific Committee for Toxicity, Ecotoxicity and the Environment (SCTEE) determined the highest emission rates of phthalate dissolution from toys to be 61μg/g/day or 7 - 15 μg/cm^2 (INRS, 1998).

2.4.1.6 Tributyltin compounds (TBTs)

2.4.1.6.1 Chronic sources in the Region

The main source of TBTs in the region is through their release from antifouling paintings in ships, although from January 2003, when the new IMO Convention that banned the use of TBT compounds in the ship paints will enter into force, the situation would change. As far as the present is concerned, there are no available data about the annual amount of TBT released to the Mediterranean Sea. An effort has been made in this report to estimate the releases of TBTs to the Mediterranean Sea due to maritime activities.

The total discharges of TBT may be estimated on the basis of leaching rates. The International Maritime Organisation (IMO) has recommended a maximum leaching rate of 4 μg/cm^2/day at 25ºC. Therefore, the first step was to estimate the number of ships longer than 25 metres. The sea traffic of ships that met the requirements was considered. On one hand, approximately 20% of merchant marine sail across the Mediterranean Sea, representing some 17000 ships. On the other hand, it is supposed that more than 4000 ships smaller than 500 tonnes but longer than 25 metres also circulate in this area. So the number of ships considered in this study amounts to 21000. The average surface in touch with the water that has been considered for each unit is about 700 m^2, so the surface susceptive of discharging is 14700000 m^2.

It must be remarked that the discharge rate considered for the estimation of losses of TBTs into the sea has been revised upward, bearing in mind that the leaching rate given in the IMO regulations is the maximum value. So, having considered the former rate as well as the total surface of ships, we obtain the following approximate

release rate: 588 kg/day. This results in an approximate annual release of 214 tonnes of TBT from commercial shipping.

2.4.1.6.2 Hot spots for TBTs in the Region

According to the previous discussions, the hot spots for TBT release in the Mediterranean will be associated with the major commercial harbours in the Region. We can stretch further the previous calculations and deduce where are the Mediterranean areas, particularly around harbours, with larger inputs.

Following the MEDPOL practice, the Mediterranean Sea has been divided in different areas because of the difficulty of estimating the exact percentage discharged in the main harbours. Then, an estimation is done of the sea traffic in each zone for ships larger than 25 m and with a metallic boat hull and the results are shown in Table 2.17 (next page).

Hence the main TBT sources to the Mediterranean are concentrated in the north-western and north-central parts of the sea and accordingly the harbours in these areas may be regarded as potential hot spots for TBT release.

2.5 EMISSIONS OF SELECTED PTSs

2.5.1 General situation in the region

An estimate of atmospheric inputs of selected PTSs in the Mediterranean region has been carried out by EMEP, taking into consideration the particular climatic and morphologic conditions of the Region. It must be mentioned, however, that the model used does not present complete reliability in the spatial distribution of contaminants. This is due to the scarcity of atmospheric data, to the climatic and orographic variability of the region (see section 1.2) and to the size of the grid used (150 x 150 km. spatial resolution), which is too large to monitor with good detail the distribution of contaminants. At further stages of the model development, a grid with 50 x 50 km. resolution has been used.

Table 2.17. Estimated distribution of TBTs in the Mediterranean Sea

Zone	**Countries (main harbours)**	**Sea traffic/Annual TBT release (tonnes)**
North-west	Spain (Marbella, Alacant, Valencia, Balearic Islands, Barcelona), Monaco, France (Marseille, Nice, Toulon), Italy (Genoa, La Spezia, Livorno)	26% / 56
Centre/North	France (Corsica), Italy (Cagliari, Catania, Palermo, Civitavecchia, Napoli, Venice, Trieste), Slovenia, Croatia, FR Yugoslavia, Albania	28% / 60
North- Oriental	Greece (Piraeus, Iraklion), Turkey (Istanbul, Izmir, Anatolian Peninsula)	16% / 34
Southeast	Syria, Israel (Haifa), Lebanon (Beirut), Cyprus (Famagusta, Limassol), Egypt (Port Said, Alexandria)	13% / 28
South-central	Lybia (Banghazi, Marsa al Burayqah, Tripoli, El Brega), Malta (La Valletta), Tunisia (oriental coast)	3% / 6
Southwest	Tunisia (Tunis), Algeria (Alger), Morocco (Ceuta, Melilla, Algeciras)	14% / 30

The EMEP emission data is based mainly on the official information reported by countries with an unified methodology for PTSs emission inventories, and on emission expert estimates, intended to fill the large gaps in official information. The data for 1995 is presented in Table 2.18, but the extended data set for the period 1970-1995 is presented in the Report Annexes shown in the website of the project: www.chem.unep.ch/pts.

2.5.1.1 PCB Emissions

The total amount of PCBs released to the environment in the North Hemisphere is about 100000 tonnes (from which the 75% between 1955 and 1970). At this moment there are no available data about emissions in the

North-African countries. The data reported in Table 2.18 indicate the limitations of the approach, derived from some important inconsistencies between the officially reported data and the model estimates, mainly because some official data include emissions from industries but not diffused emissions from all electric equipments in use and contaminated surface.

In general, a temporal decreasing trend has been observed for all developed countries of the Region, and an increasing emission trend for developing countries like the ones emerging from the FR Yugoslavia, although emissions from these countries are 5-10 times lower than the ones from the more developed countries.

Table 2.18. Experts estimates and official data (UN/ECE reported) of PTS emissions in European countries for 1995 (in kg/y)

Country	**PCBs**	**HCB**	**PCDD/Fs**	**γ –HCH^{+}**	***Official data***
Albania	146	55	2.67	463	
Bosnia &Herzegovina *	231	50	21.7	567	
Croatia *	238	78	22.4	472	
France	20347	1285	1119	560000	60 (PCBs); 1785 (PCDD/Fs)
Greece	221	175	122	5863	
Italy	6054	795	799	2230	
FYR Macedonia *	97	30	9.12	69	
Portugal	557	145	34.4	13189	
Slovenia *	123	15	11.6	169	4.9 (PCDD/F)
Spain	8721	1172	305	122909	6088 (HCB); 157 (PCDD/Fs)
FR Yugoslavia *	574	137	53.9	1694	

*Estimated on the basis of spatial emission distribution (Pacyna et al., 1999) in the FR Yugoslavia. $^{+}$Estimate for 1996.

On the other hand, the rate of PCB depositions has decreased by a factor of ten since 1970. However, this decrease is lower than the overall decrease of anthropogenic emissions in the MSC-E countries, probably because of re-emission from secondary sources.

2.5.1.2 HCB emissions

With regard to emissions of HCB it is of worth to point out that the estimate of the pollutant import from outside the EMEP grid is of importance. In 2000 a first attempt of the assessment of HCB long-range transport for 1970-98 was made (see section 4.1.2.1).

In Table 2.18, the available emission official data (corresponding to Spain) and the estimates made by MSC-East for the emissions of this compound are presented. In this case, the model estimates indicate an overall decrease of the HCB emissions in the Region and a reasonable agreement between the estimated and officially reported data for Spain.

2.5.1.3 PCDD/Fs Emission

Similar estimates have been made for the MSC-E countries and they have been compared to the officially reported data to UN/ECE. As it can be seen in Table 2.18, there is a reasonable agreement between the two sets of data (within a factor 2). The data shown in the Annex (www.chem.unep.ch/pts) indicate a tendency to increase in the developing countries of the MSC-E area, and a decrease in dioxins emissions in the more developed countries. However, the overall rate of decrease is less than expected from the rates of abatement of anthropogenic emissions. This is probably because there are a number of smaller sources, besides municipal waste incinerators, that have not addressed the problem.

2.5.1.4 γ-HCH emissions

The comparison between the officially reported data for lindane and the emission estimates for the Mediterranean countries of the MSC-E area (Table 2.18) would indicate a decrease on the emissions of a factor of 3.5.

The spatial distribution of these emissions in the MSC-E area would indicate that France constitutes a hot spot. Bintein and Devillers (1996) made a regional estimate of lindane emissions for France, indicating a contribution of 715 t/y from the north-western regions from a total of 1646 t/y for the whole country.

2.5.1.5 BFRs emissions

The knowledge of emissions of brominated flame retardants is rather limited. Model estimates indicate that the major source of BFRs is their evaporation from products in use. BFRs are particularly emitted to in-door environment from products in service. Several studies confirm that the most obvious sources of emissions to the air would be from products where the flame retardants are used as additive. This is the case of computer monitors or other elements from TV sets.

In 1991, Ball et al. (1991) analysed the emissions of PBDT and, according to his experimental results, the maximum rate emitted from a TV set was 192 ng/unit/3 days while the maximum rate from a PC monitor was 889ng/unit/3 days. The total content of PBDEs in a TV unit can be roughly estimated to be 180 g while in a PC there are some 340 g. The content of TBBPA is approximately 180 g for TVs and 204 g for PCs (Danish EPA, 1999).

The possible emission per year from the former products in service by volatilisation can be estimated applying emission factors for each substance. For the calculation it will be assumed that the accumulated amount of the selected BFRs (PBDEs and TBBPA) from TV sets and PCs in service in 2001 correspond to 10 years of consumption. The worst case emissions of BFRs have been considered, obtained from an EU risk assessment.

Consequently, in the following tables the emission rate is applied to a total-service life of 10 years and the total amount of PBDE and TBBPA emitted to the air from TV sets and PCs is broken down by country.

The results indicate that the EU Member States are those having larger emissions due to their larger BNP. It is expected that developing countries, with the measure that their economies grow, increase their proportion of TV sets, PCs and other household goods which contain BFRs. The main sources of emissions are DeBDE from TV sets.

Table 2.19. BFRs emissions from televisions in service for ten years
(International Telecommunication Union, 2002a)

Country	**TV units* (x1000)**	**TBPPA Emissions (tn)**	**DeBDE Emissions (tn)**	**OcBDE Emissions (tn)**	**PeDBE Emissions (tn)**
Albania	480	0.02	3.28	0.47	0.34
Algeria	3400	0.15	23.26	3.30	2.39
Andorra	36	0.00	0.25	0.03	0.03
Bosnia	440	0.02	3.01	0.43	0.31
Croatia	1310	0.06	8.96	1.27	0.92
Cyprus	122	0.01	0.83	0.12	0.09
Egypt	12000	0.54	82.08	11.66	8.42
France	37000	1.67	253.08	35.96	25.97
Greece	5200	0.23	35.57	5.05	3.65
Israel	2100	0.09	14.36	2.04	1.47
Italy	28300	1.27	193.57	27.51	19.87
Jordan	560	0.03	3.83	0.54	0.39
Lebanon	1170	0.05	8.00	1.14	0.82
Lybia	770	0.03	5.27	0.75	0.54
FYR Macedonia	570	0.03	3.90	0.55	0.40
Malta	218	0.01	1.49	0.21	0.15
Morocco	4700	0.21	32.15	4.57	3.30
Palestine	427	0.02	2.92	0.42	0.30
Portugal	6319	0.28	43.22	6.14	4.44
Slovenia	730	0.03	4.99	0.71	0.51
Spain	24000	1.08	164.16	23.33	16.85
Syrian Arab R.	1080	0.05	7.39	1.05	0.76
Tunisia	1900	0.09	13.00	1.85	1.33
Turkey	29500	1.33	201.78	28.67	20.71
FR Yugoslavia	3000	0.14	20.52	2.92	2.11
Total	165332	7.44	1130.87	160.70	116.06

*It has been considered that only 5% of televisions contain TBPPA as additives

Table 2.20. BFRs emission from computers at home in service for ten years
(International Telecommunication Union, 2002b)

Country	PC Units* (x1000)	TBPPA Emissions (tn)	DeBDE Emissions (tn)	OcBDE Emissions (tn)	PeDBE Emissions (tn)
Albania	30	0.02	0.04	0.06	0.04
Algeria	220	0.15	0.28	0.40	0.29
Croatia	400	0.27	0.52	0.73	0.53
Cyprus	170	0.11	0.22	0.31	0.23
Egypt	1000	0.66	1.29	1.84	1.33
France	20000	13.26	25.84	36.72	26.52
Greece	860	0.57	1.11	1.58	1.14
Israel	1600	1.06	2.07	2.94	2.12
Italy	11300	7.49	14.60	20.75	14.98
Jordan	170	0.11	0.22	0.31	0.23
Lebanon	200	0.13	0.26	0.37	0.27
Malta	90	0.06	0.12	0.17	0.12
Morocco	400	0.27	0.52	0.73	0.53
Portugal	1210	0.80	1.56	2.22	1.60
Slovenia	550	0.36	0.71	1.01	0.73
Spain	6800	4.51	8.79	12.48	9.02
Syria	270	0.18	0.35	0.50	0.36
Tunisia	230	0.15	0.30	0.42	0.30
Turkey	2700	1.79	3.49	4.96	3.58
FR Yugoslavia	250	0.17	0.32	0.46	0.33
Total	48450	32.12	62.60	88.95	64.24

* It has been considered that 65% of computers contain TBBPA

2.6 SUMMARY OF MOST SIGNIFICANT REGIONAL PTS

The main sources, environmental vectors and reservoirs of PTSs for the Region are summarised in Table 2.21. The most important sources as agreed upon at the Technical Regional Workshop under this project held in Athens (2002) are shown in bold. The Table includes only the main direct sources, although there are important indirect sources due to transfers between different reservoirs, particularly through atmospheric deposition.

For PTS pesticides, including lindane, the sources are multiple and diffuse. Although, these compounds have a tendency to disappear as a result of the implementation of the PIC procedure and the associated conventions, there is a worrisome lack of control regarding the existing stockpiles in the countries of the Mediterranean region. The use of lindane is severely restricted in the Region, but in countries like France and Spain the estimated atmospheric emissions are quite large.

DDT is still being used in the Region as 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.

For PCBs, atmospheric emissions show a decreasing trend in the MSC-E countries of the Region which coincide with the more industrialised and consequently with the larger amounts of PCBs containing equipment. However, there is a clear lack of reliable information concerning the amounts of equipment in use and the status of the stockpiles of faced out equipment and PCBs oils. Potential hot spots have arisen from the destruction of electrical and military equipment during the Balkans conflict.

For dioxins and furans, the main sources derive from thermal sources. The controls on incineration plants have achieved a decrease on the emission levels from municipal waste incineration. However, other remaining sources are the metallurgical industry, the uncontrolled combustion of waste in landfills and wood combustion. There is a need for a comprehensive Regional Inventory, which should include most of the thermal sources. Emission estimates indicate a decrease during the last decade in the MSC-E countries of the Region.

Table 2.21. Main sources, environmental vectors and reservoirs for PTS in the Region.

Compound type	*Air sources*	*Soil sources*	*Freshwater sources*	*Seawater sources*
Pesticides	**Agriculture use, spraying/land application**	**Stockpiles**, production waste **DDT, dicofol production**	**Runoff from agriculture use. DDT, dicofol production.**	**Major rivers and coastal runoff**
PCBs	**Emissions from equipment and stocks** Sewage sludge incineration	**Equipment stocks and landfills** Sewage sludge	Leakage from equipment	**Major rivers and coastal runoff** Sewage sludge dumping
PCCDs	**Emissions from combustion**	By-products of PCBs		Major rivers and coastal runoff
PAHs	**Emissions from combustion, oil, traffic** Sewage sludge incineration	**Sewage sludge** Timber preservation	**Oil spills, sewage runoff**	**Oil spills in shipping and refineries** Sewage sludge dumping
BFRs	**Emissions from the use of electrical and electronic equipment**	Landfilling of obsolete equipment		
Alkylphenolethoxylates		Sludges from wastewater treatment plants	**Runoff from industrial and domestic detergent usage**	**Major rivers and coastal runoff**
Phthalates	**Emissions from treated PVC**	Landfilling of materials		
TBT				**Release of antifouling paint from shipping**

The main source for PAHs in the Region appear to be oil shipping operations, they could be as large as 1000 tonnes per year. The estimated PAHs emissions in the Mediterranean are of the same order of magnitude than the overall riverine inputs (some 40 tonnes per year). Inputs from coastal refinery operations are less important, of the order of 1 tonne per year. PAHs emissions in the region are uncertain, ranging between 40 and 700 tonnes per year depending on the estimate.

Release from antifouling painting in commercial shipping is the source of TBTs in the Region. The present release rates estimates are in the order of some 240 tonnes per year. Commercial harbours in the North-western and Adriatic areas constitute potential hot spots.

Emissions of brominated flame retardants into the atmosphere is very much linked to the consumption of electrical and electronic equipment in the Region. The patterns of economical development would indicate that the potential sources are bound to increase in the Region as a result of increased wealth.

The per capita consumption of detergents in the Region is relatively high due to both the water hardness and cultural reasons. The estimated total amount of detergent being used in the Region in year 2000 was around 6 million tonnes. This has an impact on the release of poorly biodegradable organics (PBOs), including non-ionic surfactants in the Region, which is estimated to be in the range of 167000 tonnes per year. This is a substantial input of PTSs in the Mediterranean area. The five EU countries of the Region contribute to 50% of both the total detergent consumption and the PBO release.

In terms of setting priorities to reduce PTSs sources in the Mediterranean region, it would appear that pesticide stockpiles should be better inventoried, particularly in the Southern countries of the region. A better control on PCB inventories and the implementation of reasonable destruction plans is also a key issue. The remaining

stockpiles in the northern part of the region are enormous and contribute to the remaining emissions in the area. The negative impact of the Balkans conflict in the widespread of PCBs in the region will have to be addressed.

Another priority objective would be a better control in the activities associated to shipping and its mismanagement of oil transportation to effectively reduce PAHs emissions in the area. The same industrial sector is responsible for the release of sizeable amounts of TBTs into the Mediterranean sea, although the issue is being addressed in recent MEDPOL protocols

2.7 DATA GAPS

As mentioned before, great gaps exist in the data for PTSs sources in the Mediterranean Region. Most of the countries in the area 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 have not got the capabilities to monitor industrial sources in a comprehensive fashion and are only faced with the outcome of the industrial mismanagement practices (i.e. PCBs containing apparatus landfilling, abandoned stocks, etc.). There is a clear need to promote a PTSs source monitoring programme at regional level in association with the industrial sector. This can only be achieved by intensive consumer pressure, as occurs with the AISE code implementation for domestic detergents.

The uncertainty of PTSs emission estimates are conditioned mainly by a number of reasons:

- There are no data available (a comprehensive monitoring programme would be required);
- A wide range of emission factor values (even for one and the same kind of activity);
- Incomplete information on consumption (fuel, chemicals, other substances);
- Incomplete information on product output;
- Quantity and method of pesticide application in different countries;
- No data on material flow (goods and waste related with POPs or PTS);
- No pollution release transfer register (PRTR) on PTS available for the Region.

The use of emission factors, calculated for similar industrial processes in other countries may be used (in some cases) to estimate the possible PTSs release into the environment through air emissions and liquid discharges. However, it has to be recognised that the use of emission factors will produce data with a degree of uncertainty, because of the differences in industrial technology between different countries. This is particularly valid in the Mediterranean Region, where technological differences may be very important, especially in small and medium enterprises.

Discrepancies (in some cases rather appreciable) between used emission estimates (Pacyna et al., 1999) and official data testify to a necessity of reporting by countries more complete information on emissions (estimation methodology used, emission factors, total emission splitting by sectors, etc.).

In Eastern European countries there are data gaps with respect to pesticide stockpiles due to the little co-ordination of work on this issue. No inventory data have been published yet for these regions, but early indicators suggest that very large stockpiles exist. Apocryphal reports suggest that about 70000-100000 tonnes of obsolete pesticides are held in these countries. In locations upstream to the Black Sea basin and related rivers, or in the region close to Turkey and the Middle East there are important diffuse (non point) sources of obsolete pesticides as runoff from agriculture, including HCHs and also DDT. These could indicate improper uses or unsafe disposal.

In the Middle East there are some uncontrolled sources of by-products such as PCDD/PCDFs as a result from waste incineration and improper disposal. More data are needed.

Military and civilian sites and dumpsites with electrical equipment, as relevant sources of PCBs are present in the region: from Turkey to Israel, Lebanon, Italy and especially in Spain. There are also many local sources of other relevant PTSs in the region not adequately addressed. The survey and identification of these sites within the Mediterranean region should be made to properly address the dimensions of the problems and to identify concrete action. This should follow the policy already accepted by countries under the Barcelona Convention or a similar provision for the non-Mediterranean countries inserted in region IV for the present exercise.

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3 ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

A considerable amount of data is available on the occurrence of PTSs in the region, although with a very uneven distribution in terms of compartmental, geographical and temporal coverages, as well as analytical quality, particularly for the older ones (UNEP/FAO/WHO/IAEA, 1990). The data reported here is not intended to be exhaustive, but comprehensive enough for providing information about current levels of PTSs in the different matrices. Data basically refer to the last decade and where possible the temporal variability is also assessed.

3.1 CONCENTRATIONS OF PTS IN ABIOTIC COMPARTMENTS

3.1.1 Air and precipitation

The atmospheric compartment is one of the least studied in the region probably due to methodological difficulties. Data are basically restricted to HCB, HCHs, PCBs, PCDD/Fs and PAHs, and, except for PAHs which have been determined in a large number of countries, results are mainly from urban areas. The other measurements received do not qualify for a global assessment. Only in France has a systematic determination of pesticides been carried out in a few urban and rural areas since the end of the 80s.

3.1.1.1 HCB

In France, HCB concentrations ranged from 9-2400 pg/m^3, with mean levels in continental air of 300 pg/m^3 (Chevreuil et al., 1996; Sanusi et al., 2000) and of 161 to 240 pg/m^3 in remote areas (Pyrennes) (Nerin et al., 1996). Total fallout measured by Chevreuil et al. (1996) in France was in the range of 0.7 – 4.5 ng/L.

Based on modelling calculations, the Meteorological Synthesising Centre-East (MSC-E) has estimated mean concentrations in natural media of all northern countries of the Mediterranean region, for 1998 (Dutchak et al., 2002). Air concentrations range from 39 to 66 pg/m^3, with a slight decreasing West-East trend and the lower values for Malta and Cyprus.

3.1.1.2 PCBs

Data reported during the 90's on atmospheric concentrations of PCBs in the Mediterranean region is summarised in Table 3.1. The values found in Crete (15.7 and 1.2 pg/m^3, gaseous and particulate, respectively) may constitute the background value for the region.

The mean annual PCBs concentration in air reaches its maximum (0.8 ng/m^3) in the centre of Europe and decreases to averages of 0.34 and 0.16 ng/m^3 in coastal and open sea air, respectively (UNEP/MAP/WMO, 2001).

Table 3.1. Levels of PCBs in different components of the Mediterranean atmosphere

Matrix	Location	Sampling	PCBs conc.	References
Air	Mediterranean Sea	1989-1990	Σ PCB av. 0.49 ng/m^3	Iwata et al., 1993
	France (Paris area)	1986-1990	Σ7 cong. 0.6- 2 ng/m^3	Granier and Chevreuil, 1991
	Crete (rural area)	1999	Σ7 cong. 17 pg/m^3 (g+p)	Mandalakis et al., 2002
Rain water	Monaco	1985	Σ PCB 24 ng/L	Villeneuve and Cattini, 1986
	France (Paris area)	1986-2001	Σ7 cong. 10 - 120 ng/L	Chevreuil et al., 2001
Snow	Spain (Pyrenees)	1998	∑7 cong. 0.22 ng/L	Carrera et al., 2001
Snow and rain water	Croatia	1993	Σ PCB < 1 – 203 ng/L	Fingler et al., 1994

Total atmospheric fallout has been measured in Paris since 1986. Over 15 years, in spite of varying instant contamination, the average value remained approximately constant (40 ng/L as Σ7 congeners), but the present yearly variability is higher than in 1986 (Chevreuil et al., 2001).

3.1.1.3 PCDD/PCDFs

Concentrations of PCDD/PCDFs in ambient air are available only for four countries in the region (Table 3.2). Data have also been obtained from a remote place (Crete) with values of 2.5-3.3 and 1.7-2.9 fg I-TEQ/m^3 for

the vapor and particulate phases, respectively. As it can be seen, air concentrations are similar in the four countries. Levels in rural areas are lower than those in urban areas but not very different. The influence of industrial plants or incinerators is reflected in higher PCDD/Fs concentrations in some industrial areas.

In this respect, Seveso (Milan, Italy) should be considered as a particular area. After the accident of July 1976, the area was divided in three zones according to the levels of contamination. The first (zone A), presented a soil concentration of 2,3,7,8-TCDD > 50 μg/m^2, and zones B and R, of 5-50 μg/m^2 and < 5 μg/m^2, respectively. A recent investigation (Fattore et al, 1997), collecting long-term air samples during the four seasons of the year, revealed that annual TEQs were 240, 350 and 220 fg ITEQ/m^3 in zones A and B of Seveso, and in Milan, respectively. Levels detected in Milan were comparable with those of other industrialised cities.

Table 3.2. Summary of PCDD/Fs air concentrations from Mediterranean countries (ambient air as fg I-TEQ/m^3)

Country	Ambient air			References
	Rural	Urban	Industrial	
Greece	2-178	4-119	-	Mandalakis et al., 2002
Italy	2-6	11-480	-	Turrio-Baldassarri et al., 2001
Portugal	24-244	36-548	-	Coutinho et al., 2001
Spain	5-125	13-357	18-954	Abad et al., 2002

3.1.1.4 HCHs

Atmospheric lindane concentrations varied from 0.75-1.5 ng/m^3 with no significant differences between urban and rural sites, in France (Chevreuil et al., 1996; Sanusi et al., 2000).

HCHs have also been determined in Spain, close to an industrial solid waste dump (Sabiñanigo, Huesca) (39 - 77 ng/m^3 of α-HCH and 28 - 58 ng/m^3 of γ-HCH) and in a remote area (Pyrennes) (≤ 3 pg/m^3 of γ-HCH) (Nerín et al., 1996). Mean annual concentrations over the Mediterranean were estimated to be around 0.5 ng/m^3 (UNEP/MAP/WMO, 2001).

In spite of its prohibition in agriculture, lindane was still detected in the Paris fallout, in 2000. However, its average concentration decreased from 29 ng/L in 1986 to 15 ng/L in 2000 (Teil et al., 2002). In Croatia, the average concentration was 38 ng/L (Fingler et al., 1994).

3.1.1.5 Polycyclic aromatic hydrocarbons (PAHs)

The determination of atmospheric PAHs is hindered by many problems, the most common derived from sampling. Therefore, it is difficult to integrate the existing information into a coherent data set.

3.1.1.5.1 Dry deposition

PAHs concentrations have been reported in dry deposition in a number of urban areas as well as in remote places, including the open Mediterranean Sea (Table 3.3). 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 than in rural areas. The higher values are found in particular places like stack gases, tunnels of motorways, open burning sites, etc.

3.1.1.5.2 Rainfall (Bulk precipitation)

PAHs contamination of total atmospheric fallout (Σ14 compounds) was determined in the centre of Paris, from November 1999 to October 2000, and ranged from 51 to 995 ng/L, which represented a flux of 0.18 to 2.1 ng/m^2/day (Ollivon et al., 2001). Total concentrations in bulk precipitation samples from the main plain of Northern Greece were in the range of 0.8-781 ng/L with the higher values in the cold months (Manoli et al., 2000).

3.1.2 Fresh and wastewaters

3.1.2.1 Chlorinated pesticides

Cyclodiene pesticides (dieldrin, aldrin, endrin, heptachlor) have been reported in river water samples collected during the 80's and 90's in many countries in a wide range of values (<0.1 – 228 ng/L), but only in France as part of a continued monitoring activity. Therefore, it is not possible to assess the environmental significance of the reported values, as they do not correspond to representative river conditions. Concentrations of DDT ranged from 0.1 to 40 ng/L in rivers from Egypt, France, Italy and Spain, with values up to 83 ng/L in Po River (Italy).

Lindane and HCB have been found at levels ranging from 0.7-111 and 0.1-36 ng/L, respectively. Chlordane, toxaphene and endosulfan have only rarely been reported in the region.

Table 3.3. Concentrations of PAHs in aerosol samples from different cities and reference sites.

Location	Sampling period	PAHs	Conc. (ng/m^3)	Reference
Mediterranean Sea				
NW Coastal stations	1990	Σ10-14 PAHs	0.2-4	Conde et al., 1993
Algeria				
Algiers (downtown)	Wint./Sum. 1999	Σ18 PAHs BaP	59.9 / 13.7 0.4-2.3	Yassaa et al., 2001a
Oued Smar landfill	Wint./Sum. 1999	Σ18 PAHs BaP	136.5 / 24.9 0.3-3.9	Yassaa et al., 2001b
Egypt				
Cairo (urban area)	Wint./Sum.	Σ12PAHs BaP	14.8 / 7.5 0.1-0.2	Hassanein et al., 2001
Alexandria	Summer 1997-98	Σ39PAHs BaP	32 0.95	Barakat, unpubl.
France				
Paris (urban)	Winter 90-98	Σ9 PAHs BaP	4-24 0.4-3.2	Person, 2000
Lille (traffic sites)	1990-2000	BaP	0-1.2	Inst. Pasteur, 2000
Paris -Urban area -Motorway	 Wint./Sum. 1999 Wint./Sum. 1999	 Σ9 PAHs Σ9 PAHs	 13.7-18.4 / 5.6-7 33.3 / 27.1	AIRPARIF, 2001
Normandie -Industrial site -Rural area	 Winter 1996 Winter 1999	 BaP BaP	 1.88-6.99 0.13-0.99	INERIS, 1997
Greece				
Thessaloniki	1987-1988	Σ9 PAHs BaP	22-55 2-6	Viras et al., 1991
North Greece towns	Wint./Sum. 96-97	Σ13 PAHs	5-60 / 0.4-8.1	Papageorgopoulou et al., 1999
Crete -Finokalia	2000-2001 (N=26)	Σ10 PAHs BaP	11.3 (V), 0.8 (P) 0.003(V), 0.025(P)	Mandalakis et al., 2002
Italy				
Rome	1993-1998	Σ7PAHs BaP	5.96-7.33 1.2	Menichini et al., 1999
Bologna	1991-1993	BaP	0-174 (av. = 22.7)	Roda et al., 1994
Naples	1996-1997	PAHs BaP	2-130 0.31-3.8	Caricchia et al., 1999
Genoa -Traffic sites	1997-1999 1994-1999	Σ4 PAHs BaP	0.8-19.1 1.1-2.0	Valerio et al., 2000
Portugal				
East Coast (Aveiro)	August 1996	ΣPAHs	10-30	Alves et al., 2001
Spain				
Barcelona	Wint./Sum. 1991	Σ14PAHs BaP	240-310 / 10-32 0.76-22	Lipiatou et al., 1997
Madrid (traffic area)	Winter 93	Σ13PAHs	4.2-48.2	Kayali et al., 1995
Zaragoza	Wint./Sum. 99-01	Σ7PAHs BaP	12.5-18 / 3-6.5 0.09-1.65	Mastral et al., 2002
Syria				
Damascus	1999-2000	Σ18 PAHs BaP	14.8-45.7 0.9-2.7	Dimashki et al., 1996
FR Yugoslavia (Serbia & Montenegro)				
Belgrade	2000	BaP	0.2-0.6	Matić et al., 2001

Three cases of freshwater pollution in the vicinity of lindane factories have been reported in the 90's in the region (see section 3.5.2). Lindane has also been detected in 11.6% of the 1314 groundwater samples analysed from the Calvados Department, with concentrations ranging between 20-50 ng/L (Bintein and Devillers, 1996).

Residues of organochlorine pesticides in drinking water supplies of different cities (e.g Barcelona, Paris, Nicosia, Cairo, Istanbul and Tel-Aviv) were found to be absent or significantly below the permissible levels.

3.1.2.2 PCBs

The accurate assessment of PCB levels in freshwaters is precluded by the different units used in the studies performed until early 90's. The most relevant problem in the region concerning the aquatic environment is probably the contamination of several aquifers in the Balkans area during the Kosovo war (see section 3.5.1). However, the ecological disaster with greatest impact 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 (380 ng/L in 1988).

Concentrations of up to 120 ng/L (Σ7 cong.) were found in the wastewaters of Barcelona, Marseille, Toulon and Nice. An extensive study of the evolution of PCBs in wastewater treatment plants has been carried out in France and summarised in Table 3.5.

3.1.2.3 PCDD/PCDFs

PCDD/Fs have been determined in landfill leachates in Catalonia (Spain) and in the Ebro river with values of 6.4 and 0.01-0.05 pg ITEQ/L, respectively (Cabes et al., 1999). In general, the profiles were characterised by the large predominance of octachlorinated dioxin congeners.

3.1.2.4 Polycyclic aromatic hydrocarbons (PAHs)

Total concentrations of Σ15 PAHs in suspended matter of river waters collected in the 90's were in the range of <35-16600 ng/g dw (Tronczynski et al., 1999), whereas a study carried out in 1994-95 in the Rhone River found concentrations in the range of 100-500 ng/g (av. 300 ng/g dw, Σ7 PAHs) (Sicre and Fernandes, 1996).

A study of the evolution of PAHs in wastewater treatment plants has been carried out in France and summarised in Table 3.4. The levels of PAHs in ground waters measured between 1991-95 in the area of Paris were all <0.2 μg/L.

Table 3.4. Concentrations of PCBs and PAHs in wastewaters in France

Location	Sampling	PCBs (ng/L)	PAHs (ng/L)	References
25 WW plants (Seine watershed)	1990	(Σ7 cong) Input: 130 Output: 54		ADEME, 1998
11 WW plants (east of France)	1990-93	(Σ7 cong) Input: 280 Output: 53	(Σ6 PAHs) Input <100-2000 Output <100-1000	
Paris: wet weather	1999	(Σ7 cong) 15-26	(Σ15 PAHs) Input: 860 Output: 18	Teil et al., 2001;
dry weather		(Σ7 cong) 32-53 15-26	(Σ6 PAHs) 573 - 1180 90 - 899	Teil et al., 2000

3.1.2.5 Phthalates

Phthalates have been barely determined in freshwaters. Levels of 2.1-4.6 μg/L have been found in the mid course of the Seine River (Romaña, pers. com.) and in the Ebro River (0.7 μg/L of DEHP) (Peñalver et al., 2000). A continued survey of phthalates has been carried out in the major dams and rivers of Cyprus, since 1992 and the maximum concentrations detected for individual phthalates ranged from 5 up to 117 μg/L (Michaelidou, unpubl.).

3.1.2.6 Chlorophenols

Chlorophenols are monitored monthly in Portugal in 46 river water stations covering the whole country (see section 5.1.1). Pentachlorophenol was found in 19% of the samples collected in 1999 at concentrations between 0.1 - 1.0 μg/L (Marcolino and Vianha, unpubl.).

3.1.2.7 Alkylphenols

Nonylphenol (NP) and their ethoxylate derivatives were first studied in the Krka River estuary (Croatia). The concentrations of NP in municipal wastewaters varied within the range of <5-419 μg/L, being the concentration range in the estuary <20-1200 ng/L (Kvestak and Ahel, 1994). In Spain, NP were encountered in all water samples analysed at the vicinity of urban discharges and sewage treatment plants from Catalonia at levels of 6 - 144 μg/L (Petrovic et al., 2002). Measurable concentrations of NP were also found in 80% of the Portuguese river water samples. Concentrations ranged from 0.13-6.41 μg/L.

Recent studies have shown that total concentrations of alkylphenols in Israeli rivers, groundwaters, and coastal waters are in the range of 12.5-74.6, trace-20.2 and 4.2-25.0 μg/L, respectively (Zoller, 2001). Finally, water samples analysed in the Venice Lagoon (Italy) showed NPEO oligomers at an overall concentration range of 0.6-4.5 μg/L (Marcomini et al., 1990).

3.1.2.8 Organomercury compounds

The dynamics of the MeHg in the aquatic environment has been a subject of special interest in Slovenia. Idrija is the second largest mine of Hg in the world and even 10 years after its closure, the Idrijca and Soča rivers continue to supply about 1.5 tonnes of Hg per year to the Gulf of Trieste. The anoxic conditions of the bottom waters of the North Adriatic and the seasonal temperature stratification, favour the transformation of inorganic Hg into MeHg, which is the responsible for the elevated Hg levels in marine organisms in the region.

3.1.3 Seawater

Most of the first data published until the late 80's on organic pollutants in sea water lied below the analytical sensitivity of the method used, so the significance of the data sets is limited. More recently, the use of large water volume sampling devices has provided accurate data on levels and budgets of PTS in the marine environment (see section 4.3.2).

3.1.3.1 Chlorinated pesticides

Some surveys have been carried out in estuaries and coastal waters. α-HCH, β-HCH and lindane were detected in significant amounts (1-30 ng/L) in the marine wetlands of Amvrakikos and Thermaikos Gulfs in Greece (Albanis et al., 1994; 1995a). Similar levels were reported in coastal waters of Alexandria and Abu-Quir (Abd-Allah and Abbas, 1994; Abd-allah, 1999). Lindane levels off shore in the Eastern Mediterranean ranged from 0.06 to 0.12 ng/L, and values even lower were found in the Western basin, although along the Spanish coast 1.3-2 ng/L of HCHs were found (Prats et al., 1992).

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.

3.1.3.2 PCBs

An extensive review of data obtained during the 80's has been published by Tolosa et al. (1995). 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. Predictably, the highest concentrations were reported in urban and industrial wastewaters (e.g. from Marseille and Barcelona) as well as in river discharges (e.g. from the Rhône). Accordingly, decreasing concentration gradients have also been found in transects offshore from these sources.

PCB concentrations in the suspended particulate matter from coastal and open Western Mediterranean waters were in 1990 of 5-35 pg/L, of the same order of magnitude as those reported in other regions, e.g. North Sea and North Atlantic. 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) and a relatively important enrichment (8.4 pg/L) in open sea stations located in higher productivity frontal zones (Dachs et al., 1997). The dissolved PCBs (Σ12 congeners) amounted 28-63 pg/L.

3.1.3.3 Polycyclic aromatic hydrocarbons (PAHs)

A large number of determinations of aromatic hydrocarbons in sea water were performed in the 80's within the MEDPOL Program, following the ICES procedure. However, recent data are usually referred to individual compounds, and, therefore, not comparable with previous bulk data.

In 1997, levels of PAHs in samples from the North Aegean Sea were found to be 0.01 to 0.03 μg/L. Along the Turkish coast, concentrations vary over a wider range (0.02 to 40 μg/L), with high concentrations from offshore

samples caused most probably from direct discharges from the ships. In 1999, the concentrations of 16 PAHs were found in the range of 0.2-7.4 ng/L in sea water along the coast of İzmit Bay (Marmara Sea, Turkey) (Kolankaya, unpubl.). Coastal waters sampled at 1 mile from the main Portuguese estuarine systems presented concentrations of 2-3 ring PAHs in the range of 0.5 - 9.5 ng/L (Vinhas et al., 2000).

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, maximising 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 PAHs content 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.

3.1.3.4 Organotin compounds

MEDPOL organised in 1988 a survey to monitor butyltins in seawater and sediments of marinas and harbours, to be representative of the various contaminated sites along the Mediterranean previous to the TBT regulation. The areas investigated were the French Mediterranean and Northern Tyrrhenian coasts, the Nile Delta area, and the Southern coast of Turkey. The concentrations of TBT in seawater from harbours and marinas on average vary between 100 and 1000 ng/L (Gabrielides et al., 1990).

In the Spanish Mediterranean coast, butyl and phenyltin compounds were determined for the first time in 1988 (Tolosa et al*.,* 1992). Highest concentrations were found in marinas (TBT: 74-369 ng/L; TPhT: 3-68 ng/L). In the SW Spanish waters (Cadiz Bay) TBT ranged from 100-400 ng/L and no phenyltin species were found (Gómez-Ariza et al*.,* 1992).

A later survey conducted in the NW Mediterranean coastline (Cote d'Azur) found water concentrations reaching to 460 ng/L for TBT in all marinas. Triphenyltin (TPhT) and TBT degradation products were also detected, but at lower concentrations than TBT (Tolosa et al., 1996). In another study carried out in the Eastern and Western Harbours of Alexandria, the concentrations of TBT and TPhT were in the ranges of 18-83 ng/L and 30-135 ng/L, respectively, also proving recent inputs of these compounds (Abd-Allah, 1995).

A campaign conducted by IFREMER in 1997 confirmed that contamination of French coast was still a problem because 75% of the measurements were above the threshold of 1 ng/L, which is known to cause toxic effects for some marine species. Another study conducted in 1998 measured TBT concentrations in the NW Mediterranean open waters (France) as high as 0.47 ng/L, 20 km off-shore, and never lower than 0.08 ng/L in the open sea. Contamination of abyssal deep waters reached to a maximum of 0.04 ng/L at a depth of 1200 m (Michel and Averty, 1999).

3.1.4 Soils and sewage sludges

3.1.4.1 Chlorinated pesticides and PCBs

Surveys of DDTs and PCBs in soils are very scanty and mainly related to the studies carried out after the Kosovo war. Lindane has also been a problem in the Balkan countries in relation with some abandoned stockpiles (see section 3.5).

Sewage sludges are monitored for PCBs in countries like France were they are largely used (60%) in agriculture. The EU establishes a maximum concentration of 0.8 mg/kg of PCBs (Σ7). The values found in 50 wastewater plants of the East of France were between 0.05 – 1.13 mg/kg and 0.5 mg/kg in the region of Paris. The mean value in sludges disposed in agriculture was of 0.19 mg/kg (Table 3.5).

Table 3.5.- Concentrations of PCBs and PAHs in sewage sludges in France

Location	Sampling	PCBs (µg/g dw)	PAHs (µg/g dw)	References
Mean of 50 plants (East of France)	1994	(Σ7 cong.) 0.05-1.13		ADEME, 1998
Agricultural area (Chalons en Champagne)	1996		0.72 (Σ6 PAHs)	Palayer, 1997
Industrial area (Le Havre)	1996		10.8 (Σ6 PAHs)	Palayer, 1997
Mean in agricultural recycling	2000	(Σ7 cong.) 0.19	1.23 (Σ Flu, BaF, BaP)	ADEME, 2001
Paris (*Achères*) annual mean	2000	(Σ7 cong.) 0.50	1.80 (Σ Flu, BaF, BaP)	(Data from SIAAP)

3.1.4.2 PCDD/PCDFs

Data about levels of PCDD/Fs in soils are available for the five EU countries of the region (Table 3.6). In general, data come from studies where the concentrations of PCDD/Fs were measured around areas influenced by potential point sources, such as waste incinerators or industrial plants. Soil concentrations are similar in the five countries, with logical urban-rural gradients. Soils under the influence of strong emitting sources (e.g. uncontrolled combustion) present the high levels.

Table 3.6. Summary of PCDD/Fs concentrations in soils from Mediterranean countries (expressed as ng I-TEQ/kg dw).

Country	Backgrd.	Forest	Pasture	Arable	Rural	Urban	Influenced by point sources	References
France	0.02-0.35				0.09-1.0	0.2-17	2-60	ADEME, 1998
Greece	2						34-1144	Martens et al., 1998
Italy	0.06-4.31	5.31	0.1-43	0.08-3.1		1.0-6.2	0.9-130	Fachetti, 1998
Portugal					0.79-0.85	2.04-16.4		Coutinho et al., 2002
Spain	0.27-2.24	0.72-1.16			0.12-8.40	0.15-24.2	0.1-1080	Eljarrat et al., 2001

Concentrations in sewage sludges from rural and urban wastewater treatment plants sampled during the 90's in Catalonia (Spain) range from 5.6 to 90 ng I-TEQ/kg dw. The comparison of these levels with those detected in sludges sampled and archived during the 70's and 80's (which show levels between 29 and 8300 ng I-TEQ/kg dw) seems to indicate a decline in PCDD/Fs concentrations in this type of matrix (Eljarrat et al., 1999). The values found in the other EU member states range from 15-40 ng ITEQ/kg dw.

The use of sewage sludge for fertilising soils is a quite common practice in some countries. Molina et al. (2000) studied the evolution of PCDD/Fs in sewage sludge-amended soils used in the restoration of degraded lands. Their results revealed that polluted sewage sludge increases PCDD/Fs concentration in soils and that these compounds are persistent in soil after long periods of time (> 2 years).

3.1.4.3 PAHs

The distribution of PAHs in solid wastes, soil and aquifer sediment beneath the municipal solid waste landfill of Zagreb (Croatia) has been studied. Results suggested that despite their high concentration in solid waste (0.39-3.88 μg/g), higher PAHs (>4 rings) usually do not pose a major risk to groundwater due to the efficient biological elimination in landfills and an efficient sorption on organic-rich soils immediately beneath the landfill (Ahel and Tepic, 2000). In the Novi Sad region (FRY) soils were found to contain up to 2.44-8.53 μg/g of PAHs (∑16) (av. 5.48 μg/g) after the war period (section 3.5.1) (Sekulic, 2001).

Concentrations of PAHs in sewage sludges from rural and urban areas in France are presented in Table 3.5. The European threshold values for their use in agriculture are: 0.53 μg/g Flu, 0.39 μg/g BaF and 0.31 μg/g BaP.

3.1.4.4 Alkylphenols

High concentrations of NP (170-600 mg/kg) have been found in digested sewage sludges from wastewater treatment plants in the Catalonian region (Spain) (Petrovic et al., 2002).

3.1.5 Sediments

3.1.5.1 Aldrin, dieldrin, endrin, heptachlor and chlordane

Cyclodiene pesticides have been extensively reported in sediments collected during the 80's in the Nile River (Egypt), associated with agricultural practices. More recently, lower levels of heptachlor (0.01-0.93 ng/g dw) and total chlordane (sum of γ and α-chlordane) (0.4-18.5 ng/g dw) were reported in sediments from the Nile River and the Manzala Lake (Yamashita et al., 2000). In coastal sediments, cyclodiene pesticides were found to be in the range of <0.1-72 ng/g (Abd-Allah and Abbas, 1994), whereas values up to 44 ng/g dw were reported for total chlordane (sum of γ and α-chlordane) in the Alexandria harbour sediments (Barakat et al., 2002).

Cyclodiene pesticides were found in the Ebro River sediments all along the course at concentrations ranging from 0.02 to 1.7 ng/g dw (mean 0.4 ± 0.6 ng/g). Aldrin was found only in 46% of the samples (Fernandez et al., 1999). In Israel, levels were <0.5 ng/g in coastal, estuarine and river sediments, but noticeable in surface sediments of Lake Kinneret for dieldrin (1.6-9.9 ng/g) and heptachlor (2.1-59.9 ng/g) (Zimand, 2002). 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 ng/g on dry basis (Michaelidou and Christodoulidou, unpublished data).

3.1.5.2 HCB

HCB is widely distributed in the Western Mediterranean. The higher concentrations have been reported for the Gulf of Fos, the Rhone and the Ebro Deltas (30-39 and 19 ng/g dw, respectively). In the coastal shelf the values were below 1 ng/g (Prats et al., 1992; Tolosa et al., 1995).

HCB was found in shallow sediments of the Venice Lagoon (Italy) at concentrations ranging from 0.85-1.11 ng/g dw (Bernstein et al., 2002) and in 4 out of 9 sampling locations of river sediments in Cyprus, at levels ranging from 0.1-4.8 ng/g dw (Michaelidou and Christodoulidou, 1998, unpublished data).

HCB residues were reported in sediments from the Nile River, in the range of 3.8-4.5 ng/g dw (Yamashita et al., 2000). In Alexandria region, HCB residues in sediments from Abu-Quir and El-Mex Bays exhibited concentrations in the range 5-60 ng/g dw (Abd-Allah and Abbas, 1994), whereas lower levels (<5 ng/g dw) were reported recently in sediments from Lake Maryut and Alexandria harbour (Barakat et al., 2002).

3.1.5.3 DDT and PCBs

Sediments constitute an important sink for DDT and PCBs entering the marine environment. A mapping of DDT and PCBs of the Western Mediterranean basin in bottom sediments (around 100 samples) has revealed the widespread occurrence of these pollutants in the region and allowed a mass balance assessment (Tolosa et al., 1995 and 1997) (see section 4.3.2). Localised inputs or "hot spots" have been identified near sewage outfalls from highly industrialised and populated cities (e.g. Marseille, Barcelona and Naples) and the freshwater discharges like the Po, Rhône (229 ng/g Σ9 PCB cong. and 227 ng/g DDTs) and Ebro (34 ng/g Σ9 PCB cong. and 47 ng/g DDTs) rivers. However, beyond the zone of influence of these discharges, concentrations drop rapidly reflecting the enhanced sedimentation processes, which take place at the freshwater-seawater interface. The levels of DDTs and PCBs in the deep basin were of 0.5-1.2 and 1-2 ng/g dw (Σ9 cong.), respectively. More recent data is shown in Table 3.7.

Table 3.7. Levels of DDT and PCBs in estuarine and coastal sediment samples of the Mediterranean region

Country	Location	Sampling	DDTs (ng/g dw)	PCBs (ng/g dw)	References
Albania	Adriatic coast	1993		1 to 5	Koci, 1998
Cyprus	Dams	1997- 98	ΣDDTs: 19- 660	2-158	Michaelidou unpubl.
Egypt	Nile River	1993	DDT: 7; DDE : 45		Yamashita et al., 2000
	Manzala Lake	1993	ΣDDTs: 5-640	125 - 330	Yamashita et al., 2000
	Maryiut Lake	1998	ΣDDTs: 2-157	4.2-304	Barakat et al., unpubl.
	Coastal Bays	1990	ΣDDTs: 32 - 223	39 - 744	Abd-Allah et al., 1994
	Alexandria Harbour	1998	ΣDDTs: av. 87 (<0.25 – 885)	0.9-1210 (av. 260)	Barakat et al., 2002
France	Rhone delta	1994-96	DDT: 5-15		IFREMER, 1998
	Coastal cities (Marseille,…)		DDE: 16 (av.) DDT: 11 (av.)		
	Coastal lagoons		DDE: 1-2.3 DDT: 2-15		
Greece	Northern estuaries	1992 -93	ΣDDTs: 0.3-60		Albanis et al. 1994, 1995a
Morocco	Med. coast	1996	ΣDDTs: 0.1-1.8	0.1-1.8	Pavoni et al., 2002
Portugal (estuaries)	Guadiana	2001	Σ DDTs: 0.03-11.7	0.04-2.4	Ferreira et al, 2002
	Sado, Tagus	1987-89	Σ DDTs: 0.1-21	0.1-87	Castro and Vale, 1995
	Mondego	1998	Σ DDTs: 0.4-1.2	0.2-5.2	Vale et al., 2002
Spain (rivers)	Ebro (bed)	1995-96	Σ DDTs: 0.4 to 7.9	14.1 (av.)	Fernandez et al., 1999
	Ebro (delta)	1990	Σ DDTs: 47 (av.)		Tolosa et al., 1995
	Guadalquivir		Σ DDTs: 18 (av.)	12.2 (av.)	Hernandez et al, 1992
FR Yugoslavia	Danube	2001	ΣDDTs: 3.20	0-774 (Σ7cong.)	Jaroslav Cerny Inst, unp.
	Adriatic coast	1994	ΣDDTs: 0.1 – 1.5	1.2 – 3.8	Vojinovic et al., 2002

3.1.5.4 PCDD/PCDFs

Some data of PCDD/Fs concentrations in sediments are available for Italy, Spain and Portugal. In Italy, the most studied area has been the Venice Lagoon (see section 3.1.7.3). In addition, the first data on PCDD/Fs levels in Po River sediments have been recently published. Concentrations range from 1-2 ng WHO-TEQ/kg dw to 10-11 ng WHO-TEQ/kg dw (Fattore et al., 1997).

Sediments sampled in the Catalan coast in the late 80's - early 90's, showed concentrations in the range 0.4-8 ng ITEQ/kg dw (Eljarrat et al. 2001). The influence of a sewage sludge dumping site increased these levels to 57 ng ITEQ/kg dw. In Portugal, data are only available from three river sediments in the Oporto region. PCDD/Fs concentrations range from 0.54 to 3.39 ng ITEQ/kg dw. In general, profiles show higher concentrations of those congeners with high chlorination degree, mainly OCDDs and OCDFs.

3.1.5.5 HCHs

HCHs were detected during the 80's in coastal sediments from the Western, Central and Eastern part of the Mediterranean, with mean values of 0.5-2.5 ng/g (Jeftic, 1993). A comparison of the concentrations found in recent studies, in various areas of the Mediterranean, is presented in Table 3.8. Concentrations up to 100 ng/g, and therefore to be taken into consideration as a result agricultural pollutants of the coast of Portugal (e.g. Sado, Duoro, Lima, Mondego, etc.).

Table 3.8. Levels of γ-HCH in sediment samples from different locations in the Mediterranean region

Country	Location	Sampling	Conc. (ng/g dw)	References
Egypt	AbuQuir and El-Mex Bays	1992	10-51 (30)	Abdallah and Abbas, 1994
	Nile River and Manzala Lake	1993	0.07-2.7 (0.6)	Yamashita et al., 2000
	Alexandria Harbour	1999	<0.25-2.1	Barakat et al., 2002
France	Seine River	2000	0.5-1.2	Romaña, pers. com.
Greece	Thermaikos Gulf	1992 - 1993	7-140 (α+γ-HCH)	Albanis et al., 1994
	Amvrakikos Gulf	1992 - 1993	0.1-29 (α+γ-HCH)	Albanis et al., 1995a
Israel	Lake Kinneret	2001	14.5 - 45.6	Zimand, 2002
Spain	Ebro prodelta	1990	0.02-0.94 (ΣHCHs)	Tolosa et al., 1995
	Ebro River	1995-1996	0.007 (ΣHCHs)	Fernández et al., 1999
	Off-Barcelona	1990	0.02-1.22 (ΣHCHs)	Tolosa et al., 1995

3.1.5.6 Endosulfan

Mean concentrations of α- and β-endosulfan in different sites of the coastal lagoon of Mar Menor (Spain) were in the ranges of 1.67-86 and 1.83-248 ng/g, respectively (Perez-Ruzafa et al., 2000). In Israel, levels of endosulfan were reported to be lower than 2 ng/g in coastal, estuarine and river sediments, while levels of 33-276 ng/g were reported in surface sediments from Lake Kinneret (Zimand, 2002). Endosulfan II (<0.25-22 ng/g dw) was detected in 44% of the 23 samples collected in 1999 from Alexandria harbour (Barakat, unpubl.).

3.1.5.7 Polycyclic aromatic hydrocarbons

PAHs are widespread in coastal zones and clearly associated to urban and industrial inputs. An increasing trend of pyrolytic PAHs in transects from the coastal areas towards the open sea indicate the predominance of atmospheric inputs in the latter, which account for 80-90% of the total in the deep sea basins. Concentrations of PAHs reported in sediments from different locations of the Mediterranean region are presented in Table 3.9.

3.1.5.8 Phthalates

Data is very scanty. Levels of 6-9 μg/g dw of DEHP were found off-shore Barcelona (Spain) close to the urban sewage outlet. DM, DE, DB phthalates were found at concentrations in the order of 0.1 of μg/g dw each (Garcia et al., unpubl.). Phthalates were also detected in all sediment samples collected in the major dams of Cyprus (1997-98). The total concentrations ranged from 70 ng/g to 447 ng/g dw.

3.1.5.9 Alkylphenols

Data is scarce in the region. Sediment samples were analysed in the Venice Lagoon, being the sum of NP, NP1EO and NP2EO in the range 0.15-13.7 μg/g dw (Marcomini et al., 1990). On the other hand, in sediments collected along the Spanish Mediterranean coast, concentrations ranged from <10 to 480 μg/kg dw of NP. In the Atlantic coast the values were similar. OP was only found in some samples (21 – 145 μg/g dw) (Petrovic et

al., 2002). Levels up to 66-81 µg/g dw. of NP were found off-shore Barcelona (Spain) close to the urban sewage outlet (Garcia et al., unpubl.).

Table 3.9. Concentration levels of PAHs in coastal sediments from the Mediterranean region

Location	Sampling	PAHs	Conc. (µg/g dw)	References
NW Mediterranean Sea				
	1987-91 1996-98	Σ22 PAHs Σ14 PAHs	0.06-4.84 0.001-20 (3.31)	Tolosa et al., 1996 LPTC Bordeaux
Algeria				
Algiers Bay -Off the coast			117 to 1820 19 to 96	Sellali et al., 1998
Cyprus				
Rivers	1997-98		0.07 to 1.09	Michaelidou, unpubl.
Egypt				
Alexandria Harbour	1998	Σ39 PAHs	0.008 to 131 (28.7)	Barakat et al., 2002
Maryut Lake	1998	Σ39 PAHs	0.4 to 4.0 (1.1)	Barakat et al., unpubl.
France				
French coasts	1996	Σ14 PAHs	0.01-0.36	Baumard et al., 1998
Harbours	1996	Σ14 PAHs	0.055-6.94	Baumard et al., 1998
Greece				
Thermaikos Gulf	1991		0.5-0.9	Kilikidis et al., 1994
Israel				
Coasts and rivers Industrial outfalls	1995 1995		2.76-7.76 0.32-36.6	Zimand, 2002
Italy				
North Adriatic coast	1990	Σ10 PAHs	0.02 to 0.5	Guzzella and De Paolis, 1994
Venice Lagoon	1996-99	Σ15 PAHs	0.57-3.20	Bernstein et al., 2002
Morocco				
Mediterranean coast	1996	Σ16 PAHs	0.01-0.55 (av. 0.02)	Pavoni et al., 2002
Portugal				
Main River Estuaries	1995-98	Σ5 PAHs	n.d.-5.97	Vinhas et al., 2000
Slovenian coast				
Koper area	1996	Σ22 PAHs	0.04 and 0.68	Notar et al., 2001
Spain				
Spanish coasts	1996	Σ14 PAHs	0.005-0.84	Baumard et al., 1998
Harbours	1996	Σ14 PAHs	1.74-8.42	Baumard et al., 1998
Tunisia				
Sfax Bay			1865	Louati et al., 2001
Turkey				
Bosphorus	1995	Σ17 PAHs	0.01-0.53	Readman et al., 2002
FR Yugoslavia (Serbia & Montenegro)				
Danube	2000	Σ16 PAHs	0.266-123.5	Dalmacija et al., 2000

3.1.5.10 Organotin compounds

The 1988 MEDPOL pilot survey on TBT (section 3.1.3.4) 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 (IFREMER, 1996).

Studies have also been performed in many coastal sites (e.g. Egypt, Malta, France, Spain, Italy, etc.) (Bressa et al., 1997; Barakat et al., 2002; Díez et al., 2002) with reported values of 1 to 2067 ng Sn/g dw for TBT, indicating 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.

A comparative study of the organotin occurrence in the sewage sludge disposal sites offshore Spanish cities shows that domestic primary sewage sludge effluents can contribute to coastal organotin pollution (100 ng/g of TBT). Nevertheless, sewage sludge is a secondary source of contamination in the coastal environment compared with antifouling paints (Gomez-Ariza et al., 1995).

3.1.5.11 Organomercury compounds

The Gulf of Trieste is one of the most mercury-contaminated areas in the Mediterranean Sea. It is characterised by high mercury inputs from the Isonzo River whose tributary, the Idrijca River, drains the mercury mining area of Idrija in Slovenia where extraction activity has taken place for nearly 500 years. This appears, therefore, to be one of the most suitable sites for studying processes that affect Hg cycling in the marine environment and for determining whether sediments might act as secondary sources of mercury species in the water column.

A recent study (1995-1997) aimed for assessing the extent of contamination of the Gulf of Trieste showed that the major source of inorganic mercury is still the Isonzo River while the major source of methyl mercury is the bottom sediment of the Gulf (Horvat et al., 1999).

3.1.6 Temporal trends

3.1.6.1 Chlorinated pesticides

Decreasing trends have generally been observed for organochlorine insecticides in surface streams during the 80's and 90's. This is the case, for example, for the Danube River and its tributaries in Vojvodina (FR Yugoslavia); the Nile (Egypt), where levels of DDT decreased by 100 fold in the period 1982-1993, although this difference can be partially attributed to the higher accuracy in the analytical methods; the Seine (France), with a sharp decrease for the drins and DDT since 1985, and for lindane since 1993, etc.

Figure 3.1 shows the temporal trend of DDTs (DDT+DDE) concentrations in sediments from the Eastern Adriatic Sea (Picer and Picer, 1991). Temporal trends of chlorinated pesticides have also been assessed using dated sediment cores collected in the mouths of the rivers (e.g. Ebro, Nile, etc.), showing increasing discharges until mid 80's and further decrease, although HCHs are still increasing at present times in the Nile.

3.1.6.2 PCBs

Concentrations reported at the mouths of the Ebro and Rhone Rivers in 1993 were consistently lower than those found during the previous decade. During the period 1974-82 concentrations were also reduced by a factor of 3 off-shore Monaco (Burns et al. 1985).

Temporal variability of PCBs contamination has also been assessed through analyses of dated sediment cores from the Rhône and Ebro areas (Tolosa et al., 1995). In the Rhône area, maximum PCBs concentration was identified during the period 1960-75, whereas near the Ebro the maximum was still in the surface, corresponding to the period 1975-90. These data suggests that the restricted use of PCBs in 1976 was more effective in France than in Spain. Indeed, the factory located upstream from the Ebro river may be the sole reason for this difference. The surface sediments of the Adriatic coast (Figure 3.1) did not show a temporal trend (Picer and Picer, 1991).

Long-term trends of contamination for some pollutants and media for a number of countries have been estimated by the MSC-East Centre from field data and emission expert estimates. Figures show that the downward concentration trends follow the emission reductions, although soil concentrations decrease at much slower rates (http://www.msceast.org/countries/index.html).

3.1.6.3 PAHs

Atmospheric PAH concentrations were measured weekly for 24 h at 4 sites in the urban area of Paris (France), during winter, from 1990 to 1998 (AIRPARIF). The average particulate concentration of BaP ranged from 0.4 to 3.2 ng/m^3 and showed a decreasing trend down to twice lower during this period.

Sediment cores have also been sampled for assessing temporal trends of PAHs. Sediments from the Piallassa Baiona coastal lagoon (North Adriatic) and from the Rhone and Ebro prodeltas showed maximum accumulation rates of PAHs in the 1920-1940 and the 1975-1990 periods, although with a steep decrease since mid 80's.

Concentrations of PAHs in sea water samples obtained from various areas of the Mediterranean Sea have statistically significant differences from year to year, but levels do not show any significant yearly trend. Moreover, as shown in Table 3.9, the concentrations in NW Mediterranean surface sediments remained within the same range during the last decade.

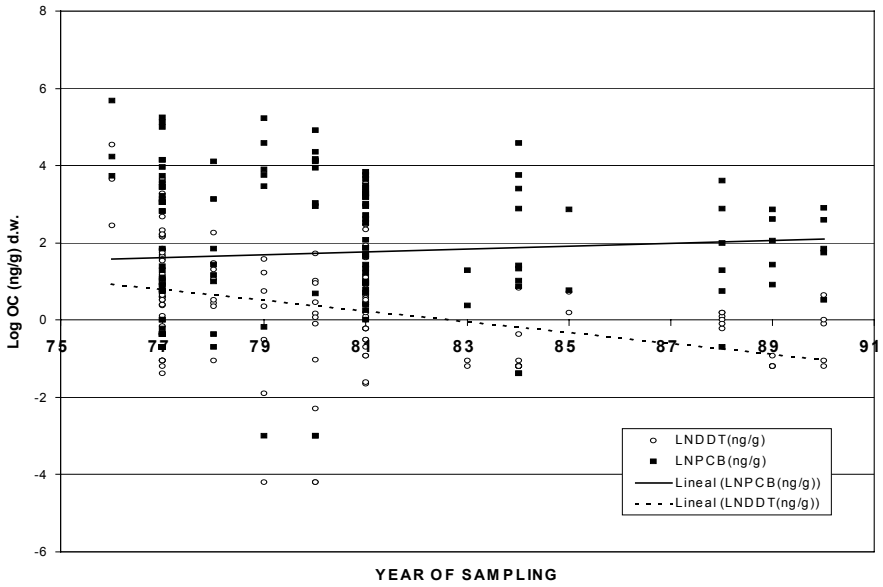

Figure 3.1. Temporal trend of DDT and PCB levels in Eastern Adriatic coastal sediments

3.1.6.4 Organotin compounds

The comparison of data on sediments collected in the late 80's and in 1999 in the Catalan coast (Tolosa et al., 1992) reveals that organotin regulations established in the Mediterranean region in 1991 on the use of TBT-based antifouling paints have been effective in marinas, but not significantly in commercial and fishing harbours. Surveys conducted in areas of the South Atlantic coast of Spain (Gómez-Ariza et al., 1995) and the Mediterranean coast of France (Tolosa et al., 1996) also reveal a decline in the TBT concentration in seawater but still exceeding the non-effect level for the most sensitive species.

3.2 CONCENTRATIONS OF PTS IN BIOTA, INCLUDING HUMANS

3.2.1 Terrestrial biota

3.2.1.1 Vegetation

Using compartmental modelling, the Meteorological Synthesising Centre-East has estimated mean concentrations of HCB in natural media of all northern countries of the Mediterranean region, which are reflected in vegetation (Dutchak et al., 2002). Calculated mean concentrations range from 0.03 ng/g in Turkey to 0.57 ng/g in France.

Leafy vegetables (cabbage and lettuce) and, particularly, conifer needle species have been mainly used as biomonitors to evaluate the pattern of PTSs contamination. HCB, HCHs and DDTs have been measured in pine needles in Greece and more extensively in Italy, Croatia and France. The results are summarised in Table 3.10.

Table 3.10. Concentration of some organochlorinated hydrocarbons 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	Reference
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)	Krauthacker et al., 2001
France (Paris)		7-27	59-69			190-680 (av. 340)	Granier et al., 1992
Greece	5.0-7.2						Calamari et al., 1999
Italy (North):							
- Industrial	2.2-5	1.4-26	3.9-10	1.6-12.4	2.6-11	30-360	Gaggi et al., 1985
- Alps	0.5-3	1.1-4.5	0.6-4.9	0.6-3.2	0.6-5.0		

The sampling sites in Italy cover the whole country, from the North (Alps and Milano) to the South (Taranto). The highest levels of HCB in pine needles were found in Milano, while the lowest were in the Alpine region, far from urban pollution. Conversely, HCHs levels in vegetation were lower in the Northern industrialised area than in Central Italy (e.g. Siena, Pisa), where there is widespread agricultural activity.

PCBs are widespread environmental contaminants but there are few data in vegetation as shown in Table 3.10. Higher levels were found in sites considered as "hot-spots" where there is an evidence of a PCB-pollution source (e.g. electrical transformers).

PCCD/Fs have been found in pine needles collected in urban and rural sites revealing that they are excellent biomonitors for dioxins contamination (Di Guardo et al., 1999). 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.

The Seveso area (Italy) was of particular concern for PCDD/Fs contamination of vegetables and human risk assessment (Arnoldi et al., 1999). The vegetables analysed are zucchini, cabbages and cucumbers and the most abundant isomers were hepta and octacloro dioxins indicating that atmospheric deposition plays an important role in determining levels in vegetables.

3.2.1.2 Animals

Surprisingly there is no recent information on most chlorinated pesticides in terrestrial animals, considering that these are at the top of the food chain. Only some studies have been performed in Italy, involving foxes, rabbits and barn swallows.

3.2.1.2.1 DDT and metabolites

Mean DDT values (op'- and pp'-DDT, DDE and DDD) were 0.55 μg/g in muscle (n=18) and 0.14 μg/g in fat of *Vulpes vulpes* (fox) from Pisa, 1.16 μg/g in muscle (n=36) and 0.49 μg/g in fat of foxes from Siena, while specimens from Grosseto contained 4.17 μg/g in muscle (n=3) and 0.67 μg/g in fat (Corsolini et al., 2000a).

In barn swallows (*Hirundo rustica*) collected in 1995 in agricultural areas around Milan (Northern Italy), mean pp'-DDE levels in liver and muscle were 95 and 75 ng/g ww, respectively (Kannan et al., 2001).

3.2.1.2.2 HCB

HCB in red foxes (*Vulpes vulpes*) sampled in 1992-1993 from three variously impacted areas of Tuscany ranged from an average of 0.08 μg/g ww in fat (n=13) of foxes from Pisa (industrialised area) to 1.06 μg/g ww in muscle (n=3) of those from Grosseto (agricultural area) (Corsolini et al., 2000a).

3.2.1.2.3 PCBs

ΣPCBs ranged between 0.6-8.0 ng/g ww (mean: 2 μg/g; n=10) in red foxes (*Vulpes vulpes*) from Central Italy collected in 1991-1992. TEQs were calculated on 13 dioxin-like PCB congeners (range: 17.8-1379.6 pg/g; mean: 177.8 pg/g) (Corsolini et al., 1995a). PCBs were also detected in adipose and muscle tissues of red foxes (*V. vulpes*) sampled in 1992-1993 in three areas of the Tuscany region. Mean concentrations on lipid basis were 20.2-38 μg/g in muscle and 7.2-7.5 μg/g in fat (Corsolini et al., 2000a).

Barn swallows (*Hirundo rustica*) collected in 1995 from agricultural areas around Milan (Italy) contained mean values of 1230 ng/g ww in liver and 716 ng/g ww in muscle. Toxic equivalents, calculated as the sum of TEQs of coplanar PCBs, PCDD/Fs and PCNs, ranged 14.1-19.7 pg/g ww in swallow tissues (Kannan et al., 2001).

3.2.1.2.4 PCDD/PCDFs

The liver of some rabbits fed for 3-4 months with grass cut in four areas selected for their specific contamination (Seveso area) was analysed to detect the dioxins contamination. The highest concentration (27-31 pg I-TEQ/g ww) was detected in rabbits that were fed with grass cut over basins that contain materials and debris of the ICMESA accident. The rabbits fed with grass that should be contaminated mostly by deposition of traffic pollution were less contaminated (5-13 pg I-TEQ/g ww).

PCDD/Fs in barn swallows (*Hirundo rustica*) collected in 1995 from agricultural areas around Milan (Northern Italy) were below the limits of detection (Kannan et al., 2001).

3.2.2 Freshwater environment: fish and aquatic birds

3.2.2.1 Aldrin, Dieldrin, Endrin, Heptachlor and Heptachlor epoxide

Concentrations of aldrin, dieldrin and heptachlor in gills of fish (*S.galileum*) from different sites in Lake Kinneret (Israel) were found in the range 0.5-106.5 ng/g (Zimand, 2002). In Egypt, the levels of pesticides in fish were generally lower and below the acceptable tolerance levels for human consumption.

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) and heptachlor epoxide (1 – 57 ng/g dw) were measured in unhatched Audouin gull eggs from Aegean Sea (North-eastern Mediterranean) colonies in 1997 and 1998, whereas dieldrin was below the detection limit (Goutner et al., 2001). Lower residue values of aldrin (0.01 – 0.3 ng/g dw), heptachlor (0.3 – 0.9 ng/g dw) and heptachlor epoxide (3.8 – 8.6 ng/g dw) were found in four Greek wetlands of international importance (the Evros and Axios Deltas, and Kerkini and Prespa Lakes), using the cormorant *Phalacrocorax carbosinesis* (Konstantinou et al., 2000).

3.2.2.2 DDT

The zebra mussel, *Dreissena polymorpha*, has been used by Galassi et al. (1994) to monitor the Po River basin. The maximum level of DDT was found in Lake Magiore at the mouth of the River Toce (3120 ng/g ww) which may indicate a point source, identified as a DDT manufacturer located at Pieve Vergonte. Zebra mussel was also used in the Seine River which exhibited a DDE conc. of 8.4-29 ng/g dw (Chevreuil et al., 1996).

Data available for different Po River fish species vary from 17 ng/g ww (eel) to 4030 ng/g fat weight (barbel) (Galassi et al., 1994; Bressa et al., 1997; Vigano et al., 2000). Roach catched in the Seine River in 1996 contained 4.1 ng/g ww of DDE (Chevreuil, pers. com.).

In Croatia, levels of DDTs in various rivers and fish species are between 1 and 147 ng/g (Radakovic et al., 1992). In the FR Yugoslavia, perch, carp and pike from the tributaries of the Danube River in the region of Vojvodina exhibited levels ranging 1.7-49 ng/g (Vojinovic-Miloradov et al., 2002). In Egypt, DDTs in fish species from the River Nile and coastal lakes range from 1 to 850 ng/g (Dogheim et al. 1996a; Yamashita et al., 2000; Abd-Allah and Ali, 1994; Badawy and Wahaab, 1997). Levels of DDTs (1-31 ng/g ww) measured in fish samples collected during 1995-1996 from the local markets indicated a decline in DDT concentrations.

A number of studies have focused on the use of eggs of aquatic birds as biomonitors. Levels of pp'-DDE in eggs of avocet and fish-eating birds of the Po River Delta are shown in Table 3.11. Eggs of *Egretta garzetta,* collected in the Göksu Delta (Turkey), were also analysed for DDTs (1254, 787 and 85 ng/g dw of p,p'-DDT, p,p'-DDD and p,p'-DDE, respectively) (Ayaş et al., 1997).

Table 3.11. Mean organochlorine concentrations (in ng/g ww) in eggs of avocet and fish-eating birds of the River Po Delta (Focardi, 2002).

Species	PCBs	p,p'-DDE	HCB
3.2.2.2.1.1.1.1.1 Phalacrocorax sp.	477 - 7085	206 - 1281	1.13 - 3.82
Sterna sp.	1060 - 2551	316 - 349	2.01 3.17
Larus ridibundus	5041	960	5.13
Egretta garzetta	1314	372	1.02
Recurvirostra avosetta	329	198	1.97

DDTs were determined in eggs of Dalmatian Pelican (*Pelecanus crispus*) as well as in eels (*Anguila anguila*) the main pelican prey, collected at the wetlands of Amvrakikos Gulf (Greece) during 1992-93 (Albanis et al., 1995b). DDTs 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 Northern Greek wetlands, using the cormorant *Phalacrocorax carbo*(Konstantinou et al., 2000).

The Balearic shearwater *Puffinus mauretanicus,* which is a species of special concern in the area because of its status of endemic threatened seabird, has shown levels of 3-2544 ng/g dw of pp'-DDT (3-1937 pp'-DDE) (Ruiz et al. 2002). It is outstanding the lack of information for the South and South-Eastern basin. Only recently, some data corresponding to *Larus audouinii* from the Chafarinas Islands has been obtained (DDTs: 1360 ng/g dw) (Ruiz pers. com.). The mean level of this species in the Ebro Delta was 4610 ng/g dw (n=56)(Pator et al., 1995).

Comparison between Western and Eastern Mediterranean basins has been approached using the Audouin's Gull (*Larus audouinii*) eggs. Levels are significantly higher in the Western than in the Eastern basin.

3.2.2.3 HCB

Data are available for different fish species (*Alburnus alburnus, Silurus glanis, Rutilus pigus, Leuciscus cephalus, Perca fluviatilis*) from Po River showing contamination in the range of 4-21 ng/g fresh tissue or 26-130 ng/g fat basis (Galassi et al., 1994). 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., 1996; Bressa et al., 1997). HCB residues found in eggs of avocet and fish-eating birds of the Po River Delta are reported in Table 3.11.

In France, the concentrations of HCB in roach (*Rutilus rutilus*) collected in 1991 in the Seine river were in the range of 3.8-274 ng/g dw, whereas lower concentrations (3.1-6.1 ng/g dw) were reported in zebra mussel (Chevreuil et al., 1995 and 1996b). HCB has also been found in trouts from isolated lakes in the Pyrenees (0.10-0.22 ng/g), where only atmospheric inputs can be expected (Sanchez et al., 1993).

3.2.2.4 PCBs

Levels of PCBs 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 fat weight, significantly lower than those found in a different selection of species (*Alburnus alburnus, Silurus glanis, Rutilus pigus, Leuciscus cephalus, Perca fluviatilis*) in early 90's (Galassi et al., 1994, Viganò et al., 2000). In the Seine River (France) PCBs (Σ7 cong.) were found in roach at concentrations of 40.5 ng/g ww (Chevreuil, pers. com.).

In Croatia, PCBs levels in fish species from various rivers are between 70 to 95700 ng/g ww (Radakovic et al., 1992). Recently, a serious contamination of the Kupa River (Slovenia) resulting from improper disposal of the waste discharged by an electrical capacitor manufacturing plant was observed. Concentrations of PCBs in fish ranged from 90 to 1590 ng/g (Aroclor eq.) (Picer et al., 1995). In the FR Yugoslavia, perch, carp and pike from the tributaries of the Danube River in the region of Vojvodina exhibited levels ranging 6.0-25.5 ng/g (Vojinovic-Miloradov et al., 2002). In Egypt, fish from coastal lakes exhibited PCB levels from 6 to 54 ng/g ww (Badawy and Wahaab, 1997; Abd-Allah and Ali, 1994; UNEP/FAO/WHO/IAEA, 1990).

Evidence of long range atmospheric transport of PCBs over the region has been obtained by the occurrence of the more volatile congeners in trouts captured in remote lakes from the Pyrenees, at 2200m of altitude. Concentrations of the 28 more abundant congeners were in the range 2.7-7.5 ng/g ww (Sanchez et al., 1993).

A number of papers have been published on PCBs have in eggs of fish-eating birds. Table 3.11 shows data from the Po River Delta. Koci et al. (2000) determined PCBs residues in eggs of a series of migratory birds (*Sterna* and *Pelecanus* sp.) inhabiting the Karavasta lagoon, a natural protected area in Albania. Concentrations of total PCB congeners were in the range of 145-656 ng/g ww. In turn, the mean concentration in eels liver (*Anguilla* sp.) was 9 ng/g ww.

Levels of eight PCB congeners (IUPAC Nos. 8, 20, 28, 52, 101, 118, 138, 180) were measured (2-349 ng/g dw) in unhatched Audouin gull eggs from Aegean Sea (NE Mediterranean) colonies in 1997 and 1998 (Goutner et al. 2001) and in four Northern Greek wetlands, using the cormorant (*Phalacrocorax carbo*) eggs as a suitable bioindicator (Konstantinou et al. 2000). The median of total PCBs were significantly different among the areas, being unexpectedly high in Prespa Lake (68.4 ng/g) and low in Evros Delta samples (12.2 ng/g).

Comparison between Western and Eastern Mediterranean basins has also been approached using the Audouin's Gull (*Larus audouinii*) eggs. Trends for total PCB are similar to those obtained for total DDT, but in this case the differences are even larger, indicating a higher impact of industrial PTSs sources for the Western basin.

3.2.2.5 HCHs

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). The zebra mussel, also used as sentinel organism in the Seine river, contained, in 1992, 0.5-63 ng/g dw of lindane (Chevreuil et al., 1996b). A concentration of 0.9 ng γ-HCH/g fat has been reported for rainbow trout from the Po River (Galassi et al., 1996). Concentrations slightly lower were found in trouts from high altitude lakes in the Pyrenees (0.1-0.3 ng/g), suggesting an effective long range transport of this pollutant (Sanchez et al., 1993).

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. Levels were higher in the coastal lagoon of Manzala (1.3-5.1, 3.0-7.2 and 0.6-2.1 ng/g ww, respectively) (Badawy and Wahaab, 1997; Yamashita 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 wetlands of Amvrakikos Gulf (Greece) during 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 in eels (Albanis et al., 1995b).

Levels of 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 the Aegean Sea (NE Mediterranean) colonies in 1997 and 1998 (Goutner et al. 2001). Slightly lower residue values of these compounds were also found in four Northern Greek wetlands, using the cormorant *Phalacrocorax carbo* as a suitable bioindicator (Konstantinou et al. 2000).

3.2.2.6 PAHs

Total concentrations of 15 PAHs in roach (*Rutilus rutilus*) and zebra mussels collected in 1996 -1998 in the Seine River (France) were in the range of 23-136 ng/g dw and 0.6-1.1 ng/g dw, respectively (Blanchard et al., 1999).

Frogs have been proposed as a new indicator of pollution in aquatic and terrestrial systems, in Serbia (FR Yugoslavia). High concentrations of PAHs were found in liver (Vojinovic-Miloradov et al., 1996).

3.2.3 Marine environment: bivalves, fish and marine mammals

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. In the Mediterranean Sea, the bivalve *Mytilus galloprovincialis* and the benthic red mullet (*Mullus sp.*), have been largely used, preferentially reflecting contamination from the water column and sedimentary compartments, respectively.

3.2.3.1 Aldrin, Dieldrin, Endrin, Heptachlor and Heptachlor epoxide

Cyclodiene pesticides have been determined during the last 20 years in a large number of organisms, mainly bivalves and fish, in coastal areas of Spain, Egypt, Morocco, in the middle and north Adriatic Sea, Greece, Turkey, etc. (UNEP/FAO/WHO/IAEA, 1990). Concentrations of aldrin, dieldrin, endrin and heptachlor in *Mullus barbatus* were in the low ng/g range. More recently, values of 0.1-1.0 ng/g ww have been reported, for example, in samples collected in the coasts of Greece and Turkey (Giouranovits et al., 1994; Kucuksezgin et al., 2001). *Mullus barbatus* has also been monitored in Cyprus coastal waters and the values found between 0.86-1.46 ng/g dw for aldrin, 0.62-2.51 ng/g dw for dieldrin, 0.25-0.34 ng/g dw for endrin, and 0.94-1.19ng/g dw for heptachlor, with a slight temporal decreasing trend from 1993 to1999 (Gabrielides, pers. com.).

3.2.3.2 DDT

A summary of the concentrations of DDTs in different organisms based on data from the MEDPOL database is shown in Fig. 3.2. In general, p,p'-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. Concentrations up to 230 ng/g ww of total DDTs (DDT+DDE) were found, for example, in red mullet in the area of influence of Barcelona, whereas the lowest (<1 ng/g ww) were found in Corsica and Sardinia Islands (Porte et al., 2002).

The mean values of total DDTs found in mussels in the French Atlantic and Mediterranean coasts during 1995-99 were 6 ng/g dw (0.7-45 ng/g) and 24.4 ng/g dw (1.2-157 ng/g), respectively (IFREMER, 2001), indicating the higher presence of DDT in the Mediterranean basin. Levels in the range of 7-29 ng/g ww were found in mussels collected during the 90's in the Morocco coast.

Concentrations of DDTs from 1 to 25 ng/g ww were found in bivalves (oysters and clams) collected in the Sado and Formosa estuaries (Portugal) (Ferreira et al., 1994 and 1998).

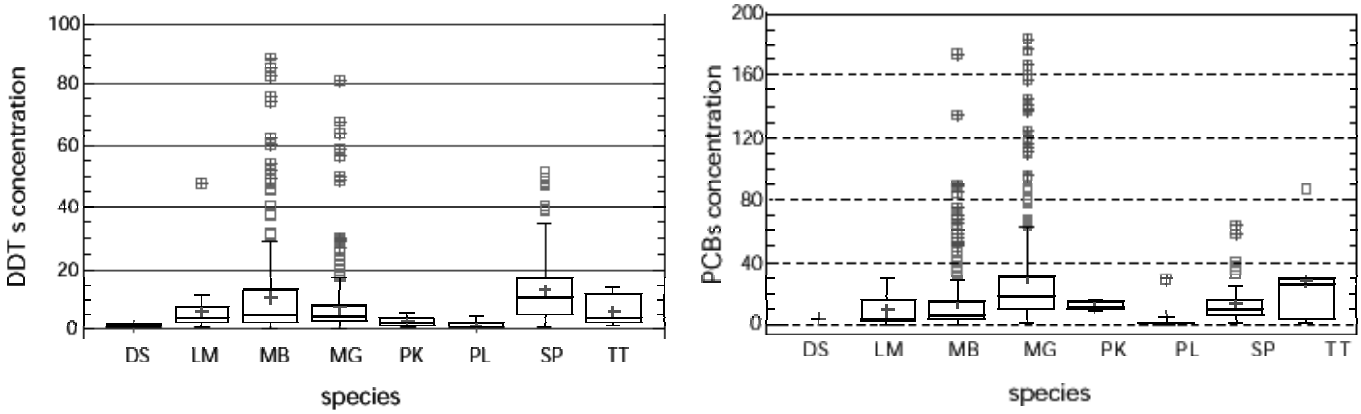

Figure 3.2. Concentrations of DDTs and PCBs (ng/g ww) in selected species from the Mediterranean Sea. DS: *Diplodus sargus*; LM: *Lithognatus mormyrus*; MB: *Mullus barbatus*; MG: *Mytilus galloprovincialis*; PK: *Penaeus keraturus*; PL: *Parapenaeus longirostris*; SP: *Sardina pilchardus*; TT: *Thunnus thynnus*.

The Adriatic Sea was also an area largely investigated. 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 of DDTs were 124 ng/g and 37 ng/g for the Istrian coast and

Rijeka Bay, respectively. Concentrations in *Mullus barbatus* from the Montenegro Coast (South Adriatic) varied for DDE (0.01 to 4.95 ng/g ww) and DDT (4.17 to 15.14 ng/g ww). Finally, bivalves, red mullet, mackerel, anchovy and squid samples from the northern, central, and southern Adriatic exhibited DDE levels from 0.7 to 32.4 ng/g fw. The highest levels were found in mackerel, red mullet and anchovy (17.7-32.4 ng/g ww, 8.1-9.8 ng/g ww, and 6.4-11.9 ng/g ww, respectively) (Bayarri et al., 2001). In molluscs from open sea areas of the Venice Lagoon, levels between 0.2-2.7 ng DDE/g ww have been found (di Domenico et al., 1997).

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.

DDTs were also measured in a variety of mesopelagic and deep sea fish species collected in the Western Mediterranean. The concentrations shown in Table 3.12 can be considered as the background values for the region

Table 3.12. Concentrations (in ng/g ww) of organochlorinated compounds in samples of fish tissues collected in the NW Mediterranean

Fish species	Habitat	DDTs (DDT+DDE)	HCB	PCBs (Σ7 cong.)	References
Mullus sp.	Coastal	4.4 - 16.8	1.6 - 6.7	8.7 - 20.3	Pastor et al. 1996
Dicentrarchus sp.		2.6 - 4.0	0.6 - 0.8	4.4 - 6.2	
Lepidorombus sp.	Mesopelagic	0.8 ± 0.2		2.1 ± 0.3	Garcia et al. 2000
Phycis sp.		0.4 ± 0.1		1.0 ± 0.2	
Lepidion sp.	Deep sea	6.0 - 7.1	0.14 – 0.17	8.3 – 9.4	Porte et al. 2000
Coryphaenoides sp.		1.9 - 4.3	0.25 – 0.67	2.5 – 4.6	
Bathypterois sp.		5.0 – 10.2	0.12 – 0.25	6.0 – 10.0	
Mora moro		7.4 – 12.6		9.0 – 16.2	Solé et al. 2001

DDTs were 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 1987-1993 and in Bottlenose and Risso's dolphins found dead along the Italian coast in 1992 (Corsolini et al., 1995). DDT concentrations measured in blubber ranged from 8.0 to 550 μg/g ww (mean: 170 μg/g) in bottlenose (*Tursiops truncatus*) and 5.2 to 400 μg/g ww (mean: 200 μg/g) in Risso's dolphins (*Grampus griseus*). In sharks (*Prionace glauca* and *Alopias vulpinus*) DDT ranged between 14 and 300 ng/g ww (mean: 78.2) while in bluefin tuna (*Thunnus thynnus*) levels ranged 56-780 ng/g ww (mean: 256) (Corsolini et al., 1995).

Levels of p,p'-DDE were measured in bluefin tuna (*Thunnus thynnus thynnus*), swordfish (*Xiphias gladius*) and cormorants (*Phalacrocorax carbo*) collected off the Italian coast in 1999. Mean concentrations of p,p'-DDE on ww basis in tuna was 82 ng/g in liver, 49 ng/g in muscle and 135 ng/g in fat. In swordfish p,p'-DDE was 135 ng/g in liver and ranged 45-69 ng/g ww in muscle (mean: 57 ng/g), while in cormorant livers concentrations ranged 144-190 ng/g ww (mean: 166 ng/g). (Kannan et al., 2001).

3.2.3.3 HCB

HCB has been widely distributed in Western Mediterranean fish species, as shown in Table 3.12. Measurable amounts of HCB have also been found in red mullet collected along the NW coast, with levels along the Spanish coast (0.24-2.80 ng/g ww) slightly higher than in the French one (0.42-0.97 ng/g ww). The highest levels were found in the vicinity of the Ebro Delta, probably by the existence of an industrial source upstream of the river.

HCB was also found in mussels collected in the Atlantic coast of Morocco (2.5-3.0 ng/g ww) (Fahri et al., 1995) and in red mullet from Cyprus (0.69 ng/g dw) (Gabrielides, pers. com.).

Storelli and Marcotrigiano (2000) investigated the occurrence of organochlorine pesticides in tissues of some specimens of the Mediterranean turtle *Caretta caretta* beached along the Adriatic Sea, Italy. The concentrations of HCB in the liver of all specimens varied from 0.02 - 0.08 μg/g and in the kidney from 0.01- 0.04 μg/g.

3.2.3.4 PCBs

A summary of the distribution of PCBs in different Mediterranean organisms based on data from the MEDPOL database is shown in Fig. 3.2. The levels of PCBs found in mussels and mullets from the Western Mediterranean during the 70's and 80's have been reviewed and discussed by Tolosa et al. (1997). It appears that rivers and

wastewater discharges are the major sources of PCBs in coastal areas. “Hot spots" (av. 527 ng/g dw) have been identified at enclosed locations along the French coast (Toulon, Thau, Sete, Cannes, Monaco), off industrial and highly populated cities (Marseille, Barcelona and Genova), and at the mouths of the Rhône and Ebro rivers.

Most recent data shows concentrations in the Eastern Mediterranean coast (< 2 ng/g ww for mussels, and between the detection limit and 10.0 ng/g ww for *Mullus* sp.)(Giouranovits et al., 1994; Kucuksezgin et al., 2001) much lower than those found in the Western basin. The levels in the Atlantic coast are also slightly higher than in the Mediterranean (IFREMER, 2001). Levels of PCBs (Σ19 cong.) in bivalves and benthic fish collected in the Atlantic coast of Portugal were in the range of 1-12 ng/g ww (Ferreira et al., 1994 and 1998).

The accumulation of PCBs in red mullet, mackerel and anchovy from the northern, central, and southern Adriatic revealed detectable differences among species and sites. The higher concentrations were found in the northern area and in mackerel (94 -177 ng/g ww) (Bayarri et al., 2001). PCBs levels in fish and bivalves collected from the Egyptian Mediterranean coast and Nile estuary ranged from 18 to 32 ng/g, and 28 to 37 ng/g, respectively, (Abd-Allah et al., 1998). Representative concentrations of PCBs in Mediterranean pelagic and deep sea fish are shown in Table 3.12.

PCBs were also determined in the blubber and liver of striped dolphins affected by the 1990 morbillivirus epizootic in the Mediterranean Sea (Corsolini et al., 1995). PCBs levels were found to be significantly higher in the individuals that succumbed to the epizootic than in a 'healthy' population sampled before or after the event. The levels were also higher than those found in animals showing reproductive failure and physiological impairment following prolonged PCBs exposure, thus suggesting that the contamination by PCBs may be a major causative factor for the large-scale deaths of dolphins in the Mediterranean Sea.

Levels of chlorinated pesticides and PCBs have also been determined in tissues of dolphins (*Stenella sp.)* beached along the Adriatic and Ionian coasts of Apulia - Southern Italy. The results obtained confirm that the accumulation of contaminants is higher in Mediterranean dolphins than in similar species living in the Atlantic.

Tissues from a number of cetaceans stranded along the Italian coasts in the period 1987-1993, and of Bottlenose and Risso's dolphins found dead along the Italian coast in 1992 were also sampled and analysed for PCBs. TEQs calculated on 13 dioxin-like PCB congeners ranged 3325-53470 pg/g (mean: 18840 pg/g) in bottlenose and 912-40612 pg/g (mean: 20838 pg/g) in Risso’s dolphin (Corsolini et al., 1995b).

PCBs were analysed in bluefin tuna, swordfish and cormorants sampled in autumn 1999 off the Italian coast. Concentrations of total PCBs in livers of bluefin tuna (*Thunnus thynnus*) ranged 224-1660 ng/g ww (mean: 934) or 5670-14400 ng/g lipid basis. Mean concentrations of tuna muscle and fat were 280 ng/g and 817 ng/g ww, respectively. Mean PCBs values in pooled samples of liver and muscle of swordfish (*Xiphias gladius*) were 745 and 329 ng/g ww, respectively (Kannan et al., 2001).

Corsolini et al. (2000b) investigated the presence of PCBs in stranded specimens of the Mediterranean loggerhead turtle *Caretta caretta* found along the Italian Adriatic coast in 1994. ΣPCBs ranged 69-205 ng/g ww (mean: 119 ng/g) in liver, 10-19 ng/g ww (mean: 15 ng/g) in muscle and 136-563 ng/g ww (mean: 334 ng/g) in fat.

3.2.3.5 PCDD/PCDFs

Total PCDD/Fs in samples of selected marine species from the Adriatic Sea are presented on Table 3.13 (Bayarri et al., 2001). In general, I-TEQ findings were greater for species collected in the northern area and for those situated at higher levels in the trophic web (mackerel > red mullet > anchovy).

Table 3.13.- Total PCDD/PCDFs concentration levels in marine organisms from the Adriatic Sea

Species	**%fat**	**PCDDs** (pg/g ww)	**PCDFs** (pg/g ww)	**PCDD/Fs** (pg TEQ/g)
Anchovy	1.8-3.3	0.33-0.50	0.71-1.53	0.23-0.47
Squid	1.2-1.9	0.20-0.30	0.48-0.83	0.12-0.25
Mussel	1.4-1.6	0.49-1.54	0.89-1.52	0.11-0.24
Lobster	0.5-0.7	0.46-0.69	0.62-0.77	0.09-0.14
Marckerel	5.6-8.7	0.32-0.53	2.38-3.05	0.59-1.07
Red mullet	4.3-4.9	0.29-0.60	0.99-1.49	0.37-0.56
Clam	0.9-1.1	0.38-0.53	0.38-1.38	0.07-0.13

PCDD/Fs were also analysed in bluefin tuna (*Thunnus thynnus thynnus*), swordfish (*Xiphias gladius*) and cormorants (*Phalacrocorax carbo*) collected off the Italian coast in 1999. Concentrations in tuna were less than the limits of detection which varied from 1-75 pg/g ww. PCDD/F congeners were below the detection limits in swordfish. 1,2,3,7,8-PeCDD and 1,2,3,6,7,8-HxCDD and 2,3,4,7,8-PeCDF and 1,2,3,6,7,8-HxCDF were detected in livers of some cormorants (Kannan et al., 2001).

3.2.3.6 HCHs

Isomeric ratios (α/γ) below 1 have usually been found in bivalves and benthic fishes. A large survey of mussels performed during 1995-99 in the French Atlantic and Mediterranean coasts (over 700 samples) have shown mean values of 0.8/3.6 ng/g dw and 0.5/2.0 ng/g dw for α/γ-HCHs, respectively (IFREMER, 2001). Mussels from the coast of Morocco exhibited values of 0.5-6.4 ng/g ww.

Concentrations of lindane in the range of 0.1 - 0.6 ng/g ww have been reported for mussels and red mullet from the Spanish coast. An extensive survey of *Mullus barbatus* carried out between 1986 and 1991 in 8 coastal stations of the Aegean Sea revealed concentrations of α and γ-HCH of 0.1-0.5 ng/g ww and 0.6-3.5 ng/g ww, respectively. Lindane was also found in red mullet (*Mullus barbatus*) collected between 1993-99 in the Cyprus coast (0.6-1.3 ng/g dw) (Gabrielides, pers. com.).

3.2.3.7 Polycyclic aromatic hydrocarbons

Concentrations of PAHs in marine biota indicate a high degree of contamination of certain areas of the region. Data given for the Ligurian Sea for *Mytilus* sp. range from 14 to 571 ng/g dw (UNEP/WHO, 1995). In more recent studies, Baumard et al. (1998) determined the 14 priority PAHs in mussel tissues (*Mytilus* sp.) and fish livers (*Serranus* and *Mullus* sp.) of specimens collected in the French and Spanish Mediterranean coasts and found values of 25-82, 27-87 and 15-49 ng/g dw, respectively, although values up to 390 ng/g dw were found in mussels collected inside harbours. Similar determinations carried out in deep sea fish from the NW Mediterranean basin (*Mora* sp.) showed liver concentrations of 7-16 ng/g ww (Solé et al., 2000).

A large survey of mussels carried out during 1995-99 in the French Mediterranean and Atlantic coasts gave mean values of 590 and 411 ng/g dw (Σ16 PAHs), respecively (IFREMER, 2001). A survey carried out recently in bivalves (*Perna perna*) from 18 stations along the Atlantic coast of Morocco gave results from 3.4-34.6 ng/g (Σ14 PAHs) with values up to 87-109 ng/g ww in the vicinities of the cities of Agadir and El Jadida (Moukrim, 2002). Values of 170-750 ng/g dw were found in mussels from the Thermaikos Gulf (Greece) (Kilikidis et al., 1994). The concentrations of 16 PAHs in mussels collected in 1999 from Izmit Bay (Turkey) were found in the range 1.25-34.0 ng/g (Telli-Karakoç et al., 2002).

In Israel, total concentrations of PAHs in livers of coastal fish collected in 1997 were reported to be in the range 97-987 ng/g dw. Total PAHs in benthic fauna (*D. trunculus, Patella sp.* and *M. coralina*) collected from Haifa Bay during the period 1995-1998 were reported in the range 54-267 ng/g dw (Zimand, 2002).

Blubber samples were collected in 1993 and 1996 from live specimens of fin whales *(Balenoptera physalus)* and stripped dolphins *(Stenella coeruleoalba)* from the Ligurian and Ionian Seas. In whales, the median value of total PAHs was 350 ng/g ww while median carcinogenic PAH values were 114 ng/g ww, in dolphins. The median values of total and carcinogenic PAHs were 938 and 670 ng/g ww, respectively (Marsili et al., 2001).

3.2.3.8 Alkylphenols

Nonylphenol (NP), octylphenol (OP), and their ethoxylates were detected in edible molluscs, cuttlefishes and squids, caught from 15 harbours along the Italian coast in 1997. NP reached the maximum concentration of 696 ng/g ww in the squids from the central Adriatic Sea. Levels were lower in mussels and clams (246-270 ng/g fresh tissue). OP generally occurred at levels 30 times lower than NP (Ferrara et al., 2001).

3.2.3.9 Organotin compounds

The first survey in Spain was conducted in 1988 in the NE Mediterranean coast (Tolosa et al., 1992). Clams (*Tapes decussatus*) and mussels (*Mytilus galloprovinciatis*) were collected in marinas and mariculture areas where concentrations of TBT were found in the range of 900 ng/g and 200 ng/g ww, respectively. A survey conducted ten years later (Morcillo et al*.,* 1997) still showed elevated concentrations of TBT (1200-5400 ng/g). In the SW of Spain, levels of TBT in bivalves were generally <400 ng/g (Gomez-Ariza et al., 1995).

Mussels collected along the Portuguese coast exhibited, in certain places (e.g. Lagos and Viana do Castelo), values of 200-838 ng/g of TBT and no traces of MBT and DBT, indicating recent inputs of this compound. TPhT was also found at high concentrations (up to 800 ng/g).

Levels of respectively 11-44 and 6-9 ng BTs (DBT+TBT)/g fresh tissue have been found in fish (sea bass, salmon, trout, etc.) and in shellfish (mussels) from the Naples province, sampled in the period 1997-1998 (Amodio-Cocchieri et al., 2000). Mussels and clams collected in the Alexandria harbours were also analysed and exhibited concentrations of 93-420 ng/g of TBT, respectively (Abd-Allah, 1995).

Concentrations of TBT and its degradation products, MBT and DBT, were determined in the liver and kidney of striped dolphins (*Stenella coeruleoalba*), bottlenose dolphins (*Tursiops truncatus*) and in a foetus of the common dolphin (*Delphinus delphi*) stranded along the western Italian and Greek coasts in 1992-1994. Butyltin compounds were detected in almost all samples analysed and were higher in kidney (780-8050 ng/g ww) than in liver (150-1020 ng/g). The high levels found in a foetal sample, suggest that organotin compounds are transferred from mother to foetus (Focardi et al., 2000). The same compounds have been found in mean concentrations of 47 ng/g ww in muscle of bluefin tuna from the Egadi Islands (Kannan et al., 1996).

3.2.3.10 Organomercury compounds

Mercury (organic and inorganic) was monitored in marine organisms since the inception of the MEDPOL programme. Initial results indicated that mercury concentrations in Mediterranean species were generally higher than those found in organisms from the Atlantic. These higher concentrations were attributed to the higher natural background levels of mercury in the Mediterranean and not to anthropogenic contamination.

In 1996, a large survey of methyl mercury in mussels and oysters along the French coast was carried out as part of the National Monitoring Network (Claisse et al., 2001). The concentrations found were similar in both species, and ranged from 8 to 238 ng/g dw with a mean of 64 ± 35 ng/g. The higher values were found along the Brittany coast and the Rhone delta, although they were all below the WHO guideline.

A collection of 15 kinds fish samples (115) was performed at the Zagreb fish market during 1997. The mean content of total mercury and organic mercury in pooled samples was 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. This concentration did not exceed the maximum allowed level of 500 ng/g for total and 400 ng/g for organic mercury in any of the samples examined.

Total mercury and methyl mercury concentrations were also 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 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).

3.2.4 Levels in food

3.2.4.1 Chlorinated pesticides

Food pesticide residues have been extensively determined in all countries for regulatory purposes but data is not easily available. In Egypt, 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 were found in around 50% of the samples at levels of 0.04 and 0.02 mg/kg, respectively, close to the MRL (Dogheim et al., 1996a,b; 1999).

In Turkey, residue analysis has been conducted on milk, butter and wheat with 60-90% of positive results but below the MDL (e.g. total DDTs in wheat samples: 0.05 mg/kg) (Kara et al., 1999; Yentur et al., 2001). DDT, HCHs, chlordane and HCB residues were found in canned fish but much below the MRL values.

In the FR Yugoslavia measurements were carried out in 1662 meat samples during a 5-year period (Spiric and Saicic, 1999). Among lamb samples, 2.5% contained lindane residues exceeding the MRL, with a mean of 4.7 ng/g. In Croatia, raw cow's 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).

Organochlorine residues were also investigated in Spain in milk, dairy products, meat and meat products (229 samples of lamb, pork, beef and poultry) with results below the RL (Martinez et al., 1997). Data on pesticide residues in fruit, cereals and vegetables provided by the Italian National Health Service (1993-1994), have shown no detectable residues of the pesticides analysed ("drins", chlordane, DDT, HCB and HCHs).

Monitoring of pesticide residues in agricultural products in Slovenia was performed over the past twenty years. Over more than 1000 samples, the permitted level was exceeded in 3.3% of the samples analysed. The analyses showed that DDT values were reduced by a factor of ten in seven years.

In Cyprus, chlorinated pesticides are currently determined in milk, meat, and vegetables. Concentrations are from 0-20% of the MRL, the higher values corresponding to dieldrin and DDT (Michaelidou and Ziegler, unpubl.).

3.2.4.2 PCBs

Data from Mediterranean countries presented in Table 3.14 were provided for Spain (Fernandez et al., 2001), France (AFSSA, 2001) Croatia (Cerkvenik et al., 2000) and Egypt (Abd-Allah and Ahmed, 1993). PCBs were also analysed in Cyprus in meat and milk, in 1999-00, with values below the detection level (1-5 μg/kg in meat fat and 0.6 μg/kg in milk) (Michaelidou and Ziegler, unpubl.).

Table 3.14. Concentration of PCBs in various type of food in Mediterranean countries (collected between 1990 and 2001)

Foodstuffs	**DL-PCB (pg WHO-TEQ/g fat)**					**Σ7 PCB ng/g fat**			
	- N	Mean	sd	range	Country	N	Mean	range	Country
Milk	-18	0.40	0.5		Spain	-108	5	2 – 140	Croatia
						-25	1.83, 2.63 (cow, buffalo)		Egypt
Dairy products	-7	1.33	1.84		Spain				
- Butter	-7	1.54	1.54		Spain				
- Cheese	-16	4.36	5.89		Spain				
- Yoghurt	-5	0.69	0.30		Spain				
- Cream	-7	0.35	0.07		Spain				
Fish and sea foods									
-Marine fish	-16			0.77-13.3	Spain				
-	-111	0.36	0.90		France	-89	25	2.1-121	France
- Trout	-56	13.6		5.94-28.9	France	-56	143	45-274	France
-Molluscs	-9	2.29	2.32		Spain	-50	122	9-300	France
Meat	-8	0.20	0.29		Spain				
Meat products	-16	0.34	0.38		Spain				

3.2.4.3 PCDD/Fs

Monitoring programmes on food products were implemented in Spain, in 1992 and in France in 1995. Samples were collected in markets from the overall country, covering the period 1992-2001. The current database (Table 3.15) shows national average concentrations of PCDD/Fs in more than 300 and 450 food samples in Spain and France, respectively (Fernandez et al, 2001, AFSSA 2001).

Table 3.15. Concentration of PCDD/Fs in various types of food from Spanish and French markets, collected between 1998 and 2001, expressed in pg WHO-TEQs/g fat or g fw*

Type of food	**Egypt**	**Italy**	**Spain**			**France**		
			n	Mean	sd	n	Mean	sd
Cow's milk			16	1.34	0.76	148	0.65	0.29
Cheese			7	1.54	1.54	55	0.77	0.36
Yoghurt			16	1.85	1.20	19	1.16	0.67
Butter	0.41-29.9	0.45-1.2	7	0.97	0.63	16	0.92	0.44
Eggs		0.2-3.3	7	3.24	5.18	14	1.51	1.70
Beef meat	0.94		8	1.25	0.87	13	0.8	0.39
Pork meat		0.4-0.7	10	2.16	2.81	6	0.16	0.16
Cured meat			16	1.93	2. 80	14	0.25	0.22
Poultry			11	6.15	5.86	6	0.60	0.29
Wild marine fish			18	3.47	1.85	29	4.64	6.67
Salmons						11	5.15	1.63
Trouts						56	3.94	4.03
Molluscs			16	8.67	7.06	5	50.3	6.38
Cereals*						4	0.012	0.005
Bread*						4	0.01	0.03
Fruits*						5	0.010	0.011
Vegetables*						7	0.032	0.036

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. However, when the concentration of dioxin-like PCBs is added to the contribution of PCDD/Fs, the total WHO-TEQs increase significantly, and almost all the food types investigated are over the mentioned maximum levels.

Complementary data for other Mediterranean countries (Egypt and Italy) are presented in Table 3.15 (Rainer and Saad, 1994, Report SCOOP Task 1999).

3.2.4.4 Endosulfan

No endosulfan was found in 120 samples of raw and pasteurised (HT-ST and UHT) cow's milk collected from 3 regions in Italy (Capei and Neri, 1998) as well as in north-western Spain (De la Riva and Anadon, 1991), and in 229 samples of meat products of different species (lamb, pork, beef and poultry) (Herrera et al., 1994). However, high values were shown in red pepper and eggplant (87.3 and 72.4 ng/g, respectively) (Fallico and Ferrante, 1993) from Catania (Italy) and in vegetables (potatoes, grapes, etc.) from Cyprus (<10 – 85 ng/g).

3.2.4.5 PAHs

Sources of PAHs in food are due to natural constituents, contaminants from food chain, environmental exposure (air particles deposits, sediments, water column), but mainly from food processing. A national food monitoring programme was initiated in France in 2000 and a tentative food intake estimation was carried out by the AFSSA. From 6 to 16 PAHs were measured in oils (5.1 ng/kg), bread (1.2 ng/kg), fish (1.6 ng/kg), vegetables (0.5 ng/kg), raw and grilled meat (0.3 and 11.5 ng/kg, respectively), sausages (2.9 ng/kg) and chorizo (13.8 ng/kg).

In Italy, analyses of various foodstuffs carried out in 1994 gave values of B(a)P in the range of 0.001-0.030 ng/g ww in vegetables, fruits, bread and cheese, whereas in oil and chocolate were of 0.10-0.33 ng/g ww (Lodovici et al., 1995). Meat exhibited values of 0.45-0.61 ng/g ww and barbecued beef of 1.44 ng/g ww. Apparently, the main contributor for food intake is meat and especially grilled and fried meat, indicating the importance of food heating processes.

3.2.4.6 Phthalates

Phthalate plasticisers have been primarily determined in foodstuff plastic packages for their potential transfer to human diet. In Italy, contamination by phthalate esters was found in Sicilian and Calabrian citrus (lemon, orange and mandarin) essential oils, produced in the crop years 1994-1996, at levels up to a maximum of 62 mg/L of di-isobutyl phthalate (DiBP) and 30 mg/L of bis(2-ethylhexyl)phthalate (DEHP) (Bella et al., 1999).

Also in Italy, dibutyl phthalate (DBP) was detected in 97, 80, 95, 100, and 49% of cheese, salted meat, vegetable soup, potato chips, and milk samples, respectively. No DBP was recovered from jams and baby food. The mean levels of contamination with DBP were 0.07-2.80 μg/g. DEHP was found in 80, 71, 94, and 52% of salted meat, jam, baby food, and milk samples, respectively, and in all the cheese and vegetable soup samples. The mean DEHP values were 0.21-2.38 μg/g (Amodio-Cocchieri, 1986).

Retail dairy products from Spain were contaminated with <0.01-0.55 μg/g DEHP with a maximum level of total phthalates of 3.0 μg/g in cream samples (Sharman et al., 1995).

3.2.4.7 Organomercury compounds

Total mercury and methylmercury concentrations from long-term monitoring of the terrestrial soil-vegetation-herbivore-carnivore food chain with regard to accumulation and transformation processes were studied in Slovenia, the second larger producer of mercury in the world. The results obtained indicated that vegetation mediates significant transfer of Me-Hg to herbivores, and this becomes subject to further accumulation in the higher trophic levels of this food chain (Gnamus et al., 2001).

A large monitoring of food contamination and intake of mercury and methyl-mercury was also carried out in France by the AFSSA in 2002. The main food contributors were fish (47%) and fruits and vegetables (19%).

3.2.5 Temporal trends

3.2.5.1 DDT

Two surveys conducted along the Mediterranean coast of France and Italy, in 1973/1974 and in 1988/1989 (Villeneuve et al., 1999) showed that DDTs levels 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). It is interesting to notice that levels of DDTs detected in red mullet in the Spanish coast are

similar to those found 10 years earlier by Porte and Albaigés (1993), which may well reflect the high persistence of DDT residues associated to sediments in the region.

The Adriatic Sea has also been extensively monitored from this perspective. Decreasing trends of HCB and p,p'-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 (Fig. 3.3). In Fig. 3.4 are also shown the annual trends of DDTs in benthic and epibenthic fish from 1974 until 1991 (Picer and Picer, 1995). Recent reported levels of DDT in fish collected from different coastal areas in Egypt also suggest a concentrations decline during the 90's (Abd-Allah et al., 1998).

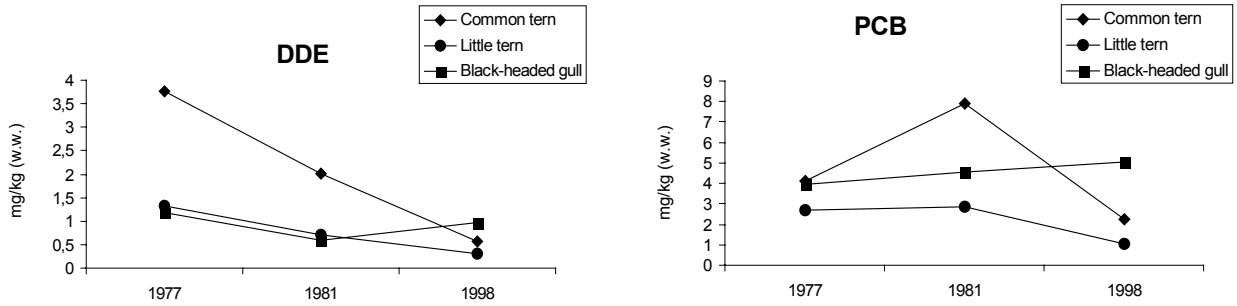

Fig. 3.3. Temporal trends of mean organochlorine concentrations in eggs of fish-eating birds of the River Po Delta (Focardi, 2002).

3.2.5.2 PCBs

The concentrations of PCBs in different marine samples (e.g. plankton, faecal pellets and mussels) collected along the French coast exhibited reduction factors of 2.8-3.6 between mid 70's and late 80's. Two surveys conducted along the Mediterranean coast of France and Italy, in 1973/1974 and in 1988/1989 (Villeneuve et al., 1999) also showed a PCBs decrease by a factor of 5 in 15 years, following the gradual cessation of PCBs production.

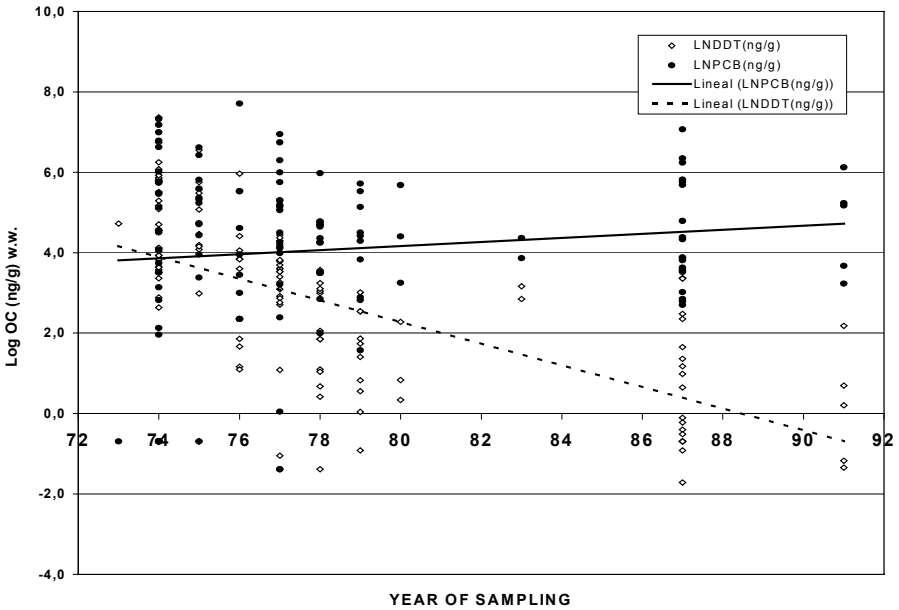

Fig. 3.4. Yearly trend of DDT and PCBs level in the eastern Adriatic coastal epibenthic and benthic fish

However, in other areas the trends were not so evident. As shown in Fig. 3.3 the PCBs levels in little tern and black-headed gull eggs did not vary significantly. PCBs concentrations have also remained constant in benthic fish from the Adriatic coasts during the last 20 years (Fig. 3.4) (Picer and Picer, 1995). 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. Similar trends were observed in the French monitoring network of coastal pollution using bivalves as sentinel organisms (IFREMER, 2000). In Table 3.16 are shown the number of increasing and decreasing trends in the Atlantic and Mediterranean coasts in the different sampling stations. In general, it can be seen that during the period 1979-1998 the decreasing trends were in the order: ΣDDT > HCHs > PCBs > PAHs.

Table 3.16. Number of trends by contaminant observed in the RNO Atlantic and Mediterranean sampling sites (for mussels or oysters) (1979 - 1998)

	RNO Atlantic			RNO Mediterranean		
Contaminant	Up Trend	Down Trend	No Trend	Up Trend	Down Trend	No Trend
(PCB) CB 153	0	22	57	0	4	19
ΣDDT	0	62	17	0	16	7
α-HCH	0	55	24	0	13	10
γ-HCH (Lindane)	0	40	39	0	16	7
ΣPAH	0	12	67	0	5	17

In summary, it appears that a decline of PCBs has been achieved, consistently with the regulatory restrictions on the use of these compounds, although they remain still in significant amounts in some coastal areas of the Mediterranean Sea where localised chronic contamination exists.

3.2.5.3 PCDD/Fs

An important trend to be assessed in the case of dioxins is the reduction of levels in the vicinities of incineration plants after the activity is improved or discontinued. In this respect, farm milk is generally used as a biomonitor of dioxin sources. In France, cow milk from a general survey ranged from 0.64-2.4 pg TEQ/g fat in comparison with milk produced in the vicinity of metallurgic and metal reclamation (0.4-3.8 pg TEQ/g fat) and MSWI (4.5-70 pg TEQ/g fat). A case study carried out in the vicinity of a MSWI indicated that mowing and discarded grass after closure of the plant led to recovering background levels of dioxins. Then, the dioxins level in milk from cows after remediation decreased within the 9 following months from more than 10 pg TEQ/g fat to background levels (lower than 3 pg TEQ/g fat) (AFSSA, 2002).

A decreasing trend in concentration of PCDD/PCDFs in dairy products collected in Spanish markets from 1993 until 2000 has been observed. These results agree with those observed in other European countries.

3.2.6 Levels in humans

The available data, describing the concentrations of the selected PTS in the general population, represent a basis of information quite inhomogeneous in terms of both the chemicals specifically monitored and the monitoring geographical pattern. In fact, the data assessed mostly refer to some chlorinated pesticides, PCBs and PCDD/Fs, whereas a general paucity or absence of data is observed for the other chemicals of the list, to make an evaluation of health risks feasible. The analysis of information at a country level shows that most of it refers to a few countries (i.e. Egypt, Croatia, France, Italy, Spain, Turkey and FR Yugoslavia).

Since in data evaluation a crucial role is played by the way they were reported (i.e. fresh weight or lipid basis), an effort was made, where possible, to express all the collected data on a lipid basis in order to facilitate comparison between levels in different tissues, different individuals and different years. Information useful to define the power of the study (i.e. sample size) and the statistical design have also been taken into account.

As to sample typology, breast milk, blood, and adipose tissue were the human tissues better characterised in terms of contamination from PTS. In particular, 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. Mother's 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, the number of breast-fed infants has been shown to progressively and considerably decrease the body burden of PTS (especially PCDD/Fs and PCBs) while an increase in mother's age is generally correlated with a significant increase in PTS body burden.

3.2.6.1 Aldrin, dieldrin and endrin

Data has only been reported for human milk in few countries. Fig. 3.5 shows the situation in the years 1987-1990 in Egypt, France and Turkey (Dogheim et al., 1991; Bordet et al., 1993; Üstünbaş et al., 1994). Dieldrin levels became undetectable in Egypt in 1994.

Recent data on human milk contamination in Jordan report levels of about 860, 1400 and 3300 ng/g fat of aldrin, dieldrin and endrin, respectively (Nasir et al., 1998).

3.2.6.2 Chlordane

Few data are available for chlordane in human milk. A study carried out in France in 1990 (Bordet et al., 1993), reporting levels of 78 ng/g fat α-chlordane and of 6 ng/g fat γ-chlordane, and a study carried out in Jordan in 1996 (Nasir et al., 1998), reporting levels of 460 ng/g fat α-chlordane and of 590 ng/g fat γ-chlordane are the only ones identified.

Human adipose tissue samples collected in Madrid (Spain) in early 90's did not contain chlordane at measurable levels (Hernandez et al., 1992).

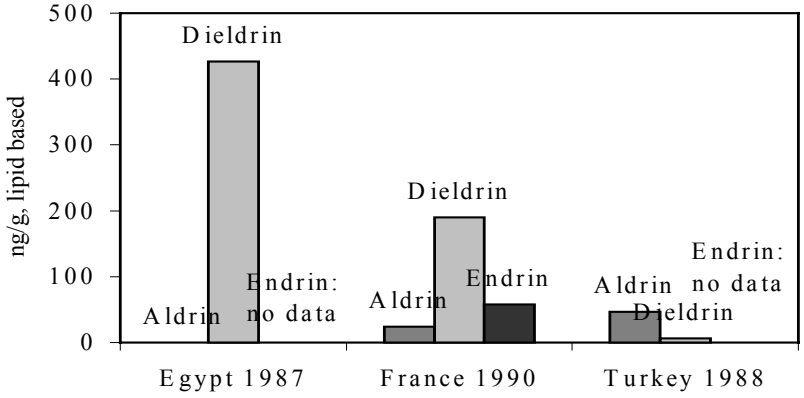

Figure 3.5. Levels of aldrin, dieldrin, endrin in human milk

3.2.6.3 Heptachlor and heptachlor epoxide

In Turkey, heptachlor and heptachlor epoxide were found in human milk samples of 51 mothers working in agriculture in the Region of Kayseri at levels of 198 and 11 ng/g fat (Üstünbaş et al., 1994). Heptachlor epoxide levels of 78 and 69 ng/ fat were also found in Van and Manisa, respectively (Ergin, pers. com.).

Values of 700 and 580 ng/g fat of heptachlor and heptachlor epoxide, respectively, were attained in human milk samples collected in Jordan in 1989-90, although they decreased to 500 and 190, respectively, in 1997 (Alawi et al., 1992; Nasir et al., 1998).

Adipose tissues have also been analysed. Mean levels of 121 ng/g fat heptachlor epoxide have been detected in Manisa residents (Turkey) (Cok et al., 1998), while levels of 62 ng/g fat had previously been reported for Ankara citizens. This difference is possibly due to the fact that in the Manisa area, agriculture is the predominant activity and samples had been collected before the use of heptachlor was prohibited.

3.2.6.4 DDTs

Figure 3.6 shows p,p'-DDT and p,p'-DDE levels in human milk from different countries, in the period 1990-1995 (Krauthacker et al., 1998; Bordet et al., 1993; Larsen et al., 1994; Hernandez et al., 1993). A considerable difference in contamination may be observed among them, although the large predominance of the p,p'-DDE in all samples suggests the absence of recent DDT sources.

In Israel, contamination levels of 79 ng/g p,p'-DDT and 8.5 ng/g p,p'-DDE (fresh weight) have been reported in 1985 (Weisenberg et al., 1985). DDTs were the most frequently found pesticide in human milk sampled in Cairo area with levels up to 240 ng/g fresh weight in samples collected in 1994 (Dogheim et al., 1996a).

Mean concentration of total DDTs in 60 human milk samples collected in 1993 from 20 Egyptian governorates was found to be of 24 ng/g whole milk basis (Fig. 3.7) (Saleh et al., 1996). The highest levels, up to 42-55 ng/g were found in the Delta region, and attributed to the higher agricultural activity. In none of the samples where DDT was detected were the WHO recommended limits (1986) exceeded.

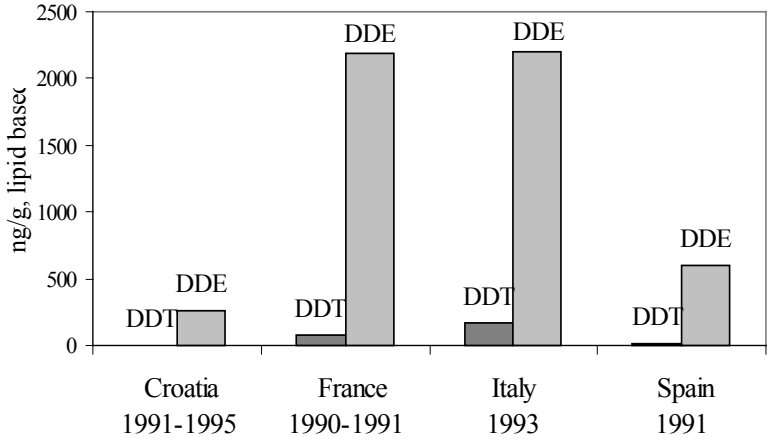

Figure 3.6. Levels of DDT and DDE in human milk

Recent data from four Governorates in Jordan show levels of 5-18 ng/g fat DDTs (Akeel, pers. com.). For the same area, these compounds had been reported to be in the range of 1060-2640 ng/g fat in a study carried out in 1993-1994 (Alawi et al., 1996), whereas p,p'-DDT was 450 ng/g fat. Another study reports levels of p,p'-DDE and p,p'-DDT of 6350 ng/g fat (Nasir et al., 1998).

In Turkey, levels of 410 ng/g fat p,p'-DDT and 2389 ng/g fat p,p'-DDE were detected in milk samples from the Kayseri Region (Üstünbaş et al., 1994), while levels of 72-141 ng/g fat p,p'-DDT and 1850-2260 ng/g fat p,p'-DDE were found in Van and Manisa areas (Ergin, pers. com.). In Northern Greece, levels of 35 ng/g fat p,p'-DDT have been found in the early 80's, while levels of the same compound of 65.9 ng/g fat have been detected in samples from the region of Patras collected in 1995-97 (Schinas et al., 2000).

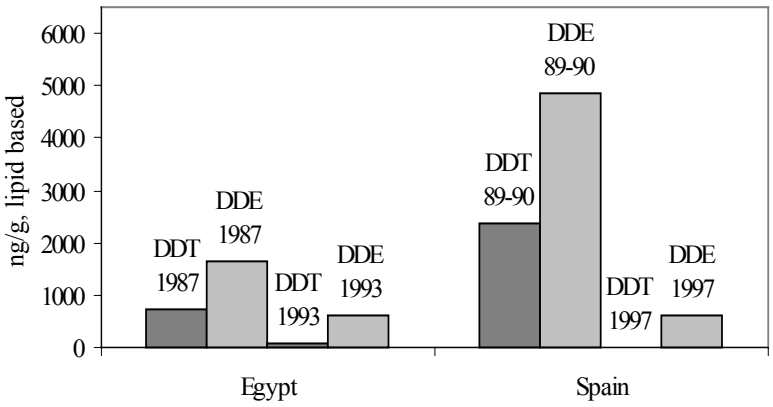

Figure 3.7. Temporal trends of DDT levels in human milk

p,p'-DDE and p,p'-DDT mean levels in colostrum from Novi Sad (FR Yugoslavia) were of 13.1 and 0.5 ng/g (fresh weight) respectively, in 1993, whereas the same compounds were about 69.4 and 20 ng/g in samples collected in 1982 in the same area (Vukavić et al., 1997).

Decreasing temporal trends are generally observed, reflecting the effectiveness of the restrictions imposed on the DDT use since the mid 70's. Representative trends for Spain and Egypt are shown in Fig. 3.7 (Dogheim et al., 1991; Saleh et al., 1996; Hernandez et al., 1993).

Available data from Spain indicate that in the years 1989-1993 levels of DDT and DDE in the adipose tissue of the general population were in the range of 0.7-1.5 μg/g fat and of 3.7-6.3 μg/g fat, respectively (Camps et al., 1989; Catalan et al., 1993). Mean concentrations of p,p'-DDE in adipose tissue collected in 1991-1992 in Central Italy was 2.52 μg/g ww (Corsolini et al., 1995a). In 1997-2000 mean DDT concentration was 1.9 μg/g ww. Levels and age were found to be positively correlated (Mariottini et al., 2002). Data for Jordan on adult population indicate DDT and DDE contamination levels of about 1.3 μg/g fat and of 92 μg/g fat, respectively, in early 90's, while recent data indicate mean values in the range of 0.5-1.3 μg/g fat and of 1.8-3.6 μg/g fat for the same compounds (Alawi et al., 1999). Serum levels of 3.4, 0.2 and 0.6 ng/mL 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 DDT and 9.41 DDE ng/mL have been found in specimens from general population sampled in 1992-1995 (Porta, 1999).

3.2.6.5 HCB

Considerable differences in HCB levels in human milk are observed among different countries, as shown in Table 3.17, covering a 10 years span (Krauthacker et al., 1991; Dogheim et al., 1991; Weisenberg et al., 1985; Üstünbaş et al., 1994; Krauthacker et al., 1998; Bordet et al., 1993; Larsen et al., 1994; Hernandez et al., 1993; Nasir et al., 1998).

Table 3.17. Mean levels of HCB in human milk

Country	Year	Conc. (ng/g lipid based)
Croatia	1987	50
	1991-1995	13
Egypt	1985	490
France	1990-1991	147
Israel	1985	80
Italy	1993	217
Jordan	1990-97	290
Spain	1991	0.8
Turkey	1988	84
	1995-96	44-58

Temporal trends may be derived only in a very few cases, and appear to vary according to the country considered. Decreasing trends were observed in Croatia (Table 3.17) but not so evident in the case of Jordan or Turkey (Ergin, 2002).

In Italy, HCB levels in adipose tissues were about 310 ng/g fat in the years 1985-1986, whereas in 1997-2000, concentrations in Central Italy averaged 335 ng/g ww, and were positively correlated to age (Mariottini et al.,

2002). 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 (Camps et al., 1989; Catalan et al., 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 (Cok, 1998). Finally, 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 (Alawi et al., 1999).

Blood levels of 300 ng/L serum have also been reported for general population in Croatia in 1994-1995 (Krauthacker et al., 1996).

3.2.6.6 PCBs

Literature data show a considerable dishomogeneity in terms of kind and numbers of congeners analysed. Table 3.18. shows the mean PCBs levels for some countries, expressed as the sum of the six marker congeners as well as the coplanar congeners (WHO, 1996; Bordet et al., 1993; Larsen et al., 1994).

Table 3.18. Mean concentrations (1987-1990) of PCBs and PCDD/Fs in human milk

Country	PCBs Marker congeners (ng/g lipid base)	PCBs Coplanar (pgTEQ/g lipid base)	PCDD/Fs (pgTEQ/g lipid base)
Albania	54.3	1.14	4.88
Croatia	219	4.62	12.8
France	411	4.79	23.1
Italy	290	10.3	25.6
Spain	458	7.93	22.3

Data on blood contamination of the general population are available for the period 1994-1996 for Israel and Palestine (Schecter et al., 1997), indicating levels of coplanar congeners in the range of 7-12 pgTEQ/g fat. For Croatia, levels of about 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 ng/mL (mean value of 4.9 ng/mL) as the sum of the seven marker congeners (Ministère de la Santé, France, 1989).

The three most abundant congeners (#138, 153, 180) have been reported in human blood in Spain (3.7 ng/mL) (Porta, 1999) and in follicular fluid from healthy women from Rome (900 pg/g fat) (De Felip et al., 2001).

3.2.6.7 PCDD/PCDFs

Human milk has been the object of a number of studies in the last two decades, because of the sanitary concern associated to the exposure of breast-fed infants to these contaminants. The monitoring programmes periodically carried out by WHO on a number of countries are a very valuable source of high quality data, being the selection of mothers based on strict criteria.

The contamination levels in pooled milk samples in the period 1987-1990 for certain countries are shown in Table 3.18 (Gonzalez et al., 1996; EU-SCOOP Task 3.2.5, 2000). Studies on human milk contamination have also been published for other non-European countries, like Egypt, Israel and Palestine (Fig. 3.8) (Schecter et al., 1997; Malisch et al., 2000). A decreasing trend has also been observed for European countries (Fig. 3.9).

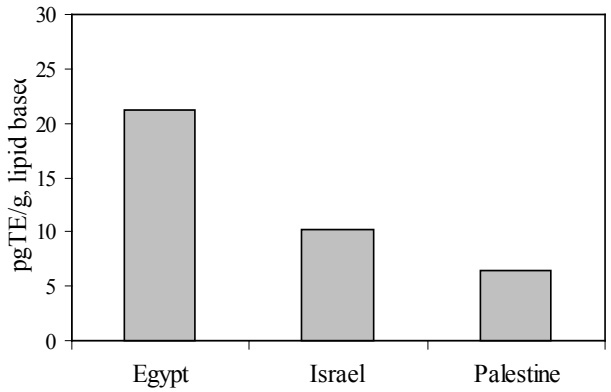

Figure 3.8. PCDD/Fs in human milk (1996-1997)

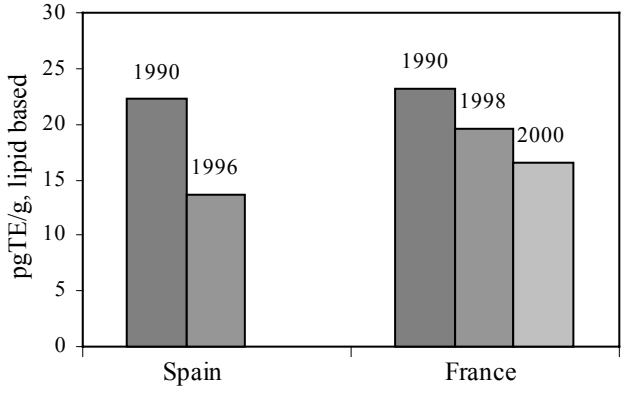

Figure 3.9. Trends of PCDD/Fs levels in human milk

Data on fat are available for France, reporting contamination levels in the general population of about 36 pgTEQ/g fat in 1999 (Arfi et al., 2001) and for Spain, showing levels of about 45 and 36 pgTEQ/g fat in 1993 and 1996, respectively (Gonzalez et al., 1993; Schumacher et al., 1999a).

Data on blood contamination in Israel and Palestine in 1996 have been published (Schecter et al., 1997), showing levels of PCDD/Fs in the range of 26.6-32 pgTEQ/g fat and of 8.44-16.9, respectively. A study carried out on blood samples from general population in Spain has shown an increase in PCDD/Fs body-burden as a function of age as already highlighted in a number of studies (Schuhmacher et al., 1999b).

3.2.6.8 HCHs

An overview of human milk contamination by HCHs in different countries in two consecutive time periods is shown in Figures 3.10 (1985-1990) and 3.11 (1990-1997) (Krauthacker et al., 1991, 1998; Dogheim et al., 1991; Weisenberg et al., 1985; Alawi et al., 1992; Üstünbaş et al., 1994; Saleh et al., 1996; Bordet et al., 1993; Larsen et al., 1994; Nasir et al., 1998; Hernandez et al., 1993).

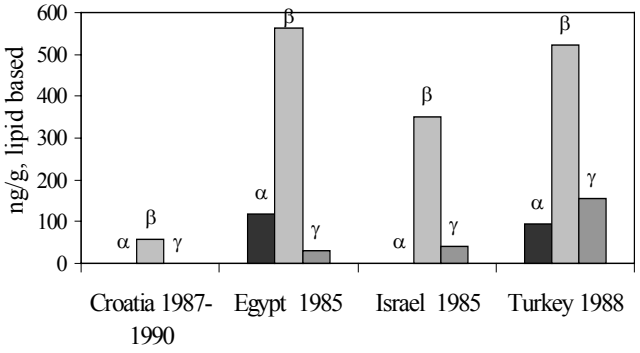

Figure 3.10. Levels of α,β,γ - HCH in human milk (1985-1990)

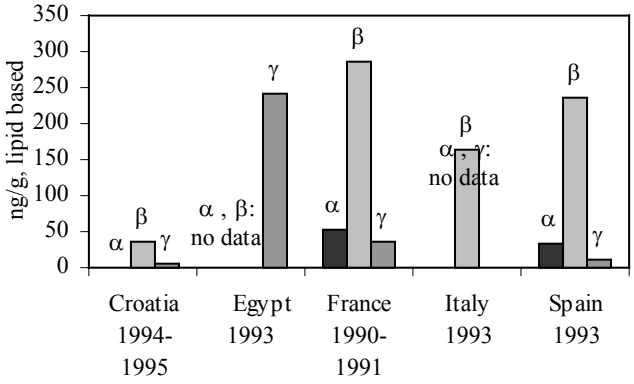

Figure 3.11. Levels of α,β,γ - HCH in human milk (1990-1997)

When focusing on the most toxic isomer, γ–HCH, it is possible to observe a temporal trend for some countries (e.g. Turkey, Greece and Spain). In Novi Sad (FR Yugoslavia), ΣHCHs have been determined in colostrum samples in 1982 and ten years later, in 1993, giving values of 1.7 and 1.3 ng/mL, respectively (Vukavic, 1997).

Data available for adipose tissue from the general population in Spain indicate levels of β- and γ-HCH in the range of 1160-3060 and 50-80 ng/g fat, respectively, in the years 1989-1993 (Camps et al., 1989; Catalan et al., 1993). Available data for Turkey in 1985-1986 indicate a contamination of β- and γ-HCH of about 1500 and 2 ng/g fat, respectively. For the same compounds, 374 and 43 ng/g fat were found in samples collected from Manisa residents in 1995-96 (Ergin, pers. com.). In Jordan were reported levels of β- and γ-HCH around 870 and 130 ng/g fat, respectively, while recent data indicate mean contamination values of 857-1332 and 90-330 ng/g, for the same compounds (Alawi et al., 1999).

Serum levels of 1.2 ng/mL β-HCH and 0.3 ng/mL γ-HCH have been found in general population in Zagreb (Croatia), in 1994-1995 (Krauthacker et al., 1996).

3.2.6.9 PBBs and PBDEs

Only one study concerning the occurrence of these chemicals in human adipose tissue has been reported in the region, which was conducted in Spain (Meneses et al., 1999). Tetra-, penta- and hexabrominated diphenyl ethers were found in all samples, at average concentrations of 1.36, 0.93 and 1.83 ng/g lipid, respectively. These values were similar to those found in northern European countries.

3.2.6.10 PAHs

General population exposure to PAHs mainly occurs from atmospheric pollution and diet, this latter accounting for about 90% of the total exposure (Lagorio et al., 2000).

Sanitary risk from human exposure is mainly due to continuous exposure rather than to bioaccumulation, since biological persistence is generally rather low. PAHs half-lives in humans are in fact in the range of days/hours, and metabolism is responsible of the formation of toxicologically active (carcinogenic) metabolites. Because of the lack of persistence and to the complexity of PAH mixtures, human exposure is usually characterised in terms of "internal dose" rather than of "body-burden", by the use of biomarkers of exposure, mainly 1-OH pyrene in urine and DNA adducts in peripheral blood lymphocytes.

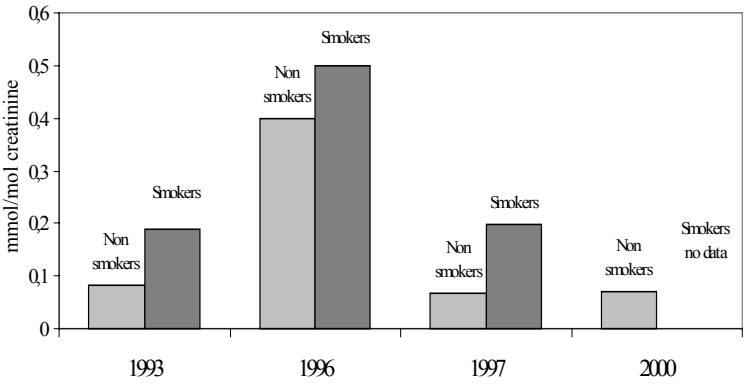

Figure 3.12. 1-hydroxypyrene in human urine in Italy

Data on urinary 1-OHPy excretion in some groups of the general population are available for Italy (Sartorelli et al., 1994; Merlo et al., 1998; Pavanello et al., 2000) and Turkey (Karahalil et al., 1998). Due to the relevance of smoking in determining individual exposure, literature data hereafter reported always make a distinction between smokers and non smokers. Figure 3.12 show contamination levels in different years, referred to both smokers and non-smokers.

Levels of DNA-adducts in lymphocytes formed after oxidative activation are used as a qualitative marker of exposure, mostly in assessing risk of carcinogen exposure. Because of the large interindividual differences, adduct levels can only be compared on a group basis, resulting in insignificant comparisons on a country and/or temporal basis. As an example of what has been found for general population, a few data are reported. Data available for Greece indicate a level of 1.39 adducts/10^8 nucleotides for non smoking students in 1997-98 (Georgiadis et al., 2001). In 1996, levels in Italy were about 2.2 adducts/10^8 nucleotides in low-traffic exposed non-smokers and 2.4 adducts/10^8 nucleotides in low-traffic exposed smokers (Yang et al., 1996).

3.3 EVIDENCE OF HARMFUL EFFECTS

The basic approach of risk assessment is to measure the amount of chemical or chemicals present in the environment and then to relate that to the expected adverse effects caused by this amount of chemical, on the basis of bioassays conducted under laboratory conditions. Alternatively, a hazard assessment can estimate the ecotoxicological threshold and set quality standards/objectives (QS/QO) or predicted no effect concentrations (PNEC) for each chemical. The proposed EU QO for fresh and marine waters can be found in Bro-Rasmussen et al. (1994), and PNECs for priority chemicals are available from the ECB. These values are generic values for Europe, covering the Mediterranean region. Similarly, the risk for humans can be established from the comparison of exposure levels with those expected to be safe from toxicity studies. Maximum tolerable exposure to xenobiotics, e.g. as tolerable daily intake (TDI), are available from different European and international organisations.

These threshold levels are considered to be safe even for combined exposures to several contaminants (if exposure from those with a similar mode of action is combined). However, the evaluation of concentrations above threshold is very complex. Interpreting measured concentrations versus observed effects in the complex multistressor reality, which includes not only chemical exposure but also other factors, is very difficult. Only for hot spots and accidental episodes can cause-effect relationships be established through toxicological diagnosis. Nevertheless, associations between exposure levels and some ecological effects have been observed in some cases within the Region, as reported below.

3.3.1 Existence of regionally derived ecotoxicological data and appropriate test species

3.3.1.1 Terrestrial biota: vegetation and animals

Assessing the risk of chemicals on terrestrial ecosystems is challenging as several receptors and exposure patterns must be considered. The receptor approaches (e.g. Tarazona et al., 2002) can be applied to the Region when enough information is available (Ramos et al., 2000).

Exposure via soil is relevant for soil microorganisms, plants and soil dwelling invertebrates. For pesticides and biocides, real data are now required, while for industrial chemicals, extrapolations from aquatic toxicity are considered in some cases. Some additional information can be obtained from studies on contaminated soil, although the information for the Region is scarce. Plants can also be exposed via atmospheric deposition, very recently, specific requests have been included for pesticides, but this regulation does not cover PTSs.

Much work has been carried out on the incorporation of PTSs into grasses and vegetables, as part of investigations into PTS transfer from air, soil and water to vertebrates including humans in food chain contamination studies.

Regarding invertebrates, studies used to focus on earthworms but test on other groups have been recently standardised. Typical endpoints are mortality and reproduction but biomarkers based on enzymatic activities and DNA adducts have also been considered. For insecticides, the efficacy trials and the studies on beneficial arthropods offer information on ground and foliar invertebrates including bees. Studies conducted on typical Mediterranean crops offer specific information for the region however, not all studies are public particularly for the PTS pesticides banned in Europe.

Alteration of reproduction of top predator birds (eagles and falcons) in the terrestrial food chains were the first observed environmental effects of DDT and other chlorinated pesticides. The Mediterranean Region combines a huge biodiversity with a large number of endangered species. Monitoring data indicates a significant exposure of birds to several PTSs in the Region, and chemical pollution is included among the list of factors affecting the success of these species. Recovery of some prey species has been observed in recent years after several chlorinated pesticides were banned. Therefore, there are indications of possible impact of PTSs on bird populations but no conclusive evidence allowing quantifying the role of these chemicals within the multitude of factors affecting population dynamics.

Toxicological information on mammals is available for all PTSs as it is essential for the human health assessment. This information can also be used for setting ecotoxicological thresholds in wild populations. However, differences in the toxicokinetics and toxicodynamics of laboratory versus wild mammals must be considered. Regarding effect assessment in the Region, the situation is similar to that presented for birds, showing indications of possible effects but no clear evidence of cause-effect relationships other than for hot spots.

3.3.1.2 Freshwater environment: fish and aquatic birds

Different biotic indices, based on the direct observation of changes in the populations structure in terms of biodiversity (number of species) and population size for each species, are applied in several Mediterranean countries as direct bio-assessment techniques. However, these indices are strongly related to changes in environmental conditions (e.g. temperature, oxygen concentration, productivity) and, therefore, not specific of PTSs effects, except for hot spots.

Ambient water toxicity assessments, Toxicity Identification Evaluations, and toxicological diagnosis have been applied in the Region (Muñoz et al., 1994) but with relatively low incidence. Fish kills are relatively frequent, but the role of PTSs in these events is mainly concentrated to areas downstream from specific discharges. The biomarker methodology has also been applied with some difficulty by Water Agencies. In the early 90's, EROD activities were measured in a wide range of fish species in France. More recently, biomarkers in molluscs species (e.g. *Corbicula, Unio, Dressenia*) were found to be sensitive to PTSs (PAHs and PCBs) in laboratory exposures and field experiments with caged animals (Mora et al., 1999).

Among sub-lethal effects affecting river fish, endocrine disruption may be the one more directly related to PTSs. For example, the benthic cyprinid *Barbus plebejus,* captured from the middle Po River showed profound inter-sexual alterations (50% of the individuals). These effects can be related to the high levels of NP measured in Po river sediments, although the contribution of natural and synthetic estrogens cannot be excluded (Viganò et al., 2001). Bioassays based on induction of vitellogenine synthesis in primary culture of trout hepatocytes clearly demonstrated the ability of PCBs, TCDDs and PAHs to elicit or antagonise the estradiol effect.

In France, in the Seine-Maritime region, cyprinids of the species *Rutilus rutilus* showed inter-sex gonads, with the incidence of inter-sexuality ranging 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.

A third example of endocrine disruption likely related to PTSs, has been recently identified in two tributaries of the Llobregat River (Spain) (Solé et al., 2000). In male specimens of another cyprinid species (*Cyprinus carpio*), a significant induction of plasma vitellogenine (Vtg) was found. Higher levels of Vtg were found downstream from sewage treatment plants, with a meaningful correlation between NP present in water and Vtg response. Although the high levels of NP (up to 644 µg/L) found in that area strongly suggest that NP can be responsible for the estrogenic alterations, again the contribution of other estrogen agonists cannot be excluded.

Due to the widespread occurrence of PTSs 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 knowledge of the dimensions and consequences of this problem both in freshwater and marine environments.

A particular challenge for risk assessment is posed by estuarine systems, especially by the diversity of habitats and environmental conditions. A limited number of standard tests (water and sediments) exist, particularly for long-term effects assessment, and experimental designs are weak for many of them. Therefore, a research effort is needed to produce more information about toxicity, especially in estuaries, but also more work is needed about how to use toxicological information in risk assessment in these systems (see section 3.5.4).

3.3.1.3 Marine environment: fish and marine mammals

As it has been reported in section 3.2.1.3., the amount of data available on levels of PTS in marine biota is not negligible. However, information on the fate and toxicity of these and other chemicals that are currently released into the marine environment is scarce, and very few monitoring programs have addressed the integrated use of chemical analyses with ecotoxicological assessment.

3.3.1.3.1 Oil pollution

In assessing the effects of oil pollution, one should distinguish the impact of chronic pollution, which is the most common in the marine environment, from the episodic spills. In this case, the impact and the recovery of the ecosystems affected vary considerably. Both biotic and abiotic factors govern the extent of the biological consequences of each oil spill and it is the interaction and relative contribution of these factors which are important.

Danovaro et al. (1995) studied the meiofauna response to Agip Abruzzo oil spill in sub-tidal sediments of the Ligurian Sea, where about 30000 tonnes of crude oil were released in front of the Livorno harbour and caused a decline in meiofauna density relative to the pre-pollution conditions. Statistical analyses indicated that the structural characteristics of meiobenthos collected after two weeks were almost indistinguishable from pre-pollution, demonstrating the high resilience of these meiobenthos assemblages. High crude oil toxicity was also found by testing Erika oil samples with mussel larvae and algae, although the acute effects seem to decrease rapidly due to oil dilution and degradation.

The effects of chronic oil pollution are more difficult to be assessed as they usually co-exist with other forms of pollution. It is well documented that even 1μg/L of water-soluble oil component can harm sensitive organisms like larvae hatched from fish eggs. Exposure to low boiling hydrocarbons of 12 μg/L, halves the rate at which mussels can assimilate food. Low salinities and high temperatures enhance the effect. Bearing in mind the temperature in certain Mediterranean coastal areas, it is expected that chronic effects occur although at present there is little or practically no information on this subject. Long-term, sub-lethal effects were recently assessed by using the biomarker methodology. Results from Aegean Sea and Erika studies found that after a period of 6-12 months the biochemical markers returned to initial values, indicating no differences with original long-term contamination (Porte et al., 2000, Narbonne et al., 2001).

3.3.1.3.2 Other PTSs

At the end of the 80's, France and Italy incorporated for the first time the use of biomarkers as tools for assessing sub-lethal effects on marine organisms in a monitoring program (GICBEM 1986-1993). Later, in 1994-1995, a series of international coastal monitoring programs started (BIOMAR 1994-1998, MEDPOL 1995-now, BEEP 2000-2003), involving the measurement of a range of biomarkers in bivalves (*mussels*) and benthic fish (*Mullus barbatus, Serranus cabrilla and Dicentrachus labrax*) in Mediterranean areas exhibiting significant pollution gradients (e.g. harbours, urban sites, etc.) in comparison with cleaner areas (e.g. Corsica and Sardinia). Following the same strategy, a monitoring network (REMER) was recently initiated in Morocco.

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 PAHs 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 Mediterranean coast.

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 Orbetello Lagoon (Frenzilli et al., 2001).

The BIOMAR program demonstrated the ability of a multimarker approach to build indices of marine contamination impact (Narbonne et al., 1999). For each site, a global response index was calculated as the sum of the response index of each of the five selected biomarkers. As a result of the calculation method, the impact of coastal pollution at each site can be classified in a five level scale.

In addition to biochemical and cellular effects, several studies indicate disruption of normal endocrine function in the Mediterranean area. A series of field investigations with marine invertebrates suggests that tributyl and triphenyltin compounds can induce imposex. The monitoring of a gastropod (*Bolinus brandaris*) along the Catalan coast (NW Mediterranean) showed that imposex was a widespread phenomenon (Solé et al., 1998). Imposex has also been described in the gastropod *Nucella lapillus* collected in the Galicia coast (Ruiz et al., 1998), in the whelks *Stramonita haemastoma* and *Hexaplex trunculus* in Israel (Rilov et al*.,* 2000) and Italy (Terlizzi et al*.,* 1998), and in Malta (Axiak et al*.,* 2000). Five neogastropod species collected in a TBT-polluted site, near the port of Faro (Portugal), were examined in 1996 for imposex with positive results (Gibbs et al*.,* 1997). Imposex was also found in the species *Hinia reticulata* in Portuguese coastal waters and on the south part of the Tagus River (Pessoa et al., 1997). Also, in Portugal, oyster shell anomalies in *Crassostrea angulata* were found in the Sado and Tagus estuaries (Phelps and Page, 1997).

A wide variety of the PTS 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. Recently, new evidence based on monitoring hormone and vitellogenin levels together with gonad histology indicate 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.

Despite the difficulty to directly attribute population responses to pollutants, there are some indications that coastal fish assemblages respond to the impact caused by sewage discharge or mussel fisheries in SE Italy. But still more data is required at the population, community and ecosystem level to assess the health of the Mediterranean. The two approaches (individual and ecosystem health) are not exclusive, but the fact that the type of studies involved are very different usually means that they are not conducted in tandem. Actually, it is difficult to extrapolate from a cellular response caused by chronic exposure, and assess its effect on a whole organism or an ecosystem, as it is also difficult to extrapolate from an acute response resulting from a lethal concentration of a stressor to low-level effects occurring over long exposure periods.

In marine mammals, PCBs 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. Although recent mobilisation of lipid reserves was found to have occurred in some of the diseased dolphins, this had little effect on their PCBs blubber levels and cannot explain the observed difference with the healthy individuals. Three hypotheses were put forward to explain the apparent link between high PCBs levels and mortality caused by the epizootic: (i) depressed immuno-competence caused by PCBs leading to an increase in individual susceptibility to the morbillivirus infection, (ii) mobilisation of fat reserves leading to increased PCBs levels in blood which, in turn, may produce a liver lesion capable of increasing the individual's susceptibility to the morbillivirus infection, and (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 PCBs levels and susceptibility to the morbillivirus infection.

3.3.2 Human health effects

For many PTSs, toxicological effects are still unknown or not fully clarified, and mechanistic information is lacking. Moreover, even for those PTSs whose human health hazard has been characterised (i.e. PAHs), no risk assessment is actually feasible due to the lack of exposure data in most countries. Food being the main exposure route to PTSs, data on PTSs daily intakes are of major relevance and represent the necessary basis to develop an adequate risk assessment. Some food exposure estimates are reported below.

3.3.2.1 Pesticides

3.3.2.1.1 Aldrin, dieldrin, endrin and heptachlor

Exposure to these pesticides mostly happens from eating contaminated foods, such as root crops, fish, or seafood, but also from water. Human breast milk may be a major route of exposure for nursing infants. The total daily intake of aldrin and dieldrin from food has been estimated to be 0.5 µg/day (aldrin + dieldrin) per person in Spain in 1990-91 (Urieta et al. 1996). In one study in Egypt in 1995 (Zeinab et al. 1998), aldrin and

dieldrin were found to be completely absent in the composite diet. In the same study, the daily intake of endrin, heptachlor and heptachlor epoxide were found to be completely absent in the composite diet.

At high levels of exposure, aldrin, dieldrin and endrin mainly affect the central nervous system (EHC 91, 1989; EHC 130, 1992). Ingesting moderate levels of aldrin or dieldrin over a long period may also cause convulsions as a consequence of their bioaccumulation. The effects of exposure to low levels of aldrin or dieldrin over a long time are not known. Some workers exposed to these insecticides had reversible nervous system effects with excitation leading to convulsions. Studies in animals indicated that these compounds may be immunotoxic. The International Agency for Research on Cancer (IARC) determined that aldrin, dieldrin and endrin are not classifiable as to their carcinogenicity to humans (Group 3, IARC 1987).

Heptachlor and heptachlor epoxide are moderately toxic to humans and animals and can damage the nervous system (EHC 41, 1984). A few reports showed that people who accidentally swallowed pesticides containing heptachlor, or who spilled pesticides on their clothes became dizzy, confused, or had convulsions. IARC has classified heptachlor as possibly carcinogenic to humans (Group 2B, IARC 1991).

3.3.2.1.2 DDT

Exposure to DDT, DDE, and DDD occurs mainly from residues in food. The total daily intake of DDT, DDE, and DDD from food has been estimated to be 1.4 µg/day (DDT+DDE+DDD) per person in Spain in 1990-91 (Urieta et al. 1996) and 2.01 µg/day (DDT) in Italy in 1997 (Camoni et al. 2001). In one study in Egypt in 1995, DDT was found to be absent in the composite diet and only DDE was present at 2.18 µg/day (Zeinab et al. 1998). In FR Yugoslavia the daily intake for new-borns in the period 1993-94 was estimated in 3.29 µg of DDE and 0.21 µg of DDT (Vukavic et al., 1997).

Acute exposure of DDT mainly affects the nervous system (EHC 9, 1979). Animal studies show that long-term exposure to DDT may affect the liver, while short-term exposure to DDT in food may have a harmful effect on reproduction. DDT has been shown to have an estrogen-like activity, which is probably responsible for its impact on reproduction in laboratory animals. As a consequence, it has been classified as a substance for which there is evidence of endocrine disruption in an intact organism (COM, 1999).

In animals, oral exposure to large amounts of DDT over a short time mostly affects the nervous system and can cause liver cancer. Tests in animals also suggest that short-term exposure to DDT in food may have a harmful effect on reproduction. DDT has been shown to have an estrogen-like activity. Studies of DDT-exposed workers did not show increases in deaths or cancers, but these studies are considered biased by a number of factors and hence inconclusive. IARC has determined that DDT, DDE, and DDD are possibly carcinogenic in humans (Group 2B, IARC 1991).

3.3.2.2 Industrial compounds

3.3.2.2.1 Hexachlorobenzene (HCB)

The intake of HCB by adults in the general population is predominantly from the diet (about 90%). In utero exposure occurs through mother's blood; breast lactation may also be a significant route of exposure. The total daily intake of HCB from food has been estimated to be 0.2 µg/day per person in Spain in 1990-91 (Urieta et al. 1996). In Egypt, in 1995, HCB was found to be completely absent in the composite diet (Zeinab et al. 1998).

HCB has little capability to directly induce gene mutation, chromosomal damage and DNA repair (EHC 195, 1997). However, it has been tentatively shown that it may play a role, together with other organochlorine compounds such as p,p'DDT, p,p'DDE and some PCBs, in the pathogenesis of exocrine pancreatic cancer through modulation of K-ras activation (Grimalt et al., 1993; Porta et al., 1996). Hexachlorobenzene has been classified as a substance for which there is evidence of endocrine disruption in an intact organism (COM, 1999) and as possibly as being carcinogenic to humans (Group 2B, IARC 2001).

3.3.2.2.2 PCBs

Human exposure to PCBs mostly results from the consumption of contaminated food. Total daily intake of PCBs from food has been estimated to be 2-4µg per person in Italy (Turrio-Baldassarri et al., 1998). Infants are exposed through lactation and a study carried out in FR Yugoslavia with 88 new-borns estimated 1.75µg to be the daily intake of PCBs (Vukavic et al., 1997).

The toxicological evaluation of PCBs presents many problems. PCBs usually occur as mixtures of many congeners each characterised by a range of toxicological activities strictly depending on the degree and pattern of chloro-substitution. "Dioxin-like" congeners are characterised by dioxin-like activity, while other congeners may cause more subtle effects, among which is endocrine disruption (COM 1999). The acute toxicity of

commercial PCB mixtures (Aroclors, etc.) is generally low (EHC 140, 1992). PCBs induce production of various enzymes in the liver and can produce changes in the immune system, behavioural alterations, impaired reproduction, liver, stomach, and thyroid gland injuries. Some PCBs can mimic or block the action of hormones from the thyroid and other endocrine glands.

The most commonly observed health effects in people exposed to large amounts of PCBs are skin conditions such as acne and rashes. Studies in exposed workers have shown changes in blood and urine that may indicate liver damage. Few studies of workers indicate that PCBs were associated with certain kinds of cancer in humans, such as cancer of the liver and biliary tract. Both EPA and IARC have determined that PCBs are probably carcinogenic to humans (Group 2A, IARC 1987).

3.3.2.3 Unintentional by-products

3.3.2.3.1 PCDD/PCDFs

Over 90% of human exposure to PCDD/PCDFs is estimated to occur through the diet, with food from animal origin being the predominant source. The daily intake of PCDD/PCDFs from food has been estimated to be 210 pg I-TE per person in Spain (Domingo et al. 1998) and 97 per person in France (EU SCOOP, 2000). For Italy, a daily intake of 45 pg I-TE per person has been calculated (EU SCOOP, 2000) considering the only contributions from food being of animal origin (a daily intake of about 60 pg I-TE may be assumed when contributions from the other foodstuffs are added).

Toxicological effects reported for PCDD/PCDFs refer to the 2,3,7,8-substituted compounds. A variety of effects have been reported in animal studies following exposure to these compounds (IARC 1997; WHO, 1998). The most extensive data set is available for 2,3,7,8-TCDD; less information is available for the other congeners. Among the most sensitive endpoints of 2,3,7,8-TCDD are endometriosis, neurobehavioral, developmental and reproductive effects and immunotoxic effects.

The lowest doses giving rise to statistically significant effects in the most sensitive endpoints following exposure, have resulted in body burdens (3 to 73 ng of TCDD/kg) in the exposed animals. These results overlap, at the lower end, with the range of body burdens expressed as TEQ that are found in the general population in industrialised countries exposed to background levels of PCDD/PCDFs.

Of the many non-cancer effects evaluated in exposed adult populations (e.g. herbicide producers and subjects exposed in incidents like Seveso, Italy) many were transient effects disappearing after the end of exposure. The only effect that correlates consistently with high exposure of humans to TCDDs was cloracne. A few conditions appear to be in excess among the exposed cohorts when compared to unexposed reference groups including alterations in metabolic parameters, as well as mortality from cardiovascular and non-malignant liver disease.

PCDD/PCDFs have been classified as substances for which there is evidence of endocrine disruption in an intact organism (COM, 1999). 2,3,7,8-TCDD has been shown to be carcinogenic in several species of laboratory animals at multiple sites. In humans, the epidemiological evidence from the most highly exposed cohorts studied produces the strongest evidence of increased risks for all cancers combined, along with less strong evidence of increased risks for cancers of particular sites. IARC concluded that 2,3,7,8-TCDD is carcinogenic to humans (Group 1). Other polychlorinated dibenzodioxins and dibenzofurans are not classifiable as to their carcinogenicity to humans (Group 3, IARC 1997).

3.3.2.4 Other PTSs of concern in the region

3.3.2.4.1 HCHs

Diet accounts for over 90% of the total exposure of HCHs in industrialised countries. The total daily intake of lindane from food has been estimated to be 2.9 µg/day per person in Spain in 1990-91 (Urieta et al. 1996)), 1.75 µg/day in Italy in 1997 (Camoni et al. 2001); and 11.9 µg/day in Egypt in 1995 (Zeinab et al. 1998). In FR Yugoslavia the total daily intake of lindane in new-borns was estimated in 1993-94 in 0.35µg (Vukavic et al., 1997). In France, despite the wide occurrence of lindane in the environment and food chain, neither the limit of maximum residues nor the acceptable daily intake were exceeded in recent years (Bintein and Devillers, 1996).

The acute oral toxicity of lindane is moderate: the central nervous system is the main target of toxicity (EHC 124, 1991). Mutagenicity was not shown in a number of studies. Lindane has been classified as a substance for which there is evidence of endocrine disruption in an intact organism (COM 1999), and as a possible carcinogen for humans (IARC, 1987).

3.3.2.4.2 PAHs

The main sources of general population exposure are: vehicular traffic, residential heating, smoke from open fireplaces and cooking, tobacco smoke, contaminated food and drinking-water, and the use of PAHs-contaminated products. The calculated total daily intake of PAHs from food has been estimated to be 3 µg/day (1.4 µg/day carcinogenic PAHs) per person in Italy (Lodovici et al., 1995).

The acute toxicity of PAHs appears to be moderate to low (EHC 202, 1998). Short-term studies showed adverse haematological effects. Systemic effects caused by long-term treatment with PAHs have been described only rarely, because the end-point of most studies has been carcinogenicity. Significant toxic effects are manifested at doses at which carcinogenic responses are also triggered. In studies of adverse effects on the skin after dermal application, non- or weakly carcinogenic PAHs were inactive, whereas carcinogenic compounds caused hyperkeratosis. Benz[*a*]anthracene, benzo[*a*]pyrene, dibenz[*ah*]anthracene, and naphthalene are embryotoxic to mice and rats. Benzo[*a*]pyrene also have teratogenic and reproductive effects.

PAHs have also been studied extensively in assays for genotoxicity and cell transformation; most of the PAHs are genotoxic or probably genotoxic. The only compounds for which negative results were found in all assays were anthracene, fluorene, and naphthalene. Owing to inconsistent results, phenanthrene and pyrene could not be reliably classified for genotoxicity. PAHs have generally been reported to have immunosuppressive effects.

Because of the complex profile of PAHs in the environment and in workplaces, human exposure to pure, individual PAHs has been limited to scientific experiments with volunteers, except in the case of naphthalene which is used as a moth-repellent for clothing. After dermal application, anthracene, fluoranthene, phenanthrene and benzo[*a*]pyrene induced specific skin reactions, which were classified as neoplasic proliferations.

IARC (IARC, 1987) has determined the following: benz[a]anthracene, dibenz[*a*,*h*]anthracene and benzo[*a*]pyrene as probably carcinogenic to humans (Group 2A); benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, dibenzo[*ae*]pyrene, dibenzo[*ah*]pyrene, dibenzo[*ai*]pyrene, dibenzo[*al*]pyrene, and indeno[1,2,3-*cd*]pyrene as possibly carcinogenic to humans (Group 2B); and anthracene, benzo[*ghi*]perylene, benzo[*e*]pyrene, dibenzo[*h*,*rst*]pentaphene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene as not carcinogenic to humans (Group 3).

3.3.2.4.3 Alkylphenols

Exposure to alkylphenols occurs mainly from food. The dietary daily intake of alkylphenols has been estimated to be 80 µg/day per person in Italy in 1995 (Ferrara et al. 2001). The acute oral toxicity of alkylphenols is usually low. Long-term oral exposure causes an increase in liver and kidney weight without significant histopathological alterations. Alkylphenols are not genotoxic. Nonyl-phenol and 4-tert-octyl-phenol have been classified as substances for which "there is evidence of endocrine disruption in an intact organism" (COM 1999) because of their estrogenic activity.

3.3.2.4.4 Organomercury compounds

Mercury compounds are neurotoxic. The clinical manifestations of methylmercury poisoning are quite extensive and include disturbances in sensory, motor and cognitive functions. As seafood is the main source of mercury for humans, and because of the often reported high levels of methylmercury in fish and shellfish, monitoring of the general population exposure is needed. Monitoring should be aimed to define the risk for some groups of the general population, such as heavy fish consumers and vulnerable groups (in particular young children and pregnant women). On this basis, a study was initiated by MEDPOL in the early 80's, aimed to assess the risk for the Mediterranean population in general. Italy, Croatia and Greece were the countries selected for this study. The investigation was carried out on the high-risk group of fishermen and their families. After preliminary screening of more than 4000 people through dietary surveys, a total of 1098 hair samples (659 from Greece, 241 from Italy and 198 from Croatia) were analysed for total mercury and, where appropriate, for methyl mercury. The results confirmed that there is a positive correlation between seafood consumption and levels of total mercury and methyl mercury in hair.

On the basis of the levels of methylmecury in hair in relation to blood concentrations consistent with no detectable adverse effects in the adult population, the individuals from the study in Croatia were not considered at risk. Only very few people in the other countries exceeded these levels without reaching the hair concentrations associated with a 5% risk of neurological damage (WHO/FAO/UNEP, 1989).

The importance of fish as vector of Me-Hg exposure focused the interest of risk managers to the high predators species, mainly pelagic carnivorous (e.g. tuna, sword fish, etc.). According to the mean annual per capita fish consumption, the mean weekly mercury intake is of 49.8 µg in Spain and of 19.0 µg in Croatia.

3.4 COMPARISON OF MEASURED DATA

3.4.1 General assessment of ecosystems effects

As shown in the previous sections of this chapter, PTSs are widely spread in the different environmental compartments of the region. The application of low-tier risk assessment models based on the comparisons between measured levels of PTSs and accepted environmental quality standards (Table 3.19) or ecotoxicological thresholds (see Annex II) may provide a primary guideline for the identification of hot spots. However, the real impact of their occurrence in the environment is more difficult to estimate because the effects are expected to be in the most cases, the outcome of a multi-factorial stressor where toxic chemicals are just one of the elements.

Table 3.19. Guideline environmental quality values for PTSs in some compartments.

PTS	drinking water[1]	Water[2]	sludge for use on land (EU draft)	Soil[3] (Neth.)	Air (WHO)
aldrin	0.1 µg/L	10 ng/L		0.0025 mg/kg	
endrin	0.1 µg/L	5 ng/L		0.001 mg/kg	
dieldrin	0.1 µg/L	10 ng/L		0.0005 mg/kg	
heptachlor	0.1 µg/L				
chlordane	0.1 µg/L				
mirex	0.1 µg/L				
toxaphene	0.1 µg/L				
DDT	0.1 µg/L	10 µg/L p,p'DDT 25 µg/L total DDT		0.0025 mg/kg	
HCB	0.1 µg/L	0.03 µg/L		0.0025 mg/kg	
PCBs[4]	0.5 µg/L		0.8 mg/kg	0.02 mg/kg	
PCDD/F			100 ng TEQ/kg		
HCH		100 ng/L		0.05 µg/kg	
PAHs	0.2 µ/L 0.01 µ/L (BaP)		6 mg/kg	1 mg/kg	0.087 µg/m^3 0.7 ng/m^3 (BaP)
TBT		10 ng/L (WHO)			
Phthalates			100 mg/kg	0.1 mg/kg	
Alkylphenols			50 mg/kg		

[1]maximum values allowed in drinking water (Directive 98/83). [2]EU quality objectives.
[3] target values after remediation. [4] Σ7 cong. (28, 52, 101, 118, 138, 153, 180)

In general, water and soil concentrations of PTSs are much lower than the reference values. Therefore, at first glance, no adverse effects would be expected althought some hot-spots can be identified. The case of B(a)P in air is less evident, although the data quoted in table 3.3 is just representative of a few samples. On the other hand, the fact that PTSs may accumulate in parts of the environment and, in particular, the elevated capability of biomagnification through the food web and sub-lethal long-term effects, may represent the true hazard. Therefore, conceptual approaches for specific exposure routes, such as those associated with suspended matter, sediments, and food chains, are required as the starting point for any assessment.

It is clear that the exposure of higher organisms to PTSs represents one of the major concerns. This has been evidenced by measurements and confirmed by biomarkers and related techniques. However, excluding very local incidents (e.g. imposex in coastal enclosures), no conclusive evidence on cause-effect relationships can be presented.

As the marine environment is one of the sinks for PTSs, the Mediterranean Action Plan assessed the risks associated with current levels and loads of organohalogen compounds in marine biota (UNEP/FAO/WHO/IAEA, 1990). The main conclusions were as follows:

Based on the limited data available on chlorinated pesticides it was concluded to be unlikely that present levels of aldrin, dieldrin, endrin, heptachlor and heptachlor epoxide in the Mediterranean would adversely affect

marine organisms. It was found equally unlikely that marine seabirds or mammals were at risk. The small database available indicates levels well below those of concern in the Mediterranean. Furthermore, there is little cause for concern in relation to the potential impact of HCB and HCHs on the marine organisms in the sea. Similarly, the maximum concentrations of DDT found in marine species were comfortably below those reported to cause effects on reproduction or other sublethal effects. With regard to marine birds and reproduction disturbances associated with egg shell thinning, the assessment document concludes that there is nothing in concentration levels that suggests that populations of marine birds in the Mediterranean are at risk, and no indication that their numbers are in decline. However, some recent studies confirm exposure levels to PTSs in the Region and body burdens of concern have been detected for organochlorinated pesticides and PCBs (Herrera et al., 2000; Mateucci et al., 2001; Berny et al., 2002) particularly for inland systems.

Very recently, Miniero et al. (2002) have assessed the risk of dioxin-like chemicals for aquatic birds, fish and marine mammals. The application of mammalian TEFs, derived from rodent bioassays, to the assessment of risks in aquatic mammals presents some obvious drawbacks. In fact, TEFs should take into account differences in metabolism, typical of terrestrial organisms fit to aquatic life, their species and endpoint dependency. In general foraquatic mammals, exposure data are given for blubber concentrations that result approximately two orders of magnitude more contaminated than the brain. For mammals, 2.8 pg/g ww of 2,3,7,8-TCDD, based on a maternal body burden, would likely represent this threshold resulting in adverse effects on the reproductive system. This concentration, expressed in TEQs on a ww basis, is more than one order of magnitude lower than the concentration found in the blubber of dead specimens of *Tursiops truncatus* and *G. griseus*.

By applying the same procedure on a body burden basis to fish LOAEL, a threshold concentration in eggs of 4 pg/g ww of 2,3,7,8-TCDD causing a defined adverse effect is obtained. This level, expressed in TEQs, results in more than one order of magnitude lower levels than the concentration found in the eggs of the two sharks *Centrophorus granulosus* and *Squalus bainvillei*. In birds, it has been found that *Larus audonii* eggs exhibit a concentration of 0.73 ng TCDD/g ww, approximately six times higher than the LD_{50} of 0.15 ng/g capable to induce mortality and eliciting a significant increase in the incidence of the developmental abnormalities in chicken of *Gallus domesticus*. Apart from the high sensitivity characteristic of this species, the concentrations found in the herring gull eggs appear to be of concern.

In summary, and based on the small number of toxicological evaluations and on the concentrations of some PTSs in fish, marine mammals, and aquatic and terrestrial birds, adverse effects on some systems may be expected. These effects will add to those already described in section 3.3.1 regarding inter-sexual alterations of aquatic organisms.

3.4.2 General assessment of health criteria

Except for professionally exposed workers, diet is the main route of human exposure to PTS (up to 90 %). As a consequence, a risk assessment may be carried out by comparing PTS dietary intakes with their pertinent Tolerable Daily Intakes (TDIs) established at the international level by expert groups considering the probability of specific health damages. The results for some EU countries are shown in Table 3.20. Additional data can be found in section 3.3.2.

For PAHs and mercury, the mean exposure is about 30% of TDI but for methylmercury, the food intake is more close to the TDI. In this case, certain consumers can exceed the TDI, such as young children 3-8 years old (133%) and the high consumers of pelagic carnivorous old fish (2500%) .For chlorinated compounds, mean intake levels are far below (less than 5%) the corresponding TDIs, except in the case of PCBs and dioxins for which recent data available for France and Italy indicate mean intakes close to TDIs. In this regard it is worthwhile to emphasise that exposure of specific groups of the population (infants, fish consumers) may largely exceed TDIs (3-4 times as reported by AFSSA).

For DL-PCBs expressed as TEQs, the food exposure is twice the WHO (1998) TDI for dioxins and DL-PCBs. For total PCBs, the dietary intake based on Italian TDIs study is about 2 times the TDI recently revised by the WHO and given in Aroclor equivalents. This observation is well correlated with the over-exposure found for DL-PCBs. Thus, the new TDI of PCBs revised by the WHO appeared to be pertinent for risk-assessment of total PCBs. The EU SCOOP report indicated that fish and fish products contributed to 70% of the food exposure of DL-PCBs.

Table 3.20. PTS TDIs vs/ corresponding dietary intakes

PTS	TDI xg/kg/day	Organisation	Food intake Mean /adults	Source
DDT	20 µg	WHO	16 ng (0.08%)	Italy
HCHs	0.3 µg	WHO	5.3 ng (1.8%)	Italy
Chlordane	0.5 µg	WHO		
Dioxins (I-TEQ)	1 pg	WHO	1 pg (100%)	Italy
			1.03 pg (103%)	France
			3.5 pg (350%)	Spain (Catalonia)
PCB-DL (I-TEQ)	1.3 pg	WHO	2.5 pg (192%)	EU
Σ PCB (Aroclor 1260 Eq)	0.02 µg	WHO*	36.8 ng (180%)	Italy
PAHs (BaP Eq)	14 ng	DVS 10-4 RIVM	5 ng (36%)	France
Hg	0.7 µg	WHO	0.25 µg (36%)	France
Me Hg	0.47 µg	WHO	0.34 µg (72%)	France

**Temporary TDI proposed at the international PCB meeting in Brno, May 2002*.

There is no systematic data for most of the other countries of the region. However, an interesting study made in FR Yugoslavia in 1993-94 concluded that the estimated average daily intake for healthy new-borns was significantly lower than in 1982-83 for DDE, DDT, total DDT and total PCBs; significantly higher for β-HCH but not for γ-HCH; and nearly equal in both periods for α-HCH. Estimated average daily intake (ADI) of total DDT and γ-HCH was below the WHO values in both periods, and decreased to below the limit values for PCBs in 1993-94 (Vukavic et al., 1997).

The data from the monitoring of PTSs in different areas of the Balkans (see section 3.5) clearly show levels of some PTSs in environmental matrices (mainly soil and sediment), and eventually biota, higher than the background levels generally found in the environment. Therefore, the ability of PTSs to enter the foodchain and to biomagnify along them makes the hypothesis of a high human exposure to these compounds highly plausible, and the correlated damage for health worthwhile to be explored.

3.5 CASE STUDIES

The following studies have been selected to illustrate different situations of PTSs sources in the Region which can also be considered as hot spots. They underline the variety of sources, either urban, industrial or accidental, and the approaches followed towards a better knowledge of each problem.

3.5.1 PCBs contamination after the war in Kosovo

The long conflict between the different nations of the Former Republic of Yugoslavia throughout the 90's and NATO's Kosovo intervention in spring 1999, not only had dramatic humanitarian consequences but also detrimental effects on the environment. The burning or damaging of industrial and military targets resulted in the release of a large number of hazardous chemical substances, including PTSs. It was estimated, for example, that over 1000 electro-transformer stations, containing PCBs oil, were damaged during the war.

The karst area of the coast of Croatia was of particular concern for groundwater pollution. A large number of transformer stations were damaged in Delnice, Zadar, Šibenik, Split and Dubrovnik. In a study performed in 1996, significant levels of PCBs were found in soils from Šibenik (over 2000 mg/kg dw), Zadar and Dubrovnik areas. Daily PCBs and DDT intakes were studied among fishermen and their families who consume fish from the coast of Zadar in significant quantities. It was found that many of them (especially those assumed to consume fish caught from the Marina and Vruljica stations, in Zadar area) ingested more than the acceptable daily PCBs intake of 1 µg/kg/day (Picer and Picer , 1998).

The cities of Pancevo, Novi Sad, Belgrade, Kragujevac, etc., in Serbia, were also severely attacked during the NATO's intervention, causing numerous industrial accidents. For example, after the heavy bombardment of Kragujevac, 2500 kg of PCBs-based oil from the transformers of the automobile industry ZASTAVA were spilled. Very high levels of PCBs and PCDD/Fs were found in samples taken around the transformers of the power plant (70-74 g/kg of PCBs and 10200 ng ITEQ/kg of PCDD/Fs). Underground water reservoirs were found to contain 0.7 mg/L of PCBs, but there were no traces in drinking water in this locality. On the other

hand, sediments from the Lepenica river (close to the factory) contained high levels of PCBs (2.4 mg/kg), and the contents in water was 18.7 ng/L. The factory is still storing 5-6 tonnes of waste oil containing PCBs.

The oil refineries of Pancevo and Novi Sad were also destroyed and around 150000 tonnes of crude oil and oil products were burnt or leaked. Average contents of total PAHs in soils of the Novi Sad region were of 5.5 mg/kg two years after the aggression (2001), a value which is above the lowest risk level (Table 3.25) and could affect the safety of the crops grown in the area. Residues of DDTs were also found in all soil samples in levels that exceeded the Maximum Tolerable Concentration, according to the Official Register of the Republic of Serbia (11/1990), although this area was already heavily polluted before bombing (Vojinovic-Miloradov et al., 2002).

Water quality of the Sava and the Danube rivers was also assessed right after the accidents by monitoring the PCBs levels in freshwater fish. The concentrations of PCBs in fish tissues from the Sava river were in the range of 8-177 μg/kg ww, and from the Danube 2-196 μg/kg ww, which is well below the maximum residue limit for PCBs in fish (3 mg/kg). However, PCBs have a long half-life in the environment, and it can be expected that concentrations in fish will rise.

In order to collect and analyse the consequences for the environment and human settlements of the military actions in the Balkans region, the Balkans Task Force (BTF) was established in early May 1999 (UNEP/UNCHS, 2000). The BTF studied the impact of the conflict on the environmental situation in three countries: FR Yugoslavia, FYR of Macedonia and Albania, and identified the main environmental concerns. More recently, the European Commission has recognised these problems and approved the research proposal APOPSBAL, to be developed in 12 institutions of Croatia (3), Slovenia, Bosnia and Herzegovina, Kosovo, FR Yugoslavia (3), Austria, Czech Republic and Greece. These investigations will provide more precise data about the pollution, especially by PCBs, of the war-damaged area in the Former Republic of Yugoslavia.

3.5.2 The fate of HCHs close to production sites.

The production and storage of obsolete stocks of lindane have been the cause of severe pollution problems in the Region, which deserve consideration. Major contamination episodes occurred in the vicinity of three factories, as a result of the industrial emissions and the disposal of the production residues. The sites were located in a rural area near the small village of Sabiñanigo (Huesca, Spain), in Durres (Albania) and Skopje (FYR of Macedonia).

During the 90's a lindane factory was installed close to the village of Sabiñanigo, and close also to the Gallego river (av. 37.7 m^3/s), one of the most important tributaries of the Ebro river. The up and downstream waters were currently monitored when the factory was still working. No HCHs were found in the upper part of the river, but high concentrations were found for α-HCH (1.06 μg/L) and γ-HCH (0.76 μg/L) downstream. Both values were well over the maximum established limit and the factory was definitely closed.

The analysis of suspended solids during the sampling dates showed values of 2.8 mg/kg of α-HCH, 4.5 mg/kg of β-HCH and 3.8 mg/kg of γ-HCH. The analysis of river sediments carried out in the same sampling points during the same period showed the maximum values also near the factory and the waste dumps. A relative increase of α- and β-isomers was observed, the former having the highest content in the solid waste withthe latter being the least soluble and the most stable. The decrease in the pollution levels along the river was not as sharp as the variation of the concentration of α-HCH.

After 5 months without industrial activity, the same points were monitored again and considerably lower values were found. In fact, α-HCH was lower than 0.08 μg/L and γ-HCH was below 0.20 μg/L (Nerín et al., 1992). This gives a timescale for natural environmental recovery.

On the other hand, the Durres chemical plant produced lindane (6-10 tonnes per year) until it was closed in 1990. Since then, families have been living in the area with their houses built using contaminated bricks from the old indane production buildings 20 m away. They are also keeping domestic animals, such as cows, sheep and goats, inside the plant area. A well with a depth of about 6 m is located inside the plant and is being used to water the animals and irrigate vegetables.

A preliminary study of HCH levels conducted during the 90's showed concentrations of 225 mg/kg of HCHs in the topsoil inside the plant. This level decreased rapidly to about 40 mg/kg at a distance of 200 m from the plant. However, at a distance of 800 m, a soil sample still showed concentrations of 15 mg/kg of total HCHs. Sediment samples from the channels and 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, clearly documenting the spreading of HCH isomers into the environment.

The further results of HCH analysis conducted within the UNEP assessment (2000) in some samples from the area are shown in Table 3.21. The conclusion of this assessment was that the former chemical plant in Durres is one of the worst environmental hot spots in the Balkans.

Table 3.21. Levels of HCHs in samples analysed in UNEP assessment (2000).

Sample	Total HCHs	γ-HCH (Lindane)
Soil from Lindane production area	8790 mg/kg	3140 mg/kg
Soil from dichromate plant	2.21 mg/kg	0.71 mg/kg
Water from well 6 m deep	4 μg/L	
Sheep's milk	12.8 mg/kg	0.13 mg/kg
Sheep's wool	0.31 mg/kg	
Pepper from house 20 m away	not detected	

Another area of concern was detected in a three-building site located approximately 1.5 km from the former plant which stores approximately 500 tonnes of HCHs. Leakage from corroded drums, inappropriate storage of bags containing chemicals, etc. suggest soil and groundwater contamination.

Finally, the Organic Chemical Industry of Skopje (OHIS A.D.) produced for some time technical HCH and lindane. The production of lindane ceased in 1977 and in the 1980's the plant's equipment was dismantled leaving behind two empty buildings. The floors and walls were not cleaned and soil remediation did not take place around the buildings. Most of the remaining residues of production were dumped on site. Approximately 10000 tonnes of technical mixture of HCHs have been stored for 20 years. The HCH dumps were to be covered with a mixed soil of clay, sand and gravel and covered with grass. The supporting concrete sidewalls were not as high as the dump and some parts of the walls were missing or damaged. Groundwater analyses performed between the OHIS site and the Vardar River show high HCH concentrations.

3.5.3 PTS in the Venice Lagoon

The Venice Lagoon (Italy) (Fig. 3.13) is particularly polluted by the presence of an important industrial district (Marghera Harbour), by the untreated domestic wastes and the motorboats continuously crossing the lagoon. The lagoon ecosystem is damaged because of severe eutrofication and chemical pollution.

Large projects have been undertaken over the last few years with the aim of providing a comprehensive state of the environment according to the European Environmental Agency (EEA) guidelines (i.e. DPSIR approach). The projects were conceived to support regulatory actions and interventions envisaged to reduce the overall input of PTSs into the lagoon and, particularly, to enforce the definition of the quality objectives for the lagoon and to set maximum allowable annual loads of PTSs.

The survey of PTSs in the lagoon top sediment (15 cm) included the examination of 150 stations distributed all over the northern, central, and southern lagoon in both shallow (<1 m deep) and deeper (shipping canals) bottoms (*MAP project*). The mean concentrations and loads of PTS in the shallow bottoms are reported in Table 3.22. The lagoon canals inside the industrial district of Porto Marghera, as well as the canals inside the historical centre of Venice, were identified as hot spots, i.e. concentrations of PTSs were typically 100-2000 times higher than in the rest of the lagoon (e.g. PCDD/Fs mean concentration in the industrial canals was 83000±307000 ng/kg dw) (Frignani et al., 2001).

The transfer of PTSs from the catchment area to the lagoon was also investigated (*DRAIN project*). Based on statistical analysis of time series of rainfall events on the drainage basin, the 1999 year turned out to be representative of the average annual rainfall recorded over the last 30 years. The riverine contributions to the total annual loads of the selected PTSs are reported in Table 3.13

The contribution of atmospheric deposition was estimated by collecting monthly bulk (dry and wet) deposition in one

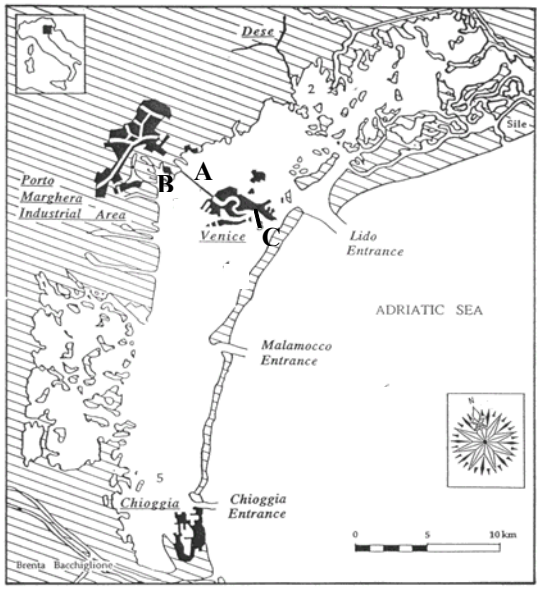

Figure 3.13 Map of Venice Lagoon showing the sampling stations A, B and C.

site near an industrial area (Porto Marghera), another site in the city of Venice, and the remaining two sites in the southern and northern ends of the Lagoon (Valle Figheri and Valle Dogà, respectively). Although a significant variability was observed for the determined PTSs, calculated PCDD/Fs fluxes to the lagoon resulted to be rather homogeneous, the median range being ~25-35 pg/m^2/d, whereas in the station located close to the industrial zone the flux was ~60 pg/m^2/d. PCBs deposition in the industrial fallout sampling site and in the Venice town centre was ~3-4 ng/m^2/d, that is almost three times higher than the value measured at north and south lagoon stations. HCB loading (~4 ng/m^2/d) was almost four times higher in the industrial zone than in the other sites (~1 ng/m^2/d). PAHs loadings in the city of Venice and in the industrial area were ~700 ng/m^2/d, respectively. The overall median of 2,3,7,8-TCDD equivalents (TEQ) of PCDD/Fs was 1.3 pg/m^2/d (range 0-9.2) while dioxin like PCBs contributed for another 0.3-0.4 pg I-TEQ/m^2/d.

Table 3.22. Mean concentrations and loads of PTSs in the 15 cm top sediment of shallow lagoon bottoms.

			North. Lagoon (n=21)	Central Lagoon (n=31)	South. Lagoon (n=29)	Whole Lagoon
Total PCBs (Aroclor PCBs)	Conc. Load	µg/kg dw tonnes	6.6 0.11	11.4 0.24	7.4 0.17	8.2 0.50
OC Pesticides[a]	Conc. Load	µg/kg dw tonnes	1.2 0.02	2.6 0.05	1.4 0.03	1.7 0.10
Total PAHs[b]	Conc. Load	µg/kg dw tonnes	570 10	3200 66	1100 25	1600 97
PCDD/Fs	Conc. Load	ng/kg dw kg	115 2.0	340 7.1	100 2.3	180 11.1
Sum dioxin-like PCBs	Conc. Load	ng/kg dw kg	1600 28	3300 70	1200 27	2000 120
HCB	Conc. Load	µg/kg dw kg	0.86 15	1.11 23	0.99 22	0.95 58

[a] aldrin, endrin, dieldrin, heptachlor, heptachlorepoxide, DDE, DDD, DDT, α-HCH and β-HCH

[b] naphthalene, acenaphtylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b-k)fluoranthene, benzo(a)pyrene, indeno(123,cd)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene.

The estimated external loads of PTSs (i.e. riverine and atmospheric) into the Lagoon of Venice presented in Table 3.23, suggest that the non-point sources are actually more important than the point ones, which marks the difference between present and past situation. Both water and air emissions must be included in environmental protection policy planning.

Table 3.23. Major point (industrial) and non point (riverine and atmospheric) annual loads (kg/year) of PTS in the lagoon of Venice (year 1999).

PTS	Riverine loads	Atmospheric deposition	Porto Marghera effluents
Total PAHs	<100	100±40	5
PCDD/Fs	0.013	0.01±0.004	
PCDD/Fs (TEQ)	0.0001	0.0003	0.0044
ΣPCB dioxin-like	0.4	1.0	
HCB	0.9	1.7	

A large variety of sediment cores were analysed in order to reconstruct the temporal development of PTSs in the Lagoon. The results concerning PCDD/Fs, dioxin-like PCBs, and HCB found in three radio-dated cores from the central lagoon (Fig. 3.13) allow a close comparison of the first (1930-1960) and second (1960-nowadays) industrial development periods of Porto Marghera industrial district and the examination of the contamination development in a canal of the Historical Centre where the last dredging dates back to the 50's. While a decreasing trend of concentration and fluxes of the halogenated pollutants was found in core A, cores B and C showed a continued increase over the time of PCBs and HCB fluxes. PCDD/Fs fluxes decreased significantly in the most recent sediment layers (Marcomini et al., 1999).

3.5.4 The Seine estuary

Estuarine systems are biologically rich ecosystems subject to complex behaviour patterns. The spatio-temporal variability of the parameters and processes which characterise these environments complicate both their scientific approach and their appropriate management. The Atlantic rivers, moreover, are subject to the consequences of the tidal effect, namely the salinity gradient and the capacity to accumulate suspended particles in the turbidity maximum zone. Together, these features determine the distribution of biological communities and the fate of fine particles and associated compounds. These phenomena also modify the speciation and flux of some chemical pollutants. In fact, estuaries are the zones where generally the highest concentration of contaminants are found, in the *continuum* river basin/estuary/coastal waters.

Since the biology of the estuary is rather simple and only some species play an important role in the ecosystem, it can be used as an excellent field laboratory for testing the "Risk assessment" methodology. The "Seine Estuary Program" (http://seine-aval.crihan.fr/) has provided important knowledge about the Seine estuary behaviour and the status of contamination by PTSs, including emission sources, levels in abiotic and biotic compartments (more than 15 species sampled) and food web transfer, understanding the behaviour of PTSs crossing estuaries, mathematical modelling, ecotoxicological and epidemiological information for estuarine species and ecosystem status and dynamics.

On one hand, the program has provided key concepts for understanding the role of an estuary and explaining the consequences of chemical contamination for biota. On the other, it was proved that an estuary acts like a good waste treatment plant and plays an important role as a reactor and/or speciation transformer of PTSs.

The Seine estuary offers ample possibilities for developing the PEC/PNEC methodology, intended for protecting the estuarine ecosystem. However, the PNEC provided today for fresh and marine waters using the TGD prescriptions are based on ecotoxicological data obtained from fresh water species. Thus, the idea behind the project is to define a PNEC for estuaries, and use specific ecotoxicological data for estuarine species.

The experience of the Seine program shows that there is a need for:

- More ecotoxicological data on estuarine species, giving preference to chronic tests,
- Standardisation of tests in water and sediment,
- Specific evaluation factors in estuarine environment, because fresh water and sea water factors are not necessarily adaptable.

In summary, due to the lack of laboratory and field data, research is needed to produce more information for risk assessment in estuaries.

3.6 CONCLUSIONS AND RECOMMENDATIONS

3.6.1 Levels

A substantial amount of information exists on the distribution of PTSs in the different environmental compartments of the Region. In consequence, some areas of concern have been identified, which include estuaries (e.g. Seine, Rhone, Ebro, Po and Nile), coastal enclosures (e.g. Izmit Bay, Venice Lagoon, etc.), coastal areas (e.g. NW Mediterranean and Northern Adriatic), inland waters (e.g. Po, Ebro, Seine, Kupa and Lepenica rivers) and dumpsites (e.g. Durres, Skopje, Alger, Mustaganem, etc.). Apart from areas of intense local contamination, compounds of regional concern are PCBs, DDT, HCHs, PAHs, HCB and TBTs. Other compounds, e.g., phthalates, alkylphenols and PBDE/PBBs, are suspected to be ubiquitous but data are lacking.

Few spatial and long-term temporal trend monitorings of fish, mussels and seabird eggs have been carried out in the Northern Mediterranean. A general decline of DDTs has been reported for marine biota along the Mediterranean coast of France and Italy, and from the Adriatic Sea between 1970's and 1990's, which is consistent with the regulatory restrictions on production and use of this compound. PCBs, in general, do not exhibit such clear trend.

Despite the extensive information existing on PTSs levels and trends, data are often missing for some compartments particularly: atmosphere, ground and drinking waters, sewage sludges and soils, and storages (industrial products, pesticides). Moreover, significant geographical data gaps occur particularly in the South and South-eastern Mediterranean basin.

Apparently, data obtained is mainly the result of research campaigns rather than the existence of monitoring networks. When data exists, particularly in governmental agencies or institutions, they are not easily available

and, in many occasions, data series are discontinued and have not been quality assessed. Most of data for chlorinated pesticides, for example, was obtained in the 80's and levels usually show an extremely large span of concentrations, which may reflect more the result of analytical inconsistencies than real differences of level of pollution.

Available data on PTSs levels in human tissues show a substantial paucity which appears even more striking if compared to the amount of data available for environmental matrices, biota and food. A representative study of a general healthy population living in a wide geographic area has never been conducted in any country of the region. Most countries in the region lack population indicators on the impact that environmental contamination has on human health.

A major step towards the filling of the existing data gaps in the Region will be the activation of monitoring programs at three levels:

- Analysis of abiotic samples or sentinel species to identify hot spots and transport pathways. Monitoring activities should be established in the corresponding countries to fill the geographical data gaps and ensuring the continuation of existing time trend series. Regional surveys of emerging PTSs and compounds actually on the market or those difficult to analyse (e.g., PCDD/Fs) should be particularly envisaged.
- Analysis of food to evaluate the general exposure of the population and to detect abnormal increases due to different cases of contamination. Monitoring design should allow to assess any correlation of PTSs body-burden with factors 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 PTSs. The data obtained should allow the validation of exposure models.

Domestic and regional monitoring efforts should continue to study multi-media transport across air, rivers, seas, and soil, and the resultant environmental and human concentration levels.

According to the regional experts, future monitoring strategies should address the following:

- Intensive monitoring of temporal trends in appropriate abiotic and biotic media at a few key locations, and occasionally over wider areas, and continuation of existing time trend series which have proven to be useful and informative.
- Standardised sampling and analytical methods in order to compare results in the studies carried out in different countries must be implemented. Monitoring programs should include improved quality assurance/quality control protocols, possibly linked to other international programs, and contain reporting procedures and analysis of data.
- Monitoring strategies need to be adequate to the technical and economical possibilities of the different countries. Regional accredited laboratories may assist contracted monitoring institutions in the development of quality assurance systems. In any case, a regional network of national inter-calibrated laboratories contributing to regional monitoring could better improve data quality and fill data gaps.

The achievement of these goals requires national/regional strategies, which should provide the basic support for an adequate environmental management of PTS.

3.6.2 Effects

A number of reports have illustrated the development of the ecotoxicology studies in the region. These studies provide guidelines for the identification of hot spots, particularly in coastal areas (e.g. Adriatic Sea, Seine, Po and Nile estuaries, Izmit Bay, Venice Lagoon, etc.) and inland waters (e.g. middle Po and Ebro rivers, MSWI in France, etc.). As a result, a range of symptoms are shown by aquatic organisms exposed to PTSs. In general, studies referring to metabolism and end-point, deal with growth, endocrine disruption, CYP and drug metabolism induction, biochemical parameters and genotoxicity. Furthermore, the combination of chemical and biological methods has provided early identification and response to new emerging problems (e.g. imposex in gastropods).

Laboratory studies have shown bird species to be susceptible to exposure to PTSs displaying decreased egg production, embryotoxicity and thickness of the egg-shell but field evidence in the region is very limited. Effects of PTSs were also studied in mammals, particularly in laboratory rats and mice. The laboratory findings appear to be applicable to wild populations of mammals in field observations and experiments. Exposure of marine mammals to certain PTS has been demonstrated.

Different approaches have been proposed for risk assessment: PEC/PENEC, Toxicity Exposure Ratios (TERs), Hazard Quotients (HQs), intrinsic properties of chemicals (PBT), development and application of Environmental Quality Standards (multi media) and Reliable Environmental Data. Lower tier assessments are generic and can be applied to the region. However, most higher tier scenarios have been developed in northern European countries and there is a need for their adaptation and testing also in the southern countries.

For humans, the lack of solid data on food PTSs intakes strongly limits the risk-assessment. There is an urgent need for extensive food exposure study, taking as example the best studies performed in some countries (market basket and TDS), and the areas more heavily contaminated. Moreover, epidemiological population survey must take into account not only the morbidity data but also more subtle effects such as parameters linked to reproduction (histological and functional aspects) and neurologic functions, especially in young children (brain development, behaviour, etc.).

The following specific recommendations were proposed by the experts:

- There is a lack of toxicological and ecotoxicological data for many PTSs in the region. This holds not only for new classes of PTSs (e.g. alkylphenols, PBDEs, phthalates, PAHs, etc.) but also for those which have been under focus for many years. Special attention should be paid to chronic toxicity studies and to the incorporation of biomarkers/bioassays in environmental quality indices.
- There is need for a uniform approach and framework for evaluation and monitoring of receiving waters in the region. Water Quality Indices should be improved (various types of indices have been developed which need to be evaluated and integrated). Multidisciplinary approaches should be applied, especially for estuaries and deltas.
- Specific research to quantify the role of PTSs on the impacts observed on endangered species and ecosystems is considered urgent for setting the programmes for maintaining the biovidersity of the Region.
- Sediment exposure (reservoirs) and effects to aquatic biota are important and should be assessed by the particular hydrogeographical characteristics of the region. In this respect, mesocosm studies (validation of biological parameters and biomarkers) should be encouraged.
- Modelling is a complementary tool for risk assessment and is barely applied in the region. Monitoring and modelling will require much attention particularly for improving the estimates of the fate and effects of emissions and pools of existing PTSs. A task of particular importance will be the improvement of communication between existing chemical and toxicological information for PTSs and ecosystem and trophic web models.

The experience in recent decades in the European Union and the UN/ECE has demonstrated the advantages of an integrated science based approach, linking population, activities, emissions, transport and effects in a coherent international co-operative risk assessment framework. Such an approach is cost effective in making better use of available scientific and technical resources and in helping policy makers to design effective environmental policy.

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4 ASSESSMENT OF MAJOR PATHWAYS OF PTS TRANSPORT

The objective of this chapter is to provide a basic understanding of the physical processes that contribute to the transport and determine the global distribution of PTSs in the Mediterranean region. As it has already been reported in the previo

us section, data on levels of PTSs in the different compartments, although abundant, are rather fragmentary, both spatially and temporally, to enable the establishment of relationships between the measured environmental levels with the sources, and the identification of major regional transport pathways. However, from the available information and using multimedia models, the distribution of pollutants between the main environmental compartments can be estimated.

A representative picture for soil, sea water and forest litter for the Northern Mediterranean countries has been obtained by the EMEP/MSC-E Centre and shown in Figure 4.1 (Dutchak et al., 2002). In the diagram it can be seen that different pollutants tend to be accumulated in proper media. Thus, PCBs, B[*a*]P and PCDD/Fs are mainly accumulated in the terrestrial compartment (soil and forest litter) whereas the main reservoir for γ-HCH and HCB is the marine environment.

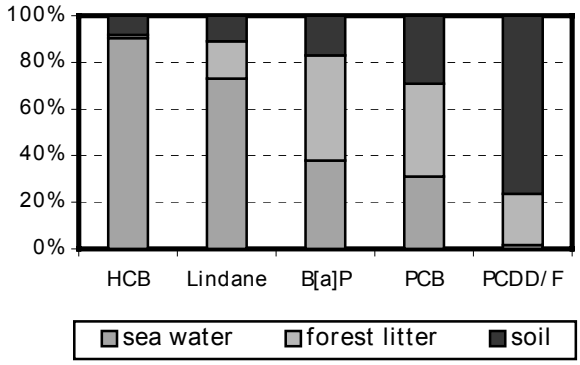

Figure 4.1. Distribution of certain PTS between different environment media within the Northern region by the end of 1998

The atmospheric and aquatic compartments, both marine and continental, may play a major role in the global distribution of PTSs in the region. The knowledge of the water circulation in the Mediterranean Sea and of the regional meteorology is well established (see sections 1.2.1 and 1.2.4) but only recently a number of studies have intended to document processes that connect the general circulations at the Basin level to pollution episodes. These will be summarised in the following sections, as well as the use of biological indicators for assessing the long range transport of PTSs.

4.1 ATMOSPHERIC CIRCULATION AND DEPOSITION OF PTS

4.1.1 Regionally specific features and modelling approaches

The physiographic characteristics of the Mediterranean Region and the prevailing climatic conditions have as a result, the development of a complicated atmospheric flow pattern. Its main characteristics are the strong northern component, almost during all seasons. This is due to differential heating between the land of North Africa (almost bare soil), the Mediterranean waters (daily cycle of SST) and the land of South Europe (with mixed-type vegetation cover). This northerly flow is pronounced during the warm period of the year. On the other hand, a second path of transport has been identified from Western towards the Eastern Mediterranean with a stronger component during the cold period of the year.

During summer, atmospheric circulation patterns are dominated by two large, semi-permanent, weather systems located at each end of the basin. At the Western edge is the Azores Anticyclone, and over the Eastern borders is the low pressure system which extends from the Middle East to the whole of South-western Asia, i.e., the Monsoon system. "Classic" frontal systems approaching from the Atlantic travel mainly North of the Alps and, approximately mid-way between the two major weather systems, the "average flow" is diverted southwards over

the Great Hungarian Plain and further South, into North Africa, via the Adriatic and Ionian Seas and/or the Black Sea, Aegean and the Levantine Basin.

Subordinate to these larger weather structures, other meso-scale systems develop during the day with important compensatory subsidences, i.e., the Iberian, Italian and Anatolian Thermal Low systems, which can strongly modify the regional flows during the day. In fact, depending on the mountain-coast geometry, their slopes propitiate the development of strong seabreezes, up-slope winds or combinations of these. Under these conditions the slopes act as orographic chimneys that link the surface winds directly with their return flows aloft to create vertical re-circulations. Depending on the surface properties (semi-arid), the same conditions also favour the formation of extensive and deep convective cells and/or Thermal Lows over the major land masses. Thus, the development of "mountain gap winds", either as a result of "subsidence aided" drainage flows during the night, large scale compensatory subsidences during the day and/or large scale channelling, is also a feature of the entire region (Gangoiti et al., 2001).

Figure 4.2 shows a summary of the specific meteorological processes for the whole Mediterranean Basin in summer and their links from the local to the sub-continental scales (Millán et al. 1997).

The ozone paths include: (#1) transport along the coast of Portugal under strong subsidence during the day, (#2) inflow of air into the Gulf of Lions followed by re-circulation along the Spanish East Coast and outflow through Gibraltar, and (#3) recirculation of air masses along the Italian coast, and transition from the combined sea-breezes and up-slope winds to storms along the Apennines in the late afternoon. The effects of the Atlas Mountains may include: upper tropospheric injections over the Northern Atlas of air masses aged along path (#2), as well as those following path (#4), i.e. transport towards the Canary Islands with deep convective-orographic recirculations along the Southern Atlas, or combinations of these.

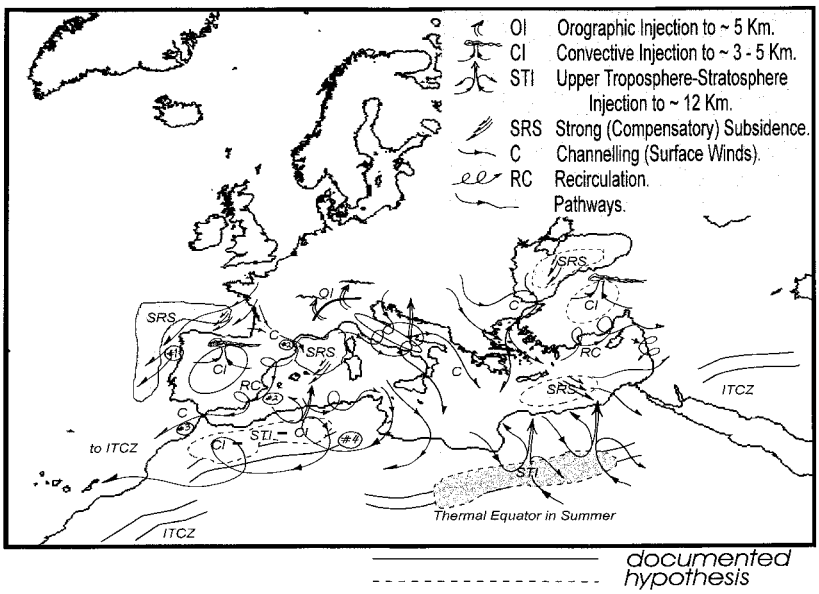

Fig 4.2. Conceptual model of the atmospheric circulations in the Mediterranean Basin in summer. The graphs show mechanisms which have a diurnal cycle and are well developed by mid-afternoon. The recirculations represent processes with spatial continuity along the coastal areas (Millán et al., 1997).

A particularly well identified and significant pattern of atmospheric circulation in the Eastern basin is the consistent flow directed from South and Eastern Europe towards the North African Coast and the Middle East which results in the transport of polluted air masses from Europe towards North Africa and the Middle East, as shown in Fig. 4.3 (Kallos et al., 1998).

The main path of such transport of air pollutants has been identified to be from the Eastern part of Europe towards the Black Sea, initially, and then farther across the Aegean Sea to the Middle East and North Africa. A secondary path is from the Central and Western part of the Mediterranean towards the East. Because of the absence of significant wet removal processes and the insolation, the oxidising processes are considered as very important. It has also been found that the time scales for such transport processes are approximately 2-4 days, which are shorter than the life cycle of ozone formed during the photochemical processes of urban plumes. Urban plumes from cities near the coast could be injected into the free troposphere with the aid of the upslope flows or within the stable marine boundary layer. In both cases, the urban plumes can travel over large

distances (even hundreds of kilometres) keeping most of their characteristics resulting in a massive upward transport of "aged" pollutants. Such kind of transport, with this time and space scales are considered as very important for several places in the Mediterranean Region. In addition to the above mentioned processes, Saharan dust particles play an important role in the atmospheric and aquatic systems, although its influence on the transport and deposition of PTSs has not been assessed.

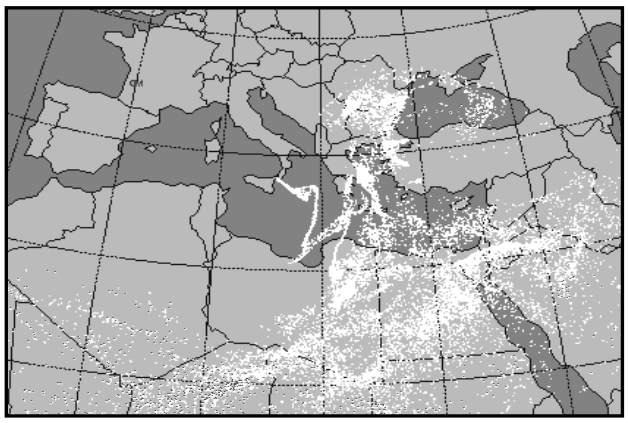

Fig. 4.3. Dispersion pattern over the E. Mediterranean and North Africa. White dots represent particles located within the lowest 5 km of the troposphere (Kallos et al., 1998).

The following conclusions can be drawn from the above observations with potential implications in the atmospheric fate of PTSs:

- Some locations of the Mediterranean Region act as "temporal reservoirs" where air pollutants are "concentrated", "aged enough" before they are re-advected again (e.g. Black Sea, Western Mediterranean).
- In general, the time scales of transport of air masses from Europe towards the Middle East is approximately 2-3 days.
- The transport from the Western Mediterranean towards SE Europe is in the range of 1-2 days, and towards the Middle East and NE Africa slightly longer (3-4 days).
- The recirculatory nature of the air masses in the Western Mediterranean Basin requires approximately 5 days for the renewal of 50% of the air mass below ~ 3000m, and 7-10 days for the renewal of 80%.
- The air quality in urban areas of SE Europe, N Africa and Middle East is affected significantly by the long-range transport patterns described because the time scales are still within the life span of most of air pollutants.
- Venting of urban or industrial plumes located near the coastal zone occurs through two different paths:

  - Towards the free troposphere with the aid of the upslope flows during the day-hours.
  - Towards the marine boundary layer where they are trapped and travel long distances until they reach land.

In order to assess the distribution and transport pathways of PTSs at a regional level, the Meteorological Synthesising Centre-East has developed a multi-compartment model for the EMEP region, describing processes in and exchange between basic environmental compartments (atmosphere, soil, seawater and vegetation). For the calculation of the long-range atmospheric transport of PTSs, a three-dimensional Eulerian transport model ASIMD (**AS**ymmetric **I**mproved **M**o**D**el) is used. The spatial resolution of the model is 150x150 km^2 , and at present there exists a grid modification for B[*a*]P with a resolution of 50x50 km^2.

The model outputs are: distributions of PTSs between environmental media and mass balance calculations; spatial distribution of concentrations and deposition; long-term trends; and transboundary transport assessment. Model parameterisations have been elaborated for PAHs (B[*a*]P), HCHs (γ-HCH), PCBs, HCB, and PCDD/Fs (www.msceast.org), although it should be taken into account that the model has been calibrated on only few sites where PTSs are determined and these are located in Northern Europe.

On the other hand, for an easier characterisation of the atmospheric deposition in the Mediterranean Sea, the MEDPOL Program has divided the basin into 11 sub-basins, as shown in Figure 4.4 and in data reported below.

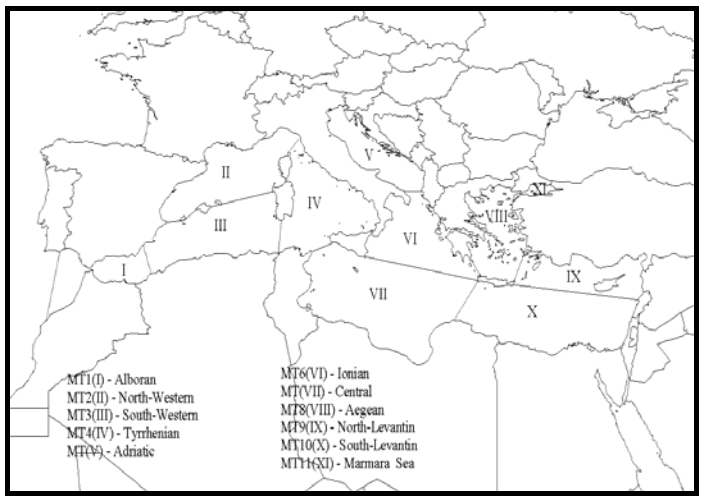

Figure 4.4. MEDPOL Mediterranean Sea sub-basins

4.1.2 Organochlorine pesticides and other PTSs

Atmospheric circulation and deposition estimates of PTSs in the Mediterranean Region are scarce. First calculations were reported by GESAMP (1989) for the Mediterranean Sea, based on very few data, but concluding that 80-95% of total inputs of PTSs (e.g. HCB, HCHs, DDT, chlordane and PCBs) were atmospheric. More recently, calculations have been performed for certain semi-volatile PTSs by the EMEP/MSC-E, using the ASIMD transport model with the limitations already pointed out. The results are shown below.

4.1.2.1 HCB

Based on published data, average emission and deposition fluxes have been generated (Dutchak et al., 2002) (Table 4.1). As it can be seen, only France, Italy and Spain account for 82% of the total emission of HCB in the region which is of 3970 kg/year. The countries of the Balkan area exhibit a negative balance in the sense that deposition is relatively enhanced with respect to the corresponding emission.

Table 4.1. Mean HCB emission and deposition (dry+wet) estimates for some countries of the Mediterranean region (1998)

Country	Emission flux g/km^2/y	Total emissions kg/y	Deposition flux g/km^2/y	Total deposition kg/y
Albania	1.88	60	0.15	4.46
Bosnia&Herzegovina	0.99	50	0.16	8.03
Croatia	1.28	80	0.18	10.88
France	2.34	1290	0.21	113.91
Greece	1.31	180	0.07	9.63
Italy	2.61	800	0.16	48.33
FYR Macedonia	1.19	30	0.15	3.77
Portugal	1.61	150	0.06	5.42
Slovenia	0.84	20	0.31	5.68
Spain	2.34	1170	0.11	52.90
Turkey	0.00	--	0.05	37.65
FR Yugoslavia	1.34	140	0.20	20.88

Field studies carried out in the region of Paris (France) (Granier et al., 1992) have shown that HCB deposition has been slightly increasing from 1993 to 2000 to around 2.9 g/km^2/y. This figure can be considered as representative of an urban-industrial area.

4.1.2.2 PCBs

Simulation of atmospheric deposition of PCBs was performed for the period of 29 years using meteorological data from 1970-98, with a preliminary run for the period 1940-70 in order to get initial concentrations in the compartments (Shatalov et al., 2000). The parameterisation of physical-chemical properties of PCBs was fulfilled on the basis of the PCB-153 congener, which certainly leads to some uncertainties. Therefore, the results are only indicative. The PCBs deposition map is presented in Figure 4.5 with the maximum rates (20 g/km^2/yr) in the centre of Europe, where the maximum emission occurs according to emission estimates. These amount 113 tons per year for the 41 countries considered.

From this hot area, an apparent north-south gradient is observed with estimated values in the range of 0.1 – 1 g/km^2/yr over the Mediterranean Sea (UNEP/MAP/WMO, 2001). In the French continental environment, median concentration values of total atmospheric fallout varied only 2 times in relation with urban locations revealing the significance of the atmospheric transport. Maximal depositions were observed in Paris (28 g/km^2/yr) but equivalent to those found in other rainy areas like the Vosges mountains, in the German border (Ollivon et al., 2001). Apparently, since the last 15 years, in spite of varying instant contamination, the average concentration has remained stable (Chevreuil et al., 2001).

During the period 1970-1996 considered in the EMEP study, the total mass in the environment decreased from 3424 tonnes to 2895 tonnes, hence showing a role of re-emission processes. After 1990 re-emission (modelled) is higher than deposition and adds about 66% to anthropogenic direct emissions (estimated). The mass exported outside the EMEP grid represents about 75% of the total anthropogenic PCBs emissions during the 28 years, the degradated mass 28%, and the mass remaining in the system 14%. This remaining mass in 1997 is mainly in soil and vegetation (42%+43%) and partly in the sea (15%, not only the Mediterranean), only 0.06% remains in air. Soil appears to be the most inertial reservoir.

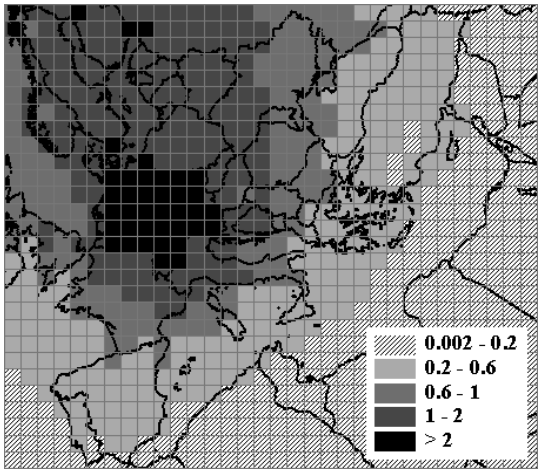

Figure 4.5. Distribution of PCBs deposition in Europe in 1999 (in g/km^2/yr).

The estimated average deposition fluxes into each Mediterranean sub-basin is shown in Table 4.2 (UNEP/MAP/WMO, 2001). The maximum deposition value is observed in region V, and the minimum in region I. The dry and wet fluxes exhibit significant seasonal variations, mainly following the air temperature, because the distribution of PCBs between the aerosol and gas phases are temperature dependant. Thus, net gaseous flux over sea probably becomes negative in summer because at high temperatures PCBs tend to evaporate from sea surface more readily. In any case, over the sea the wet deposition is the main flux and it is also correlated with the precipitation rate (both for gaseous and particulate phases).

Based on these estimates, the total deposition on the sub-basins has been calculated (Figure 4.6), representing about 1100 kg/year for the whole basin. However, from field data, Tolosa et al. (1997) have calculated that the sedimentation rate in the deep Western basin ranges from 0.5 – 3 g/km^2/y that contributes to the removal of around 5 tonnes/year from the water column. Moreover, Mandalakis et al. (2002) have determined the deposition fluxes of PCBs on the Eastern Mediterranean from a station located in the Crete island. The wet-only deposition flux was 1.40±0.31 g/km^2/y and the corresponding dry-only deposition flux was 0.17±0.10 g/km^2/y, thus representing a net input of around 700 kg of PCBs/year. The main reason for these major discrepancies are basically inaccurate emission data and shortage of measurements in the region, as well as the restricted number of physico-chemical properties of PCB congeners used in the model.

Table 4.2. PCBs deposition fluxes (g/km^2/yr) on the Mediterranean Sea and its sub-basins

Sub-basins	Net dry deposition	Wet deposition	Total deposition
mt1	0.05	0.06	0.10
mt2	0.21	0.44	0.64
mt3	0.10	0.20	0.30
mt4	0.16	0.37	0.53
mt5	0.22	0.67	0.89
mt6	0.11	0.24	0.33
mt7	0.08	0.12	0.19
mt8	0.09	0.22	0.31
mt9	0.07	0.16	0.23
mt10	0.05	0.07	0.13
mt11	0.12	0.35	0.46
Average	**0.10**	**0.22**	**0.33**

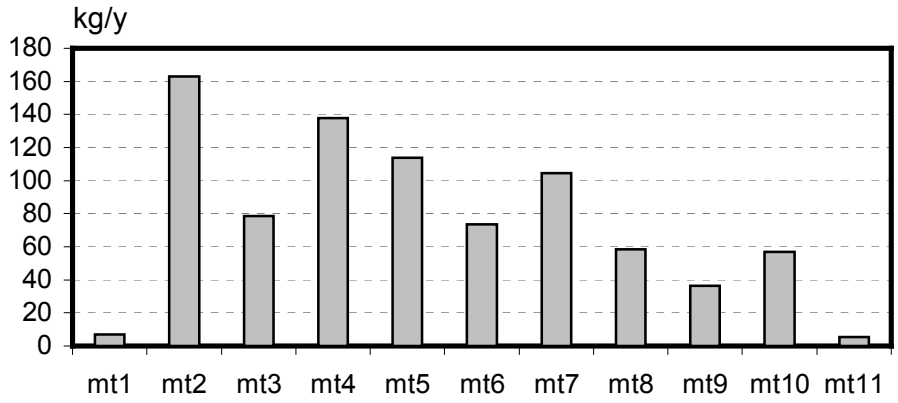

Figure 4.6. Mean PCBs deposition (1987-1996) into the Mediterranean sub-basins (mt), in kg/yr.

4.1.2.5. PCDD/PCDFs

The 2002 annual report of MSC-East (Shatalov et al., 2002) presents the calculation of concentrations of PCDD/Fs in the EMEP region as well as their deposition. In fact the results are given for one indicator congener, namely 2,3,4,7,8-PeCDF, after demonstration that it is a good indicator for the overall behaviour of total PCDD/Fs weighted by their toxicity (I-TEQ). However, the following results are only indicative because of uncertainties in the emission data and lack of measurements in the region. Calculations were led for 30 years (1970-1999) and showed typical levels of 1 to 10 fg ITEQ/m^3 for air concentrations over land, with higher levels in Italy (13.7 fg on average), and typical levels of 2 to 20 pg ITEQ pg/L in the Mediterranean Sea, with higher levels near the coasts of France and Italy.

About 40% of the total amount of PCDD/Fs emitted are transported outside the EMEP region. At the end of the model run (1999) 77 % of the remaining dioxins/furans are in the soil compartment - where their half-life is estimated to be 60 years - whereas less than 1% is in the sea and 1% remains in the air. These figures show the major role of air pollution transfer at a regional and possibly global scales, with a major role of soil as a reservoir. The significant reduction of direct anthropogenic emissions since 1982 is the cause of an overall re-emission from soil to air which is superior to deposition, but deposition at sea still exists. In the 1999 EMEP annual report the total deposition calculated for the Mediterranean Sea is 492 g ITEQ for year 1996.

4.1.2.3 Lindane

Following the same model used for PCBs, and assuming that lindane was present in the atmosphere only in the gas phase, calculations covering the period of ten years (1987-1996) were performed in order to reveal accumulation trends in various compartments (UNEP/MAP/WMO, 2001). In another study (Shatalov et al., 2001) where the time period is 28 years (1970-1997) and the vegetation, as well as sea currents, are added to the model the results are probably more reliable.

Regions of maximum deposition correspond to regions of maximum emissions. The lindane deposition map is presented in Figure 4.7 with the maximum rates (80 g/km^2/yr) in the centre of Europe, concurrently with the emission estimates which amount around 900 tonnes per year (see section 2.2).

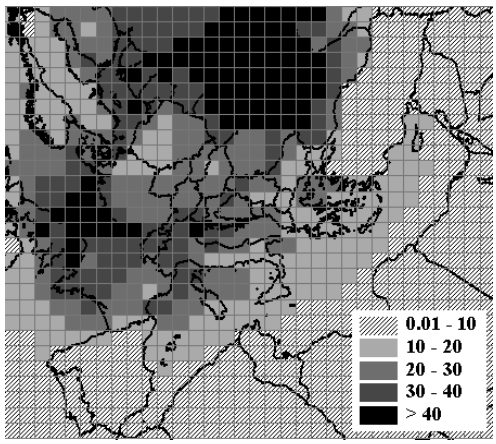

Figure 4.7. Distribution of lindane deposition in Europe in 1999 (in g/km^2/yr).

Concentrations decrease away from emission sources. Thus, the EMEP results show maximum concentrations of lindane in air in France (3-4 ng/m^3), with a decreasing trend towards the rural areas. Air concentrations of lindane decrease in the southern direction to about 0.5 ng/m^3 in the Mediterranean. On the other hand, deposition appeared to decrease also from 77 to 12 g/km^2/yr throughout the 90's (Chevreuil *et al*., 2001).

The major part of lindane falls at the continental part of the EMEP grid (20% was degraded in the soil and 2% retained) but a significant part was deposited onto the marine area of the grid (9% was degraded inside the sea and 8% remained in the sea after 10 years). Therefore, the sea becomes the most important reservoir for lindane at the continental level, since the half-life in this compartment is higher (five years). A major part of the emission is transported outside the EMEP grid (64% for 28 years).

Table 4.3 displays the lindane deposition fluxes map for the Mediterranean between 1987-1996. Maximum densities of dry and wet deposition are characteristic of sub-basin V (Adriatic), because of its location near to emission sources. The average density of deposition onto Mediterranean Sea is 12 g/km^2/year for dry deposition, 4 g/km^2/year for wet deposition, and 16 g/km^2/year for total deposition. Figure 4.8 shows the total deposition on the Mediterranean sub-basins, which follows a similar pattern to that of the PCBs deposition.

During the calculation period an average of about 55 tonnes of lindane (about 4% of annual emission) were deposited on the Mediterranean Sea each year, the major part of that amount (40 tonnes) corresponding to net dry deposition.

Table 4.3. Lindane deposition fluxes (g/km^2/yr) for the Mediterranean Sea and its sub-basins

Sub-basins	Net dry deposition	Wet deposition	Total deposition
mt1	2.7	0.7	3.3
mt2	19.0	7.8	26.8
mt3	9.0	2.7	11.6
mt4	17.2	5.7	22.9
mt5	24.1	13.2	37.2
mt6	13.5	4.1	17.6
mt7	9.2	1.5	10.7
mt8	17.9	5.3	23.1
mt9	11.8	2.6	14.4
mt10	8.5	1.0	9.6
mt11	23.0	9.9	32.9
Average	**12.33**	**3.61**	**16. 4**

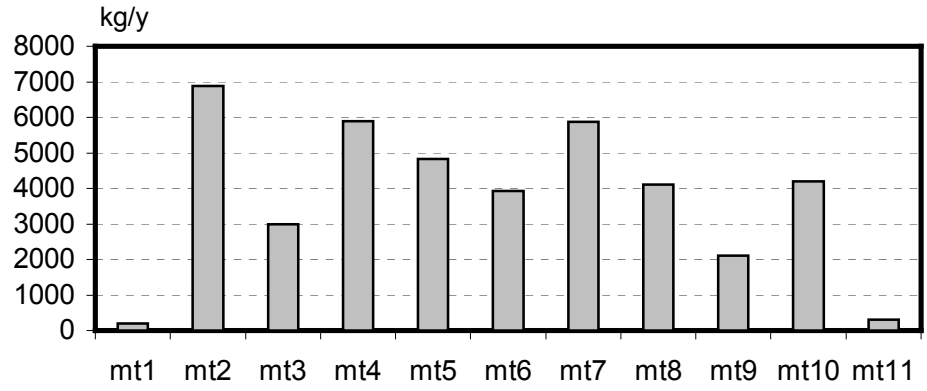

Figure 4.8 Lindane deposition into the Mediterranean (mt) sub-basins, in kg/yr

4.1.2.4 PAHs

An evaluation of transboundary transport of PAHs between countries of the region has been carried out for 1998 on the basis of the "source-receptor" approach. Calculations have been performed for B[*a*]P as the most representative component of this class of compounds. A summary of the preliminary results is shown in Table 4.4 (http://www.msceast.org/countries/index.html).

Table 4.4. B[*a*]P depositions from some European countries (main sources) to countries (receptors) of Mediterranean region (receptors) for 1998

Countries-receptors	**Depositions from European countries (main sources), kg**					
Albania	Albania 25.5	Bosnia&Herz. 16.74	Italy 29	FYR Macedonia 53.55	FR Yugoslavia 134	Other 96.51
Bosnia&Herz.	Bosnia&Herz. 981	Croatia 236	Hungary 125	Italy 85.9	FR Yugoslavia 261	Other 364.21
Croatia	Bosnia&Herz. 234	Croatia 753	Hungary 218	Italy 131.6	Slovenia 225	Other 599.42
Cyprus	Bulgaria 1.1	Greece 1.5	Italy 1.2	Romania 1.37	Ukraine 1.7	Other 5.43
France	France 6922	Germany 537	Italy 218	Spain 324.5	United Kingdom 297	Other 676
Greece	Bulgaria 232	Greece 343	Romania 90.9	FYR Macedonia 96.7	FR Yugoslavia 112	Other 301.2
Italy	Austria 153	France 383.5	Germany 152	Italy 2617	Poland 151.5	Other 818.6
Malta	France 0.1	Italy 0.2 kg	Poland 0.06	Spain 0.04	FR Yugoslavia 0.03	Other 0.27
Slovenia	Austria 110	Croatia 93.7	Hungary 36.2	Italy 63.9	Slovenia 383.5	Other 155.2
Spain	France 306	Germany 26.5	Portugal 148	Spain 2102	United Kingdom, 47	Other 73.4
FYR Macedonia	Bulgaria 99.8	Greece 19.6	Romania 26	FYR Macedonia 306.4	FR Yugoslavia 156	Other 84.14
Turkey	Armenia 388	Georgia 254.6	Romania 224	Russian Federation 437	Ukraine 416	Other 848.3
FR Yugoslavia	Bosnia&Herz. 221	Hungary 204.7	Romania 246	FYR Macedonia 128	FR Yugoslavia 2659	Other 754.2
Africa	France 142	Greece 81.2	Italy 184.3	Spain 131	FR Yugoslavia 63.9	Other 469.7

The emissions of some European countries (sources) make a substantial contribution to the depositions of others (receptors). Greece and Turkey are particularly affected by emissions from the former Eastern European countries. The Table also includes a first estimate of deposition over the North African countries.

This assessment of transboundary transport has also enabled the consideration of the contributions of depositions of B[*a*]P to the Mediterranean Sea (Fig. 4.9). It is shown that most of them take place from Italy (1499 kg, 24%), France (885 kg, 14%) and Spain (523 kg, 8%).

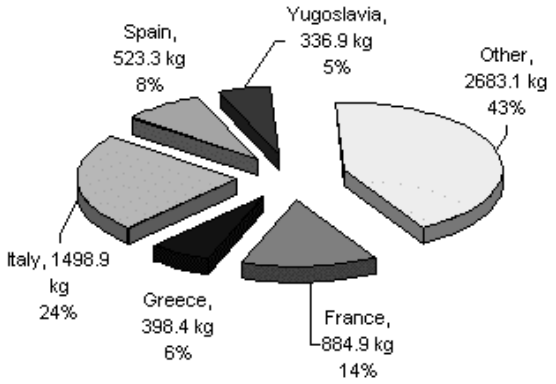

Figure 4.9. Deposition of B[*a*]P to the Mediterranean Sea

Estimated B[*a*]P depositions to the individual sub-basins have also been calculated and shown in Figure 4.10. Higher depositions are obtained for Tyrrhenian (mt4, 926 kg), Adriatic (mt5, 942 kg), North-Western (mt2, 829 kg) and Central (mt7, 851 kg) sub-basins.

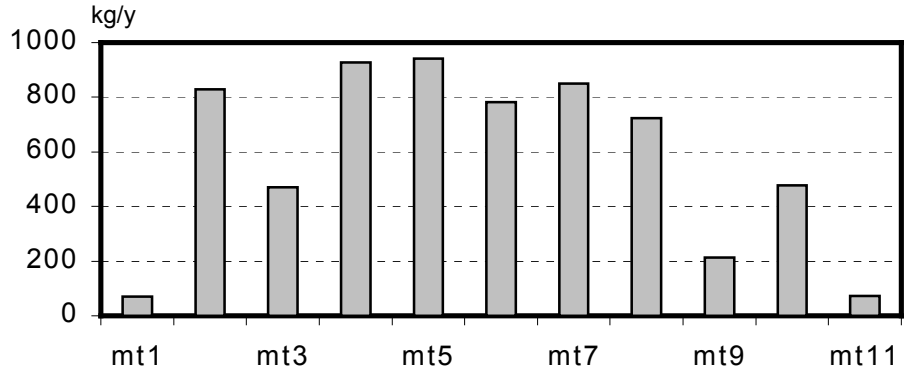

Figure 4.9. B[a]P depositions to the Mediterranean sub-basins for 1999 (in kg/y)

Despite the uncertainties of these calculations it appears that PTSs sources located in the countries of the region contribute significantly to the atmospheric deposition in the Mediterranean Sea, and that the maximum deposition densities correspond to the North-Western basin, the Adriatic and the Marmara Sea, although the total amount in the latter is small due to the reduced dimensions.

4.2 RIVER AND WASTEWATER DISCHARGES OF PTSs

4.2.1 Regionally specific features

About 100 rivers contributing significantly to the transport of pollutants in the Mediterranean Region have been identified. The nature and impact of the waters discharged into the Atlantic and the Mediterranean differ appreciably, depending on both the hydrologic regime and the dominant uses of their respective catchment areas (Meybeck and Ragu, 1997).

The Mediterranean hydrology is very heterogeneous, ranging from alpine regime with early summer maximum to the semiarid regime with a gradual increase of summer draught and development of episodic floods. The Mediterranean rivers are characterised by very high variations of day to day and year to year discharges (Figures 4.10). Moreover, these have formed deltas in their mouths (e.g. Ebro, Rhone, Po and Nile) whereas the Atlantic ones (e.g. Seine, Loire, Gironde and Tagus) constitute estuaries of macrotidal type, with the subsequent differences in transport and deposition of hydrophobic pollutants in the coastal waters. Finally,

some streams are basically affected by urban/industrial discharges (e.g. Seine) whereas others are by industrial/agriculture (e.g. Rhône and Po) or urban/agriculture (e.g. Nile) drainages.

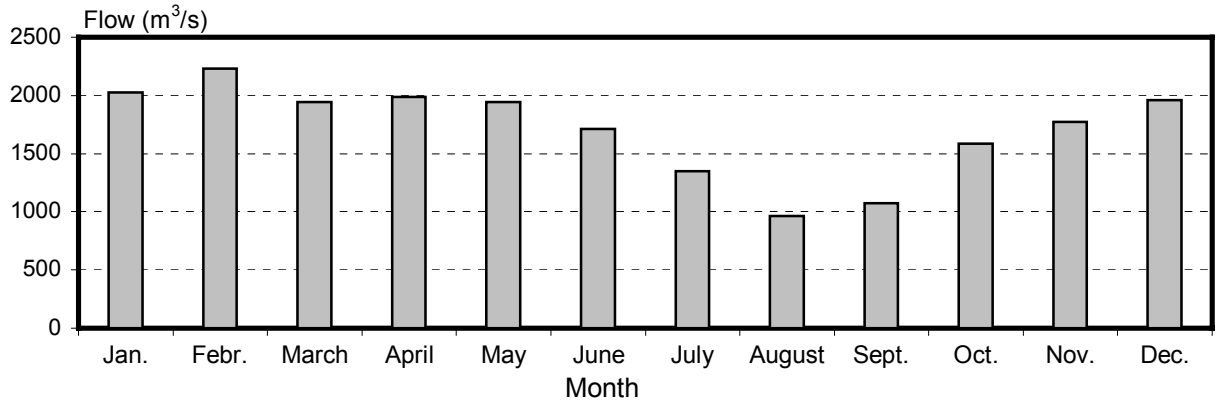

Figure 4.10. Monthly mean flow (1970-2000) of the Rhône River (France) at Beaucaire.

The impact on coastal waters is geographically limited to the continental shelf waters and sediments. The lack of tides and slow circulation in the Mediterranean basin reduce the advective transport of pollutants from river inputs and urban run-off to the open sea. In the Atlantic rivers, the mixing waters zones within the estuaries are the areas most heavily affected. The marine impact, in both cases, depends largely on deposits of suspended matter and flow conditions which are very variable. General characteristics of representative rivers of the region are given in Table 4.5. The quoted sediment yields usually refer to the conditions before the existence of major dams that were constructed in many of the river basins

Table 4.5. Water and suspended sediment discharges of major rivers in the region

River	Area 10^3 km^2	Qact km^3/year	Sediment t/km^2/y	Country
Po	70.00	48.90	217	Italy
Rhone	95.60	48.07	324	France
Drini	14.17	11.39	1173	Albania
Neretva	10.02	11.01	--	Croatia
Buna	5.19	10.09	486	Albania/Serbia
Ebro	85.55	9.24	214	Spain
Tevere	16.55	7.38	453	Italy
Adige	11.95	7.29	133	Italy
Seyhan	20.00	7.20	236	Turkey
Evros	55.0	6.80	--	Greece/Turkey
Axios	24.7	4.90	1220	Greece
Isser	31.6	6.12	193	Algeria
Moulouya	51.0	1.58	250	Morocco
Nile	2870	6.00	42	Egypt
Seine	78.7	13.72	--	France
Loire	128.0	29.50	--	France
Gironde	80.0	28.38	--	France
Tagus	80.65	12.00	--	Spain/Portugal
Douro	98.0	17.15	--	Spain/Portugal
Guadalquivir	63.97	5.17	--	Spain

In this respect, it is necessary to mention that, although not well established, the water and sediment inputs to the sea have decreased in the order of 30-40% over the last 50 years in the Mediterranean region due to

damming and irrigation, thereby also reducing the impact of these rivers on coastal waters. The south Levantine and south-west Aegean Seas and the central and northern Levantine basins are probably those most affected by this reduction.

Besides the global transport of pollutants through the open sea waters, which in the case of the Mediterranean follows the anticyclonic currents, parallel to the coast, the transboundary transport concerns also continental waters. In the region, however, this potential problem is limited to few cases because the drainage basins of most of the rivers are within each country. Those are the rivers sourcing in Spain and crossing Portugal in the lower ends (Douro and Tagus). The Nile goes by Uganda and Sudan before entering Egypt. The Danube is also crossing the northern part of Serbia in its middle course. Portugal receives 48% of its water in transboundary rivers from Spain

Intensive and usually inadequate use of river waters for industrial and irrigation activities has resulted in serious deterioration in the quality of inland waters. The runoff processes are very important in the mobilisation and transport of PTSs even though these are difficult to quantify. The vulnerability of inland waterways to drought-related pollution, and the need for measures to protect against domestic and industrial wastewaters, have led most countries to give priority to reducing sources of river pollution, rather than those affecting coastal waters. Application of the European directive on wastewaters should soon see a reduction of at least 50% in levels of pollution caused by domestic discharge, compared with the levels of the 1970's.

4.2.2 Organochlorine pesticides and other PTSs

High pesticide concentrations have been found in some specific studies and are believed to occur in many small rivers which are affected by intensive agriculture. The type of pesticides may vary from one river to another and from one country to another. However, most rivers are not adequately monitored for PTSs in order to assess loads, even though they are very important.

During MEDPOL Phase I (1975–1980), it was attempted through the project MED X to estimate the quantity and nature of riverine inputs in the region. The project met with considerable difficulties. Country responses were geographically almost restricted to the northern Mediterranean. Sampling frequency, sample pre-treatment, analytical methods and reporting formats varied widely. Some pollutants were rarely analysed (metals, specific organics, organochlorines). Field measurements of domestic sewage and industrial wastewater were very limited. No field measurements on agricultural run-off were available. From 68 rivers registered, only 30 were adequately monitored but not for PTSs.

In view of the limitations and difficulties encountered, assessments of the pollution loads from land based source (LBS) categories have been carried out, largely, by indirect computations and extrapolations. They have been worked out taking into account demographic statistics, the GNP of the countries, industrial production and manpower, and agricultural data. The time allowed for this ambitious project was too short for any in-depth study of each and all pollution sources in the Mediterranean. For this reason and by the fact that the results were pooled for each of the eleven UNEP Mediterranean regions, the project did not fulfil the requirements of its first objective, to provide the basis for national management and control plans.

Due to the difficulties and the uncertainties involved in the complex computations and extrapolations carried out, the results could not be better than rough estimates reliable within an error margin of one order of magnitude. Some of these results were proved, at a later stage, to be even worse. Only a comparative assessment of the regional contributions to the pollution load could be made. The results showed that the heaviest loads are discharged into the north-western basin with one-third of the total pollution load. The Adriatic Sea receives about one-quarter of the total load. Moderate pollution loads are encountered in the Tyrrhenian and the Aegean Seas, as they receive each about 10% of the total load. The other Mediterranean Sea areas each account for no more than 5% of the total.

More recently, accurate estimates have been obtained for some French rivers using linear regression and average weighted flow models. A survey was carried out during 1994-95 at the lower course of the Rhone River, far from the any marine influence. An important conclusion was that the large supply of fresh water (>70%) and consequently of dissolved species, corresponds to the medium-low flow regimes, whereas the contribution of large flows (>5000 m^3/s) represents less than 10% of the total input. On the contrary, these regimes contribute with about 80% of the total input of suspended particles. All pollutants, and notably PTSs attached to the particles, are carried to the sea in such episodic events. A preliminary survey has also been recently conducted in the Seine River, only for dissolved PTSs.

The calculation included dieldrin, aldrin, endosulfan, heptachlor, HCB, α-HCH, γ-HCH, pp'-DDE and PCBs (Σ7 congeners) as reported in Table 4.6. The load of lindane was consistent with the use of this compound in the preceding years (1500 tonnes/year) but the DDE is reflecting the leaching of the existing environmental stock.

Table 4.6. PTSs inputs (in kg/year) of the Rhone and Seine Rivers into the sea

River		Dieldrin	Aldrin	DDTs	PCBs (Σ 7 cong)	HCB	α-HCH	γ-HCH
Rhone (1994-95)*	Dissolved	-	-	230	-	14	124	360
	Particulate	33	-	51	304	157	23	21
Seine (2000)	Dissolved	13	6.3	6.3	-	6.5	79	85

* *Qualité des Eaux du Rhône, Evolution 1969-1995*, July 1999, Agence de l'Eau Rhône-Méditerranée-Corse.

Similar calculations performed in the Ebro River in the 80's gave inputs one order of magnitude lower, consistent with the difference in water flows (dieldrin and aldrin, 1 kg/year; DDTs, 8 kg/year; chlordane, 2 kg/year; PCBs, 12-25 kg/year; HCB about 30 kg/year; and endosulfan, 1.5 kg/year) (Cid et al., 1990). An input of 157 kg/year of PCBs (Σ7 cong) has been reported in 1999 for the Guadalquivir (OSPAR, 2001). In a study carried out in 1993 in Turkey to assess the riverine pollutant loads to the Black Sea has provided figures in the order of 11 tonnes of aldrin, 31 tonnes of dieldrin, 180 tonnes of endrin and 500 tonnes of DDT per year, being the Sakarya river the most important source (Tuncer et al., 1998). Considering the other data, it is possible that these figures are largely overestimated. In fact, the determination of river inputs requires not only reliable analytical data but also an optimisation of the sampling strategy and statistical evaluation of data (modelling), due to the large variability of hydrologic regimes of the Mediterranean rivers.

As mentioned before, contaminated coastal sediments arise from freshwater discharges. However, beyond the zone of influence of these discharges, concentrations drop rapidly reflecting 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 basin.

An analysis of general trends in concentrations of some pollutants in French rivers over a decade reveals a marked stability in measured levels, with irregular tendencies to improvement and deterioration. Compared with the situation during the 1970's, progress in the reduction of sources of domestic and industrial pollution has certainly been observed (see section 3.1.6).

4.3 MEDITERRANEAN SEAWATER EXCHANGES

4.3.1 Regionally specific features

The Mediterranean Sea is a semi-enclosed basin having interactions with the adjacent Atlantic Ocean and Black Sea through the Gibraltar and Turkish straits, so that sea water exchanges may play a role in the transboundary transport of PTSs.

The **Eastern Atlantic** has a permanent exchange of waters with the Mediterranean Sea through the Strait of Gibraltar (see section 1.2.4). This exchange results from the evaporation of the Mediterranean waters, which become more dense than those of the North Atlantic, and generate an inflow of fresher and lighter Atlantic upper waters into the Mediterranean and an outflow of more saline and denser deep Mediterranean water to the Atlantic (Hopkins, 1999). Despite its initially very high density, the Mediterranean water outflow does not reach the bottom of the North Atlantic because it entrains a substantial volume of the overlying Atlantic waters while still in the Gulf of Cadiz. Thus, the resultant mixed Mediterranean waters become neutrally buoyant at depths between 900 and 1200 m and finally reach the open North-central Atlantic, in the form of water lenses (*eddies*).

On the other hand, the **Black Sea** is connected with the Mediterranean through the Sea of Marmara where there is a surface outflow of less saline waters from the Black Sea and an inflow of denser Mediterranean waters which results in the formation of a permanent halocline/pycnocline at depths of 100-150m in the Black Sea. The annual volume of the outflow (658 km^3/y) from the Black Sea is nearly twice of the salty water import

(337 km^3/y) via the Bosphorus undercurrent, but this counterflow system is balanced at the Dardanelles exit (1331 km^3/y upper flow; 1010 km^3/y underflow).

The Black Sea has a very large catchment area, receiving extraordinary amounts of nutrients, pollutants as well as fresh water and sediment inputs from the rivers, draining half of Europe and some parts of Asia. Moreover, during recent years, the number of tankers as well as the amount of hazardous materials transported across the Sea and through the Turkish Straits had increased (from 4248 in 1996 to 6093 in 2000), and this will continue as the amount of oil production from Caspian region increases.

Taking into account these particular hydrogeographical conditions, a major question has raised concerning the significance of these water exchanges in the transboundary transport of pollutants.

4.3.2 Assessment of PTSs budgets and inventories in the Mediterranean Sea

Although there is a significant lack of data, particularly for certain compartments such as the atmosphere, for establishing a global mass balance of PTSs in the Mediterranean basin, a first attempt is possible in certain areas and for certain compounds, like PCBs and PAHs. This is a first step in the identification of the major processes contributing to their long range transport and persistence in the region.

4.3.2.1 PCBs

From the concentrations reported in the literature and mainly summarised in chapter 3 it can be inferred that:

- coastal sediments account for 55% of the total PCBs accumulated in sediments even though the continental shelf contributes only to 15% of the total surface area of the Western basin (Tolosa et al. 1997).
- In seawater, PCBs show a surface enrichment depth-depletion vertical profile, which is consistent with entry into surface waters followed by a rapid downward transport in association with large sinking particles. Sediment trap measurements in open sea and coastal waters suggest that the removal flux of PCBs from the photic zone by sinking particles is much higher than the accumulation flux in the sediment, which implies recycling in deep waters and at the sediment-water interface.
- While the coastal zone seems to be a source of PCBs to the atmosphere, the open sea is a sink for atmospheric PCBs due to the low PCBs concentration in the dissolved phase. However, there are major uncertainties in the estimations of atmospheric inputs and outputs, mainly due to the very few available measurements of gas phase concentrations.

Taking into consideration the concentrations and fluxes measured as well as the volumes of the different compartments, the budgets and inventories shown in Tables 4.7 and 4.8 have been calculated for the Western Mediterranean (Tolosa et al., 1997). It is interesting to notice that the PCBs inventory in the water column is of the same order of magnitude as the inventory in surface sediment, but probably much smaller than the complete sediment inventory, which cannot presently be estimated.

Table 4.7. PCBs and PAHs budgets for the Western Mediterranean Sea.

		PCBs*		**PAHs****	
		In (kg/y)	Out (kg/y)	In (kg/y)	Out (kg/y)
Rivers		1000	-	3850	-
Atmosphere	Precipitation	4470	-	13350	-
	Dry deposition	7930	-	5050	-
Air-water exchange	Absorption	32000	-	-	-
	Evaporation	-	22000	-	-
Water exchange	Gibraltar	5100	960	34290	17535
	Sicily	1830	5360	10620	27650
Particle flux		14000	-	76600	-
Sediment accumulation	Shelf	-	2950	-	41000
	Basin	-	2390	-	47600
Total		52330	33660	95480	133785

* Σ 7 ICES congeners. **Σ phenanthrene, fluoranthene, pyrene, benzofluoranthenes and b(a)pyrene.

The residence time of PCBs in surface waters (0.6 years) is much shorter than that of deep sea waters (2.2 years) due mainly to the lack of removal processes in the deep waters. This implies that deep sea waters and sediments are both important sinks for PCBs, contributing to their persistence in the Mediterranean.

The enrichment of organic pollutants in surface sea waters controls the direction of exchange through the Gibraltar Strait. Apparently, even though concentrations are generally lower in the Atlantic than in the Mediterranean, they are enriched in surface Atlantic waters that enters the Mediterranean whereas deep waters with low PCB concentrations exit through Gibraltar Strait to the Atlantic Ocean, giving a net input to the Mediterranean (Dachs et al., 1997).

A recent study (Marti et al., 2001) has also confirmed the preservation of the Mediterranean water signature at the Atlantic mid-depths. An input of 1.7 t/y of commercial Aroclor PCB mixture has tentatively been calculated as the contribution of suspended particles in these Mediterranean waters to the North-eastern Atlantic. Taking into account that most PCBs are in the dissolved phase (see section 3.1.3.4), the total amount may achieve about 10 t/y.

Table 4.8. PCBs and PAHs inventories for the Western Mediterranean Sea.

		Inventories (kg)	**Residence time (years)**
PCBs	Surface water (0-200 m)	21850	-
	Deep water	23560	-
	Sediment	38650	-
PAHs	Surface water (0-200 m)	57700	0.6
	Deep water	109600	2.2
	Sediment	681000	1.35

In the Eastern Mediterranean the following and consistently lower estimates have been made (Mandalakis et al., 2002). From long range transport 6084 kg of PCBs enter the area each year. Through wet and dry deposition 1019 kg/y and 219 kg/y are removed, respectively, from the atmosphere, and through photochemical processes (OH radical reactions) 4140 kg/y are destroyed. Finally, a quantity of 705 kg/y is absorbed by the sea. The remaining quantity in the atmosphere is 125 kg in the gas and 4.3 kg in the particulate phase.

4.3.2.2 PAHs

Contrary to PCBs and other chlorinated PTSs, the PAHs composition in aerosols from the region has been well characterised (Sicre et al., 1987, Simo et al., 1991, Lipiatou and Albaiges, 1994). Relatively low concentrations of alkyl-PAHs suggests that combustion is the prevalent source in the Western Mediterranean, in contrast to the Eastern basin which show a predominance of uncombusted sources (Gogou et al., 1994).

The PAHs profiles found in the photic zone of the water column are analogous to those found in the gas phase implying that air-water exchange must play a major role. In contrast, the sediments are dominated by pyrolytic PAHs such as pyrene, and benzofluoranthenes. A detailed analyses of PAHs concentrations and accumulation rates in the north-western Mediterranean basin pointed out the importance of coastal sediments as a sink of PAHs with about half of the accumulation on the continental shelf (Tolosa et al. 1996, Lipiatou et al. 1997).

PAH budgets and inventories for the Western Mediterranean basin are summarised in Tables 4.7 and 4.8. There is an advective transport through the Gibraltar and Sicily Straits, which results in a net input and output of 16755 and 1730 kg/y, respectively (Dachs et al., 1997). This exchange is strongly influenced by the vertical distribution in the water column with net input or output being in the direction of the superficial waters. A recent study (Marti et al*.,* 2001) has also confirmed the preservation of the Mediterranean water signature at the Atlantic mid-depths. An input of 8 t/y of pyrolitic PAHs has tentatively been calculated as the contribution of suspended particles in these Mediterranean waters to the North-eastern Atlantic.

The inventory in the water column underscores the importance of deep sea water as a sink and reservoir of PAHs in this marine environment. Even though deep sea waters contain an important fraction of total PAHs in the basin, most of the inventory for PAHs is in the sediment, the top few cm accounting for 680 tonnes (Tolosa et al. 1996).

In summary, the major evidence are:

- Atmospheric long range transport and deposition into surface waters play a major role in the widespread distribution of PAHs in the western Mediterranean.
- Phase association explains the high persistence of soot-related PAHs. Sediments provide the dominant sink for combustion PAHs whereas other PAHs such as alkylated phenanthrene seem to be efficiently degraded.
- Biological processes, especially the sinking of organically rich particles, contribute to observed distributions of PAHs in the water column.
- An important fraction of the PAHs inventory is in deep sea waters, where slower degradation may increase PAH persistence in the environment.

In the Eastern Mediterranean, wet and dry deposition processes are responsible for the elimination of 254 tonnes/y and 79 tonnes/y of PAHs, respectively. Through air-sea exchange processes 1178 tonnes/y are absorbed from the atmosphere on the sea surface. The remaining quantities in the atmosphere are 32 tonnes in the gas phase and 1.3 tonnes in the particulate phase (Mandalakis et al., 2002).

As far as the Black Sea is concerned, the inflow of persistent pollutants to the Marmara upper layer and further to the Mediterranean is not known but recently a first estimate of oil inputs, amounting 463 tonnes/y of petrogenic PAHs has been made (Yilmaz, 2002). This quantity is almost one order of magnitude higher than the total annual input from land-based sources (mainly rivers) on the Turkish Mediterranean coast. Data also shows that during 1985-1995 there has been a significant increase in the PAHs concentrations in the Turkish Straits system.

4.4 BIOLOGICAL INDICATORS OF LONG RANGE TRANSPORT OF PTS

The assessment of long-range transport of PTSs using biological indicators deserves consideration. Accumulation of PTSs in biota is a well known process, and it will continue for a long time as a result of the environmental redistribution pathways after a substance has been banned. Indicator species can be identified and monitored for spatial and temporal trends assessment. In this respect, the following have been tentatively used in the region: terrestrial vegetation, fish inhabiting remote places like alpine lakes and the deep sea, and eggs from sea birds, which constitute large colonies widely distributed in the region.

4.4.1 Vegetation

The ambient temperature has recently been considered to play an important role in the global distribution of persistent organochlorinated hydrocarbons, such as DDTs, HCHs and HCB (Wania and Mackay, 1996). Although the latitude span of the region is not large enough to identify the known as the single or multi-hop transport pathways, the effect of temperature on altitude has been subject to several studies (Tremolada et al., 1994). Vegetation (pine needles and lichens) has been sampled in the Alps at different altitudes, between 200 m and 4000 m. The foliage concentration of organochlorinated hydrocarbons showed a dilution effect going from the plain to the highest altitudes and in function of the distance from emission zones.

4.4.2 Fish

The concentrations of HCB, PCBs and total DDTs have been measured in muscle of different fish species from remote lakes (Sanchez et al., 1993; Grimalt et al., 2001) and the Mediterranean deep sea basin (Porte et al. 2000), in order to display the long range transport of these pollutants within the region. The selected species were *Salmo trutta* for the alpine lakes (2000 m altitude), *Mullus barbatus, Serranus cabrilla* and *Diplodus annularis,* from the coastal area (30-50 m depth), *Micromesistius poutassou, Lepidorombus boscii* and *Phycis blennoides,* hemipelagic species (100-200 m depth.), and *Lepidion lepidion* and *Alepocephalus rostratus*, from the deep-sea basin (1500-2000 m depth) (see section 3.2.3).

Site pollution gradients were clearly observed in coastal fish, particularly in benthic species (e.g. *M. barbatus*), whereas no such gradients were detected in species living in more remote habitats (e.g. *L. biscii* and *L. lepidion*). Tissue residues decreased with the distance from the source, although some benthic deep-sea fish exhibited levels in the range of those observed in fish from shallower waters, directly affected by anthropogenic activities. The preferential accumulation of highly chlorinated PCB congeners in the deep-sea species and of

the lower chlorinated congeners in fish from alpine lakes is consistent with the transport pathways of these compounds.

4.4.3 Sea birds

Median of total DDT levels in the Mediterranean Sea, North Atlantic and Arctic Sea birds have shown that levels in the Mediterranean are significantly higher, indicating a regional/local pollutant source.

Median PCB levels are also significantly higher in the eggs of Mediterranean seabirds than elsewhere, only the Herring Gull (*Larus argentatus*) in the North Atlantic reached higher levels, similar to those found in Audouin's Gull (*Larus audouinii*) eggs from Capraia Island in the Tuscan archipelago (Italy) (Leonzio et al. 1989). However, when considering the DDT/PCB ratios, the Mediterranean shows an intermediate position between the heavily industrialised North Atlantic and the pristine Arctic, where DDTs are the predominant chlorinated pollutants. A spatial West-East concentration trend in the Mediterranean populations has been observed and already discussed in section 3.2.2.

4.5 SUMMARY AND DATA GAPS

Although the knowledge of the water circulation in the Mediterranean Sea and of the regional meteorology is well established, only recently a series of studies have started to document processes that connect the general circulations at the basin level to pollution episodes. These have evidenced the role that the atmospheric and aquatic compartments may play in the transport of PTSs within the region and outside.

The physiographic characteristics of the Mediterranean Region and the prevailing climatic conditions have as a result the development of a complicated atmospheric circulation pattern. Its main characteristics is a strong northern component, particularly pronounced during the warm period of the year, due to differential heating between the land of North Africa (almost bare soil), the Mediterranean waters and the land of South Europe (with mixed-type vegetation cover). On the other hand, a second path of transport has been identified from Western towards the Eastern Mediterranean with a stronger component during the cold period of the year.

Air masses from Europe reach the mid-tropospheric layers of the Equatorial Zone within a time period of 3-4 days. These processes are further complicated by the appearance of desert dust particles, the role of which on the environmental fate of PTSs is unknown. Moreover, there are indications of a massive upward transport of various aged pollutants in the coastal zones which may also involve the cycling of PTSs, although this aspect has not been investigated. Some locations of the Mediterranean Region act as "temporal reservoirs" where air pollutants are "stored", and "aged enough" before they are re-advected again (e.g. Black Sea, Western Mediterranean).

Modelling of long range transport of PTSs, namely PCBs, HCB, lindane and B[*a*]P, has been developed by the MSC-East Centre, from EMEP data, and deposition values have been estimated. However, the scarcity of data for the air, soil and seawater compartments, even for well-known PTSs, and the weak data coverage of the southern part of the region (all EMEP sites are located in Northern Europe, hence outside the Mediterranean Region), do not allow an accurate assessment of sources and receptors in the region and the transport pathways. In general, it is difficult to assess what source(s) are controlling environmental levels and whether they can be further controlled or affected by long range transport processes.

Despite these major uncertainties that may reach to one order of magnitude, it appears that PTSs sources located in countries outside of the region contribute significantly to the atmospheric deposition in the Mediterranean Sea, and that the maximum deposition densities correspond to the North-Western basin, the Adriatic and the Marmara Sea, although the total amount in the latter is small due to its reduced dimensions.

Riverine and urban wastewater discharges have been identified also as major land-based PTSs sources amenable to transboundary transport. In this respect, it is known that substantially contaminated sediments arise from freshwater discharges from the major rivers (e.g. Rhône, Po, Ebro, Seine, etc) and sewage outfalls from highly industrialised and populated cities (e.g. Marseille, Barcelona, Naples, etc.). These pollutant inputs are greatly influenced in the region by the basin's hydrology which is very heterogeneous, ranging from an alpine regime of early summer high flows to a typical Mediterranean regime of winter high flows and summer low flows with its episodic floods. Recent studies indicate that most part of riverine PTSs discharges are linked with flooding with suspended solids.

The characteristic variations of the water regimes of Mediterranean rivers and the lack of long temporal series render it difficult to evaluate the impact of these discharges, even though they have been recognised of

importance. A better knowledge of flows to the coastal areas should imply the definition of sampling strategies and the subsequent adoption of measurement protocols. A particular improvement of this knowledge is needed in order to unable a better evaluation of the impact of the some thirty medium-sized rivers on the open sea.

It should be pointed out however, that beyond the zone of influence of these land-based discharges, concentrations drop rapidly as a result of the enhanced sedimentation processes which take place at the freshwater-seawater interface. In spite of this, marine currents may transport the pollutants to long distances and signatures are found in remote sediments and biota. In fact, an important fraction of the PCBs and PAHs inventories is in deep sea waters, where slower degradation may increase persistence in the environment. The residence time of PCBs in deep sea waters is higher than in the surface (aprox. 2.2 years) due mainly to the lack of removal processes. This implies that deep sea waters and sediments are both important sinks for PCBs, contributing to their persistence in the Mediterranean. Apparently, the Western basin and the Northern Adriatic may be important sinks for PTSs.

The long-range transport of PTSs to sites where they may be accumulated constitutes, in summary, a potential environmental threat that deserves consideration. Terrestrial and marine indicator species can be identified and monitored for spatial and temporal trends assessment. In this respect, the following have been used tentatively in the region: terrestrial vegetation, fish inhabiting remote places like alpine lakes and the deep sea, and eggs from sea birds, which constitute large colonies widely distributed in the region.

The scarcity of emission data from the Mediterranean countries, the shortage of measurements of good quality, and the weaknesses of the models are the major limitations of the present knowledge of transboundary transport processes of PTSs in the region. To improve it, there is a need to establish an integrated assessment framework embedded in reporting obligations resulting from binding agreements among concerned parties sharing a common objective. Existing structures such as MEDPOL and SAP, PIC, LRTAP and the Stockholm Convention can provide a framework but joint reporting and common work on inventories, transport and impact models and monitoring should be envisaged in practical and detailed terms and be funded nationally and internationally

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5 PRELIMINARY ASSESSMENT OF THE REGIONAL CAPACITY AND NEEDS TO MANAGE PTS

The present chapter gives an overview of the regional capacity to analyse the presence of PTSs in the environment, the existence of alternatives and reduction measures, and the regulations and their enforcement. As these issues are pertinent at the national but also at the regional level, both aspects will be considered. The information indicates that Mediterranean countries have an acceptable level of awareness regarding the necessity to reduce adverse impacts of the bad management of PTSs. However, implementation and enforcement of the adequate instruments is lacking in many countries or need to be significantly improved. The national and regional monitoring programmes and institutional/legal frameworks will be particularly assessed.

5.1 EXISTING CAPACITY TO MONITOR PTS

The data presented in Chapter 3 illustrates the capacity installed in the Region for monitoring PTSs. Preliminary evidence is that data is primarily produced by academic (research) institutions as a result of scientific interest or in response to certain pollution incidents (e.g. spills) rather than for environmental management purposes. This leads to a rather sparse geographical and temporal data coverage. The different compartments and the chemicals considered are also barely homogeneous in terms of data available. The MEDPOL Programme for the marine environment, issued from the Barcelona Convention, could be the exception, although in many cases the monitoring surveys are discontinued and the quality of data is difficult to assess.

It is clear that the context in which data has been generated do not satisfy the requirements of a monitoring programme, although it contains some of the necessary technical elements. Even in the countries where surveillance networks are operational, these do not cover most of the PTSs considered in this assessment. An adequate implementation relies on instruments that should be developed at the national level and can be promoted or co-ordinated regionally. The current situation is summarised below.

5.1.1 The National surveillance networks

5.1.1.1 Algeria

Under the auspices of the Ministries for Higher Education and Scientific Research and for Environment, analysis of pesticides, PAHs, PCBs, dioxins and furans in water, air, soil and coastal sediment samples have been implemented in the country at research level (Faculty of Chemistry at Houari Boumediene University, National Institute for Marine Sciences (ISMAL), etc.). The National Institute of Plants Protection (INPV, Institut National de la Protection des Végétaux) controls and approves the use of pesticides and provides technical support and expertise in bio-ecological studies. However, PTSs are not routinely monitored in the country.

5.1.1.2 Croatia

PTSs monitoring is not conducted at state level. Organochlorine pesticides (e.g. HCB, HCHs, DDTs, drins and endosulfan) and PCDD/Fs are determined in a limited number of samples for research purposes. These include human milk, blood and urine, as well as in air, water, food and vegetation. These activities are mainly conducted by the Institute for Medical Research and Institute Ruder Boskovic, while analysis for control purposes are conducted by the National and Regional Institutes for Public Health.

5.1.1.3 Cyprus

A comprehensive monitoring program addressing specifically the PTSs in air does not exist. However, emission limits for dioxins are specified on the permits issued by the competent authority for certain industrial installations, and therefore these establishments are obliged to provide monitoring data for these compounds.

The main co-ordinated monitoring program for water supply systems (surface and ground water) was designed in 1988 and jointly undertaken by the State General Laboratory (SGL), the Water Development Department (WDD) and the Department of Medical & Public Health Services (DMPHS). Since 2001, it is based on an integrated investigation approach focusing into developing capacities for Early Warning and Response System for both accidental and emerging pollution.

The monitoring network for the quality of the marine environment, including certain PTSs (PCBs, DDT and other chlorinated hydrocarbons) in marine organisms, is carried out by the Department of Fisheries and Marine Research at the Ministry of Agriculture, Natural Resources and Environment as part of the MEDPOL Program.

Recently, the National Food Contamination Monitoring System has been designed, which includes organochlorine pesticides, PCBs and PAHs in milk, potatoes, lettuce, celery, parsley and wheat.

5.1.1.4 Egypt

An Environmental Information Monitoring Program (EIMP) (1998-2002) is implemented by the Egyptian Environment Agency (EEAA) with support from the Danish international development assistance. The program aims at establishing national environmental monitoring programs for ambient air and coastal waters. The program has a site posted on the Internet, however, no data has yet been shown. Other activities addressing hazardous wastes and including some PTSs are planned (see section 5.2).

5.1.1.5 France

Air monitoring is performed by 39 local associations, under the co-ordination of the Ministry of Environment and the Laboratoire Central de la Qualité de l'Air but measurements of "new" PTSs are still scarce. In two cities (Lille and Paris) the measurement of PAHs began more than 15 years ago, and a pilot study in 6 more cities began in 2001. The measurement of pesticides was also undertaken recently in some networks. Besides, measurements of dioxins at the vicinity of local sources are carried out, but rarely as a regular monitoring.

The IFEN (French Institute for Environment) and the Ministry of Environment have implemented in 1997 the monitoring network of pesticides in water, in close collaboration with the Ministry of Health and the six National Water Agencies. The number of points for surface and ground waters are 400 and 1140, respectively, and roughly double for drinking waters. Among the 275 substances measured there are: aldrin, endrin, dieldrin, heptachlor, chlordane, α- and γ-HCH, HCB, endosulfan, DDTs, PCP and atrazine. Besides local studies performed by different institutions, regular monitoring of PCBs and PAHs is also carried out at national level in agricultural soils amended by sewage sludges.

The French monitoring network for the quality of the marine environment RNO (Réseau National d'Observation) is a monitoring program carried out by IFREMER (http://www.ifremer.fr) on behalf the French Ministry of Environment. The program started in 1974, and included seawater samples until 1978, when monitoring was extended to biota and sediments. The network encompasses 80 shellfish sampling sites along the Atlantic and Mediterranean French coasts, which are visited fourth a year. The stations are also sampled every 10 years for sediments. Contaminants measured are DDT, DDD, DDE, lindane (γ-HCH), α-HCH, PCBs (Σ7 congeners) and PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene.

The monitoring of biological effects is limited to research studies for the moment: EROD (Ethoxyresorufine-o-deethylase) in fish in the bay of Seine and different biomarkers in mussels on the Mediterranean coast.

5.1.1.6 Italy

The first Italian Monitoring Programme for marine and coastal environment was made in place from the 1996 – 2000 and the results can be found in the website of the Ministry for the Environment and Territory (www.minambiente.it). Italy is also under the provision of MEDPOL monitoring system.

Additionally, every Region, Province and Municipality are responsible of other specific monitoring activities including urban air and soils. The National Agency for the Environment Protection and Territory (APAT) is in charge of co-ordinating the regional system of the Agency (ARPA) to investigate acute episodes or to control specifically air, soil and water. The solid wastes report and the monitoring conducted on disposal sites and wastes incineration are available in the website: www.sinanet.it.

5.1.1.7 Jordan

Monitoring of organochlorine pesticide residues in drinking water is been conducted by the Water Authority in the country for over 10 years as part of a national project and in co-operation with the laboratories of the Royal Scientific Society in Amman. The General Corporation for Environmental Protection (GCEP) has been also in charge of activities for implementing projects over a number of years that aimed at determining levels of pesticides in agricultural products, animal products and mothers milk. Those studies were conducted during early 1990 for three years and repeated again for three years as from 2000. Pesticide residues on agricultural crops are been tested for and monitored by the Ministry of Agriculture laboratories since early 1980's. Dioxins, PCBs and other toxic substances are not been monitored in any of the known compartments so far

5.1.1.8 Lebanon

There is neither comprehensive monitoring programme for PTSs nor a national survey of the obsolete pesticides stocks and their location. The recent ratification of the Stockholm Convention will probably modify this situation.

5.1.1.9 FYR of Macedonia

There is no monitoring of PTSs in the FYR of Macedonia. The National Implementation Plan, issued from the GEF project on the implementation of the Stockholm Convention will contain a monitoring plan for POPs in the country.

5.1.1.10 Malta

Monitoring is carried out by various entities as follows: Ministry of Health - indoor air quality, bathing waters quality, control of foodstuffs in the market; Ministry of Health and Water Services Corporation - quality of ground and drinking water; Ministry of Agriculture and Fisheries - contamination of soils and vegetation with plant protection products (tests for pesticide residues on selected vegetables are carried once a month), veterinary inspection and monitoring; Ministry of Home Affairs and the Environment - air pollution monitoring, marine pollution studies and any other form of pollution.

5.1.1.11 Portugal

A systematic monitoring programme is being performed in Portugal since April 1999 to identify "hot spots" in water courses with high concentrations of semi-volatile and volatile organic compounds. Water, sediment and biota (mussels and fish) are collected and analysed in order to establish:

- the main polluted areas of Portugal
- the most ubiquitous compounds detected
- the geographical and temporal distribution of the pollutants detected in water, sediment and biota
- the agricultural or industrial origin of pollution detected

Compounds analysed are all included in the EU Black List (Directive 76/464/EEC) encompassing, among others, PAHs, PCBs, organochlorinated pesticides, atrazine and organotin compounds. The stations (46) covering all the country are sampled monthly for water and annually for sediments and biota.

5.1.1.12 Slovenia

Monitoring responsibilities are distributed in different Departments. However, these activities are not performed on a comprehensive scheduled basis. They are mainly planned as a result of incidental circumstances. This was the case of the ecological disaster of the pollution of the River Krupa by PCBs resulting from wastes dumped during the manufacture of transformers by Iskra in Semič. From 1983 to 1997, air, water, soil and sediments were monitored, and now water and sediment in the Krupa, Lahinja and Kolpa rivers are monitored for PCBs twice a year.

From 1987 to 1996, in its system of measures for monitoring the contamination of agricultural products, the Agricultural Institute of Slovenia (AIS) conducted chlorinated pesticides analysis on 1131 samples of various edible products and arable soils. A program is underway in Slovenia for monitoring levels of aldrin, dieldrin, heptachlor, DDT and HCB in food. Finally, measurements of PCDD/Fs are also made in places involving incineration and smelting processes.

5.1.1.13 Spain

The Spanish Network of Atmospheric Pollution Monitoring was set up to comply with the requirements of the programs EMEP and CAMP, resulting from the International Conventions of Geneva and OSPAR. The inventory of emissions of contaminants to the atmosphere is called CORINE - AIRE. It includes measures of the following PTSs: HCHs, pentachlorophenol, HCB, PCDD/Fs and PAHs. The inventory for the period 1996-1998 was finalised in 2000.

The integrated network for quality of waters (Red ICA) includes all the existing networks related with the quality of waters in Spain. It is being revised to respond to the new needs of quality control, mainly those related with the new European Water Framework Directive. The authorities in charge of each river basin district control water status and compliance of discharges in inland waters. Marine waters are controlled by the Regional Authorities. Until now, PTSs have not been routinely included in the surveys.

According to the European Directive 96/61/EC on Integrated Pollution Prevention and Control, the European Pollutant Emission Register (EPER) is being established in Spain. The report will be of open access and it will include data on emissions to air and water of all pollutants and activities specified in the European Decision 2000/479/EC.

5.1.1.14 Tunisia

The Ministry of Environment had implemented in 1999 a monitoring program of surveillance of the quality of the Medjerda Oued and the lagoon of Korba (Cap Bon). The aim of this network is the assessment of the levels and trends of the chemical contaminants and general water quality parameters, and involves sampling of waters and sediments every year. Analyses include: aldrin, endrin, dieldrin, heptachlor, α- and γ-HCH, DDTs, lindane and PCBs.

In the framework of the Barcelona Convention, the International Centre of Environmental Technologies of Tunis (CITET) under the Ministry of Environment and the co-operation of IAEA (Monaco) and the MEDPOL programme is monitoring organic pollution in the coastal marine environment.

5.1.1.15 FR Yugoslavia

Organised active monitoring network of PTSs still doesn't exist in FRY, although MAC values are regulated for meat products, vegetables, milk, etc. However, in some regions there exist constant monitoring activities in some environmental compartments (water, air, soil, biota). Actions are being done to create the organised monitoring network in accordance with EU standards. The new Ministry of the Environmental Protection and Protection of Natural Resources is being formed. New Law of the System of Environmental Protection and Protection of Natural Resources is in the process of verification. The draft law is maximally harmonised with the EU directives and will certainly enhance the implementation of monitoring activities.

5.1.2 The MEDPOL Programme

5.1.2.1 Monitoring data

When the Mediterranean Pollution Monitoring and Research Programme (MEDPOL) started in 1975 its main aim 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 PCBs and DDTs), and petroleum hydrocarbons in seawater. 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.

Phase I (1975–1980)

The mandatory programme included analysis of PCBs and DDTs in the following species: the Mediterranean mussel (*Mytilus galloprovincialis)*, the fish, red mullet (*Mullus barbatus)*, and the shrimp *Parapenaeus longirostris.* Alternative species were also accepted. The pelagic species used were bluefin tuna and swordfish.

Data were received for samples collected from 122 sampling locations which, however, did not cover the whole Mediterranean basin. For example, DDTs, even though obligatory, were reported from only six areas out of the ten into which the Mediterranean was divided. Aldrin and dieldrin were reported from four areas and lindane/HCH from three areas. Thus, data was unable to provide an assessment of the level and extent of chlorinated hydrocarbon contamination in the various regions of the Mediterranean (UNEP, 1986).

Phase II (1981-1995)

For Phase II, the countries were expected to organise national monitoring programmes that would concentrate on mandatory parameters which were similar to those in Phase I. Most countries signed agreements and received assistance for this, although only half of them included monitoring of pollution sources. However, there was no enforcement mechanism and the compliance of data submission was very limited.

Data covered mostly contaminated areas. Their quality improved through the years but not to the same extent as that for heavy metals. The first assessments published include averages of all data presented as representative of the Mediterranean, which makes comparability difficult.

Phase III (1996-2005)

MEDPOL III was adopted by the Governments in 1995 and became fully operational during the year 2000. It is objective-oriented and gives more emphasis on the managerial aspects of pollution control while it has a direct link with the implementation of the relevant protocols especially the Land-based Sources Protocol (UNEP, 1999a).

The programme is divided into the assessment and control components. The assessment component aims at the accurate evaluation of temporal trends using a small number of fixed coastal stations from the national monitoring programmes. Trend monitoring will also be organised in areas under the direct influence of pollution sources: "hot spots" (intensively polluted areas) where control measures have or will be taken. Monitoring takes place not only for levels of pollutants in the marine environment but also for loads and biological effects. Under the control component compliance monitoring takes place including health-related parameters.

As a complement to the MEDPOL monitoring programme, IAEA-MEL/RAF has launched a contamination assessment project for the south Mediterranean Sea (2000-2003). This project includes 5 North African countries: Morocco, Algeria, Tunisia, Libya and Egypt. This joint effort is helping to develop strategies and methodologies for marine contamination studies with capacity building in the region. The project is organised to collect seawater, biota and sediment samples along the coast to assess the levels of contaminants and their spatial and temporal trends.

5.1.2.2 Quality control of data

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. There are, at least, 2 organisers of inter-comparison exercises for the Mediterranean Area: IAEA-MEL organises these exercises for organochlorine pesticides and PCBs since 1975-1976 and for PAHs since 1988. The laboratories of 17 Mediterranean countries are currently participating. On the other hand, the FSR Marine Laboratory in Aberdeen (Scotland) runs QUASIMEME (quality assurance of information for marine environmental monitoring in Europe). This project was created in 1996 to support those chemical measurements required for national and international marine monitoring programmes (e.g. OSPAR Commission, HELCOM and MEDPOL). The results of these efforts are illustrated by the increasing numbers of analytes measured and less technical errors in the measurements. The report by Mee et al (1994) showed the considerable improvement obtained by the participants with time.

5.1.2.3 Capacity building

When the Mediterranean Action Plan was adopted and the Barcelona Convention signed in the mid-1970's, information on Mediterranean pollution was almost lacking. In preference to calling in outside expertise, UNEP and the Contracting Parties decided to give this responsibility to the Mediterranean scientific community and to generate the necessary information through the MEDPOL programme. However, at the time, no model of an international scientific programme at the Mediterranean scale was available. Both the tools and co-ordinating mechanisms had to be built as the programme was unfolding.

At that stage, many of the Mediterranean States lacked the capabilities needed and their research centres were unable to contribute efficiently to the research and monitoring activities. With the exception of some European laboratories, there was little experience in this field. Because of this, Phase I of MEDPOL was heavily burdened with capacity building activities. These included: donation of equipment, training of staff, consultancies to provide advice, maintenance services for analytical instruments and inter-calibration of analytical techniques. The quality assurance programme also included other activities such as the preparation of a number of reference methods.

At the end of Phase I, a Mediterranean-wide network of scientific institutions co-operating with MEDPOL was in place, the largest co-operative scientific programme ever undertaken in the region. The training, assistance and capacity building efforts continued during Phase II. From 1982 to 1989, more than 200 junior scientists from 16 countries were given short-term training through participation to training workshops, inter-calibration exercises or by on-the-job training in other Mediterranean institutions. During the same period, 530 fellowships

were granted to Mediterranean scientists to attend workshops convened either by MEDPOL or by other organisations.

5.2 REGULATION AND MANAGEMENT STRUCTURES ADDRESSING PTS

5.2.1 National

Different authorities normally handle the regulation and management of PTSs in the various countries of the Region. Pesticides are normally under the control of the Ministries of Agriculture, while the rest of PTSs are normally handled by the Environmental Ministries. The Health authorities are mainly in charge of assessing and regulating potential health effects.

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. In European countries, registration is a formal process in which pesticides are examined, in particular, for mammalian toxicity and for a range of potential environmental effects. These are based on the measured or estimated environmental behaviour of the product related to its physico-chemical properties. 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 PTSs considered that are mainly of industrial use, the effort has been put in managing their spread and subsequent destruction. Most of the countries of the Region, for example, have performed inventories of PCBs with varying degrees of comprehensiveness (see section 2.2.1). Although many of them have developed the regulation of industrial PTSs, they do not usually have the management capabilities in place.

Some interesting collaborative projects have been set up between some of the countries of the Region and development agencies to support specific management structures to handle PCBs and pesticide stocks. A more detailed view of the existing regulation and management structures in each country is given below.

5.2.1.1 Algeria

The management of chemicals in general and of chlorinated pesticides and PCBs in particular is an integrated part of the *Environment Law* 30\1983. The list of chemicals that include most of the PTSs is referred in the article 110 of the Law. The article 111 describes the permit conditions to produce and import chemicals into the country and the system to be adopted to control these chemicals in the market.

The control of the pesticides, including import, manufacture and sale, has been further regulated by the Law 87/1987 relating to plant protection. The National Commission for pest control products rules on the responses to give to each request for approval and the National Institute of Plants Protection (INPV) publishes the list of pesticides for agricultural use authorised to being put on the market.

Special measures are considered under the provisions of the Law 182\1987 regarding the management of PCBs for import, use, handling, storage and disposal of electrical devices containing PCBs compounds.

The Law 70\1988 describes the measures to be considered for the protection of occupational health during the handling of chemicals especially the issues dealing with awareness and information campaign concerning the impact of incorrect handling of the chemicals

5.2.1.2 Bosnia-Herzegovina

The last decade Bosnia and Herzegovina was dominated by political and economic changes, and a four-year war with devastating consequences. Under these circumstances, there is no effective primary or secondary legislation relating to the regulation of waste management activities, the emissions to the atmosphere and air quality, etc. However, the Federation is completing the drafting of a new environmental protection law under the EEC Project “Preparation of Environmental Law and Policy in B-H”.

5.2.1.3 Croatia

Croatia has ratified or is in process of ratification almost all international environment protection conventions and particularly those related to POPs substances, notably the Stockholm Convention. The strategy of environmental protection is described in the *Law on Environmental Protection* (1994). This law is accompanied with a number of by-laws relevant for specific environment compartments, types of pollution and sources, which include PTSs, namely the *Law on Waste* (1995), the *Law on Transport of Hazardous Materials* (1993),

the *By-law on Conditions for Handling Hazardous Waste* (1998), the *Law on Air Quality Protection* (1995), the *Law on Waters* (1990), and the *Law on Foodstuffs and Objects of Common Use Safety* (1997). An Environmental Emission Cadaster is being implemented (1996) including: solid waste generation, air pollutants emissions, wastewater discharges related to air pollution emissions.

In order to facilitate a further action on the implementation of the Stockholm Convention, a 2 year project funded by UNIDO is preparing the ground for strengthening the national capacity to manage PTSs. The main activities to be undertaken are: the elaboration of preliminary inventories of sources and emissions of POPs, including a preliminary assessment of stockpiles and contaminated waste products; the development of an Action plan for the regular monitoring and reduction of releases of unintentional by-products and to assess the exposure of the human population and the environment; to build capacity for reporting every five years on progress in phasing out PCBs; and, to support communication, information exchange, and raising awareness through a multi-stakeholder participatory processes.

5.2.1.4 Cyprus

The management of chemicals in general, including PTSs, is regulated by the following specific legislation, which has already been harmonised with the relevant Directives of the European Union:

The Pest Control Products Law of 1993, N1 (I)/93 and the Pest Control Products Regulations of 1993 and 2000. The law and the relevant regulations provide for the marketing, registration, quality control, toxicity classification, packaging and labelling of all pesticides.

The Food (Control & Sales) Laws 1996-2001, implementing regulations on the Official Control of Foodstuffs and Hygiene and of Pesticide Residues, form the Cyprus statutory instrument for fixing MRLs and control of pesticide residues in products of animal and plant origin, including fruit and vegetables. These Regulations, in force since November 2001, adopt all MRLs related Directives up to 1998 (Directive 98/82) and form the first phase of the continuous process for Pesticide Residues Regulations fully harmonised with the EU Acquits.

The Fisheries Law Cap. 135 and subsequent amendments (1961-2000) and the Fisheries Regulations (1990 – 2000) provides maximum limits for certain PTSs, pesticides and heavy metals, in marine captures.

The Dangerous Substances Law of 1981 and 2002 and the issued Regulations on classification, labelling and packing of dangerous substances and preparations includes provisions for restrictions on the use and the placing on the market of certain dangerous substances and preparations.

The Atmospheric Pollution Control Law 70/91 and the relevant Regulations and amendments provide for the control of industrial emissions, including dioxins/furans emissions.

5.2.1.5 Egypt

Chemicals and formulations used to control plant diseases, pest insects, rodents, weeds, and parasites are regulated by the *Agricultural Law* no. 53/1966. According to the Article 79, a Pesticide Committee is to be formed with the task of specifying pesticides to be used in the country, determine their specifications, procedure of their registration and condition for use. The Minister of Agriculture issues ministerial decrees that put the articles of the law into action, based on the recommendations of the Committee.

The regulation and control of chlorinated pesticides, PCBs, and other chemicals are specifically under the provisions of the *Law for hazardous materials and wastes* (4/1994), which includes a list of 323 hazardous chemicals. The Law prohibits to import hazardous wastes or to allow its entry into passage through the territory provided the Ministry of Environment is notified

The Ministry of Environment is responsible for the proper management of the hazardous wastes including the control of collection, storage, treatment and disposal, in collaboration with the producers. However, Article 5 of the Law sets up the functions of the Egyptian Environmental Affairs Agency (EEAA). The competent ministries, in co-operation with EEAA and the Ministry of Health should develop and promulgate a list of hazardous substances, which should be controlled and shall be revised from time to time as appropriate. The Agency is also responsible for the co-ordination with the other competent authorities, of the regulation and security aspects of the handling hazardous substances.

5.2.1.6 France

The EU directives and derived management structures apply for the EU countries of the Region (see Section 5.2.2.2). The competent body at national level is the "*Direction de la prévention des pollutions et des risques*" and the "*Bureau des substances et préparations chimiques*", which belong to the Environment and Landscape

Ministry. The Agriculture and Forest Ministry has also competencies on pesticides, particularly through the "*Bureau de contrôle des produits phytosanitaires*".

5.2.1.7 Greece

As in the case of France, the EU directives and derived management structures apply for the EU countries of the Region (see Section 5.2.2.2). The national authority on pesticides is the General Chemical State Laboratory, particularly the Section of Dangerous Substances and Preparations.

5.2.1.8 Israel

The *Hazardous Substances Law* of 1993 is the central legal tool for the supervision and management of hazardous substances. The law obligates anyone dealing with a hazardous substance to apply for a Poison Permit. The data provided in Poisons Permit applications and the administrative enforcement means established by the law are important tools in the Environment Ministry's efforts to widen its supervision and control over hazardous substances found in every industrial plant in Israel.

Hazardous Substances Regulations on the import and export of hazardous wastes were promulgated in 1994 and provide the legal basis for implementing the Basel Convention on the Transboundary Movement of Hazardous Wastes and their Disposal. In recent years, a variety of environmental regulations have been promulgated within the framework of the *Businesses Law* (1968), including limitations on emissions to the environment and conditions for the handling of hazardous substances and hazardous waste disposal.

Efforts are currently concentrating on drafting new regulations under the Hazardous Substances Law: on hazardous waste treatment and disposal with emphasis on recovery and reuse, on the classification of industrial plants according to quantities and types of hazardous materials, on new criteria for classification and exemption from the provisions of Poison Permits, and on industrial responsibility during hazardous substance accidents.

5.2.1.9 Italy

As for France and Greece, the EU directives and derived management structures apply for the EU countries of the Region (see Section 5.2.2.2). There are two national authorities, one for the pesticides, which is the *"Dipartimento di Alimenti, Nutrizione e Sanità Pubblica Veterinaria"* (Health Ministry), and another for the industrial chemicals the *"Dipartimento di Prevenzione"* (Health Ministry).

5.2.1.10 Jordan

The General Corporation for Environment Protection (GCEP) is the governmental organisation in charge of implementing and follow up of actions related with PTSs in Jordan. Moreover Jordan issued several laws addressing environmental and food safety issues. The *Environmental Law No. 12/1995* and the corresponding by-laws issued in 1998 cover all aspects of environmental protection, monitoring and impact assessment, as well as classification, registration and transport of hazardous substances. The *Agricultural Law No. 20/2000* addresses the protection of natural resources and food safety.

5.2.1.11 Lebanon

The import and use of pesticides which are banned in the countries of origin are forbidden and was formerly ordered by the Decrees 11/1978, which regulate the use of insecticides and 64/1988, concerning the protection of the environment and the import of various types of wastes. These regulations were updated for PTS pesticides in 1992 (decision 108/1) and in 1998 (decision 94/1) but do not include inspection activities within the country.

However, Lebanon has recently (29/7/2002) ratified the Stockholm Convention and a National Implementation Plan for the Management of Persistent Organic Pollutants will hopefully set the necessary legislation and criteria regarding surveillance activities. A collaboration agreement with FAO has also been performed to dispose a large quantity of obsolete pesticides found in a warehouse as well as a national management plan for the sound disposal of oil containing PCBs.

5.2.1.12 Malta

The major enabling Acts are the *Environment Protection Act* and Act Nº XI of 2001 which controls the use of pesticides. There are various legal notices which empower the respective ministries to inspect, monitor and control the use of these substances. At the moment further legislation in line with European Union regulations is being enacted.

5.2.1.13 FYR of Macedonia

The Ministry of Environment and Physical Planning has just established a National Unit which is collecting information from the different Government bodies in order to develop a legislative and regulatory framework for persistent organic substances, particularly chlorinated pesticides and PCBs.

5.2.1.14 Morocco

The country possesses a comprehensive legal and institutional framework for the control of pesticides. A series of legal instruments have been elaborated with the appearance of new chemicals in the market, such as the Laws 13-83 and 466-84 (1984) for controlling the validity and conformity of pesticides, the Law 3073-94 (1994) for the control of pesticides at customs level, the Law n° 42-95 (1997) on control and organisation of the trade of pesticides used in the agriculture, the Decree n°2-99-105 and 106 (1999) on approval the pesticides used in agriculture and their import, manufacture and trade, and the Decree n°2-01-1343 (2001) relating to the establishment of the committee of pesticides, constituted by the concerned departments, to give his opinion on all pesticides disposed for approval and to propose, if necessary, the reinforcement of legislation.

However, Morocco is lacking the convenient legal framework to control obsolete chemicals. Actually, a draft text is under discussion for adoption by Moroccan authorities. The text would enable the country to properly implement the Basel convention, signed in 1996.

5.2.1.15 Portugal

Similarly to the rest of the EU countries of the Region, the EU directives and derived management structures apply for the EU countries of the Region (see Section 5.2.2.2). Portugal has two national authorities. For pesticides is the *"Direçao Geral de Proteçao das Culturas"*, and for the industrial chemicals there is the *"Divisao de Riscos Industriais e Compostos Químicas"* (Environment Ministry).

5.2.1.16 Spain

The EU directives and derived management structures apply for the EU countries of the Region (see Section 5.2.2.2). The competent authorities in the implementation of European Directives on dangerous substances and formulations (including plant protection products and biocides) are the Ministry of Environment, the Ministry of Health and Consumption, and the Ministry of Agriculture, Fishing and Feeding, the last one related with plant protection products. A specific National Plan for management of PCBs was approved in 1999.

Environmental risk assessment, classification and labelling is responsibility of the Ministry of Environment. The Ministry of Health and Consumption is in charge of human health risk assessment, classification and labelling.

5.2.1.17 Syria

Syria started in 1952 the registration of pesticides by the Ministry of Agriculture (Legislative decree No165/T), which was developed in 1990 to include clauses of banning or restricted use. In 1988, the Minister of Health created a register of pesticides used in Public Health. A National Committee on chemical safety and another on management of wastes have the responsibility of approval and special classification of dangerous wastes and of developing technical guidelines for their correct management (Decision No 378/2001 of the Minister of Environment).

In addition to the contents of these regulations, there are several decrees issued by different public administrative sections, regarding the correct management of chemical, dangerous materials and wastes, that are also of application. The Minister of Environment issued a decree No. 477/SB/1998 on the prohibition of dumping, destruction or landfilling of materials or wastes in land, rivers, or sea, without prior consent.

5.2.1.18 Tunisia

The trade, distribution, and use of pesticides for agricultural purposes are regulated in a systematic manner since 1961. Any pesticide that is imported or formulated in the country has to be registered by the Ministry of Agriculture and authorisation is given for one or more specific usage. The implementation of these regulations is not always rigorous, particularly the regulations that govern the labelling, conditioning, handling, transport and storage of these products. Pesticides used for public health purposes are also subject to registration with the Ministry of Public Health.

Obsolete pesticides, PCBs, and by-products with PTSs characteristics are considered hazardous wastes (decree No. 2000-2339) and their management and disposal regulated by Law No. 96-41. The law states that Companies that produce hazardous wastes have to communicate to the Ministry of Environment details on their

origin, quantities, destinations and the measures taken to limit their production. Records are maintained for 10 years. New industrial, agriculture and commercial developments are subject to authorisation by the Ministry of Environment following the conduction of an environmental impact assessment study.

5.2.1.19 Turkey

All pesticides that are produced in Turkey or that will be imported are under the control of the Turkish Ministry of Agriculture and Rural Affairs. This is in accordance with the *Law for Agricultural Pest Control and Quarantine* (No.6968) and regulations based on this law, in terms of their formulation and material content.

The Regulation for the Authorisation of Pesticides and Similar substances used in Agricultural Pest Control, which constitutes a base for the authorisation of pesticides in Turkey, came into force in 17 February 1999. This regulation includes a number of items to be taken into consideration in the authorisation of pesticides as in accordance with the recommendations by the FAO, the European Union and other countries.

5.2.1.20 FR Yugoslavia (Serbia and Montenegro)

The Federal Commission for Pesticide registration, registers pesticides for plant protection in agriculture and forestry, according to the legislative the *Law on plant protection* (Sl.list SRJ, 24/98). The Federal Ministry for Health and the Environment is responsible for registration of active substances and their division into poison groups and for cancellation of licenses for application within the territory, according to the *Law of production and application of toxic substances* (Sl.list SRJ, 15/95). However, FR Yugoslavia is in the process of the identification of responsibilities of all sectors in the application of the international conventions concerning PTSs and, therefore, of the definition of National Implementation Plans for managing PTSs, with the revision of the national legislation and the introduction of a cadaster on POPs.

5.2.2 Regional

The different countries of the region are incorporated and therefore constrained by some of the following institutional and regulatory frameworks, the Barcelona Convention and the EU Directives.

5.2.2.1 The Barcelona Convention and its associated Protocols

In 1975, the Mediterranean countries and the EEC adopted the Mediterranean Action Plan (MAP) and in 1976 the Convention for the Protection of the Mediterranean Sea Against Pollution (the Barcelona Convention). Being a framework convention, it envisages the preparation of technical protocols. Actually, six protocols have been adopted by the Mediterranean countries:

- the Protocol for the Prevention of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft ("Dumping Protocol") (1976),
- the Protocol Concerning Co-operation in Combating Pollution of the Mediterranean Sea by oil and other Harmful Substances in Cases of Emergency ("Emergency Protocol") (1976),
- the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources ("Land Based Sources Protocol") (1980),
- the Protocol Concerning Specially Protected Areas ("SPA Protocol") (1982).
- the Protocol for the Protection of the Mediterranean Sea Against Pollution Resulting from Exploration and Exploitation of the Continental Shelf and the Seabed and its Subsoil ("Offshore Protocol") (1994), and
- the Protocol on the Prevention of Pollution of the Mediterranean Sea by Transboundary Movements of Hazardous Wastes and their Disposal ("Hazardous Wastes Protocol") (1996).

Most of these protocols have been amended as a result of the World summit for environment and development in 1992 and the GPA in 1995. Actually, discussions are ongoing concerning the appropriate rules and procedures to be applied for the determination of liability and compensation for damage resulting from pollution of the marine environment in the Mediterranean Sea. These discussions may result in the establishment of a new Protocol.

The most important legal instrument regarding PTSs and the reduction of their inputs into the marine environment is the amended LBS protocol. According to article 5 of the protocol "The Parties undertake to eliminate pollution deriving from land-based sources and activities, in particular to phase out inputs of the substances that are toxic, persistent and liable to bioaccumulate listed in Annex I of the Protocol. To this end,

they shall elaborate and implement, individually or jointly, as appropriate, national and regional action plans and programmes, containing measures and timetables for their implementation. Annex I contains 30 sectors of activity to be considered, 13 characteristics of substances to be taken into account and 19 categories of substances for which action plans should be prepared. These include persistent organic pollutants (POPs), other organohalogen compounds (e.g chlorinated phenols), heavy metals and organometallic compounds and hazardous wastes (e.g. used lubricating oils, batteries, etc.).

As a follow up to the provisions of the amended Protocol, the CPs to the Barcelona Convention adopted in 1997 a regional Strategic Action Plan (SAP) to address pollution from land-based activities. The main objective of SAP is to promote and provide support to the Mediterranean countries for the formulation, adoption and implementation of relevant National Action Plans (NAPs), as well as a scientifically-based long-term programme of targets to be achieved and actions to be implemented at national and regional levels.

In addition to activities directly addressing pollution, the SAP envisages the implementation of respective capacity building actions, provision of external support according to available sources, implementation of the participatory principle, and of procedures for monitoring, evaluation, reporting, feedback information and readjustments. Due to the complexity and significance of the defined targets and actions envisaged, as well as to the resulting financial, institutional and organisational implications, the implementation of an SAP requires careful planning, harmonisation and integration at national and regional levels.

The SAP operational strategy adopted by the CPs in 2001 proposes a national and regional institutional set up that would ensure the financial, technical and socio-economic sustainability of the implementation process of the Plan in the time framework (2001-2025). The strategy establishes the basis on which the Mediterranean countries would track the reduction to be achieved to comply with the SAP binding commitments. It considers the year 2003 for the establishment of a Pollutant National Budget Baseline, which is the sum of the releases of every SAP targeted pollutant that would be released from the coastal areas.

The Mediterranean countries with the support of the secretariat started the implementation, during the years 2001-2003, of a comprehensive capacity building programme financed by the GEF, FFEM and the Contracting Parties where a set of guidelines for the management of different types of pollutants and their substantial sources would be prepared, regional and national training courses would be performed together with an active search for the convenient national and international financial means that would support all the SAP National Action Plans (NAPs) to be effective in 2005. The NAPs would be elaborated on the basis of the National Diagnostic Analysis (NDA) that would be implemented by the national authorities during the year 2002-2003.

5.2.2.2 The EU Directives

The general strategy of the EU 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 Commission has proposed wide ranging legislation aimed at directly or indirectly reducing the release of PTSs into the environment, with the objective of reducing human exposure and protecting human health and the environment. Emission and source related data for most PTSs in the European countries indicate a decrease on the release of these chemicals since the legal instruments have been put in place.

Some Directives relevant for the regional PTSs strategy are:

> *Council Directive 79/117/EEC prohibiting the placing on the market and use of plant protection products containing certain active substances.*

Substances addressed are DDT, lindane, aldrin, chlordane, dieldrin, endrin, HCHs, hexachlorobenzene, camphechlor and mercury.

> *Council Directives 91/414/EEC providing the framework for the authorisation, the placing of plant protection products on the market and its use in the European Union.*

All active substances for agricultural use on the market in member states on 25 july 1993 must undergo a full evaluation verifying whether they fulfil the obligations of Article 5 and therefore can be listed in Annex I of the directive. This list contains active substances whose use in plant protection products is considered safe. Organotins are proposed to be banned as plant protection products.

Council Directive 98/8/EC on placing on the market of biocides.

After full implementation of this Directive, all active substances have to be assessed and approved at the Community level and all the biocidal products have to be authorised by the Member States. If the result of the assessment is that an active substance can be used in a biocidal product, it will be put on a positive list accompanied with the requirements on that use. Substances addressed are PCP, PAHs (creosote), TBT and lindane

Council Directive 76/769/EEC on the approximations of the laws, regulations, and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations.

National information on the import, production, stockpiling, use and export of substances is requested. Marketing and use restrictions are defined based on evaluation of risk as well as socio-economic considerations. Four priority lists (containing about 150 substances and identified Rapporteur Member States) have been established for carrying out the risk assessment work under regulation No. 793/93 (2001).

Council Directive 92/32 amending for the Directive 67/458/EEC on the approximation of the laws, regulation and administrative provisions relating to the classification, packaging and labelling of dangerous substances.

Dangerous substances, which are placed on the market have to be labelled according to their classification in Annex I, which in 2001 contains approximately 2350 existing and 214 new substances. For dangerous substances not in Annex I, the manufacturer, distributor and importer is obliged to apply a provisional classifications and labelling following the criteria in Annex VI of this directive.

Directive 2000/76/EEC on waste incineration.

Defines limit values on emissions of particles and total organic matter from incineration of all type of wastes. Substances addressed are, e.g., PAHs, PCDD/PCDFs and mercury.

Directive 96/59/EEC for the elimination of PCBs and PCTs and Directive 1999/31/EEC on the landfill of wastes.

The Directive 96/59 imposes the elimination of PCBs before December 31, 2010, and the drawing up of a stock-list of equipments containing PCBs with a volume above 5 L. Also, a national plan for decontamination and elimination is required. The Directive 1999/31 provides measures, procedures and guidance for preventing or reducing pollution of surface waters, ground water, soil and air from landfills of wastes.

Council Directive 2000/60/EC of the European Parliament and of the council establishing a framework for Community action in the field of water policy (Water Framework Directive).

This Directive contains provisions on measures aimed at progressively reducing (for priority substances) and at ceasing or phasing out (for priority hazardous substances, within 20 years) discharges, emissions and losses as well as identification of these priority substances and hazardous priority substances (emission inventories according to Article 13(4)). The EC has two years to propose control measures necessary to reach the objectives for priority (hazardous) substances. These substances will have to be monitored as mandatory parameters under the WFD.

Among the substances addressed are:

- proposed priority hazardous substances: penta-PBDE, HCB, HCHs, Hg, NP/NPEs, PAHs, Pentachlorobenzene, organotin compounds;
- proposed possible priority hazardous substances: other PBDEs, dibutyl- and diethylhexylphtalate, PCP, naphthalene, anthracene, atrazine, endosulfan, octylphenols;

Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community.

Established two lists of substances classified as hazardous. List I identified 129 substances to be eliminated from the inland and coastal waters because of their toxicity and their ability to bioaccumulate. List II contained those, which have a detrimental impact on the environment but which may be contained within a given area

depending on the characteristics and location of the area. The Directive required Member States to draw up authorisation limits for emissions of substances on both lists and set up pollution programmes.

> *Council Directive 80/68/EEC on the protection of ground water against pollution caused by certain dangerous substances.*

Replaces Article 4 of the previous Directive (76/464/EEC). Its aim is to prevent the direct or indirect introduction of substances in List I and limit the substances in List II of the Annex to groundwater supplies. It will become part of the overall approach of the draft Community Water Policy Framework Directive.

> *Council Directive 86/280/EEC on limit values and quality objectives for discharges of certain dangerous substances* included in List I of the Annex to Directive 76/464/EEC (Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community).

This Directive limit values for emission standards for the substances referred to in Article 2 in discharges from industrial plants, quality objectives in the aquatic environment, time limits for compliance, reference methods of measurement. It establishes a monitoring procedure, requires Member States to co-operate and to draw up programmes to avoid or eliminate pollution arising from the sources referred to in Article 5. The Directive applies to the waters referred to in Article 1 of Directive 76/464/EEC, with the exception of ground water. Substances addressed are: DDT, the drins, PCP, hexachlorobenzene.

> *Council Directive 96/61/EC concerning integrated pollution prevention and control (IPPC).*

The objective is to prevent or minimise air, water and soil pollution by emissions from industrial installations in the Community, in view of achieving a high level of environmental protection. This Directive requires the assessment of chemicals used in certain production processes and certain conditions for the licensing of industrial installations. Article 15 (3) of the Directive requires Member States to inventory and supply data on principal emissions and responsible sources, that is from all large facilities with one or more activities as mentioned in Annex I to this Directive. According to this Article 15 the Commission decided on the implementation of an European Pollutant Emission Register (EPER). Substances addressed include PCP, HCB, HCHs, PCDD/PCDFs and organotin compounds.

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.

Besides this regulatory framework, the European Community has also acquired new obligations by becoming a contracting party to several international conventions (see section 4.2.3).

5.2.3 International

PTSs pollution issues are covered by several Multilateral Environmental Agreements (MEA) 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.

5.2.3.1 International code of conduct on the distribution and use of pesticides

This Code of Conduct, adopted by FAO and its member countries in 1985, recognises that: *"In the absence of an effective pesticide registration process and of a governmental infrastructure for controlling the availability of pesticides, some countries importing pesticides must heavily rely on the pesticide industry to promote the safe and proper distribution and use of pesticides. In these circumstances foreign manufacturers, exporters and importers, as well as local formulators, distributors, repackers, advisers and users, must accept a share of the responsibility for safety and efficiency in distribution and use."*

The **Prior Informed Consent** (PIC) is an important component of the Code of Conduct. Under the Rotterdam convention on PIC, *"pesticides that are banned or severely restricted for reasons of health or the environment are subject to the Prior Informed Consent procedure. No pesticide in these categories should be exported to an importing country participating in the PIC procedure contrary to that country's decision...".*

Implementation of PIC Convention is carried out jointly by FAO and the International Register of Potentially Toxic Chemicals (UNEP/IRPTC) and includes almost all countries of the region (see Annex III). Pesticides under national review for PIC (FAO, 1990) are: aldrin, chlordane, heptachlor, DDT, dieldrin and HCHs (mixed isomers). The state of compliance of the various countries of Region with the Rotterdam convention is given in Annex III.

5.2.3.2 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.

Most countries of the Region comply with the Basel convention although some of the southern countries lack the appropriated management structures to implement the convention.

5.2.3.3 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 PCBs.

5.2.3.4 Convention on Long-range Transboundary Air Pollution (LRTAP)

The purpose of this Convention issued by the UN Economic Commission for Europe is to prevent, reduce and control transboundary air pollution both from existing and new sources. By covering mid-latitude regions which are the origin of a major part of the atmospheric pollution, this regional, binding agreement, and its related protocols, represents the most appropriate instrument for addressing significant components of the problem.

The Aarhus Protocol, associated to the Convention, aims at eliminating discharges, emissions and losses of POPs. It covers 16 substances, encompassing 11 pesticides, 2 industrial chemicals and 3 by-products. The Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (DDT, heptachlor, hexaclorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCHs (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that will be banned. It also obliges Parties to reduce their emissions of dioxins, furans, PAHs and HCB below their levels in 1990 (or an alternative year between 1985 and 1995). For the incineration of municipal, hazardous and medical waste, it lays down specific limit values. The protocol will enter into force as soon as it is ratified by 16 countries (10 ratifications registered in August 2002)

5.2.3.5 Convention for the Protection of the Marine Environment of the North East Atlantic, 1992 (OSPAR)

Although covering only a restricted segment of the region, the 1992 OSPAR Convention is currently one of the most applicable international agreements addressing marine pollution from various sources. The objective of the Convention is to bring to an end the discharges, emissions and losses of all hazardous substances to the marine environment by 2020. Among the chemicals or chemical groups that have been selected for priority action there are 15 compounds considered in the present assessment (see www.ospar.org). On both monitoring and source-related assessment issues, OSPAR represents a relevant agreement to be taken into account in the context of PTSs control activities.

5.2.3.6 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.

5.2.3.7 WMO Environmental Health Criteria

Over the past twenty years, the WMO has published an extensive list of environmental criteria for many of the PTSs discussed in this assessment. These criteria provide quantitative guidance for human concentrations including PTDI, TDI and TWI values.

5.2.3.8 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 PTSs. 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 (23 ratifications registered in October 2002, none from the Region).

5.2.3.9 Relations between existing MEAs

Ten of the twelve POPs covered by the Stockholm Convention (pesticides and industrial chemicals) are regulated under the Basel and the Rotterdam Conventions. The Stockholm Convention takes into account any relevant provisions in the existing international instrument on prior informed consent, in such a way that a chemical listed in Annex A of the Convention can be exported only:

- for the purpose of environmentally sound disposal;
- to a Party permitted to use that chemical under Annex A or Annex B; or
- to a country that is not a Party to the Stockholm Convention which has provided an annual certification to the exporting Party.

On the other hand, the OSPAR Convention, the Barcelona convention and its protocols, and the Aarhus POPs Protocol, aim at bringing to an end the discharge to the seas, and the production and use of some of the POPs substances covered in the Stockholm Convention.

5.3 STATUS OF IMPLEMENTATION AND ENFORCEMENT IN THE REGION

As shown in the previous section, besides the national regulatory structures, the EU directives and the regional Conventions, namely MAP and OSPAR, are the main driving forces for environmental protection in the region. However, the Mediterranean region generally lacks strong national environmental leadership and compliance of regional commitments is, in general, very irregular.

Monitoring in the Region is heterogeneous at the National level ranging from comprehensive monitoring networks in France to non-existing for many of the Southern and South-eastern countries. The EU member and proponent countries have made an effort to harmonise the monitoring programs although the degree of implementation is varying. MEDPOL is a good example of Regional collaboration in monitoring programmes although it is weakened by the lack of commitment of some of the participant countries. MEDPOL has also played a key role in developing quality criteria standards throughout the Region and it is a good example of a capacity building programme.

The regulatory status of the Region mimics the socio-economic and political structure. The legislation for PTSs management in EU members and the associated countries are regulated by the European directives, although the degree of compliance is varying within the four member States, and their investment in regional PTSs issues has been slow. On the other hand, 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 (e.g. lindane) continue to be used in practice under no control of the authorities and that even banned products such as DDT

were still being illegally imported in some of these countries. An overview of the general status of the PTSs covered in this assessment within the countries of the region is shown in Annex III.

The control and management of PTSs at national levels are quite dispersed among various authorities depending on the type of PTSs. Pesticides are usually regulated by the corresponding Agricultural Ministries, Industrial PTSs are usually left as a legacy to the new-born Environmental Ministries, while the levels and effects of PTSs in biota are either the responsibility of the Environmental or Agricultural (Veterinary) Ministries. Finally, PTSs control and regulation in foodstuff is always the responsibility of the corresponding Health Authorities. In addition, in many of the countries of the Region, environmental control and regulation is quite decentralised which implies that many of the responsibilities are transferred to regional, provincial or local authorities.

The state of implementation and compliance of the existing regulations concerning PTSs in the Region is quite varying. The available information indicate that European countries, Malta, Cyprus and Slovenia have more effective national environmental law and regulations and capabilities to undertake monitoring and enforcement activities for PTSs national and regional regulations. These countries exhibit several positive signs of high compliance of substantive obligations through their commitments to EU directives. In fact, implementation of these commitments could lead directly to implementation of Convention obligations, which takes place via three overlapping mechanisms:

- conventions sponsored implementation efforts,
- state-driven domestic implementation efforts, and
- EU-driven efforts to harmonise national environmental law and regulations.

Other Mediterranean countries exhibit low commitments to relevant national and regional regulations even though they have developed a comprehensive national legal and institutional framework for implementation of national and regional regulations. Furthermore, because these countries have ratified only few of the MEAs, they are not required to submit reports on several important requirements. As such, information about compliance of substantive obligations and implementation of the Protocols and common measures concerning PTSs remains extremely scarce and, where it exists, quite uneven in coverage and quality.

Implementation of MEAs commitments in these countries takes place via three main channels which include:

- Multi-lateral assistance programs such as those sponsored by MAP bodies, UNEP, the GEF, and multi-lateral development banks;
- State-driven domestic implementation efforts; and
- EU-driven efforts for EU candidate states and non-European countries through the Euro-Mediterranean partnership.

In general these countries are lacking the necessary technical, financial and human resources to comply with national and regional regulations. The important numbers of stockpiles of PTSs existing in the jurisdiction area of these countries could be considered as a relevant indicator that would support these facts.

Ratification of protocols remains a challenge for the region. Most of the existing MEAs have low numbers of ratifications. As an example, neither the revised Barcelona Convention, nor any of the most recent Protocols (including the revised ones), have entered into force, despite having been adopted six to seven years ago in 1995 and 1996.

5.4 EXAMPLES OF ALTERNATIVES OR MEASURES FOR REDUCTION

5.4.1 Chlorinated Pesticides

Integrated pest management (IPM) appears to be the obvious alternative to reduce the use of chlorinated pesticides in the Region. The Global IPM facility has been created jointly by FAO, World Bank, UNDP and UNEP to establish participatory IPM programmes in developing countries. The most important element of a successful IPM programme is farmer participation and training. IPM should go hand in hand with the appropriate pesticide management to allow for regulation and control, proper purchasing and marketing, good technical quality and safe handling and disposal of pesticides (CEC, 1999).

The available options for pest control consist a great deal more than the choice between chemical pesticides or the total exclusion of synthetic chemical inputs. Some of the strategies which improve pesticide PTSs management are:

- Replacement of the more hazardous pesticides with less toxic and less persistent ones.
- Selection of crop varieties which are more pest resistant.
- Improve pesticide application technology to minimise inputs and enlarge safety.
- Crop rotation
- Use of natural enemies for pest control.
- Cost-benefit analysis of the use of pesticides
- Farmer communication and consultation.

A successful IPM programme has been put in place for cotton crops. Cotton crops amount for 25% of the overall pesticide consumption, hence improved pesticide management in cotton crops has a large impact on the release of PTSs pesticides. (FAO). This would be particularly relevant for Egypt where cotton production is still quite extensive. The success of these IPM programmes resides in the fact that farmers constitute the key decision maker in the process.

The Mediterranean Region has shown a general increase in the use of pesticides due to the explosive development of protected cultivation systems (greenhouses) in the Region, particularly in South-eastern Spain, North Africa and the Middle East areas. As a consequence, crop yields have increased substantially, for instance tomato crops under plastic cover have increased from an average 60 tonnes/Ha up to 200 tonnes/Ha. This has as a result an increase also of the pest-related problems in the greenhouses. This problem is now being accelerated due to the increase of water salinity which enhances pest proliferation. To control soil borne pests, both chemical and non-chemical methods are being used, the most widely used alternative to the present PTSs uses in greenhouses is Methyl Bromide. (Besri, 2000). This is itself could constitute an additional PTSs problem in the future. Hence, integrated pest management (IPM) systems should be propagated. In order to do so, a prerequisite is to conduct a proper survey of the use of pesticides in these particularly intensive agricultural systems which are prone to generate substantial sources of PTSs.

It is not totally clear if alternative measures to the use of pesticides are being promoted within the European and Mediterranean Plant Organisation (EPPO). The following Mediterranean countries are members of EPPO: Albania, Algeria, Croatia, Cyprus, France, Greece, Israel, Italy, Jordan, Malta, Morocco, Portugal, Slovenia, Spain, Tunisia and Turkey. It is remarkable that Egypt, an important country in terms of agriculture and pesticide use, is not a member of the EPPO.

Proper handling and disposal of obsolete pesticides is a key measure for the reduction of PTSs sources in the Region. In this context the FAO has put in place programmes for the disposal and handling of obsolete pesticides in developing countries. They normally include proper repackaging and in situ storage of the obsolete pesticides prior to their export to the appropriated thermal treatment facilities in developed countries. This of course could have as a consequence the transfer of the organochlorinated PTSs to the atmosphere as secondary PTSs (dioxins and furans). Therefore, the safe storage on site is the preferred option.

5.4.2 Industrial compounds

5.4.2.1 PCBs

The handling of PCBs includes the pure compound mixtures, those diluted in oil as well as all materials (soil, metal, paper, etc.) directly or indirectly contaminated by PCBs. Therefore, the management technologies change according to the different materials. There are two kinds of alternative technologies to the use of PCBs: replacement alternatives of PCBs and chemical alternatives to PCBs. In addition, destruction is the preferred alternative to PCBs management.

Replacement alternatives

Dry isolated transformers have been proposed as alternatives to the use of PCBs-containing ones. They could avoid potential fire risks but are less suitable from the point of view of sensitivity to overload and voltage spikes. They do not seem to be viable alternatives at present (Öberg, 2002).

Chemical alternatives

The most frequently used alternatives to PCBs are mineral and silicone oils. Other alternatives are barely suitable from the point of view of PTSs control. For instance, the commercial products Pyralene, Pyrochlor and Inerteen are mixtures of chlorobenzenes and chlorobiphenyls. Inalec contains chlorinated diphenylethane. R-TempR contains a mixture of hydrocarbons and additives including perchloroethylene, tetrachlorethylene; Formel is a mixture of various chlorofluorocarbon (Öberg, 2002).

Finally, 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.

Destructive technology

The most diffused destructive technology used throughout Europe 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:

- Incomplete destruction of PCBs due to their thermal resistance which require the use of high temperature. Destruction Removal

- The generation of dioxins as secondary product. Dioxins are generally formed as recombination 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, alternative destruction technologies have been investigated. The current available technologies are: Gas Chemical Reduction, Electrochemical oxidation, molten metal and molten salt oxidation, solvated electron processes, supercritical water oxidation, plasma arc, base catalysed dechlorination and catalytic dehydrogenation. Most of these alternatives are in the R&D phase and none of these is commercially available in the Region.

Reduction strategy

Reduction strategies may require advanced technology measures involving changes in process conditions or introduction of entirely different processes. These are particularly important to suppress the generation of secondary PTSs like dioxins and furans. Reduction strategies would typically consider the following options:

- Measures involving the improvement of the control of the combustion process, these are applied to all incineration processes to minimise the generation of secondary PTSs. This applies to the non-adverted generation of dioxins and furans.
- Substitution of materials which are the source of dioxins and furans, e.g. chlorinated pesticides and chlorine-based materials and avoid chlorinated substances for bleaching. In this case the generation of dioxins is prevented at the root of the problem.
- Cleaner technology processes (i.e. chlorine free pulp making), again a measure to prevent dioxin and furan generation by substituting the generating technology.
- Avoidance of the use of additives (e.g. flame retardant in plastic) containing chlorine or bromine; although this has to be weighted against the much higher risk involved in fires.
- Separation of waste before the incineration (remove chlorine-based materials from the waste and chlorine treated wood). This would be a particularly important measure to prevent dioxin generation from garbage fires.
- Waste reduction (recycling/reuse of materials or composting of waste).

These measures have to be weighted against the potential implications related to the disappearance of some of these products in particular those that play a key safety role in the electrical and electronic equipment.

In the developing countries of the Mediterranean region and due to the lack of PCBs destruction facilities, interim storage may constitute an important element of the reduction strategy. Some of the key elements to be considered are: packaging, container preparation for shipping, labelling, transportation, monitoring activities and storage facilities (UNEP, 1999b).

5.4.3 Others

The mismanagement and lack of control of marine operations in the Mediterranean constitute one of the main sources of PTSs in the Region. As a consequence, any action taken to reduce these sources has an immediate positive consequence.

5.4.3.1 PAHs

There is no doubt that the entering to force of the MARPOL 73/78 Protocol in October1982 and its ratification by most Mediterranean countries, resulted in the decrease of oil inputs from ship operations. This is witnessed by the decrease in tar balls arriving on beaches in the Mediterranean Region. For instance, systematic monitoring of the quantity of tar along the Israeli beaches in 1975-76 showed that the mean tar content was 3600 g/m of beach from the waterline to the coastal cliff of the beach. A survey with the same methodology carried out in 1984 showed that the mean tar content was only about 139 g/m of beach front (Golik et al., 1987). The same monitoring was carried out in Cyprus where the amount of tar on beaches in the western part of the island in 1978 was about 6000 g/m^2, while this amount was reduced to 120 g/m^2 in 1988 (Loizides, 1994), and to a few grams per m^2 beach in 2000. These findings are an indication of the decrease of potential sources of PAHs in the environment from marine operations.

In addition, the use of BATs in the industrial sectors that are responsible for PAH emissions have also improved the situation. As an example, the production of coke that involves the carbonisation of hard coal by heating in absence of oxygen, results in the generation of high levels of PAHs in the oven doors. The replacement of rigid sealed doors by spring-loaded sealed ones has reduced the emissions from 82 to 13 mg/ton of coke produced, but the emissions during the oven discharge are more difficult to avoid.

5.4.3.2 TBT

The use of TBT-containing antifouling paints are now controlled or banned in many countries. France banned their use on boats of less than 25 m long in 1982. Similar regulations on the usage of TBT in paints came into effect few years later in the European Community (1989) and the Mediterranean region in 1991. The Contracting Parties to the Barcelona Convention agreed to ban the use of anti-fouling paints containing organotin compounds as from 1.7.1991 on (a) hulls of boats having an overall length of less than 25 m and (b) on all structures, equipment or apparatus used in mariculture. Finally, in October 2001, several countries have signed at IMO level, a Convention for phasing out TBT from the ships and boat paints and as antifouling in many other marine applications. This represents a concrete step towards the elimination of an uncontrollable and diffuse source of an important pollutant from the Mediterranean region.

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). A recent visit to the International Boat Fair in Barcelona (November, 2-10, 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.

5.5 TECHNOLOGY TRANSFER ISSUES

The Mediterranean region can be divided into three areas: the north side with most developed countries, the south encompassing developing countries, and the eastern part with some countries with economies in transition. In this context, there are many difficulties to address regionally the issues and the possible solutions. Technology transfer could represent a proper tool to reduce the gaps among the three areas mentioned above. However, it has to be borne in mind that the main sources of PTSs in the Region are located in the developed countries (see Chapter 2). Hence, the focus of alternative technologies and measures for reduction and control has to be in these countries, while measures to reduce the impact of stocks of obsolete pesticides and mismanaged PCBs equipment should be the preferred option for the developing countries of the Region.

Nevertheless, the dimension of future development in the Mediterranean is focused on small and medium enterprises and in revamping some of the old processes and plants in heavy industries. However, the role of large multinational conglomerates in these globalisation times cannot be forgotten. This is particularly true in the context of their growing implementation of Sustainable Development and their associated Social Responsible Investments. Hence, multinational companies, particularly those primarily responsible of past (and present) PTSs primary and secondary sources should engage in the technology transfer and capacity building

programmes in the developing countries of the Region where they operate in conjunction with Governments and NGOs.

In this context, technology transfer can be defined as the diffusion and adoption of new technical equipment, practices and know how between actors within a region or from a region to another. Most transfer in the Mediterranean region is from North to South but more South-to-South transfer needs to be developed.

Technology transfer needs attention within the following aspects: affordability, accessibility, sustainability, relevance and acceptability. Particular attention should be paid to commercial management, market development economic competitiveness and technical adaptation to local conditions. Hence, the receiver of the technology transfer should be the decision maker, rather than the giver.

Technology should be regarded not only as the equipment, but also the information, skills, know-how which are needed to fund, manufacture, install, operate and maintain the equipment. Transfer should be regarded as putting the technical concepts into practice locally in a sustainable framework so that local people can understand the technology, use it in a sustainable manner and replicate projects to speed up successful implementation. Transfer of technology also includes improvement of existing technology.

In the context of information transfer as one of the main aspects of technology transfer, the availability of documentation in the languages of the Region is critical to the success of a collaborative programme. All relevant documentation regarding the risks and alternatives to PTSs should be made available on the Internet and translated and adapted to the non-European languages of the Region. This could have a very high impact on improving the awareness of the dangers of PTSs in the Mediterranean.

The key issue for the success of technology transfer is related to capacity building in the technology recipient countries. In this context there is a clear need to establish intensive and extensive networks of scientists in the Mediterranean Region, which are able to promote and integrate the technology transfer in their socio-economical environment.

In the EU countries, companies rather than government own technology. Therefore successful technology transfer will not happen without the involvement of companies. However, commercial enterprises are at present driven by short-term profit which is in clear contradiction with any potential sustainable development. The exception are those corporations that have adhered to sustainable development principles and that could play a key role in the required changes in the Region. Hence, governments have a clear role in ensuring that technology transfer is not only driven by the market (lack of) laws but also by the general interest of the population.

The key actors of the process of the transfer of technology to improve PTSs management in the Mediterranean region are:

- The governments that have a major role to encourage, enable and ensure the transfer of technology from country to country.
- The finance institutions that should provide grants, soft loans, invest in feasibility studies, demonstrations, capacity building, information exchange and infrastructure development.
- The private sector to provide investment and technology and eventually to develop joint ventures
- The civil society to put pressure on governments and companies (through consumer action) to improve their environmental performance.
- The Regional actors: MAP, Regional Activity Centre for Cleaner Production (RAC/CP), MEDPOL, Blue Plan Regional Activity Centre (RAC/BP), EU, World Bank and UNEP.

In the context of technology transfer for PTSs management in the Region, the role of RAC/CP is particularly relevant, since its main objectives include (Macià, 2002):

- Technical support to the national focal points for Cleaner Production and consequently to advise on alternatives and reduction measures for industrial PTSs.
- The exchange of information, experiences and experts on Cleaner Production technologies and consequently the potential assistance in the dissemination of information regarding PTSs management.
- The co-operation on the definition of the Best Available Technologies (BATs) and Best Environmental Practices (BEPs) in the Mediterranean context. This is a relevant objective in order to ensure that the Technology Transfer in PTSs management is adequate to the capabilities of the technology recipient.

- Promoting demonstration projects that could show the management of key PTSs in the Region.
- Organisation and promotion of training activities that could include the required information on the development of proper guidelines for PTSs management.
- Publication and dissemination of case studies and successful activities carried by industry sectors of the Region. This could include the translation to non European languages of the relevant PTSs management information.

5.6 IDENTIFICATION OF NEEDS, FOR REGIONAL CO-OPERATION

The level of commitment and resources dedicated to assessing environmental improvement, associated with the technical, scientific and policy measures taken, can be used as an indicator of the seriousness of state officials to improve environmental protection. Three indicators could be considered to evaluate the overall capacities of the Mediterranean countries to develop proper management systems for PTSs:

- Existence of national definition and regulation of PTSs
- Existence of national inventories of PTSs
- National capacities to manage PTSs

The data clearly indicate that most of the countries do not have yet sufficient resources for an adequate implementation of these standards. In this context, regional co-operation should be strengthened for the development of national plans for the management of PTSs. These co-operative efforts can be focused on two main aspects, namely monitoring capacity and management performance, and in a number of actors, such as central government agencies, local municipalities, private firms, NGOs, and technical and scientific communities.

5.6.1 Monitoring capacity

The definition of the problem in terms of the relevant data needed is a prerequisite to find the proper management solutions. As already has been pointed out in previous sections, the Mediterranean region exhibits important data gaps regarding hazardous substances. A more comprehensive understanding of how and where hazardous substances are used and released, and in what quantities, and the situation regarding disposal and/or storage of existing stockpiles and major sources of hazardous by-products will need attending to in the region (Chapter 2). Domestic and regional monitoring efforts should continue to study multi-media transport across air, rivers, seas, and soil, and the resultant environmental and human concentration levels. Furthermore, research on environmental and human health effects needs to try and improve our understanding of the short-term and long-term effects of exposure to hazardous substances to wildlife and humans (chapters 3 and 4).

Regional co-operation may successfully stimulate the production and dissemination of technical and scientific knowledge, and also expand and sustain regional environmental assessment capacities. Such assessment work will be instrumental as a basis for prioritising issues and formulating joint policies.

For comparative reasons, further standardisation (or, at least, increased data compatibility) of research and assessment methodologies and reporting requirements is needed. This would both facilitate the compilation of reliable regional state of the environment assessments, and cross-country comparisons. However, the efforts carried out until now in quality control/quality assurance (QC/QA) in monitoring programs at regional level are not reflected in the existence of adequate data banks. For example, a number of problems have been identified associated with the submission of results by the MEDPOL participating institutions that need to be conveniently addressed:

- *Lack of comparable and transparent informatio*n. As no standard format exist to comply with the reporting obligations, a lack of comparable data is faced by the Secretariat, which encounters great difficulties when compiling the information.
- *Lack of a harmonised reporting system*. The Mediterranean Action Plan does not include a reporting system for the Contracting Parties of the Convention to comply with their reporting obligations. Only under the Emergency Protocol does a Regional Reporting System exist.
- *Lack of a concrete and precise calendar according to which Parties should submit their reportin*g. Although a reporting periodicity is stated within the Convention and its Protocols, no specific schedule exists for the Parties to submit their reports.

- *Lack of compliance* by the Parties with respect to their reporting obligations. Submission of incomplete reports and non-compliance with reporting periodicity. As no binding procedure exists, neither the Parties nor the Secretariat are worried about compliance with the reporting obligations.

It is arguable that the two main difficulties facing the development of an environmental regional policy are the lack of funds and reporting obligations. Much valuable work has been carried out but is underused in terms of practical risk reduction impact due to the difficulties in establishing and maintaining a regional network of active integrated assessment that works in an iterative manner relating monitoring, modelling, policy making and compliance. Such processes have been established at a national and European scale and it should be a priority to extend them to the Mediterranean region. The existence of such long term regular reporting practices increases the value of the effort of all components and monitoring data are more valuable if they are useful for modellers and models are more valuable if they are liked with users such as policy makers the public or scientist doing the monitoring.

Monitoring and modelling will require much attention as both are necessary to estimate the emission of PTSs, the pools of existing PTSs in the environment and their trends. Concerning modelling there is a task of particular importance in terms of establishing better working communication between existing laboratory chemical and toxicological information for PTSs and ecosystem and trophic web models. Recent work (UN/ECE/LRTAP and WHO) has indicated that for most PTSs, excluding occupational or accidental sources, the main exposure route is food for humans and wild life. Many models of terrestrial an marine ecosystems exist but few have been adapted to simulate the flow and impact of PTSs in ecosystems and the human food chain.

It should be underlined, at the end, that Information Technologies have a great potential for improving access of users of different profiles (public, scientist, industry, policy, compliance monitors) to large amounts of dispersed and diverse available information. A much more intense and effective relation between experts and models, simulating different environmental components (such as chemical toxicological and epidemiological /ecological/geophysical and transport models) or activity sectors (industry/transport/agriculture), will be needed and such communication can be simplified with Machine Learning and Evolutionary Computing tools. Similar current efforts should be spent to harness the information processing resources available in order to extract "expert common sense" from available models and data for a particular problem or application.

5.6.2 Management performance

It is obvious that the development of management structures and the implementation of national action plans cannot take place under the same conditions in all countries. The southern countries of the region are those facing major problems with regards to hazardous waste treatment capacities and safe handling of obsolete stocks and, therefore, those primarily requiring external co-operation. The problem fully remains for the treatment of organohalogen wastes, which have no recycling value and require major investments.

The conclusion, which may be drawn from this point, is that technologies for the treatment of industrial waste that could be developed are those generating a local economic activity solely based on supply and demand. Treatment technologies involving costs cannot be developed as long as they are not economically integrated in production costs. It is therefore evident that any national action plan should be preceded by the establishment of a pollutant release and transfer register. National and regional action plans should, therefore, consider the following aspects:

- Development of a systemic approach for the global management of hazardous wastes.
- Extension of registers to production flows
- The issue of environmentally rational management of hazardous industrial waste

All environmental conventions have raised the problem of the treatment of industrial effluents generated by producers or users of dangerous substances. There are three aspects, which are indivisibly linked to this issue and which are often overlooked during the implementation of conventions: the Technology/Regulation links, the Technology/Financing links and the Financing/Regulation links.

The search for solutions should therefore aim at a global approach which would integrate these three parameters. Today, however, environmental conventions have been implemented according to a pattern that does not take into consideration the close interrelation between them. It is therefore of primary importance to encourage in each country the creation of working groups bringing together the national operators of the different conventions, in order to integrate all the following aspects of the problem in a global manner:

- Financial capacity
- Technological capacity
- Harmonisation of regulations

As a key element, national action plans should take into account each country's economic situation. In this respect, the North/South financial responsibilities should be considered for an effective implementation of environmental conventions in the southern countries.

The North/South pattern as it applies to the Mediterranean region

The large debate that has been opened focuses on the historic responsibility of Northern countries, which in the absence of precautionary principles that did not exist at the time, have released substances on the market without being yet aware of their characteristics of persistent pollutants or the by-products generated by their thermal decomposition. It would be very difficult to convince them of the contrary, in the sense that it is impossible to make them responsible of the absence of the precautionary principle when they purchased these products in a situation of total technological dependence. For this reason, the financial instruments that should be provided in order to allow the countries of the South to meet with their obligations need to take into account the legitimate demands of the private sector in these countries.

In addition to the historic nature of these products, the increasingly more stringent environmental regulations in industrialised countries compel private industries in these countries to relocate their production facilities in the countries of the South and. in doing so, they also relocate emissions and transfer pollutants to these countries. This is taking place within a globalisation context where trade activities are subject to deregulation rather than regulation.

Definition of priority actions of National Plans

Experiences under way in the countries of the South demonstrate the difficulties that are associated with the implementation of PTSs related MEAs. The main difficulty, unquestionably, resides in the absence of financial instruments. In the face of this situation, priority measures should be adopted, based on cost/effectiveness criteria.

A number of measures, which meet these cost/effectiveness criteria, could be outlined as follows:

- Institutional capacity building in individual countries.
- Introduce in national environmental regulations, as a priority, the obligation to declare possession and/or use of dangerous substances which cause emissions and transfers.
- Control and reduction of waste at source. This is normally the case for dioxins.
- Promote non-polluting technologies.
- Develop containment facilities before disposal. This applies in particular to pesticides and PCBs.
- Management of obsolete stocks

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6 CONCLUSIONS

6.1 IDENTIFICATION OF THE BARRIERS

The wide variation in political and economic systems as well as historic differences has led to great discrepancies in the level of development between Mediterranean countries. The highly developed industrial countries in the North (e.g. France, Italy and Spain) and countries on the way to become industrialised (e.g. Greece and Turkey) stand in stark contrast to the countries in the south. The large spread between the northern-rim and the southern- and eastern-rim nations is also reflected in other indicators such as the public expenditure on health and education, the life expectancy at birth and the adult illiteracy rate. On the other hand, the northern countries are, in general, disbursing official development assistance to third countries not necessarily in the region, whereas those in the south are primarily receivers.

These differences have significant implications for the establishment of environmental standards in the countries of the Region because there is a clear relationship between GDP, expenditure in education and the application of environmental control and environmental management. Countries that cannot satisfy the basic needs of their citizens cannot afford to digress into environmental management systems and these are only applied once a certain GDP threshold is attained.

This socio-economic context has also important consequences when addressing the potential technology transfer issues. Proper technology transfer opportunities can be created by making emphasis on education, social and environmental awareness and through the creation of long-term networks of scientific and technical collaboration between the countries of the Region. At the same time, the opportunities created by the increased internationalisation of the markets have to be monitored by the public administrations of the receiving countries, as well as by the rest of stakeholders, so that the environmental standards are kept throughout the process. It is clear that the northern countries bear much of the responsibility of the actions taken, or not taken, today and over the past two centuries that shape the present state and delineate the future.

In spite of the diverse socio-economic development in the Region many of the countries share quite ancient cultural roots. In this cultural heritage the environment never played a relevant role, mainly because basic resources have been abundant to the primitive populations of the Region prior to the industrial era and the associated migrations. In this context, many Mediterranean countries lack at present adequate capacities and capabilities to achieve sound management of persistent toxic substances. These include:

- Inadequate institutional capabilities to manage PTSs in particular and toxic and hazardous waste in general.
- Inadequate legal framework for the proper management of chemicals and the implementation and enforcement of regulations for industrial and consumer hazardous substances.
- Inadequate technical capabilities to assess the potential toxicity and to control the nature and purity of imported or domestically produced chemicals.
- The handling of chemicals is normally done by poorly informed or trained personnel, especially operators in SMEs.
- Lack of capabilities to cope with chemical accidents, including the subsequent rehabilitation of the environment.
- There are not sufficient guidelines for labelling, packaging, handling, transport, and storage of these products.
- There is a lack of adequate management system and facilities for treatment and disposal of hazardous wastes.
- And more importantly most of the countries of the Region have no access to the adequate financial resources to support various activities for a proper management of PTSs.

There is a very low public awareness and education on the issues of PTSs and consequently no political driving force to amend the issue.

There are also many barriers, especially in developing countries, from the standpoint of the adoption of alternative technologies. Some of the alternatives are simply more expensive both in price and in the resources

required to apply them compared to the older more hazardous compounds. Some alternatives are believed to be more acutely toxic to the applicator than the PTSs and, therefore, more hazardous to the individual, thus adding a human health cost dimension.

Other barriers to adoption include education and training. Education and training on both the older compounds as well as the possible alternatives are necessary for everyone in the consumer chain including the individual users and vendors.

The infrastructure and regulations that are needed to manage the use of pesticides, as well as educate and train individuals in the use of possible alternatives is not fully developed in most of the countries of the Region. The regulatory structure that most of the developing countries of the Region have adopted is based on the developed countries regulatory structure. This structure is often not adaptable or appropriate to the particular socio-economical situation in the developing country. In addition, both financial and human resources needed to make such structures function effectively are often insufficient. Once a regulatory system is in place compatible with the resources available, then the gradual elimination of older and hazardous compounds can be initiated.

Priority to the implementation of alternative technologies should be given to the PTSs which entail a larger risk to the Regional environment. For those compounds, pilot projects should be initiated to disseminate the use of alternative technologies and/or compounds.

6.2 PRIORITY PTS ENVIRONMENTAL ISSUES IN THE REGION

The issues identified here are the result of the information collected and reported in the previous chapters of the report and of the "scoring exercise" performed by the experts participating in the Regional Workshops (Annex I). The experts were supposed to score the chemicals to be assessed from 0 to 2, for the different sections of the report (sources, levels, effects and gaps), depending on whether they were of no concern (0), of local concern (1), and of regional concern (2). The synopsis of the results from this exercise gives an overview of the various aspects of the occurrence of PTSs within the Region. Nevertheless, precaution should be taken when looking at this dataset as a basis to prioritise PTSs and hence to orientate future research and actions. In fact, judgements expressed by the experts necessarily reflect their specific experience and their knowledge/perception of the problems, also on a Country basis. Moreover, restrictions inherent to the scoring system itself may not adequately weigh Country based, field-specific information, this possibly resulting in misleading conclusions.

Table 6.1 summarises the responses provided by experts from 18 countries, organised by categories (regional concern, local concern and no concern). Obviously, a low score may imply either the chemical is of low concern or there is a data gap preventing any assessment. For example, the Mediterranean EU countries, Croatia and the FR of Yugoslavia have, in general, a rather acceptable knowledge of the different issues (sources, levels, ecotoxicological and human effects) for chlorinated pesticides, PCBs and dioxins/furans, since the experts gave scores "0-1" for the data gaps and "1-2" for the weight of the concern arisen from their presence in the environment. This was also the case with the southern countries of the region for chlorinated pesticides, which were scored "1" as well as the data gaps, but scored "2" most of the other compounds because the lack of data.

Sources: In general, organochlorine pesticides were scored with "0" based on the fact that the use and import of these compounds is already banned in most countries of the region. However, DDT and HCHs were scored with "l" because of the existing stocks and illegal use in some countries. For dioxins and furans, most experts identified a data gap, although their appraisal was based on the usual sources in other countries. Hence, they were scored with "1-2". For some compounds, such as organomercury, PBB/PBDE, endosulfan, phthalates and alkylphenols, the scores emphasised a lack of data.

Environmental levels: In general, organochlorine pesticides were scored with "0", excluding DDTs and HCHs that wer scored with "1", based on the levels detected in different compartments. However, some countries, especially in Eastern and Southern Mediterranean, noticed the absence of regular monitoring programmes for these compounds as an important data gap. This was also the case of dioxins and furans. Similar to the scoring of sources, organometallic compounds, PBB/PBDE, endosulfan, phthalates, alkylphenols and PCP, were only evaluated by a few experts because of the lack of data.

Ecotoxicological and human effects: The scoring presented in Table 6.1 reflects primarily the existence of important data gaps for most compounds.

In summary, industrial PTSs including PCBs and dioxins/furans are of Regional concern with respect to their sources and their potential effect on humans. PCBs are ubiquitous in the Mediterranean region and the status of

their management is not satisfactory. This would indicate that the measured constant temporal trends are the result of the widespread distribution of the sources in the Region and the lack of control about PCBs stocks. Dioxins and furans continue to pose a Regional threat because of the lack of proper control in combustion facilities and their generation from garbage combustion.

Pesticides are perceived mainly as local scale problems, although their environmental levels in the Region are quite homogeneous. DDTs, HCHs and HCB remain a perceived regional problem although the environmental levels indicate a decreasing trend in all vectors and compartments. Other chlorinated pesticides (i.e., "drins", mirex,…) are categorised of no concern. In fact, mirex and toxaphene have not been used in the region.

The extent and spread of the use of detergents in the Region would indicate that alkylethoxylates could constitute a Regional scale problem but proper data is lacking. The same occurs with other PTSs, like phthalates, PBDEs, PCP and organometallic compounds.

Finally, the chronic pollution by the ubiquitous PAHs has been recognised as a problem that needs to be addressed locally.

Table 6.1. Scoring results of the regionally assessed PTSs, organised by categories (regional concern, local concern and no concern).

	Sources	**Environ. levels**	**Ecotox. effects**	**Human effects**
Regional concern (score 2)	PCBs dioxins&furans	----	----	dioxins & furans
Local concern (score 1)	DDT HCB HCHs PCP* PAHs org. mercury compds.* org. tin compds. PBB/PBDE* phthalates* endosulfan* alkylphenols*	DDT HCB PCBs dioxins&furans HCHs PCP* PAHs org. mercury compds.* org. tin compds. PBB/PBDE* phthalates* endosulfan* alkylphenols*	DDT HCB PCBs dioxins&furans HCHs PAHs org. mercury compds. org. tin compds.	DDT HCB PCBs org. mercury compds.
No concern (score 0)	"drins" heptachlor chlordane mirex toxaphene	"drins" heptachlor chlordane mirex toxaphene	"drins" heptachlor chlordane mirex toxaphene PCP* phthalates* endosulfan* alkylphenols*	"drins" heptachlor chlordane mirex toxaphene HCHs* PCP* PAHs* org. tin compds* phthalates* endosulfan* alkylphenols*

* Limited concern due to lack of data

Besides these general conclusions, some specific hot spots deserving priority attention have been identified. The list is intended to be illustrative rather than exhaustive. Some of them have already been described in section 3.5.

The elimination of stockpiles of obsolete PTSs and the remediation of abandoned chemical storage facilities existing in all countries, and many of them not inventoried, is one of the first priorities for action. These exist in Albania (Durres), the FYR of Macedonia (Skopje), Algeria (Ain Temouchent, Alger, Mustaganem, Sidi bel Abbas, Tizi Ouzou, Mascara, Tipaza, etc), Syria (Hama), Morocco, Lybia, just to mention a few.

Another priority area concerns the groundwater pollution by PCBs of the karstic region of Eastern Adriatic, due to inadequate landfilling or accidents. This encompass Slovenia (Semič town, Krupa, Lahinja and Kupa

rivers), Croatia (the coastal area of Zadar and the River Dubrovačka), FR Yugoslavia (Kragujevac area), etc. In this respect, comprehensive monitoring programs should be adopted. Compounds of regional concern are PAHs, PCBs, DDT, HCHs and HCB.

In relation with the cases reported above, the exposure of the population living in these highly contaminated areas and in their surroundings should be worth to be fully characterised.

Localised inputs of PTSs have been identified from freshwater discharges in coastal areas but they have neither been quantified nor risk assessed. First, a correct estimate of PTSs loads of the major rivers of the region (e.g. Seine, Rhône, Po and Nile estuaries) is needed. Second, the environmental quality of some coastal enclosures (e.g. Izmit and Iskenderun Bays, Thermaikos Gulf, Sfax Bay, Venice Lagoon, etc.) with respect to PTSs loads should be categorised.

Sewage outfalls from highly industrialised and populated cities such as Marseille, Barcelona, Naples, Nice, Genova, Alexandria and Algiers, as well as inland waters (e.g. Po, Ebro, Llobregat, Rhone, Seine, Nile, Sava, Kupa, etc.) and waste waters from representative sewage treatment plants should be fully characterised.

The atmospheric compartment is one of the less studied in the region, and measurements are not really representative for a global assessment. Therefore, comprehensive monitoring programs in rural and urban areas should be adopted. Compounds of regional concern are dioxins/furans, PCBs, HCHs, HCB and PAHs.

Finally, field work for improving the modelling of long-range transport and transformation of PTSs over the Mediterranean Sea should be highly encouraged.

6.3 RECOMMENDATIONS FOR FUTURE ACTIVITIES

In order to tackle the problems documented previously the following technical, institutional, social and economical recommendations are formulated. Some of these recommendations are region-specific, while others are valid for all regions. Also, some are particular to the management of PTSs, while others are more general challenges to regional co-operation that have important implications for hazardous substances management, as well. In particular, five major inter-connected challenges are addressed. It is foreseen that the development is done depending on the priorities and needs identified by each of the countries of the Region.

6.3.1 Monitoring and data reporting

- A more strong and co-ordinated effort is needed to identify and survey sources, stocks and reservoirs of PTSs in the Region. This should be a first priority and a substantial part of any monitoring programme.
- It is important to generate the relevant data related to control of PTSs release into inland waters, sea, air and soil and information on polluted or contaminated sites.
- Monitoring of potential health consequences of PTSs mismanagement in the Region should also be a priority.
- To achieve the above mentioned goals, national monitoring programmes need to be implemented and co-ordinated through the existing regional monitoring programmes. Monitoring programs should include standardised sampling and analytical methods (QC/QA procedures) to improve comparability.
- Concurrently, there is also the need to establish national and internationally accredited laboratories to assist the monitoring institutions in the development of quality assurance systems. An integral part of PTSs management is the establishment of database systems within modern information technologies.
- The importance of reporting obligations for the assessment of the situation and its changes over time and for the monitoring of compliance and progress in approaching the declared objectives need to be highlighted in any national monitoring plan.

6.3.2 Technical

- Once the existing PTSs inventories are truly identified a key priority is the safe storage and subsequent disposal and re-use of PTSs in the Region. Stockpiles of PCBs and obsolete pesticides should constitute the objective of co-ordinated management efforts, technology transfer and international collaboration.
- There is a need to establish a central reserve of expertise, which could co-ordinate and actively manage the generation of data to establish emission inventories.

- It would be useful to stress the importance of adopting cleaner production processes. These include; good housekeeping procedures, toxic waste minimisation, more efficient use raw materials, substitution of toxic substances by less toxic or less concentrated alternatives and when this is inevitable proper handling and management of toxic wastes. The resources available through the RAC/CP and other regional activity centres should be used to promote cleaner alternative processes that exclude the generation of PTSs.
- Multinational corporations involved in the origin of the PTSs mismanagement problem: electrical companies, oil producers and shippers, chemical and pharmaceutical companies, etc., that operate at a Regional scale should play a proactive role in the technology transfer and educational issues as part of their Social Corporate Programmes.

6.3.3 Institutional and legal frameworks

- The Basel convention should be properly enforced to exclude the illegal transfer of obsolete pesticide and PCBs stocks between the countries of the Region.
- Update the present legislation on import/export, GATT agreements should include the required monitoring and enforcement according to the Stockholm and Barcelona Conventions.
- The countries of the Region should be encouraged to ratify related MEAs such as Stockholm and Barcelona convention.
- The enforcement of reporting obligations for the assessment of the situation and its changes over time and for the monitoring of compliance and progress in approaching the declared objectives should be a key consequence of the application of the relevant conventions.
- There is a need to strengthen the co-ordination and co-operation between transnational, regional, national and local administrations actively involved in the management of PTSs in order to avoid overlapping responsibilities.
- It is necessary to further develop the co-ordination activities between the various MEAs secretariat at regional levels to ensure proper harmonisation.

6.3.4 Public awareness

- It is necessary to integrate the diverse contamination issues for different educational levels in order to raise the general environmental and scientific literacy and promoting public awareness including the collective attitude towards municipal and industrial waste management.
- It is very important to strengthen the role of NGOs at regional and national levels. This would ensure an effective dissemination of information to the public
- Develop the education and training programme of cleaner production concepts that could be co-ordinated by the RAC/CP.
- Preparation and dissemination of relevant PTSs management information in the languages of the Region.

6.3.5 Financial

- The development of national economic instruments to support the financial requirements for the proper management of PTSs, particularly in the least affluent States of the region.
- Initiate contacts and co-operation with regional and international funding institutions to develop and support financial assistance programmes in the Mediterranean countries facing difficulties in handling and disposing stock piles of PTSs. There is still a high need for more comprehensive capacity building efforts in these countries that will require financial resources.

ANNEX I LIST OF PARTICIPANTS TO TECHNICAL MEETINGS

i. First Regional Workshop on Assessment of PTSs sources and concentrations in the environment (4-6 February 2002, Athens, Greece)

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ii. Second Regional Workshop on Assessment of (eco)toxicological impact of PTSs and transboundary transport (3-5 April 2002, Istituto Superiore di Sanità, Rome, Italy)

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iii. Priority Setting Meeting (26-28 June 2002, Barcelona, Spain)

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ANNEX II GENERAL DEFINITIONS OF PTS

i. Pesticides

Aldrin

Chemical Name: 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene ($C_{12}H_8Cl_6$). **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 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 18000 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 x 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 x 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 x 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 metabolised 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 x 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 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 x 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 is 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 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.

ii. 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 PCB 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.

iii. Unintended by-products

Polychlorinated dibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs)

Chemical Name: PCDDs ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDFs ($C_{12}H_{(8-n)}Cl_nO$) 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 characterised 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 refers to the 2,3,7,8-substituted compounds (17 congeners) that are agonist for the AhR. All the 2,3,7,8-substituted PCDDs and PCDFs plus coplanar PCBs (with no chlorine substitution at the ortho positions) show the same type of biological and toxic response. Possible effects 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. The most sensitive groups are foetus and neonatal infants.

Effects on the immune systems in the mouse have been found at doses of 10 ng/kg bw/day, while reproductive effects were seen in rhesus monkeys at 1-2 ng/kg bw/day. Biochemical effects have been seen in rats down to 0.1 ng/kg bw/day. In a re-evaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to recommend a range of 1-4 TEQ pg/kg bw, although more recently the acceptable intake value has been set monthly at 1-70 TEQ pg/kg bw.

iv. Regional specific

Hexachlorocyclohexanes (HCHs)

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. HCHs 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.

Endosulfan

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 x 10^{-4} mm Hg at 25°C; log K_{OW}: 2.23-3.62.

Discovery/Uses: Endosulfan was first introduced in 1954. It is used as a contact and stomach insecticide and acaricide in a great number of food and non-food crops (e.g. tea, vegetables, fruits, tobacco, cotton) and it controls over 100 different insect pests. Endosulfan 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-endosulfan.

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, endosulfan is rapidly broken down to the corresponding sulphate, on most fruits and vegetables, 50% of the parent residue is lost within 3 to 7 days.

Toxicity: Endosulfan 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 endosulfan than male rats. The α-isomer is considered to be more toxic than the β-isomer. There is a strong evidence of its potential for endocrine disruption.

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 x 10^{-5} mm Hg at 20°C; log K_{OW}: 3.32 – 5.86.

Discovery/Uses: It is used as insecticide (termiticide), fungicide, non-selective contact herbicide (defoliant) and, particularly as 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 persist 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, with a predominance in commercial mixtures of 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 x 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 varies 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

Properties: Solubility in water: 0.00014 -2.1 mg/L at 25ºC; vapour pressure: from 0.0015 x 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 vary 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 produce 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 x 10^{-5} (DBP) and 6.4 x 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 damaged the liver and kidney and affected the ability to reproduce. There is no evidence that DEHP causes cancer in humans but they have been reported as endocrine disrupting chemicals. The EPA proposed a Maximum Admissible Concentration (MAC) of 6 μg/L of DEHP in drinking water.

Nonyl- and Octyl-phenols

Chemical Name: NP: $C_{15}H_{24}O$; OP: $C_{14}H_{22}O$. **CAS Number**: 25154-52-3 (NP).

Properties: Solubility in water: 6.3 μg/L (NP) at 25°C; vapour pressure: 7.5 x 10^{-4} mm Hg at 20°C (NP); log K_{OW}: 4.5 (NP) and 5.92 (OP).

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 end degradation products of APEs under both aerobic and anaerobic conditions. Therefore, the major part is released to water and concentrated in sewage sludges. NPs and t-OP are persistent in the environment with half-lives of 30-60 years in marine sediments, 1-3 weeks in estuarine waters and 10-48 hours in the atmosphere. Due to their persistence they can bioaccumulate to a significant extent 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 3000 µg/L. In chronic toxicity tests the lowest NOEC are 6 µg/L in fish and 3.7 µg/L in invertebrates. The threshold for vitellogenin induction in fish is 10 µg/L for NP and 3 µg/L for OP (similar to the lowest NOEC). Alkylphenols are endocrine disrupting chemicals also in mammals.

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 x 10^{-7} mm Hg at 20°C (TBTO) 3.5 x 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 x 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 volatilisation 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 foetus. 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.

ANNEX III STATUS OF COUNTRIES TO PIC

Substance	Banned for Plant Protection Use	No Consent (year)	No information available
Aldrin	European Union (95): For uses other than plant protection written authorisation is required for import into France, Italy and Spain	Cyprus (93), Jordan (93), Lebanon (93), Malta (93), Morocco (93), Slovenia (98), Syrian Arab Republic (93), Turkey (97)	Albania, Algeria, Bosnia-Herzegovina, Egypt, Israel, Libyan Arab Jamahiriya, Tunisia.
Dieldrin	European Union (95): For uses other than plant protection written authorisation is required for import into France, Italy and Spain	Cyprus (93), Jordan (93), Lebanon (93), Malta (93), Morocco (93), Slovenia (98), Syrian Arab Republic (93), Turkey (94)	Albania, Algeria, Bosnia-Herzegovina, Egypt, Israel, Libyan Arab Jamahiriya, Tunisia.
Chlordane	European Union (95): For uses other than plant protection written authorisation is required for import into France, Italy and Spain	Cyprus (97), Jordan (95), Lebanon (93), Malta (93), Morocco (95), Slovenia (98), Syrian Arab Republic (93), Turkey (94)	Albania, Algeria, Bosnia-Herzegovina, Egypt, Israel, Libyan Arab Jamahiriya, Tunisia.
Heptachlor	European Union (95): For uses other than plant protection written authorisation is required for import into France, Italy and Spain For other uses than plant protection, national authorisation schemes apply	Cyprus (97), Jordan (95), Lebanon (93), Malta (93), Morocco (95), Slovenia (99), Syrian Arab Republic (93), Turkey (94)	Albania, Algeria, Bosnia-Herzegovina, Egypt, Israel, Libyan Arab Jamahiriya, Tunisia.
DDT	European Union (95):For uses other than plant protection written authorisation is required for import into France, Italy and Spain Slovenia (98): Not registered	Cyprus (93), Jordan (93), Lebanon (93), Malta (93), Morocco (93), Syrian Arab Republic (93), Turkey (94)	Albania, Algeria, Bosnia-Herzegovina, Egypt, Israel, Libyan Arab Jamahiriya, Tunisia.

Substance	Banned for Plant Protection Use	No Consent (year)	No information available
HCB		Bosnia and Herzegovina (97) Cyprus: There are no registered pesticides containing HCB as an active ingredient. According to national legislation, imports into Cyprus (of any pesticide containing HCB) are not allowed. European Union (00) Jordan (01), Malta (98), Slovenia (98), Syrian Arab Republic (98), Turkey (97)	Albania, Algeria, Egypt, Israel, Lebanon, Libyan Arab Jamahiriya, Morocco, Tunisia.
Gamma-HCH	Cyprus (97) → Severely restricted pesticide. Small quantities of this chemical are still imported from time to time for specific uses, i.e. wood preservative. European Union → For import prior written authorisation is required: France, Greece, Italy, Spain and Portugal. Slovenia (98) → Prohibited for Plant Protection Use Syrian Arab Republic (98)	Bosnia and Herzegovina (97) Jordan (01) Turkey (97)	Albania, Algeria, Egypt, Israel, Lebanon, Libyan Arab Jamahiriya, Malta, Morocco, Tunisia
HCH Mixed isomers	European Union (95) → Prohibit for Plant Protection Use. For uses other than plant protection, written authorisation is required for import into France, Italy, and Spain.	Cyprus (93) Jordan (93), Lebanon (93), Malta (93), Morocco (93), Syrian Arab Republic (93), Turkey (94)	Albania, Algeria, Bosnia and Herzegovina, Egypt, Israel, Libyan Arab Jamahiriya, Slovenia, Tunisia

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