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The KJIST- UNU – UNESCO  
International Workshop on

# Regional Environmental Quality in the East Asian Coastal Hydrosphere:

*Environmental Quality Guidelines and Capacity  
Development*

Held at the Kwangju Institute of Science and Technology,  
Gwangju, Korea, January 26-27, 2003

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# Preface

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This workshop focused on the regional environmental quality in the East Asian coastal hydrosphere. We believe that this is an important issue for the region and UNU is working towards the development of environmental quality guidelines and capacity building for monitoring. The workshop included presentations on various aspects of these issues and provided for a series of discussions on various aspects of the undertaking.

UNU's work on environmental monitoring and governance entered its third phase in 2002, with a new project on Monitoring of Persistent Organic Pollutants (POPs) in the East Asian Region, thanks to the generous support from Shimadzu Corporation, Japan. Many of the project participants from the nine countries in UNU's network for this project were included amongst the workshop participants, representing China, Indonesia, Japan, Korea, Malaysia, the Philippines, Singapore, Thailand and Viet Nam. This group of scientists has been working together for over six years on the collection of environmental data. UNU is proud of the achievements that have been made by this group, and we look forward to continuing to develop our work together in the years to come.

This workshop discussed the state of pollution in the region and the available environmental guidelines for interpreting data on environmental quality. We focused our discussions on ways to develop guidelines for determining environmental quality on a regional basis. I realize that this is a very challenging undertaking and we did not aim to resolve all issues in this workshop, but to take steps in this direction that will lead us to our ultimate goal. Our discussions during the second day of the workshop then focused on monitoring methodologies and ways to harmonize various monitoring activities in this region.

The workshop further aimed to enhance the existing capacity for environmental monitoring in the East Asian Hydrosphere. The two days of discussions in Gwangju were followed by a training session for young scientists, held in Japan. This training is important in order to ensure the future of our environmental monitoring activities in the region, and it is supported by UNESCO.

This workshop was generously hosted by the Kwangju Institute of Science and Technology (KJIST). This is in continuation of our excellent collaboration with KJIST that has been developing over many years. We were particularly glad to be at KJIST for the discussion of regional environmental quality, and to benefit from KJIST's considerable expertise in the field of environmental chemistry. This workshop also provided us with the opportunity to learn about the state of the science research being undertaken in Korea on this subject from researchers at KJIST and at other Korean institutes.

I would also like to acknowledge the support provided by UNESCO for organizing this workshop and hope that we can continue this collaboration in future as well.

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# Workshop Overview

## **Concept:**

During this regional workshop on environmental monitoring and governance in the East Asian coastal hydrosphere, hands-on training and substantive discussions will focus on building capacity for the monitoring of POPs in the East Asian coastal hydrosphere. Workshop participants will be selected from the region, including the UNU network.

## **Aims:**

1. A plan of action for the development and dissemination of environmental quality guidelines and information on the threats from POPs pollution in the coastal areas this region.
2. A research plan for an inter-laboratory calibration of sample analysis
3. A scoping exercise for the development of environmental quality guidelines and the potential for a regional early-warning system
4. Training for laboratory staff-members in analytical techniques

## **Activities:**

26-27 January 2003: Substantive Discussions, Kwangju Institute of Science and Technology (KJIST), Korea.

During this part of the workshop, collaborative discussions will focus on the interpretation of environmental monitoring data and the development of guidelines for environmental quality in terms of pollution in coastal and inland waters. The discussions will include consideration of existing health standards as presented by WHO and those adopted by countries in other regions. Ideas for a regional inter-laboratory calibration exercise will also be discussed.

Selected participants will travel from Kwangju, Korea, to Hadano, Japan on 28 January 2003 to attend a training session.

29-31 January 2003: Training session in analytical techniques, Hadano, Japan

This training session will be offered to the junior laboratory staff at participating institutions in the region. The training will be held in Hadano, Tokyo, at the facilities of Shimadzu Corporation, Japanese specialist manufacturers of scientific instruments. It will include practical support and instruction on the use of GCMS and other scientific equipment necessary for the collection and analysis of environmental samples. One participant for the training session will be chosen by each of the National Project Coordinators at the participating laboratories.



# Summary of Workshop Sessions and Discussions

The workshop included a series of sessions including substantive discussions on the monitoring work that is currently being carried out in this region, beginning on the first day with a review of the existing data, and a discussion of methods for its interpretation through the use of environmental guidelines. On the second day, the presentations focused on analytical techniques used by the project participants, and those that are currently being developed in Korea. The discussions during this second day concentrated on the issue of interlaboratory calibration amongst the network of laboratories. These discussions were intended to inform the design of UNU's proposed interlaboratory calibration exercise, to be conducted during the coming year. This report presents a summary of the workshop sessions in order of appearance.

**January 26, 2003**

## Session 1: Overview of Current Activities and Data on Environmental Quality in East Asia

*Chairs: Prof. M. Suzuki (UNU) and Prof. S. H. Moon (KJIST)*

During this opening session, four presentations gave an overview of the current state of knowledge regarding EDC's in East Asia. In this regard, Dr Zafar Adeel, Project Manager of the UNU project on Environmental Monitoring and Governance in the East Asian Hydrosphere - Monitoring of POPs in the East Asian Region started off the session with a presentation on the need for Environmental Quality Guidelines and Early Warning Systems to Combat Pollution in the East Asian region. Adeel proposed that countries in this region should coordinate their efforts to conduct research and monitoring for environmental pollutants, particularly POPs. He also suggested that the joint effort should include the development of environmental quality guidelines that are shared on a regional basis. Finally, the presentation underlined the need for a regional early-warning system to be developed to identify "hotspots" in areas with high or rapidly increasing pollutant levels.

The proposal from UNU was followed up by a review of the results of previous UNU monitoring activities in East Asia, presented by Caroline King. This presentation and the following discussions highlighted the fact that although UNU has collected an interesting body of data on EDC's in this region, based on common analytical techniques, the task of drawing useful comparisons and conclusions from it is complicated by the differences between the sampling plans undertaken in each country, and also by the lack of standards with which to evaluate the levels of pollutants that have been recorded. Ms Kumiko Tsukamoto then presented an Overview of Environmental Standards in East Asia, demonstrating the differences between the standards in use in nine East Asian countries for the evaluation of the EDC's that have been studied during the UNU project. Standards for drinking water, surface water, ground water, coastal water and for sediments and soil were not found in every country for all of the pollutants, and wide variations in the levels set by those countries where they do exist were found in many cases. The issues raised during these presentations regarding the ongoing work of the UNU's project on Environmental Monitoring and Governance in the East Asian Hydrosphere - Monitoring of POPs in the East Asian Region provided the basis for the rest of the day's discussions, culminating in the afternoon discussion session.

The KJIST perspective on Monitoring of EDCs in the soil and aquatic environments was presented by Prof. Kyoung-Woong Kim of K-JIST, offering valuable insights from outside the UNU project on current thinking regarding the analytical techniques for EDC monitoring and the need for establishing systematic and scientific monitoring and assessment programmes for EDCs. Prof. Kim's observed that results from the monitoring of river water and effluents from KJIST showed surprisingly high levels of EDC's emitted from the scientific laboratories. This raised a lively discussion amongst participants regarding the possible explanations for this phenomenon, and the resulting lessons that could be drawn for the design and management of environmental monitoring and analysis. Further discussions on analytical techniques were pursued on the second day of the workshop.

## Session 2: Environmental Quality Guidelines in East Asia

*Chairs: Prof. Keichiro Fuwa (UNU) and Dr. Kyunghee Choi (NIER)*

Following a review of the legal framework for regulation of chemicals in the environment and emissions, Dr Masatoshi Morita, of NIES, Japan considered the calculation methods currently used in Japan to set the levels of Acceptable Daily Intake (ADI), Tolerable Daily Intake (TDI) and Virtually Safe Dose (VSD). The use of these measurements in the setting of Environmental Quality Standard for chemicals was then considered. Dr Morita noted that there are the cases where toxicological information is not sufficient, or where for practical reasons, a full safety margin cannot be incorporated. Regarding the need to consider the protection of fishery resources and wildlife as well as human exposures, Dr Morita referred to a set of standards for environmental water quality for the protection of aquatic organisms that are currently under preparation by the Japanese Ministry of the Environment.

Environmental Standards from China were presented by Dr Yeru Huang, of the China-Japan Friendship Center for Environmental Protection, including standards in various forms for a range of different media and parameters. Insights into the history of the development and revision of these standards were also included in this presentation. For the case of Thailand, Ms Sukanya Boonchalermkit presented the Environmental Quality Standards of Thailand in relation to the Pollution Control Act (B.E. 2535 (1992)). Institutional arrangements were summarized and the various standards and classifications presented. Ms Sukanya further commented on the need for vigorous enforcement of the standards and the role of technology transfer to support the existing environmental monitoring activities in Thailand. Finally, the Malaysian experience of aquatic pollution and the use of standards were evaluated by Dr Mustafa Ali Mohammed of the University of Malaya. He found further need for research regarding the fate, distribution and behavior of pollutants in the tropical environment in order to enhance surveillance and monitoring activities for the enforcement of pollution control.

### Discussion Session

UNU proposed a joint effort to develop regionally harmonized environmental quality guidelines that could be shared on a regional basis. The initial timeframe for this work is 2003-2005. This effort would be intended to facilitate joint action to remediate existing and potential pollution through the creation of a regional early-warning system to identify "hotspots," areas with high or rapidly increasing pollutant levels.

UNU presented the following process for the development of environmental quality guidelines:

- Stock-taking
  - Overall estimate of the extent of pollution
  - Comparison of existing standards
  - Identification of gaps in scientific information & knowledge
- Defining process for regional coordination
  - Identifying key stakeholders
  - Develop a dialogue mechanisms
  - Conduct professional and thematic roundtable
  - Develop draft quality guidelines
  - Conduct peer and stakeholder reviews
  - Discussion and negotiation
  - Adoption
- Implementation
  - Facilitation of dialogue

A discussion including representatives of all nine partner laboratories to be included in the project was undertaken in order to clarify the scope and aims of the project. Regarding the implementation mechanism for the project, UNU's role as a facilitator was agreed by participants. The proposed process for the development of the environmental quality guidelines also received general approval. Participants noted that the existing UNU network could be used for the project, and suggested that it should be used to start off the project as an initial working group. The need for further capacity development was highlighted by some participants.

Further issues raised during the discussion amongst the participants included the following matters:

#### *Scope of the work to be undertaken*

- Countries to be included: Representatives from laboratories in all nine countries expressed an interest: China, Indonesia, Japan, Korea, Malaysia, the Philippines, Singapore, Thailand and Vietnam
- Consideration of the chemicals to be selected as a focus for the exercise: It was concluded amongst the participants that initially, organochlorine pesticides should be investigated in order to maintain the priority on POPs monitoring. Aldrin, Dieldrin, Endrin, DDT and Lindane. These will continue to be monitored by the group. Some data also already exists on other EDC's, including a range of phenols and phthalates.
- Major stakeholder groups to be considered: these should include ministries that are already working with the project eg Thailand, the researcher community, general public, industries and NGOs. Different groups could be involved at different stages in the process. The importance of engaging the participation and support of government officials was highlighted by participants.

#### *Creation of Environmental Quality guidelines*

- Quality guidelines should be harmonized to correlate to existing classification systems. WHO and EPA can be used as a common reference source, as well as existing environmental quality standards from those countries that already have them.
- Philosophical question raised regarding the setting of environmental quality standards: should it be based on toxicity to humans or for aquatic organisms? For example, with dioxins, the levels for toxicity vary amongst the species. Humans should be the first priority, but both need to be considered. The project could include a focus on criteria for the preservation of aquatic life in freshwater and seawater
- What is the effect to be considered harmful, and how can a lowest possible concentration that would cause this effect be identified? Some countries already have some toxicity data. Other countries do not have this kind of data. Maybe we can start with that?
- Regional harmonization of environmental quality standards: this was widely agreed as necessary. However, the issue of regional variation in climate and exposure habits was raised. For example, climatic conditions and the levels of fish consumption vary across the region and –therefore population exposures to chemicals in the environment, even at similar concentrations, can also vary.
- Additional comment: Environmental Quality Standards are an end of pipe solution. Why don't we go upstream? PRTR for each country is needed.

**January 27, 2003**

### Session 3: Environmental Monitoring and Analytical Techniques

*Chairs: Dr Masatoshi Morita (NIES) and Prof. Man-Bock Gu, (KJIST)*

In his Introduction to the UNU Project in Nine East Asian Laboratories: Comparative Monitoring Activities and Standardized Methods, starting off this session, Prof. Keichiro Fuwa, Senior Project Adviser for the UNU project on Environmental Monitoring and Governance in the East Asian Hydrosphere - Monitoring of POPs in the East Asian Region commented on the project participant's efforts to improve the accuracy of the analyses that are carried out in their individual laboratories. He highlighted the projects use of standardized methods for sample collection and analysis, as well as the use of identical equipment in all of the laboratories and round-robin tests to check the accuracy of reporting. Prof. Fuwa then called on the participants to consider the need for further improvements in accuracy through inter-laboratory calibration and improved analytical techniques.

Dr Evangeline Santiago, of the University of the Philippines presented the need for Internal Validation of Analytical Methods for OCPs, Phenols and Phthalates in Water. The presentation underlined the need to ensure the required sensitivity in terms of the instrument detection limit, the reliable detection limit and the limit of quantitation. The presentation considered accuracy in terms of % recovery of spiked samples and consistent performance in terms of precision. The procedures for determination of these limits and for the construction of a quality control chart based on the IUPAC method for the UNU project methods were presented.

A presentation on The Development of Advanced Analytical Techniques for POPs Monitoring by Prof. Hian Kee Lee, of NUS, Singapore focused upon the development of environmentally-friendly analytical technologies. Dr Lee presented work from his laboratory on the development of solvent-

minimized extraction procedures for organic environmental contaminants. In addition to environmental considerations, Dr Lee highlighted the affordability of these techniques and the fact that very little, if any, solvent or other waste is generated from them. In his presentation on Direct Extraction of Phenolic Compounds from Acid-Digested Sediment for Simultaneous GC/MS Analysis Dr Jae Ryoung Oh of KORDI considered the possibilities for parallel treatment of large numbers of samples that can be afforded by the technique, without the use of expensive special equipment or heating processes.

## Session 4: Inter-laboratory Calibration Discussion Session

In his Introduction to the Inter-laboratory Calibration Concept and Possible Approaches, Dr Zafar Adeel, Project Manager for the UNU project on Environmental Monitoring and Governance in the East Asian Hydrosphere - Monitoring of POPs in the East Asian Region, commented on the range of different laboratories that are involved in this project across the region. Adeel highlighted that conducting such collaborative environmental monitoring activities requires the research institutions to work together to assure the quality of the data generated and consistency in procedures and reporting. Whilst the project has already taken steps to address the need for standardization equipment and analytical procedures, there is still a need for quantifying the inter-laboratory differences. In this regard, Adeel proposed a systematic approach in this direction is to undertake an inter-laboratory calibration exercise that would involve double-blinded samples to be given to each laboratory.

The following discussion outlined the available approaches and concepts to be used in an inter-laboratory calibration exercise.

### *Objectives of Inter-Laboratory Calibration*

- Harmonization of methodologies
- Quantifying accuracy and precision of analysis (degree of uncertainty) in each partner lab
- Ensuring reliability and adequate quality control
- Identifying analytical and systematic problems
  - Lab-based contamination
  - Errors and variability in methodology

### *Approaches for Calibration Exercise*

- Samples preparation based on
  - Synthetic standard sample
  - “Blind” samples – 4 per laboratory
  - Method blanks
- Concentrations from MDL to observed maximum levels (after pre-specified dilution)
- Randomized identification numbers
- Common sample collection, preparation, extraction and analytical methodology
- Pre-defined data quality objectives
- Reporting in standardized format

### *Analysis of Calibration Output*

- Quantification of uncertainty
  - Sample preparation
  - Standard recovery
  - Repeatability
  - “Blind” sample concentration measurement
  - Statistical evaluation of reported results
- Identifying method detection limits
- Identifying sources of error
- Discussion on reduction/elimination of errors
- Systemic improvements in reliability

### *The following additional points were raised by participants for future activities:*

- Possibilities for linking up with other networks
- The need to check the calibration curve itself, through the analysis of an additional sample, possibly during a future exercise

## Session 5: EDC's Research in Korea

*Chairs: Dr Zafar Adeel (UNU) and Prof. Kyoung-Woong Kim, K-JIST*

The final session of the workshop was devoted to presentations on current activities in Korea for monitoring EDC's. Dr Won Joon Shim of KORDI gave a presentation on Monitoring of organic pollutants in the coastal environment of Korea. Dr Shim described a 3 year monitoring program that has been undertaken by KORDI to establish a quality-controlled data set on the spatial distribution and the scale of contamination from toxic organic chemicals in the coastal environment and selected biota samples from the South Korean coastal area. In her presentation on Strategies and Perspectives on EDCs Research in Korea, Dr. Kyunghye Choi of the National Institute of Environmental Research examined 10-year National Research Programs for EDCs (1999-2008) of the Korean Ministry of Environment and the contributions of NIER to this programme in monitoring EDC's in surface-waters.

Regarding the use risk analysis techniques to evaluate the threat from POPs, Dr. Park, President of Lab Frontier and former Director of Korea Food and Drug Administration, gave a presentation entitled 'Monitoring of POPS level in human breast milk and its risk analysis: Korean perspective'. This presentation included information regarding the average concentrations of total PCDD/Fs and Co-PCBs in breast milk from women in Korea. Based on these results, the average lifetime daily exposure dose (LADD) was estimated. Prof. Man-Bock Gu of K-JIST explored the Toxicity Monitoring and Classification of Endocrine Disrupting Chemicals (EDCs) Including Dioxins Using Recombinant Bioluminescent Bacterial Biosensors. Prof. Gu found that recombinant bacteria could monitor the toxic effects, but not the estrogenic effects of various EDCs. These effects are measured through observation of bioluminescence (BL) and cell growth rate, which depend upon the type of toxicity occurring. It was also found that the damage caused by EDCs could be further classified into several groups of mechanisms for toxic action.

Finally, Prof. Seung-Hyeon Moon, of K-JIST gave a presentation on the Electroenzymatic Degradation of Persisting Organic Pollutants. Prof. Moon pointed out that this method avoids some of the disadvantages of traditional methods for treating industrial wastewater, such as high operating costs, incompleteness of degradation, formation of hazardous by-products, and limited concentration range for applicability. This method also does not require chemical reagents or generate secondary waste during the treatment process.

# Abstracts

## The need for Environmental Quality Guidelines and Early Warning Systems to Combat Pollution in the East Asian region

**Zafar Adeel**

*United Nations University, Tokyo, Japan*

**R**apid urbanization, the green revolution in food production and industrialization have all led to adverse impacts on the environment, particularly in coastal ecosystems which are the typical sink for all land-based sources. Adverse health impacts on coastal ecosystems and species are observed throughout the region. The level of information available about the extent and distribution of pollutants, particularly those that persist in the environment (e.g., POPs), is insufficient. Another complicating factor is that guidelines or standards for environmental levels of pollutants are not present in all countries of the East Asian region. At a regional scale, this makes it difficult to subjectively evaluate the existing pollution monitoring data. The main thesis of this paper is that countries in this region should coordinate their efforts to conduct research and monitoring for environmental pollutants, particularly POPs. This joint effort should include development of environmental quality guidelines that are shared on a regional basis. This will also facilitate joint action to remediate existing and potential pollution. For this purpose, it is also proposed that a regional early-warning system be developed to identify “hotspots,” areas with high or rapidly increasing pollutant levels. Such an early-warning mechanism must be linked to a reliable and consistent monitoring network.

# The Status of Major EDC Pollutants in East Asian Waters

**Caroline King**

*United Nations University, Tokyo, Japan*

**D**uring the past three years, considerable progress has been made in the environmental monitoring of Endocrine Disruptor Compounds (EDCs) in river and seawater across East Asia. Some regional assessments have already been attempted by researchers for persistent pollutants such as DDT's and PCB's. In general, these studies have relied on the analysis of biomarkers, such as mussels and fish, most notably through the Asian Mussel Watch Programme. Comparisons have been drawn, based on the comparison of measurements taken from different parts of the region at various different times (Kannan et al 1995, Monirith et al 2000 and Tanabe et al 2000).

With support from Shimadzu Corporation, Japan, and with coordination by the United Nations University (UNU), eight laboratories in different countries across this region have been undertaking regular monitoring activities, focusing on a range of recognized EDCs. Participating laboratories are located in China, Indonesia, Korea, Malaysia, the Philippines, Singapore, Thailand and Vietnam. The results from the monitoring work in these countries have been collected together by UNU to form a regional database on environmental pollution. Drawing on these data, comparisons can be made between the different countries for levels of a range of EDC pollutants, including organochlorines, phenols and phthalates. This presentation offers an overview of the data collected so far.

Relatively high levels of pollution by organochlorines were found, particularly in Malaysia and the Philippines, compared to the other countries. In Malaysia, levels of Aldrin and Dieldrin in freshwater exceeded WHO Drinking Water Standards in some areas. Relatively high levels of Aldrin and Dieldrin were also recorded in coastal water off the Philippines, as well as high levels of Endrin and Heptachlor in both fresh and saltwater. For DDT, DDE and DDD, US EPA Criteria for Human Consumption of Water and Organisms were frequently exceeded in a number of the participating countries. Whilst in freshwater higher levels were recorded on average in Malaysia, for seawater some Vietnamese results were extremely high. Comparative levels varied amongst the countries for a range of different Hexachlorohexanes studied. Freshwater from some samples taken in the Philippines far exceeded US EPA Human Health Criteria for Lindane in Water for Consumption. From a range of alkylphenols monitored by the laboratories, by far the highest results were for 4-nonylphenol. For most alkylphenols and Bisphenol A, comparatively higher results were recorded from samples taken in coastal waters in Singapore. In freshwater, comparative levels varied amongst the other countries. Both Malaysia and the Philippines recorded levels of Pentachlorophenol in excess of the US EPA Human Health Criteria for Consumption of Water and Organisms. Indonesia and China recorded comparatively high levels of some phthalates in certain samples, although results from none of the countries reached the level of the WHO Drinking Water Standards for Di-2 ethylhexylphthalate.

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# Overview of Environmental Quality Standards in Asia

**Kumiko Tsukamoto**

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In the past few decades Asia has experienced rapid industrialization and economic growth. Although the recent development has improved the standard of living of people in the region, it also brought byproducts in the form of environmental degradation. A notable example is the deterioration of water quality in many Asian countries as a result of agricultural and industrial discharges as well as domestic sewage.

Recent research has demonstrated that some pesticides reside in the environment for prolonged periods and affect human's endocrine functions through the food chain. Although the possible effects on human health by these endocrine disrupting chemicals (EDCs) or persistent organic pollutants (POPs) are still under research, it is considered that even a very small portion of these chemicals may cause endocrine problems in living organisms including humans. Hence, it seems crucial to restrict the use of these pesticides and thus to control the quality of water and soil in the Asian region.

This presentation attempts to provide a brief overview of environmental quality standards, a quality control technique, in Asian countries. In the presentation, the following chemicals will be discussed:

1. DDT and its breakdown compounds;
2. Alkyl phenols;
3. Phthalates;
4. POPs;
5. Petroleum hydrocarbons (BTEX: Benzene, Toluene, Ethyl benzene, Xylene).

## Monitoring of Endocrine Disrupting Compounds in Soil and Aquatic Environments

**Kyoung-Woong Kim\* and Eun Gyeong Kim**

*UNU Pilot Programme on Science and Technology for Sustainability and Department of Environmental Science and Engineering, Kwangju Institute of Science and Technology (K-JIST)*

Endocrine disrupting compounds (EDCs) interfere in some ways with the endogenous hormones and may potentially cause adverse effects on the populations and the community of humans and wildlife. Various compounds such as pesticides, plasticizers, food additives and packaging materials, etc. are included in a category of EDCs. Since EDCs are closely related to human life in many ways, people are exposed to the hazard of EDCs regardless of their intention. Like hormones EDCs exert their effects at significantly low concentrations, and very sensitive and reliable analytical methods are essential to monitor those compounds.

Well-known synthetic EDCs are generally assayed using conventional analytical techniques, including liquid chromatography (LC), gas chromatography (GC), and hyphenated techniques such as gas chromatography and mass spectrometry (GC-MS). The advantages of these techniques include accuracy and precision. Soil and sediment/water samples were collected from the potentially contaminated and control areas in Korea and the retention levels of alkylphenols, chlorophenols and bisphenol A in these samples were determined by GC-MS. A standard protocol for the pretreatment and extraction of samples in the soil and aquatic environments is being developed.

## Acceptable daily intake (ADI), tolerable daily intake (TDI) and environmental standards for chemicals in Japan

**Masatoshi Morita, Ph.D.**

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**S**afety from hazardous chemicals has been secured by a network of legal regulations which enable control at various stages in the production, movement and administered by various authorities.

Major laws are summarised as follows;

Production (& import) levels: Chemicals control law(MITI), Chemical weapons law(MITI)  
Use and Distribution levels: Toxic Chemicals Law(MHWL), Pesticide Control Law(MAFF)  
Human Exposure levels: Drinking Water Law(MHWL), Food Sanitation Law(MHWL),  
Environment levels: Water Pollution Control Law(MOE), Air Pollution Control  
Law(MOE), Soil Pollution Control Law(MOE), Occupational Safety Control Law(MHWL)

These laws have different origins and histories, and are maintained by different authorities, but are often related to each other when the basis of toxicity evaluation is the same. Regulation of chemicals in the environment and in emission control is such a case that relates to Drinking Water Law, Food Sanitation Law, and Occupational Safety Law. In these laws, toxicity and risk evaluation are mainly based on chronic toxicity, i.e. they consider effects from long term exposure to small amounts of toxicant.

Because it is not possible for humans to avoid exposure to various chemicals at any level, it is necessary to define the border line that ensures reasonable safety in our modern life. Acceptable daily intake (ADI), tolerable daily intake (TDI) and Virtually safe dose (VSD) are such borders that are applied to agricultural chemicals, industrial and unintentionally produced chemicals, and carcinogenic chemicals, respectively. These values are often divided according to the route of exposure, and quality standards are set for each media following the usual rule.

The usual calculation will be introduced in this presentation. It is to be noted that the actual decision making is not simple because there are the cases where toxicological information is not sufficient, or a full safety margin cannot be taken because of practical consideration. Chemicals control is not only to be restricted to human health issues. The approach toward the protection of fishery resources and wildlife is also being considered by the Ministry of the Environment. Such an approach will be also introduced.

## Environmental Quality Standards in China

**Yeru Huang and Li Zhou**

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**S**ince 1980's, many environmental standards have been issued or promulgated in China (Table 1). All of the standards can be classified as the basic standards, the quality standards, the discharge standards or emission standard, the method standards and reference material standards. Environmental quality standards include water, ambient air, soil, physical parameter and ecological quality standards. Several environmental quality standards have been revised or supplemented during recent years. All of the environmental quality standards in China are listed in Tables 2-6, containing the standard code, executed date and numbers of pollutant items restricted in the standard.

Table 1 Environmental Standards in China

	Basic Standards	Quality Standards	Discharge Standards	Emission Standard	Method Standards	Reference Material Standards
Water quality	7	5	22	?	55	16
Ambient air quality	2	2	?	24	65	9
Solid waste	1	?	27	?	15	?
Soil	?	1	?	?	9	4
Physical parameters	1	3	7	?	6	?
Ecological quality	1	1	?	?	4	?
Radioactivity	1	?	?	15	33	?
Others	2	?	?	?	36	?

Table 2 Water quality standards in China

Standard name	Standard code	Executed date	Standard items	Version
Environmental quality standard for surface water	GB 3838-2002	20021001	71	3
Quality standard for ground water	GB/T14848-93	19941001	39	1
Sea water quality standard	GB3097-1997	19980701	35	2
Water quality standard for fisheries	GB11607-89	19900301	33	1
Standards for irrigation water quality	GB5084-92	19921001	29	2
Water quality standard for scenery and recreation area	GB12941-91	19920201	21	1

Table 3 Ambient air quality standards

Standard name	Standard code	Executed date	Standard items	Version
Ambient air quality standard	GB3095-1996	19961001	10	1
Maximum allowable concentration of pollutants in atmosphere for protection crops	GB9137-88	19881001		

Table 4 Soil quality standard in China

Standard name	Standard code	Executed date	Standard items	Version
Environmental quality standard for soils	GB15618-1995	19960301	11	1

Table 5 Quality standards for physical parameters in China

Standard name	Standard code	Executed date	Standard items	Version
Standard of vibration in urban area environment	GB10070-88	19890701		1
Standard of environmental noise of urban area	GB3096-93	19940301		1
Environment standard of aircraft noise around airport	GB9660-88	19881101		1

Table 6 Ecological quality standard in China

Standard name	Standard code	Executed date	Standard items	Version
Standard for safety application of pesticides	GB4285-89	19900201		1

## Water Quality Standards in Thailand

**Ruchaya Boonyatumanond, Sukanya Boonchalermkit**

*Environmental Research and Training Center, Thailand*

**T**he trend in the use of chemicals for improvement of industrial and agricultural products has been increasing in Thailand. Like other developing countries, Thailand has benefited from the availability of the growing spectrum of chemical products available on the market. On the other hand, many environmental problems have arisen from the use of these chemicals, such as air pollution, water pollution and solid waste. The use of pesticides, insecticides, and the disposal of hazardous chemicals introduce pollutants into the environment which have been found to affect human health.

Chemical controls need vigorous enforcement. The Thai government has defined a number of environmental laws and established "The Enhancement and Conservation of National Environmental Quality Act in B.E. 2518, 2521, 2522 and newly one is B.E.2535 (A.D.1992)". This paper highlights the Coastal Water and Surface Quality standards and the role of Pollution Control Act B.E. 2535. There are many government offices and private sector actors concerned with the Act. The Environmental Research and Training Center has been given the responsibility of providing supporting data to the Pollution Control Committee of formulation of future policies.

## The status of aquatic environment monitoring in Malaysia

**W.M. Wan Hazira, A.M. Mustafa**

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**T**he importance of monitoring levels of environmental pollution and contamination due to extensive industrial and agricultural activities is being emphasized. Toxic, ignitable, corrosive and reactive wastes from industries include acids and bases, reactive wastes and organic constituents. These scheduled wastes generated by industries show a marked increase from 1999 to 2001.

Environmental pollution from agricultural activities includes various types of organo-metallic compounds used as insecticides, herbicides, fungicides and rodenticides. There has been a steady increase in the growth of consumption crop care products from 1995 to 1999.

Categories of pollution under various environments such as river, well and marine as well as their respective standards have been established by the Department of Environment and the Ministry of Health. Using indicators like biological oxygen demand, ammoniacal nitrogen and suspended solids, river water quality in river basins from 1999 to 2001 was monitored. The results show a fluctuating trend of clean, slightly polluted and polluted water. In addition, monitoring marine water is based on physical, chemical and biological characteristics. The major pollutants detected in marine water include total suspended solids, oil and grease and E.coli.

Ground water monitoring has been given a greater priority by the Malaysian government under the Ministry of Science, Technology and Environment due to its increasing demand for domestic and industrial use. Parameters for monitoring the water quality include volatile organic compounds, pesticides, heavy metals, bacteria, phenolic compounds, total dissolved solids, pH and dissolved oxygen.

From 1999 to 2001, land use contaminants in agricultural sector, urban/suburban, golf courses and radioactive landfill have generally exceeded the acceptable value. It is of utmost importance that strict enforcement by the local authorities be carried out to ensure the levels of environmental pollution be kept below the acceptable level.

## Introduction to the UNU Project in Nine East Asian Laboratories: Comparative Monitoring Activities and Standardized Methods

**Prof. Keichiro Fuwa**

*United Nations University, Tokyo, Japan*

**T**he UNU has spent the past ten years working with different laboratories in the East Asian region. During this time, we have all made considerable progress in improving the accuracy of the data that is collected across the region. Over the past few years, we have developed a large database of comparative information on the presence of EDCs in the environment. This information was collected from analyses of environmental samples that have been conducted in nine laboratories across the region. The data that we have collected in this way is very valuable to us, because it can help us to look for trends in the distribution of pollutants, and to identify the areas where the levels of pollution are the most acute. Furthermore, as we continue to pursue our understanding of the behavior of chemicals in the environment, this regional data may help us to identify patterns in the fate and transport of pollutants across the globe.

The challenge for all environmental scientists is to obtain accurate data that can be used to compare trends in environmental effects over time and between geographical locations. The same issue confronts other scientists who are studying biological effects and population patterns in both plant and animal species, as well as those whose task it is to decipher subtle effects in weather, the behavior of particulate matter in air, the hydrology of groundwater and streams and the movements of sediments in the oceans. Each of us is contributing a tiny piece of the environmental puzzle that will allow us to understand the global changes that await us in the future. These pieces can only come together meaningfully if they are accurate enough for comparisons and deductions to be made concerning the ways in which the different media and effects relate to one-another.

In their work on environmental quality in East Asian waters, the partners in UNUs network have each been striving to improve the accuracy of the analyses that are carried out in their individual laboratories. In addition to this, in order to ensure that the data is comparable between the different monitoring programmes, over the past three years we have used standardized methods of sample collection and analysis. Thanks to the help of Shimadzu corporation, we have been able to conduct the chemical analysis using identical equipment in all of the laboratories. We have also used round-robin tests to check the accuracy of our reporting, and we have met together regularly to compare our results.

During the first day of this workshop we have seen some of the regional comparisons that have emerged from our database so far. During our project, we have already identified the differences in levels of pollutants found at different times of year in the same location, depending on the dry or rainy season. In compiling our database, we have also found that there are some variations between countries in the types of data that are being reported, particularly concerning the detection limits, and perhaps even the accuracy of the data. Our project has therefore already demonstrated that there are many conditions that can affect the data that is reported from our monitoring activities. We need to continue to work to minimize these variations in our results, in order for our data to be comparable across the region.

As we enter this new three-year phase of our project on Environmental Monitoring and Governance in the East Asian Hydrosphere: Monitoring of POPs in the East Asian Region. We will continue to focus on comparative monitoring activities, with a particular emphasis on POPs, and we hope that we will be able to produce more comparative data on this group of pollutants. The purpose of this session is to examine the ways in which we can protect the comparability of our data across the region by reducing the variations in the reported levels of pollutants. We will need to do this through the use of even more standardized methods. In the presentations that we will hear this morning, some methodological questions will be raised. We will then proceed to the discussion of a proposed inter-laboratory calibration exercise in order to enable further possible improvements in the work that we can carry out together.

## Internal Validation of Analytical Methods:for OCPs, Phenols and Phthalates in Water

**Evangeline C. Santiago and Charita S. Kwan**

*Research and Analytical Services Laboratory, Natural Sciences Research Institute, University of the Philippines*

**T**he interpretation of any analytical data is contingent on the performance of the analytical method used in generating the data.. For an analytical data to be valid, the analytical method must satisfy the data quality objectives of the activity where the analytical data will be utilized. For environmental monitoring, the analytical method to be employed must conform to the required sensitivity in terms of the reliable detection limit and limit of quantitation, accuracy in terms of % recovery of spiked samples and consistent performance in terms of precision. These characteristics of the method define the quality of the analytical data and any meaningful conclusions that can be derived from these data.

The performance of an analytical method in a laboratory can be determined by internal validation. The IUPAC method for internal validation of a method was applied to the UNU methods for organochlorine pesticides, phenols and phthalates in the Research and Analytical Services Laboratory of the University of the Philippines. Quality control (QC) charts based on the % recoveries of the surrogate standards were constructed for each group of compounds.

The procedures for determination of the Reliable Detection Limit, Limit of Quantitation, and for the construction of the QC chart for the methods will be presented

## The Development of Advanced Analytical Techniques for POPs Monitoring

**Hian Kee Lee**

*Department of Chemistry, National University of Singapore,*

**“P**ersistent Organic Pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. With the evidence of long-range transport of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment of the whole globe, the international community has now, at several occasions called for urgent global actions to reduce and eliminate releases of these chemicals” (statement from the United Nations Environment Programme web site on POPs, <http://www.chem.unep.ch/pops/>). “The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (POPs). POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. POPs circulate globally and can cause damage wherever they travel. In implementing the Convention, Governments will take measures to eliminate or reduce the release of POPs into the environment” (from the Stockholm Convention homepage, <http://www.pops.int/>).

The Stockholm Convention, and other international agreements, state that monitoring activities should be established to verify the effective implementation of such treaties and agreements, and the decrease of environmental levels of persistent pollutants. It is therefore clear that the analysis of POPs is a vital component of these exercises.

To be sure, there are already procedures to extract POPs from environmental matrices, and these are being widely used. Many, if not all, of these methods, however, are based on those technologies established many years ago, and they often generate considerable waste (eg. materials, organic solvents, etc), which is ironic considering that while attempts are made to investigate a critical

environmental problem, yet at the same time, in the process of doing so, undesirable waste products, which are potentially toxic, are being produced!

One solution to this dilemma is to develop newer, environmentally-friendlier analytical technologies. In our laboratory, we are focusing on the development of solvent-minimised extraction procedures for organic environmental contaminants. Some of these techniques can be modified for the extraction of POPs. These techniques make use of very small quantities of materials, including toxic solvents and are generally affordable to many normal laboratories. In this paper, we shall describe some examples of these procedures.

## Direct Extraction of Phenolic Compounds from Acid-Digested Sediment for Simultaneous GC/MS Analysis

**Jae Ryoung Oh\*, Donghao Li\*, and Jongman Park\*\***

*\*Korea Ocean Research and Development Institute and \*\*Department of Chemistry, Konkuk University, Korea*

**D**irect extraction of alkylphenols, chlorophenols and bisphenol A from acid-digested sediment suspension for GC/MS analysis was studied. The sediment was digested with acid while the hydrolyzed analytes were being extracted with dichloromethane. The conditions of the acid-digestion and extraction were optimized in terms of time and acidity of digestion, and extracting solvent. It was possible to complete the extraction within 20 minutes with five milliliters of 0.1M HCl digesting solution and three portions of five milliliters of dichloromethane. The recoveries of analytes were mostly around 90% with about 10% of relative standard deviations. Not only parallel treatment is possible for large numbers of sediment samples, but also any expensive special equipment and heating process are not required. The analytical characteristics of this extraction technique were compared to those of Soxhlet extraction (SE) and accelerated solvent extraction (ASE) technique. This technique was applied to real marine sediment samples and obtained satisfactory results with high recovery and sensitivity.

## Introduction to the Inter-laboratory Calibration Concept and Possible Approaches

**Zafar Adeel**

*United Nations University, Tokyo, Japan*

**M**onitoring of environmental pollutants is an important activity in the East Asian regional context and in view of increasing pollutant burdens in the coastal and freshwater ecosystems. Conducting such monitoring at a regional level requires collaboration of various laboratories and research institutions. A key challenge in this effort is to assure the quality of the data generated and consistency in procedures and reporting – a challenge already faced by UNU's project on monitoring of POPs in the East Asian hydrosphere. In addition to using the same equipment and analytical procedures, there is a need for quantifying the inter-laboratory differences. A systematic approach in this direction is to undertake an inter-laboratory calibration exercise that involves double-blinded samples given to each laboratory. This paper will outline the available approaches and concepts to be used in an upcoming inter-laboratory calibration.

## Monitoring of organic pollutants in the coastal environment of Korea

**Won Joon Shim, Sang Hee Hong, Un Hyuk Yim and Jae Ryoung Oh**

*Korea Ocean Research and Development Institute*

**M**arine pollution is becoming a widespread problem in this region as a result of the rapid growth of agricultural and industrial activities. Inputs of sewage and persistent organic pollutants (POPs), e.g. pesticides, polychlorinated biphenyls (PCBs), and PAHs, into the marine environment have a negative impact on ecosystems and fishery resources.

To protect the marine environment, especially from POPs, a comprehensive action plan is needed in the region to develop national monitoring programs. As part of this action plan, a need has been identified to carry out monitoring program of these trace organic contaminants to study the occurrence of these compounds in the coastal marine environment and to evaluate the effects of this contamination on marine organisms using validated analytical techniques.

A 3 year monitoring program was undertaken to establish a quality-controlled data set on the spatial distribution and the scale of contamination from toxic organic chemicals in the coastal environment and selected biota samples from the coastal area in order to:

- describe the present extent of environmental pollution, and
- establish a baseline for the future monitoring program.

## Strategies and Perspectives on EDCs Research in Korea

**Dr. Kyunghee Choi**

*National Institute of Environmental Research, Republic of Korea*

**M**uch research has been reported on the adverse effects of Endocrine Disrupting Chemicals (EDCs) on the ecosystem. EDCs disrupt the action of the endocrine system in the body and can cause impairment to the reproductive faculties as well as malignant growths.

Consequently, they pose the risk of immense harm to human health and the ecosystem for the next generations, and have become a key issue of international concern.

In Korea, the social and environmental concerns regarding EDCs were emerging in the public media since 1998. In order to commit the public need, an Expert Committee on EDCs has been organized to formulate a 'National Strategy on EDCs Research'. In July 1999, the Ministry of Environment released the "10-year National Research Programs for EDCs (1999-2008)". This program requires and integrates research activities of seven ministries including Environment, Food and Drug Administration, Marine and Fisheries and so on. The Programs are aiming at preparing the Ministry's basic perspectives on the problem solutions and specific lines of action on it. In this program, the research scopes are proposed and prioritization of the implementation period is specified. First, fundamental research areas, development of screening and testing methodology, monitoring of public consumption patterns, strengthening of international cooperation and establishment information exchange system are included. Second, fact-finding studies on detection in the environment and influence on wildlife are suggested. Third, for risk assessment and management, the following subjects are included; criteria set-up for safe management, gradual restriction or ban of use, reduction of release to environment, development of substitutes and remediation techniques.

National Institute of Environmental Research (NIER) has participated in the main activities of this program. Research activities performed since 1999 are;

- monitoring of contamination level in a variety of media (water, soil, air, sediment and biota) and adverse effects on ecosystem
- investigation of dioxin on small- and medium scale incinerators



- a survey has been done in order to understand the public's consciousness and consumption pattern on EDCs
- to understand the environmental fate and transport of EDCs, a single cell multimedia fate model has been constructed and evaluated. The EDCs of concern were PAHs, Organochlorine pesticides, PCBs, Alkyl phenols and Phthalates. The model will be refined in ongoing research and used to support decision-making for the proper management of EDCs

Experimental methods of EDCs have been published in 1999 by NIER and revised in 2002. For the investigation of in-depth impacts on ecosystems, a guidance manual has been prepared in 2002. Screening methods, such as uterotrophic assay and hershberger assay, were developed as highly advanced environmental technology project.

A joint research with a Japanese counterpart has been embarked upon, in accordance with a bilateral agreement made in the year 1999. Cooperative activities of implementing arrangement on joint research and cooperation concerning EDCs are:

- exchange of technical information and expertise
- sharing of research findings and development of joint research projects
- joint symposium, workshop and academic discussions on topics of mutual interest.

Continuous researches in accordance with the research plan will be carried out to the accumulation of scientific knowledge on EDCs issues. Furthermore, strengthening local, regional and international cooperation, risk reduction measure for dioxin-like chemicals will be enacted in future. Regional networks will be employed efficiently and effectively to exchange information and expertise about EDCs to number of countries in the region.

To compare data generated by different countries, common standard methods for sampling, treatment and analysis of EDCs should be agreed upon. Overall results would provide the fundamental and scientific data on future EDCs research planning and also rationale in decision making for regulatory action.

## Monitoring of POPs level in human breast milk and its risk analysis

**Jongsei Park, Shinai Choi**

*LabFrontier, Co., Ltd., Korea*

**P**ersistent organic pollutants (POPs) have spread throughout the global environment to threaten human health and damage ecosystems, with evidence of POPs contamination in wildlife, human blood, and breast milk documented worldwide.

Breast milk is an ideal medium for assessing exposures to POPs. POPs enter humans largely as contaminants of dietary animal products, where they sequester in adipose tissue, serum, and breast milk and equilibrate at similar levels on a fat weight basis. With long (5-10 year) half-lives, POPs persist in humans and in breast milk as they do in the environment. Breast milk mimics sediments of rivers or lakes as a storage reservoir for POPs, serves as an indicator of past human exposures or environmental conditions, and complements environmental monitoring data in air, water, soil, and food (Hooper K. et al., 1999).

In Korea, it is reported that the average concentrations of total PCDD/Fs and Co-PCBs in breast milk were 10.108 pg TEQ/g lipid (n=43) collected at 1st day after delivery, 2.432pgTEQ/g lipid (n=21) at 5th day, 2.105 pg TEQ/g lipid (n=19) at 30th day, and 1.605 pg TEQ/g lipid (n=21) at 100th day, 1.351 pg TEQ/g lipid (n=14) at 150th day, and 1.103 pg TEQ/g lipid (n=6) at 200th day. Based on these results, the average lifetime daily exposure dose(LADD) is estimated 1.77E-2pg/kg/day considering breast milk intake rate and body weight of Korean. The LADD is lower than 1~4 pg/kg bw-day as TDI(tolerable daily intake, WHO).

## Toxicity Monitoring and Classification of Endocrine Disrupting Chemicals (EDCs) including Dioxins using Recombinant Bioluminescent Bacterial Biosensors

**Man Bock Gu, Jiho Min, Pham Chi Hoa, and Eun Jin Kim**

*National Research Laboratory on Environmental Biotechnology and KJIST*

**F**ive different recombinant bioluminescent *Escherichia coli* strains containing the *recA* (responsive to DNA damage related stress), *fabA* (membrane damage), *katG* (oxidative damage), *grpE* (protein damage) and *lac* (constitutive expression – general toxicity) promoters fused to the bacterial *lux* operon from either *Vibrio fischeri* or *Photobacterium luminescens*, to describe the different mechanisms of toxicity that several endocrine disrupting chemicals (EDCs) including dibenzo-p-dioxins and dibenzofurans have on bacteria, as well as to determine whether bacteria can sensitively detect their presence. It was found that the recombinant bacteria could monitor the toxic effect, not estrogenic effect, due to the presence of various EDCs through the measurement of bioluminescence (BL) and cell growth rate, which depend upon the type of toxicity occurring. It was also found that the damage caused by EDCs could be classified into several groups upon their mechanisms of toxic action. In addition, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) was found to cause only DNA related damage to bacterial cells, but the four stress responsive strains showed positive responses after addition of 1,2,3,4-tetrachloro-dibenzo-p-dioxin (1,2,3,4-TCDD), while 2,3,7,8-tetrachloro-dibenzo-p-furan (2,3,7,8-TCDF) caused only DNA, oxidative and protein damage. However, 2,8-dichloro-dibenzo-p-dioxin (2,8-DCDD) was not found to induce any stresses tested for in this study, i.e. DNA, membrane, oxidative and protein damage, indicating that each congener might differentially interact with the cell, stimulating differential stress responses within them. Furthermore, using the constitutive strain, it was found that the level of cellular toxicity experienced due to the addition of these four dioxins decreased in the order of 2,3,7,8-TCDD (the most toxic), 1,2,3,4-TCDD, 2,8-DCDD and 2,3,7,8-TCDF.

## Electroenzymatic methods for degradation of POPs

**Seung-Hyeon Moon, Gha-Young Kim**

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**A**s many industries produce wastewater containing toxic pollutants, there has been increasing concern in the treatment of industrial effluents. Currently available methods for treating industrial wastewater include solvent extraction, microbial degradation, and adsorption on activated carbon, chemical oxidation and so on. Technologies such as adsorption and chemical oxidation require short retention time and relatively simple equipment. Although these methods are effective, they suffer from drawbacks such as high operating cost, incompleteness of degradation, formation of hazardous by-products, and applicability to a limited concentration range. Also, they usually require chemical reagents and/or generate secondary waste during the treatment.

Electroenzymatic process is an interesting approach to be applied for the efficient use of H<sub>2</sub>O<sub>2</sub> dependent enzymes in biocatalysis. It combines the enzymatic reaction and the electrochemical generation of the H<sub>2</sub>O<sub>2</sub> to overcome the limitation of continuous supply of H<sub>2</sub>O<sub>2</sub> in enzymatic removal of toxic organics. In an anodic oxidation for electroenzymatic process, the water molecules are first adsorbed on the anodic surface and then oxidized by the anodic electron transfer reaction. In an indirect oxidation process at the cathode, a strong oxidant such as H<sub>2</sub>O<sub>2</sub> is generated by the electrochemical reactions and provided to peroxidase enzymes immobilized on a carbon electrode which would accelerate the degradation of pollutants such as dye and TNT in the aqueous solution.

Azo dye is a group of chemicals that is largely resistant to biodegradation and persists in wastewater treatment processes. An electroenzymatic process was employed for the enzymatic removal of Orange II (Azo dye) in this study. The electroenzymatic method using immobilized horseradish peroxidase enzyme (HRP) was carried out to degrade Azo dye. It was proved that an enzyme-based electrolytic treatment process was a viable approach for the removal of Azo dye.

2,4,6 - Trinitrotoluene (TNT) has been used as a major military explosive and can be an important contaminant of soil and groundwater at many sites of TNT production and storage. TNT molecule includes three electron-withdrawing groups reducing the electron density of the aromatic ring. Thus TNT is resistant to oxidative attack by oxygenases and tends to persist in the environment. TNT can be degraded and conjugated into more complex products to some extent by a variety of microorganisms under aerobic or anaerobic conditions, but biodegradation and especially mineralization rates by microorganism were relatively low if the concentration of TNT is toxic or inhibitory to microorganisms. The disadvantages of the conventional treatment methods were overcome in an enzyme-based reactor, where lignin peroxidases catalyzed the degradation reaction with a low retention time in an electrochemical reactor.

# Poster Session

I

## Adverse Effect to Endocrine Disruptors on the Specific Tissues in the Medaka (*Oryzias latipes*)

**Jiho Min and Man Bock Gu**

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All species respond to chemical and physiological stresses by increased and/or decreased synthesis of some genes known as stress responsive genes. In this study, the expression of some biomarkers in several tissues of Japanese Medaka, *Oryzias latipes*, using RT-PCR with specific primers has been analyzed in order to study their changes in the liver, heart, intestine, spleen, gills and reproductive tissue after exposure to endocrine disruptors. Real time RT-PCR, based on the TaqMan probe method, was used to quantify these gene expressions in each specific tissue. Each tissue has been selected due to their specific role or function. It was shown that estrogen receptor, which represent the estrogenic potential due to endocrine disruptors, were expressed more highly in the ovary and testis compared with other tissues after exposure to beta-estradiol including nonylphenol and bisphenol A. However, a gene related to cellular toxicity, such as cytochrome P450 aromatase, was expressed in the liver, as well as in the reproductive tissues as expected. None of the stress- responsive genes, which were selected for this study, were detected in the heart, spleen and intestine. Meanwhile, the profiles of the gene expressions in the gills were quite different compared with those seen in the reproductive tissues and liver. It was shown that all genes related with estrogenic potential and cytotoxicity were expressed in gills. This would indicate again that the gills are highly sensitive, due to their role as a filter in exchange of dissolved gases, to any changes in environmental conditions. In conclusion, it was found that very sensitive responses to a specific chemical, according to the biomarker gene expressions, were obtained in specific tissues, and not in all tissues tested. This work suggests that the chemical specificity in a specific tissue should be considered when specific markers are sought.

II

## Biosensors for Detecting Cellular Toxicity using Constitutive Bioluminescent Bacteria

**Byoung Chan Kim, Ju Myoung Ahn and Man Bock Gu**

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Especially, bacteria test can be easily applied to toxicity measurement, because of inexpensive cost, easy detection protocol, fast reproducibility or fast response for toxicity assay. The most popular commercialized bacterial tool for toxicity measurement is MICROTOXTM. Decrease of bioluminescent intensity, on exposure to liquid samples can be used to a toxicity criterion of the samples. This method is well correlated with other invertebrate or algal methods, although each assay has different detectable range of toxicity. But culture condition of strains used for this tool is sensitive to salt concentration and so for getting consistent results, salt concentration should be considered.

To solve these problems and detect toxic materials we developed genetically engineered bacteria, which have highly constitutive expression of bioluminescence. We used bacteriophage lambda PR promoter or E.coli 16s rRNA promoter *rrnD* to fuse with pUCD615, which is promoterless vector having lux operon. We could establish high constitutive expression of bioluminescence. After mixing with toxic chemicals, the bioluminescent levels were decreased depending on increase of the chemicals concentration.

These strains can be a new alternative tool for toxicity monitoring of chemicals or water samples.

### III

Detection of oxidative damaging chemicals using recombinant bioluminescent oxidative stress inducible bacteria

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A recombinant bioluminescent *Escherichia coli* strain, EBJM1 (pqi-5::luxCDABE), containing the promoter for a member of soxRS regulon, a probable membrane protein of unknown function (pqi-5) gene fused to the *Vibrio fischeri* luxCDABE operon, was successfully constructed and characterized. The soxRS-dependent induction of pqi-5 occurs only during the exponential phase caused by paraquat, a superoxide radical-generating agent. In addition, it was compared the different patterns of oxidative stresses and response sensitivity caused by some chemicals with EBJM1 including existing oxidative stress responsive strains, EBHJ1 (sodA::luxCDABE), which is strongly induced by redox-cycling agents, such as paraquat and chromium, and DPD2511 (katG::luxCDABE), which is sensitive to hydrogen peroxide. It was found that responses from the pqi-5-, sodA- and katG-based strains were significantly different dependent upon the chemicals being tested. Therefore, EBJM1 in parallel with EBHJ1 and DPD2511 can be used to characterize and detect chemicals that cause oxidative damage.

### IV

An environmental biosensor using immobilized recombinant fluorescent mammalian cells

**Jung Eun Lee and Man Bock Gu**

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In this study, the KFC-A10 cell line, which contains c-fos SRE::GFP plasmid (pKCFG), was used. This cell line was found to be induced by toxic chemicals, especially DNA damage agents and apoptotic chemicals and produces green fluorescence protein under these toxic conditions. The EFC-500 cell line containing CMV::GFP fusion gene reduces its green fluorescence protein level under toxic conditions due to metabolic inhibition. An environmental biosensor was developed by immobilizing KFC-A10 and EFC-500 cell line within agarose matrix and confirmed that its detectable functions were well maintained for a week.

Mitomycin C and MNNG as model chemicals is used as an anti-chemotherapeutic drug, causing DNA damage by producing cross links and inhibits DNA synthesis. It has confirmed that genes which response specific cellular stress or environmental toxic chemicals with signal transduction were detected using by RT (reverse transcript)–PCR (polymerase chain reaction) . The result of RT-PCR of KFC-A10 cell line exposed to MMC and MNNG shows the DNA band pattern of control and sample exposed to mutagenic chemicals. Of using genes, there was no noticeable change when the cells were exposed to various concentrations of MMC and MNNG. On the other hand, the transcriptional activity of c-fos was significantly different when compared between cells that were and were not exposed to mutagenic chemicals.

V

## Toxicogenomic Analysis of the Environmental Hazardous Effect Using Stress Specific Functional cDNA Microarray of Medaka fish

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With the introduction of DNA microarrays, a high throughput analysis of gene expression is now possible as a replacement to the traditional time-consuming Southern-blot analysis. This cDNA microarray should be a highly favored technology in the area of molecular toxicology or analysis of environmental stresses. In this study, therefore, we developed a novel cDNA microarray for analyzing stress-specific responses in Japanese Medaka fish. In the design and fabrication of this stress specific functional cDNA microarray, 22 different genes in Medaka fish were selected from four different stress responsive groups, e.g. estrogenic, cytotoxic, and carcinogenic and etc. On a 25 x 75 mm glass surface, 23 different cDNA genes, including one yeast gene as a negative control, were spotted twice for statistical analysis of hybridization. This newly developed microarray has been tested and confirmed with other qualitative and quantitative methods, including RT-PCR and real time RT-PCR. After exposure of the fish to a well-known endocrine disrupting chemical, nonylphenol, over 1, or 10 days, the responses of the DNA chip were found to comparable with those of RT-PCR and real-time PCR analysis of the same sample. Additional chemicals, beta-estradiol, bisphenol A, phenol, and glyphosate, have been also tested and the responses confirmed with real time PCR data as well. Therefore, this chip can be used to monitor stress responses of unknown and/or known toxic chemicals using Medaka fish and may be used for the further development of other biosensors and biomarkers by utilizing the gene expression patterns for known contaminants.

VI

## Comparison of Food-borne Cadmium and Water-borne Cadmium in the Bioavailability

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Freshwater algae are normally provided as the primary source of food during *Ceriodaphnia dubia* toxicity tests. A large body of environmental literature demonstrates that algae are capable of accumulating heavy metals. Consequently, questions regarding whether or not the toxic metals incorporated in food particles (i.e. algae) influence laboratory-based toxicity tests must be addressed for a better understanding of variability that occurs in such tests and for improving the standardization of test procedures. The objective of this study was to investigate the effect of feeding Cd-laden algae on 7-day chronic toxicity tests. A continuous supply of Cd-laden algae was obtained by including Cd to the feed of a chemostat culture of *Selenastrum capricornutum*; the ability of algae to mediate Cd toxicity by making it more or less bioavailable was then determined by continuously delivering the chemostat effluent to a flow-through bioassay system containing *Ceriodaphnia dubia*. A control system introduced the same level of Cd prior to the bioassay chamber (after chemostat) was operated in parallel to assess the toxic effects resulting from a similar level of exposure to non-algal-incorporated Cd. The above bioassay test was performed at 8 different concentrations of cadmium. For each Cd concentration, number of neonates produced from *C. dubia* exposed to Cd via "food pathway" was significantly greater than that from the animals exposed to non-algal-incorporated Cd. These results were used compare the NOEL and LOEL values for the two different routes of Cd exposure.

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The effects of pH on phenanthrene solubilization and biodegradation using a biosurfactant (rhamnolipid) solution were investigated. Batch solubilization experiments were performed in the pH range 4 to 8 and the highest solubilities were detected around a pH of 4.5 to 5.5. The apparent solubility at pH 5.5 was 3.6 times greater than at pH 7 in presence of 240ppm rhamnolipid, and changes in the apparent solubility with the changes in pH are possibly related to the rhamnolipid, an anionic surfactant, forming different pH dependent structures. Two biodegradation experiments were performed in the absence (EXP #1) and the presence (EXP #2) of rhamnolipid, with the cell growth investigated using a spread plate method. The specific growth rates at pH 6 and 7 were higher than at the other pH, and the HPLC analysis data, for the total phenanthrene loss, confirmed the trends in the  $\mu$  (specific growth rate) values. In presence of rhamnolipid, maximum  $\mu$  values shifted from around pH 5 which showed maximum enhancement of solubility in the abiotic experiment, compared to the  $\mu$  values obtained without the biosurfactant. In our study, the increase in the observed specific grow rate was not as high as the increase in solubilization. The 1.44 times increase in  $\mu$  values at pH 5 was lower than the 3.6 times enhancement in the solubility at the same pH. This was supported by the fact all the solubilized phenanthrene is not bioavailable to microorganisms.

#### MATERIALS AND METHODS

The effect of pH on solubilization of phenanthrene. The effect of pH on the solubility of phenanthrene in the biosurfactant solution was determined by batch tests. Phenanthrene (100mg) was added to 45ml centrifuge tubes and 20ml of the biosurfactant solution (240-mg/l & 20000-mg/l) in deionized water at the various pHs was added. The rhamnolipid solutions pHs were adjusted to 4.5, 5, 5.5, 6, 6.5, 7, and 7.5 by the addition of HCl or NaOH solution. Triplicate samples were placed on an orbital shaker for 48 hours at room temperature (25°C). Samples were centrifuged at 4000 rpm for 10 minutes, and the supernatants were analyzed by HPLC.

The effect of pH on cell growth with biosurfactant. The biodegradation of phenanthrene was quantified in two ways: 1) direct measurement of phenanthrene loss, used to determine substrate utilization, and 2) spread plate cell counts, used to evaluate cell growth. For phenanthrene utilization experiments, 4mg of phenanthrene was dissolved in chloroform and added to the 125ml flasks (Zhang et al., 1997). Mineral salt medium (MSM) was made (Zhang et al., 1992), and the pH of the solution was adjusted with HCl or NaOH. Twenty milliliters of MSM was added to each flask, and the samples inoculated with 0.2ml aliquots of the phenanthrene degraders from precultures, to give a final cell density of approximately  $10^6$  cfu ml<sup>-1</sup>. The inoculated samples were incubated at 25 °C, in a water bath shaker at 80 rpm. The cell growth was measured by spread plate cell counts on R2A agar. The microbial populations were estimated using the spread plate method, by experimental procedures based on standard methods (APHA et al., 1992). The samples were serially diluted, and duplicate plates were prepared at each dilution ratio. The colonies were enumerated following incubation for 2 days at 30°C. At the end of the experiment, the contents of each flask were extracted with 30-ml of chloroform. The amount of phenanthrene in the extract was quantified by high-performance liquid chromatography (HPLC). HPLC analysis was performed isocratically using mobile phase of 35% water and 65% acetonitrile, at a flow rate 1ml/min, using UV detection at a wavelength of 254nm.

#### RESULTS AND DISCUSSION

Effect of pH on solubilization of phenanthrene. The phenanthrene solubility in the rhamnolipid solutions, at each pH, as determined by the centrifuge vial tests are presented in Figure 1. The highest solubilities were detected in the pH range 4.5 to 5.5 for both concentrations. The apparent solubilities at pH 5.5 with the 2000-ppm and 240-ppm rhamnolipid were 3.6 and 25.7 times greater, respectively, than those at pH 7. The effect of pH on phenanthrene solubility seems to correlate to the type of rhamnolipid aggregate present in the solution. Based on our result, vesicles may have a larger solubilizing capacity for phenanthrene.

The effect of pH on cell growth with biosurfactant. The effect of rhamnolipid and pH, on cell growth and biodegradation of phenanthrene, were monitored as described in the growth experiments above. The specific growth rates at different pHs are shown in Figure 2. Compared to the  $\mu$  values obtained without the biosurfactant, the specific growth rates were increased, and the maximum  $\mu$  values shifted from around pH 6 without the biosurfactant, to around pH 5 which showed a maximum enhancement in the solubility for the abiotic experiment. Zhang et al. (1997) reported the addition of rhamnolipids markedly increased the rate of dissolution of phenanthrene, but increased the rate of biodegradation more moderately. Also, the uptake of micellar phenanthrene requires the transfer of substrate from micelles to cells, which should be inversely related to the affinity of the substrate for micelles. In our study, the increase in the specific grow rates observed were not as high as the increase in the solubilization. The 1.44 times increase in  $\mu$  values at pH 5 was lower compared to the 3.6 times enhancement of solubility. This is supported by the fact that all of the solubilized phenanthrene is not bioavailable to the microorganisms. The trends in the  $\mu$  values were validated by the total substrate loss (%) at the end of the experiment, and this analysis shows similarly with the shift in the maximum value from pH 6 to 5 (Figure 2).



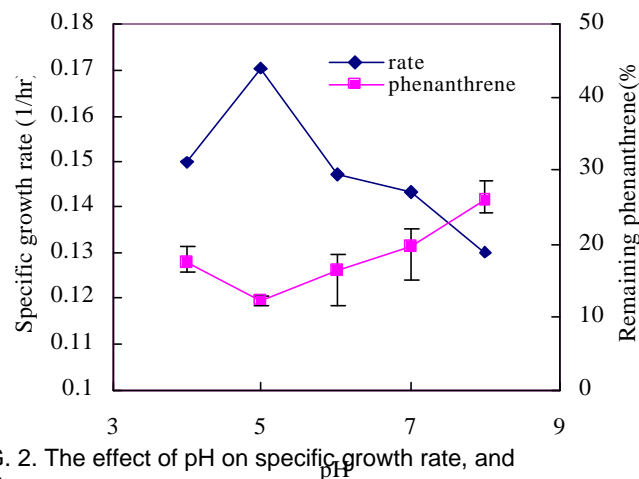
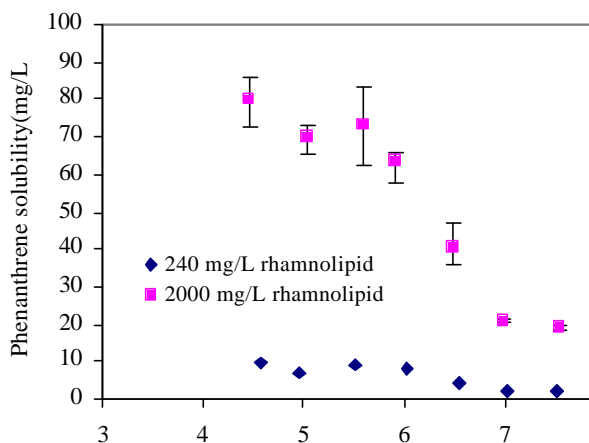


FIG. 1. The effect of pH on phenanthrene solubility in the presence of biosurfactant. FIG. 2. The effect of pH on specific growth rate, and phenanthrene biodegradation, in the presence of biosurfactant

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#### VIII

#### Fungal Biodegradation of Insecticide N,N-Diethyl-m-Toluamide (DEET) and Toxicity of Its Metabolites to *Daphnia magna*

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An insecticide N,N-diethyl-m-toluamide (DEET) was recently reported to be one of the most frequently detected compounds in water resources in United States. Industrial and domestic heavy usage is the main sources for the frequent detection of the DEET in the environments. However, with the best knowledge up to now, there have been no reports for the environmental or biological fate of the DEET and biological toxicity of the metabolites produced from the DEET to organisms. To elucidate biological fate of DEET, 5 different fungi, *Cunninghamella elegans* ATCC 36112, ATCC 9245, *Mucor ramannianus* R-56, *Aspergillus niger* VKMF-1119, and *Phanerochaete chrysosporium* BKMF-1767 were tested. The fungi were grown in the potato dextrose medium containing 1 mM DEET in the final concentration shaking with 200 rpm at 27 °C for 7 days. The metabolites were extracted with ethyl acetate in vacuo and dissolved in methanol. Analysis with high performance liquid chromatography equipped with the reverse phase C-18 column showed three and two metabolites produced from DEET by the incubation of *C. elegans* 9245 and *M. ramannianus* R-56, respectively. The metabolites were not seen in the control experiments with the strains, which did not contain DEET in the medium. Liquid Chromatography/Mass Spectrometry was used to further analyze the metabolites. The metabolites of the DEET, which showed 208 and 164 m/z [M+H]<sup>+</sup>, could be N,N-diethyl toluamide N-oxide and N-ethyl-toluamide by *M. ramannianus* R-56, respectively. *C. elegans* 9245 produced one more metabolite 180 m/z [M+H]<sup>+</sup>, which could be N-ethyl-toluamide N-oxide. In addition, freshwater zooplankton *Daphnia magna* is being subjected for the environmental toxicity evaluation of the DEET metabolites produced by the fungi.

## Arsenic removal using steel manufacturing byproducts as permeable reactive materials in mine tailing containment systems

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Steel manufacturing byproducts were tested as a means of treating mine tailing leachate with a high As concentration. Byproduct materials can be placed in situ as permeable reactive barriers to control the subsurface release of leachate from tailing containment systems. The tested materials had various compositions of elemental Fe, Fe oxides, Ca-Fe oxides and Ca hydroxides typical of different steel manufacturing processes. Among these materials, evaporation cooler dust (ECD), oxygen gas sludge (OGS), basic oxygen furnace slag (BOFS) and to a lesser degree, electrostatic precipitator dust (EPD) effectively removed both As(III) and As(V) during batch experiments. ECD, OGS and BOFS reduced As concentrations to < 0.5 mg/l from 25 mg/l As(III) or As(V) solution in 72 hrs, exhibiting higher removal capacities than zero-valent iron. High Ca concentrations and alkaline conditions (pH ca. 12) provided by the dissolution of Ca hydroxides may promote the formation of stable, sparingly soluble Ca-As compounds. When initial pH conditions were adjusted to 4, As reduction was enhanced, probably by adsorption onto iron oxides. The elution rate of retained As from OGS and ECD decreased with treatment time, and increasing the residence time in a permeable barrier strategy would be beneficial for the immobilization of As. When applied to real tailing leachate, ECD was found to be the most efficient barrier material to increase pH and to remove As and dissolved metals.

## Monitoring of PAH-Contaminated Soils Using Laser-Induced Fluorescence (LIF)

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Laser-Induced Fluorescence (LIF) is one of the most promising optical spectroscopic techniques and relies on the fact that most organic molecules, when excited with UV-light, readily reemit less energetic optical radiation. This LIF investigation of soils will provide significant advantages that reduce the time and cost for the analysis and avoid the complicate experimental procedures such as sampling, preparation and extraction. The portable and power independent system can be easily used for continuous in-situ monitoring. In spite of these advantages, the intensity of fluorescence measurements can be significantly influenced by the presence of soil grains. Therefore, for practical application of LIF into in-situ investigations of the soil, the concept of diffuse reflectance as one of the calibration procedure on fluorescence signal was introduced.

For the feasibility study, the contaminant concentrations dependence on LIF intensity was examined. Fluorescence experiments were carried out on soil specimens contaminated with the spiking solution, which consisted of PAH dissolved in dichloromethane. Phenanthrene and pyrene were selected as representative PAHs. The soils were artificially composed of silt & clay fraction and standard sand fraction. The spectra obtained are time-resolved between 0 and 50ns over the wavelength range 258 to 607nm. Although high correlation coefficient ( $R^2 > 0.97$ ) was obtained, a wide variety of physicochemical properties on soils make it difficult to predict the contaminant contents precisely. The LIF intensity increased with increasing the moisture content and sand content. In order to calibrate LIF intensity for the properties of soils, diffuse reflectance, scattering of lights induced by laser emission, was used and showed correlation enhancement between LIF intensity and PAH concentration. In order to demonstrate the relationship between LIF intensity and contaminant levels with influencing variables from soil properties, statistical approach was carried out using multiple regression and analysis of variance (ANOVA). The level of significance was 5%. The null hypothesis and alternative were:  $H_0 = b_1 = b_2 = b_3 = 0$ , or  $H_1 =$  at least one partial regression coefficients was not zero. The hypothesis that all the variables had the same effect for LIF intensity was rejected and showed that all the variables have different influence on LIF intensity respectively. In three-way ANOVA, The PAH concentration was divided into three groups such as low, medium and high concentrations, while soil moisture content into three groups of dry, common and wet group. As the same way, the hypothesis was rejected and implied that each variable has diverse effect for LIF intensity in relation to the level of factor.

**Acknowledgement**

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## Bioleaching of Arsenic from contaminated tailing using indigenous bacteria

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The bioremediation of heavy metals has received a great deal of attention in recent years, not only as a scientific novelty but also for its potential application. Generally sulfur-oxidizing bacteria such as *At. ferrooxidans*, *At. thiooxidans*, and *At. thioparus* were used in bioleaching process. However, it required an initial acid addition to lower the pH of the system to 4.0 or below and the operational cost is high. Thus, bioleaching process using indigenous bacteria was studied to overcome the disadvantages. The objectives of the studies are to investigate 1) behavior of As leaching according to C-source and O<sub>2</sub> and 2) feasibility to treat As using indigenous bacteria.

The tailings and sediment used in the experiment were taken from the Au-mining site. Variations of total As concentration and As speciation before and after bioleaching were measured. As the result of the analysis, high level of As (3290mg/kgsoil in tailings, 339mg/kgsoil in sediment) were measured. An amount of As in the tailing and sediment existed in Fe-associated fractions can be leached to ecosystem near the mining area.

In bioleaching test of tailing under anaerobic condition, the difference of leached As concentration was shown between sterilized and unsterilized samples when glucose was added as a C-source. In the case of sediment under aerobic condition, some amount of As was removed from the sediment when lactate was added as a C-source. The difference of leached As was shown according to C-sources such as acetate, lactate and glucose and supply of the oxygen such as aerobic and anaerobic conditions. From the results, it can be derived that different microbes interacted with As depending on conditions. Also it can be confirmed that a bioremediation using indigenous bacteria has possibility to treat As contamination.

## Competitive Adsorption Characteristics of Metal Ions onto Cation Exchange Resin

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Many physicochemical methods have been developed for heavy metal removal from wastewater. Among the various treatment techniques available, the most commonly used ones are reduction and precipitation, ion exchange, and adsorption. Among these methods, ion exchange is a highly popular one and has been widely practiced in industrial wastewater treatment process.

In this study, the adsorption behaviors of Co(II), Ni(II), and Cr(III) by cation exchange resin IRN 77 were investigated. The adsorption kinetics and capacities of heavy metal on the ion exchange resin were studied. Competitive adsorption onto the resin was also performed in mixture of metal solution. The results from the kinetic tests verified that equilibrium was attained within 1 hr and the pH was decreased to pH 2.6-2.9 during adsorption because the sulphonic group (-SO<sub>3</sub>H) of resin can serve as an exchangeable ion with metal cations, the pH of solution decreased during the reaction. Each metal adsorption onto the resin was well represented by Langmuir isotherms. Cobalt(II) and Ni(II), which have an equivalent electrovalence, were adsorbed to the resin with a similar adsorption amount when they coexisted in the solution. However, Cr(III) added to the solution competitively replaced Co(II) and Ni(II) which had been adsorbed onto the resin, resulting in desorption of these metals into the solution. The result was likely due to higher adsorption affinity of Cr(III) than Co(II) and Ni(II).

This implies that interactively competitive adsorption of multi-cations onto the resin should be thoroughly examined for an efficient operation of ion exchange process in treatment of industrial wastewater and demineralization of primary coolant system.

## Colloid Barrier Formation by Nanoscale Hematite Particles

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The groundwater treatment using a subsurface treatment zone has been discussed and alternative reactive treatment materials and emplacement methods are being developed (USEPA, 1996). Emplacement of permeable reactive barrier has been limited to relatively shallow depth and width. Chemical reactive barrier is alternative technique, which is now in the research stages, to immobilize contaminants. Colloidal emplacement is to inject colloids of zero valent iron to desired zone in the subsurface perpendicular to groundwater flow for target groundwater contaminants (Kaplan et al., 1997). Durmusoglu et al. (2000) formed a horizontal barrier by injecting gelling liquids to isolate the downward migration of NAPLs in the subsurface. The in-situ chemical reactive barriers are an inexpensive and more effective means of remediation than the conventional trench-and-fill barrier by excavating and refilling solid materials. The most generally proposed material for chemical reactive barriers is zero-valent iron (Fe<sup>0</sup>).

This study will, alternatively, propose to form a chemical reactive barrier to inject nanoscale hematite colloids into the subsurface environment. To minimize the colloid-facilitated transport of contaminants, injection well is installed before zones apart from contaminated plume and extraction well is installed to regulate the colloidal movement in the desired direction. This colloidal reactive barrier would form in the desired area without excavation. Hematite is an excellent adsorbent for arsenic and heavy metals. Zero valent iron lowers the pH of groundwater, removes inorganic oxyanions (CrO<sub>4</sub><sup>2-</sup>, UO<sub>2</sub><sup>2+</sup>, MoO<sub>4</sub><sup>2-</sup>, TcO<sub>4</sub><sup>-</sup>) by reductive precipitation, and arsenic (AsO<sub>4</sub><sup>2-</sup> and AsO<sub>3</sub><sup>2-</sup>) by surface precipitation or adsorption in the limited pH and Eh (Cantrell et al. 1995). Whereas hematite changes pH of groundwater slightly, and adsorb arsenic and heavy metals kinetically faster than zero valent iron.

The objectives of this study are to evaluate the effect of pore fluid velocity and pore grain size on deposition of nanoscale hematite colloids in sand column, and to determine the characteristics of As removal by the nanoscale hematite colloids.

**MATERIALS AND METHODS**

**Hematite colloids.** Hematite colloids were synthesized using the method suggested by Sugimoto et al. (1992). A concentrated Fe(OH)<sub>3</sub> gel was prepared by mixing 100 mL of 2.0 M FeCl<sub>3</sub> with 100 mL of 6 M NaOH. The gel aged at the oven (100 ± 1 °C) for 8 days and cooled to room temperature for 72h. After aging and cooling, excess salts were removed by centrifuging and redispersing the hematite colloids in deionized water, which was tested by AgCl<sub>2</sub> precipitation tests. The concentrated stock solution (pH 5.7) was used for influent of column experiments.

**Batch and Column experiment.** Stock solutions (1 mg As /L) were prepared freshly from reagent grade sodium arsenate for As (V) and sodium arsenite for As (III) (Aldrich) for each batch and column test. Deionized water was aged under N<sub>2</sub> bubbling in advance. Specifically, separate batch tests were performed for each anion using solutions of 1 mg As (V)/L in solutions of NaHCO<sub>3</sub> (1.0 mM, pH 7.38 not adjusted, and 100 mM, pH 8.21 not adjusted), Na<sub>2</sub>SO<sub>4</sub> (1.0 mM, pH 6.42 not adjusted), NaNO<sub>3</sub> (1.0 mM, pH 5.84 not adjusted), and NaCl (10 mM, pH 6.41 not adjusted). The same anion solutions were also used for the As(III) tests. Duplicates were prepared for each anion with hematite colloids and either As(V) or As(III). As concentration was fitted to the pseudo-first-order reaction equations to calculate the reaction rates. The half-lives of As in solution were estimated from the rate equations and normalized to surface area of hematite colloid.

Glass liquid chromatography columns (SPELCO) with an internal diameter of 2.5 cm and a height of 10 cm were packed with approximate 90g of washed sand and used in arsenic displacement experiments.

**RESULTS AND DISCUSSION**

**Effect of anions competition.** The dominant species of As (V) and As (III) present in the system are H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>. Anions would compete effectively for binding sites on iron-oxide because of the Lewis structures of the various species. The presence of bicarbonate at either 1.0 mM or 100 mM noticeably reduced pseudo-first-order rate constants for As(V) removal and for As(III) removal by hematite colloids, compared with 10 mM NaCl. There was no significant difference between kinetic suppression of the two concentrations of bicarbonate. Sulfate did not significantly reduce As(V) removal by hematite colloids but noticeably reduced As(III) removal. The removal rate of As(V) and of As(III) were significantly decreased with 1.0 mM nitrate compared with 10 mM NaCl. The presence of 1.0 mM nitrate is not uncommon in many contaminated groundwater resources, thus its impact on arsenic removal by a colloid barrier wall should not be completely ignored. The implication is that an excess amount of colloid barrier materials may be needed for in-situ remediation of As in groundwater.

**Colloid deposition.**

Calculations of travel distance were carried out for three kinds of grain size (0.1, 0.4, 2 mm) indicating the usual aquifer environment. As the grain size increases, the removal of hematite colloids media grains decreases, and the travel distance increases (Fig 1a). The increased pore fluid velocity (224 –611 cm/day) enhances the travel distance of colloids because of shear-induced diffusion (Fig 1b). The favorable deposition condition was kept because positively charged hematite colloids attached dominantly onto negatively charged sand.

### Colloid-facilitated transport and removal.

To demonstrate the potential for colloid-facilitated removal and deposition, a breakthrough experiment was conducted by a step input (Fig 1c). After 10 pore volumes, the influent was switched to an arsenic solution containing each 1mg As (V)/L. As in effluent solution was coupled to colloid breakthrough, indicating that colloid-facilitated transport with the removal of As. Affinity of adsorption of arsenate is strong and the arsenate attached in hematite colloids is dominant and deposited onto the sand.

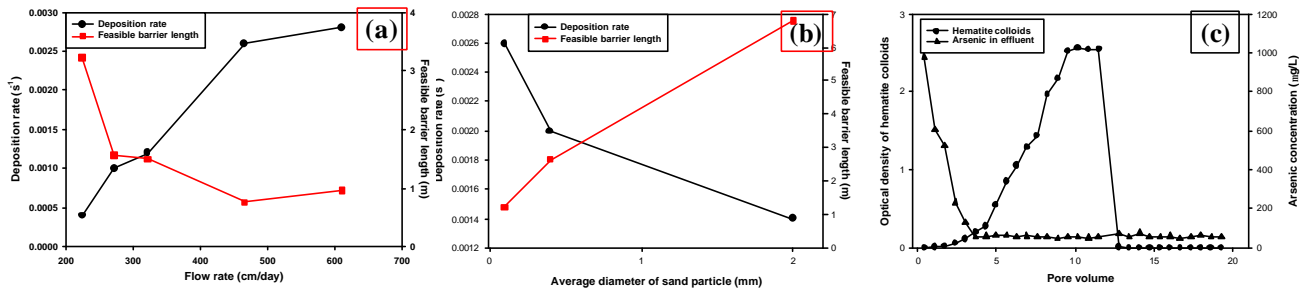


FIG. 1. Hematite colloids deposition with respect to (a) pore fluid velocity and (b) medium grain size, and (c) transport of colloids and removal of As

### ACKNOWLEDGEMENT

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## Influence of NOM on the electrokinetic soil processing for removal of heavy metals

**Won-Seok Kim, Seung-Hyeon Moon, Kyoung-Woong Kim\* and Soon-Oh Kim\*\****\* K-JIST and \*\*Department of Earth and Environmental Sciences, Korea University Republic of Korea*

Electrokinetic (EK) technique is one of the most promising decontamination processes that have high efficiency and time-effectiveness in low-permeable media such as sludge and clay soils. The significance of this method is its low operation cost and potential applicability to a wide range of contaminant types. Soil Organic Matter (SOM) is the whole of the organic material in soils, including litter, light fraction, microbial biomass, water-soluble organics, and stabilized organic matter. This study investigated the influence of NOM to the mobility and adsorption of heavy metals in the EK process.

The objective of this study is to examine the enhancement or attenuation of EK processing by Soil Organic Matter (SOM) in natural soil and to investigate the transport of SOM in electric field and the adsorption in SOM, metal and clay.

Soil used in this experiment was kaolinite, which was contaminated with 1500ppm Cd and 5000ppm of Pb up to a moisture content of 50wt.%. Concentrations of heavy metal contaminants were analyzed by ICP-AES (Thermo Jarrel Ash, USA.). The Humic Acid (HA) was used from Aldrich HA. Reactor shape is rectangular. The size of soil cell is 10cm\*10cm\*15cm. Anode electrode is platinum plate and Cathode electrode is titanium plate. DIW & HNO<sub>3</sub> was used to electrolyte. These experiments are conducted 4 tests. Pre-test is (A) & (C) and applied test is (B) & (D). (A): Electrolyte (DIW), absence HA. (C): Electrolyte (HNO<sub>3</sub>), absence HA. (B): Electrolyte (DIW), presence HA. (D): Electrolyte (HNO<sub>3</sub>), presence HA.

Removal efficiency of Cd is higher with HNO<sub>3</sub> electrolyte in cathode part than that with DIW electrolyte from buffering capacity. As HA affects the adsorption capacity, the removal efficiency of Pb is higher in the soil with HA than those without HA. NOM transferred to the anode part when EK process was applied.

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ACKNOWLEDGEMENT: This work was supported by the National Research Laboratory (NRL) program from the Korea Institute of Science and Technology Evaluation and Planning (Project NO. 2000-N-NL-01-C-185).

XV

## Effect of Aeration on Dissolution of Copper from Anoxic Sediment

**Dong Wook Kim (1), Daniel K. Cha (2)***(1) Cheonan National Technical College, Korea and (2) University of Delaware, USA*

The overall goal of this study was to test the hypothesis that the frequent increases in copper concentrations of the polishing pond at Wilmington Wastewater Treatment Plant (WWTP) during winter months is due to the sulfide oxidation process following the aeration of sediment. The normalized Cu concentrations of the sediment samples ranged from 140 mg/kg to 1580 mg/kg. Batch reactors were conducted with mixing or non-mixing sediment slurries at 25, 10, and 4 oC. The changes in copper and sulfate levels in the supernatant of sediment slurries were determined.

Dissolved Cu concentration of up to 200 µg /L was observed in a continuously aerated reactor. Increases in Cu concentrations coincided with the trend observed for sulfate concentrations, confirming that the Cu solubilization was due to sulfide oxidation. The mobilization of Cu in the aerated system increases with increasing temperature, indicating that increasing temperature accelerates the sulfide oxidation process. However, for non-aerated systems, dissolved Cu concentrations were highest in 4 oC reactor, suggesting that under oxygen-limiting conditions, the sulfide oxidation process was controlled by oxygen transfer from the atmosphere.

Results from this study strongly indicates that high Cu excursion in the polishing pond at WWTP during winter months, especially following windy days may be attributed to the increase in dissolved oxygen (DO) concentrations in the water column.

XVI

Development and application of porous hydraulic structure to improve water quality in small and middle sized streams

**Hye-Mi Lee, Jae-Young Park, Jong-Min Oh**

*Department of Environmental Science and Engineering, Kyung Hee University, Korea*

The water quality of river especially located in urban areas became deteriorated by inflow of pollutant originated from sewages and non-point sources. The direct purification method developed for treatment of inflow water has used as a very useful tool. Until now, gravel, waste plastic, or waste concrete has been used mainly as a contact media of direct purification method. These materials however have some troubles that must be overcome such as block phenomenon by low specific surface, unstable treatment efficiency by changing pollutant concentration of inflow water and low treatment efficiency for T-N and T-P. The porous concrete as a substitute material for them therefore was examined in this study because of their void ratio that could be adjusted, high treatment efficiency for pollutants by attached biofilm in their internal void and their applicability to constructions in the stream. The objectives of this study were to development porous hydraulic structures (porous weir and porous river bed materials), to estimate their physical and chemical characteristics and to investigate their purification ability of water quality in small and middle streams.

The results of this study were as follows:

- 1) Their physical and chemical characteristics were estimated to be useful to application of porous hydraulic structures in the stream
- 2) When the ordinary weir and natural river bed materials were applied to hydraulic structures ( $Q=10.0 \text{ ? /day}$ ), the average removal efficiency of SS, BOD and COD were 48.4%, 25.2% and 12.0% respectively.
- 3) When the porous weir and porous river bed materials were applied to hydraulic structures ( $Q=10.0 \text{ ? /day}$ ), the average removal efficiency of SS, BOD, COD and T-P were 83.0%, 62.1%, 45.9% and 32.3% respectively.
- 4) When the porous weir and porous river bed materials were applied to hydraulic structures ( $Q=1.0 \text{ ? /day}$ ), the average removal efficiency of SS, BOD, COD and T-P were 91.6%, 84.7%, 63.2% and 60.2% respectively.

Judging from our results, porous concrete applied to the weir from took a great role of removal efficiencies of BOD, COD and T-P.

XVII

Monitoring of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in marine sediments of the Southeastern coast, Korea

**Se-Jin Lee, Byung-Hoon Kim, Yoon-Seok Chang**

*School of Environmental Science & Engineering, Pohang University of Science and Technology, Korea*

The Korea peninsula is surrounded by the sea on the western, southern, and eastern sides and a variety of large industrial complexes and municipal cities are located and a great number of people lives along the coastal areas. Therefore, various contaminants are entering and accumulated on the bottom of the sea. Ultimately, these pollutants affect to the human as well as the aquatic environments.

Marine sediment can be a record of the current/past status of contamination and its fine particles can be a medium of spreading toxic compounds. The objective of our study is to evaluate the concentrations and distributions of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) in sediment according to the different locations, especially Southeastern coast, which exist large industrial complexes along the coast, and according to the different particle sizes in Korea.

At first, we studied the sediments collected in Masan bay in 1996 and 1997. Sediments (30g) were separated by SPLITT (Split-flow thin fractionation) technology in order to determine the concentrations and distributions of PCDD/Fs in different particle sizes (<1.0, 1.0~2.5, 2.5~5.0, 5.0~10, 10~20, and 20~53  $\mu$  in diameter). And the analysis of PCDD/Fs was accomplished according to the US EPA method 1613 and by high-resolution gas chromatography/high-resolution mass spectrometry (JMS 700T). Total concentration of PCDD/Fs increased as the particle size decreased and this trend was consistent with the previous study. It is considered that small particles have larger surface area and higher concentration of organic carbon.

Based on this research, besides Masan, the study of PCDD/Fs in the southeastern coastal areas such as Pohang, Ulsan, Pusan is now being carried out. These cities are characterized with heavy industries of steel, chemical, textile complexes, resulting that the sediments should be contaminated according to the types of



industries. We are also dividing the sediments with different particle sizes. Therefore, we can obtain the distribution picture of PCDD/Fs geographically with different sources and particles sizes of sediments.

XVIII

Restoration of fresh water ecosystem and the mechanism of water quality improvement by artificial vegetation island

**Byeon, Myeong-Seop, Jae-Jun Yoo<sup>1</sup>, Ok-Sun Kim (1), Seung-Ik Choi (2), Tae-Seok Ahn (1), (3)**

*(1) Department of Environmental Science and (2) Environmental Research Institute, Kangwon National University, Korea and (3) Kangwon Regional Environmental Technology Development Center, Korea*

Even though the main purpose of installation of artificial vegetation island (AVI) was water quality improvement, it was impossible to catch out the evidence of improvement. Under the AVI, the water quality was worse than control site by simple comparing of the chemical parameters. For example, the values of SS and COD under AVI were about two times higher than those of control site. But, the abundance of zooplankton of AVI site at extreme period was 400 times higher than that of control site. This means that the AVI is acting as a new ecosystem created by macrophyte and microorganisms. So for scrutinizing the microbial ecosystem under the AVI and possible mechanism of water quality improvement through newly created ecosystem, we measured the microbial and biological parameters at Lake Paldang, where the large AVI was installed at May, 2000.

Zooplankton and bacterial numbers and exoenzyme activities (beta-glucosidase and phosphatase) were measured biweekly from 3, November 2001 to 20, April 2002 at AVI site and control site. The zooplankton numbers of AVI site were averagely 25 times higher than those of control site. Respiratory active bacterial numbers were 3-8 times higher at AVI site, but the total bacterial number was not different at both sites. And both enzymatic activities were also higher at AVI site than those of control site.

These results suggest that the biological compositions and ecological functions of newly created ecosystem under AVI were quite different from those of control site. Moreover, this new ecosystem was operating for organic material removal by respiration of zooplankton and high activities of microorganisms. These high activities were resulted from the tight couplings of zooplankton-phytoplankton-macrophyte-bacteria relationships.

IXX

New method for detection of Microcystin-producing Cyanobacteria in lake waters by competitive PCR

**Jun-Ho Kim (1), Chi-Kyung Kim (1), Tae-Seok Ahn (2), and Dong-Hun Lee (1)**

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*(2) Department of Environmental Sciences, Kangwon National University, Chuncheon 200-701, Korea*

The microcystin produced by cyanobacteria in surface waters, such as lake and river, is a kind of serious environmental problems due to its toxicity to humans and wild lives. Several different methods have been utilized to detect the microcystin in water. However, those methods generally require expensive instruments and take a long time to detect the toxic compound. In this study, the microcystin-producing cyanobacteria were detected by a simpler molecular biological method in order to monitoring the microcystin in lake waters. Two pairs of primers, MSF/MSR and TOX2F/TOX2P, were selected on the basis of the nucleotide sequence of the genes responsible for microcystin which were reported in 12 species of cyanobacteria. The water samples taken from 10 lakes in Korea were examined for existence of the cyanobacteria by PCR using each of the primers. From all the water sample, cyanobacteria capable of producing microcystin were detected by the PCR. The HPLC also proved that microcystin was detected in those water sample. On the other hand, the mcy genes of *Microcystis aeruginosa* NIER 10010 were isolated and then amplified by PCR using each of the primers. The PCR products were inserted into pGEM T-easy vector to construct two competitor plasmids with the primers. The plasmids were reacted with the DNA isolated from each lake water by competitive PCR technique to identify the cyanobacteria. The microcystin-producing cyanobacteria in the waters could be quantified by the competitive PCR using the competitor plasmids.

XX

Recycle scheme of sewage water using planting concrete for insurance of retention of instream flow

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Recently, drying of the river flow in urban stream with rapid urbanization is getting difficult in utilization of water resource. For this reason, recycle scheme of sewage water is a useful method to prevent drying of the river flow. Therefore, the objectives of this study were that the planting concrete for improvement plan of sewage water quality was manufactured and its purification ability was evaluated to insurance of retention of instream flow.

pH of porous concrete used as a material of planting concrete was investigated because the pH is very important factor in growth of plant. Based on the result, the pH of porous concrete was maintained the range of pH 7.0 ~ 7.5 after 28 hours with and without neutralization. This range was shown to be in satisfying condition for growth of plant.

In the batch test to understand the purification ability, the removal efficiencies for DOC, NH<sub>4</sub>-N, NO<sub>3</sub>-N and PO<sub>4</sub>-P were 75%, 68%, 90% and 42%, respectively. Experiment using reactor induced sewage treatment system, the removal efficiencies for SS, BOD, COD, TN and TP were 58%, 42%, 26%, 45% and 53%, respectively.

From this result, it was proved that the planting concrete had very high efficiency for pollutant removal of in sewage water and is very useful for insurance of retention of instream flow. Accordingly, if planting concrete applies to media, them improvement of water quality and insurance of retention of instream flow will be expected.

## XI

### Effect of Aeration on Dissolution of Copper from Anoxic Sediment

**Dong Wook Kim (1) and Daniel K. Cha (2)**

*(1) Department of Environmental Engineering, Cheonan National Technical College, Korea*

*(2) Department of Civil and Environmental Engineering, University of Delaware, USA*

The overall goal of this study was to test the hypothesis that the frequent increases in copper concentrations of the polishing pond at Wilmington Wastewater Treatment Plant (WWTP) during winter months is due to the sulfide oxidation process following the aeration of sediment. The normalized Cu concentrations of the sediment samples ranged from 140 mg/kg to 1580 mg/kg. Batch reactors were conducted with mixing or non-mixing sediment slurries at 25, 10, and 4 oC. The changes in copper and sulfate levels in the supernatant of sediment slurries were determined.

Dissolved Cu concentration of up to 200 µg /L was observed in a continuously aerated reactor. Increases in Cu concentrations coincided with the trend observed for sulfate concentrations, confirming that the Cu solubilization was due to sulfide oxidation. The mobilization of Cu in the aerated system increases with increasing temperature, indicating that increasing temperature accelerates the sulfide oxidation process. However, for non-aerated systems, dissolved Cu concentrations were highest in 4 oC reactor, suggesting that under oxygen-limiting conditions, the sulfide oxidation process was controlled by oxygen transfer from the atmosphere.

Results from this study strongly indicates that high Cu excursion in the polishing pond at WWTP during winter months, especially following windy days may be attributed to the increase in dissolved oxygen (DO) concentrations in the water column.

## XII

### Geostatistical Interpretation of the Environmental Radioactivity in the Vicinity of Youngkwang Nuclear Power Plant

**So-Young Kang × Ilwon Ko × Eun-Joung Ko × Jae-Suk Lee × Seung-Hyun Moon**

**Chul-Seung Park × Kyoung-Woong Kim**

*Energy and Environment Research Center, Kwangju Institute of Science and Technology (K-JIST), Korea*

In order to investigate the influence of nuclear power plant operation on its nearby environment, soil, stream and marine sediment samples were collected in the vicinity of the Youngkwang Nuclear Power Plant in Korea, and analyzed for artificial and natural radionuclide radioactivity. From the analytical result, Cs-137 was detected in most soil samples, but it may have been derived from past nuclear weapon tests because Cs-134 having short half-live was not detected. The radioactivities of Cs-137 in the sediment samples were also detected which are within the normal range in the sediments based upon the published literature (1997-99).

For the quality control of radioactivity analysis of environmental samples, sets of marine sediments in the Gamami area were analyzed using two HPGe Gamma-ray Spectroscopes (30 % and 45 %) according to the geostatistical sampling strategy, and Cs-137 and K-40 results were interpreted by analysis of variance (ANOVA). In the two-way ANOVA, variances derived from the geochemical variation were significant, but error from sampling and analytical procedures are negligible. In conclusion, all the radioanalytical procedures of this study including sampling are proved to be acceptable.

## Development of Enhanced Uptake Capacity of Uranium in Transgenic Plants by Alteration of Citrate Synthesis

**Pei-chun Chang, and Kyoung-Woong Kim**

*Department of Environmental Science and Engineering, Kwangju Institute of Science and Technology (K-JIST)*

Plant species have shown the capacity to absorb U into the biomass. Norman(1952) even suggested that uranyl ion acts as an accessory microelement in growth of Lemna and flax roots. The plants, termed metal hyperaccumulators, can extract and accumulate more than 1000-10,000 $\mu\text{g}$  heavy metal / g of dry weight of plants (0.1-1%). The most vital main factors influencing the ability and efficiency of phytoremediation is the ability of the plant to uptake the metals from soil in prior to the accumulation in the plant tissue. Huang(1998) reported Brassica juncea had a capacity to accumulate 5,000mgKg<sup>-1</sup> U in the shoots by the enhancement of citric acid. Dushenkov(1997) reported that the bioaccumulation coefficients of Helianthus annuus based on the ratios of U concentration in the roots vs. U concentration reached 30,000 in the aqueous phase system.

The low solubility of heavy metals and radioactive nuclides in the soil is usually a limiting factor in metal extraction by plants. Adding chelating compounds that solubilize non-available heavy metal should increase metal uptake by plants. For example, Huang(1998) showed citric acid could trigger uranium hyperaccumulation in some plant species, including Brassica juncea, by more than 1000 fold within a few days. Unfortunately, side effects related to the addition of chelates, e.g. metal leaching, may occur, too. Subsequently, the citric acid-bond uranyl ions that do not be uptaken into plant roots may migrate into and contaminate ground water.

It has been shown that phytoremediation using conventional plants has some potential for use in remediation; but also that it is encumbered by limitations that prevent widespread benefits from its significant economies. Therefore, the potential of genetic engineering for enhancing the remediation capacity of plants has been recognized. Heaton(1998) engineered plants with a modified bacterial mercuric reductase gene (*merA*) and mercurial lyase (*merB*) were capable of converting ionic mercury and methylmercury to the much less toxic Hg(0), which is volatilized from plants to an enormous global atmosphere Hg(0) pool. Besides, selecting sterile plants and controlling propagation by harvesting before flowering can avoid genetic release to the ecology.

### Enhanced Uptake Capacity of Uranium in Transgenic Plants by Alteration of Citrate Synthesis

#### Theory:

Brassica juncea showed the enhanced uranium uptake capacity by addition of citric acid, but the citric bond uranyl ions, which exist out of rhizosphere, have higher probability to leach downward rather than to be uptaken by plants. The application of genetic engineering to aggrandize the citric acid exudation from roots of transgenic plants could be a plausible method to prevent the metal leaching problem.

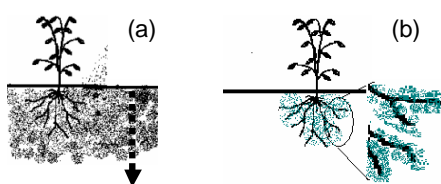


Fig 1. The sketch map of transgenic plants with enhanced citric acid exudation ability; (a) the additional citric acid-uranium complexes existing out of rhizosphere may leach downward, and (b) transgenic plants could exudates citric acid and uptake uranium immediately without leaching.

#### Method:

Constructing a chimeric gene with the coding sequence of the Pseudomonas aeruginosa citrate synthase gene (CSb) fused to the 35S promoter from the cauliflower mosaic virus to form 35S-CSb sequence. Then, introducing the 35S-CSb sequence into Brassica juncea, Helianthus annuus and Brassica napus using Ti Plasmid-derived transformation system. The presence of the transgene could be confirmed by PCR analysis (Fuente, 1997). After selection the lines harboring the transgene, tissue culture techniques will be applied to differentiate and domesticate the transgenic plants and finally test the transgenic plants in the uranium contaminated soil.

#### Result:

The seeds were obtained from Korea Research Institute of Bioscience and Biotechnology (KRIBB) and SeedBank for Wild Herbaceous Plant Species at Korea University. Figure 2 shows the pictures of seedlings of plant species in this experiment.



Fig 2. Pictures of 3-weeks old seedlings of (a) *Brassica juncea*, (b) *Brassica napus* and (c) *Helianthus annuus*.

(a)

(b)

(c)

#### Acknowledgement

This research is supported by the Korea Science and Engineering Foundation (KOSEF) through the Advanced Environmental Monitoring Research Center at K-JIST and by the Brain Korea 21 Program of the Ministry of Education.

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#### XXIV

### Contamination Level and Chemical Form of Arsenic in the Water System from Some Abandoned Au-Ag Mines

**Jin-Soo Lee, Ji-Min Yi and Hyo-Taek Chon**

*School of Civil, Urban and Geosystem Engineering, College of Engineering, Seoul National University*

The objectives of this study are to investigate the extent and degree of As contamination of waters and sediments influenced by previous Au-Ag mining activities and to assess the chemical form of As in contaminated waters and sediments. For this study natural waters (mine water, surface water and groundwater) and stream sediments were sampled in and around five Au-Ag mine (Au-bearing quartz veins) areas. The main contamination sources of As in these abandoned Au-Ag mines (Dongil, Okdong, Dongjung, Gubong and Samkwang mine) can be suggested by mine tailings and waste materials including the sulfide gangue minerals such as arsenopyrite (AsFeS). The pollution levels of As in mine water of the Dongil (524  $\mu\text{g/L}$ ) and the Samkwang mine (444  $\mu\text{g/L}$ ) were much higher than those of the Okdong (17  $\mu\text{g/L}$ ) and the Gubong mine (56  $\mu\text{g/L}$ ). Elevated levels of As in stream water were also found in the Dongil (0.9~118  $\mu\text{g/L}$ ) and the Samkwang (21~1042  $\mu\text{g/L}$ ) mine. Arsenic concentration in groundwater was highly elevated in the Dongil (0.9~64  $\mu\text{g/L}$ ), the Okdong (0.2~69  $\mu\text{g/L}$ ) and the Gubong (0.5~101  $\mu\text{g/L}$ ) mine areas. Therefore, it can be possible to the risk of arsenicosis because groundwater is used by drinking water in these study areas. Arsenate[As( $\text{V}$ ), H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>] was more dominant than arsenite[As( $\text{III}$ ), H<sub>3</sub>AsO<sub>3</sub>] in waters from the most mine areas. However, the concentration ratio of As( $\text{V}$ ) to As(total) present up to 95 % in stream water from the Okdong mine and 82 % in groundwater of the Okdong and the Dongjung mine. Arsenic showed significant correlations with cation (Ca, Cu, K, Mg) and anion (HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) in water system.

## Hydrogeochemical Characteristics of Dissolved Ions in Stream Waters and Chemical Speciation of Heavy Metals in Sediments from the Tancheon River, Korea

**Sung-Eun Lee (a), Jin-Soo Leea, Hyo-Taek Chon (a) and Kyu-Han Kim (b)**

*(a) College of Engineering, Seoul National University (b) Dept. of Science Education, Ewha Womans University*

The Tancheon river is one of large tributaries to the Han-River in Seoul, Korea. This river runs through highly urbanized and industrialized areas, joins several streams and then finally joins to the Han-River in Seoul, loading out large amounts of potential pollutants. In order to investigate the contamination level and chemical speciation of heavy metals in stream waters and sediment from the Tancheon River, river water and sediment samples were collected at 18 locations, along a distance of 69 km, between Yongin-si in Kyunggi-do and Samsung-dong in Seoul on October in 2000 (after rainy season) and April in 2001 (before rainy season). After appropriate sample preparation, stream waters and sediments were analyzed for the dissolved ions and heavy metals by IC, ICP-AES and AAS.

The levels of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^{-}$ ,  $\text{HCO}_3^{-}$  in the Tancheon River were higher than those in world average river water, but those of Cd, Fe, Mn, Pb, and Zn lower. However, high concentrations of Pb and Zn were found near densely residential areas and the Sunghnam waste water treatment plant. The relative enrichment of ion and metal was caused by the inflow of local domestic and industrial sewages. Heavy metals (Mn, Cd, Cu, Pb, Zn) concentrations in stream sediments from the Tancheon river exceeded the lower limit of tolerable level in bottom sediment established by the Ontario Ministry of the Environment (OME) of Canada. Concentrations of these metals in sediments increased from upstream to downstream due to input of anthropogenic contaminants. Especially, high levels of heavy metals were found in sediment near the Sunghnam waste water treatment plant in the Tancheon river. Heavy metals were higher elevated in sediments collected from before rainy season rather than after rainy season. From the result of sequential extraction analysis for stream sediments, relatively high proportion of Mn and Zn are present as exchangeable and carbonates fractions. This indicates that these elements are more mobile and bioavailable than other elements in water system.

## Determination of Cr(VI) using an Ion Selective Electrode with a Carrier Immobilized Membrane

**Young-Woo Choi, Yong-Jin Choi, Seung-Hyeon Moon**

*Department of Environmental Science and Engineering, Kwangju Institute of Science and Technology*

Cr(VI) is one of the hazardous heavy metals monitored in water and wastewater streams. Ion selective electrodes (ISEs) for ionic materials have been widely used with the poly(vinyl chloride) (PVC) homopolymer containing appropriate carriers. In previous studies, supported liquid membranes (SLMs) have been employed for selective determination of Cr(VI). However, the electrodes still have some serious drawbacks such as short lifetime and unstable potential drift. These are due to the leaching-out of the substances (carriers) into sample solutions during long-term measurement of Cr(VI). The objective of this study is to develop Cr(VI) sensor with a carrier-immobilized membrane for stable determination. The problems can be solved by immobilization of carriers on supporting materials. In this study, N,N,N,N-tetrakis(3-aminopropyl)-1,4-butanediamine (DABAm4) having 3rd amine groups was selected as a Cr(VI) selective monomer to be immobilized onto PVC films. A novel method for preparation of carrier-immobilized membrane was introduced by a sequential ultraviolet (UV)-induced graft polymerization and copolymerization technique.

### Results and Discussion

A novel carrier-immobilized membrane was prepared to determine Cr(VI) in waste water by sequential ultraviolet (UV)-induced graft polymerization and copolymerization technique. Hydrophobic nonporous polyvinyl chloride (PVC) membranes were made with Cr(VI) selective surface by copolymerization of DABAm4 on PVC membrane. NPOE introduced into the prepared carrier-immobilized membrane to make Cr(VI) diffusible channels was optimized as 0.5 ml/ 0.5 g PVC. A stable response of Cr(VI) using the optimized ISE was obtained repeatedly within 1 sec. detection time in the range of 0.1 - 5000 ppm. Selectivity for Cr(VI) against interfering ions increased as an order of  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_2^- > \text{NO}_3^- > \text{CO}_3^{2-} > \text{SCN}^- > \text{I}^-$ . From the result of FT-IR spectra between an initial and used membrane, it was verified that the immobilized tertiary amine groups on the membrane were sustained for a long-term experiment. Therefore, it is suggested that the ISE with the carrier-immobilized membrane is not only stable for long-term determination of Cr(VI) but feasible and reproducible for continuous monitoring of Cr(VI) in environmental waste water.

### Acknowledgements

This work was supported in part by the Korea Science and Engineering Foundation (KOSEF) through the National Research Laboratory (NRL) Program of Korea Institute of Science and Technology Evaluation and Planning (Project 2000-N-NL-01-C-185).

# Workshop Programme

## January 26, 2003

08:30 - 09:00	Participant registration and document delivery
09:00 - 09:30	Opening Ceremony Welcoming Address Dr Jung-Woong Ra, President, KJIST
09:30 - 9:40	Opening Address Prof. Motoyuki Suzuki, Vice Rector, UNU Session 1: Overview of Current Activities and Data on Environmental Quality in East Asia Chairs: Prof. M. Suzuki, UNU and Prof. S. H. Moon, KJIST
09:40 - 10:10	The need for Environmental Quality Guidelines and Early Warning Systems to Combat Pollution in the East Asian region Dr Zafar Adeel, Project Manager, UNU
10:10 - 10:40	The Status of Major EDC Pollutants in East Asian Waters Ms. Caroline King, Project Assistant, UNU
10:40 - 11:10	Overview of Environmental Standards in East Asia Ms. Kumiko Tsukamoto, UNU
11:10 - 11:40	Coffee break
11:40 - 12:10	Monitoring of EDCs in the soil and aquatic environments Prof. Kyoung-Woong Kim, K-JIST
12:10 - 13:40	Lunch  Session 2: Environmental Quality Guidelines in East Asia Chairs: Prof. Keichiro Fuwa, UNU and Dr. Kyunghee Choi, NIER
13:40 - 14:10	Acceptable Daily Intake (ADI), Tolerable Daily Intake (TDI) and Environmental Quality Standard for chemicals in Japan Dr Masatoshi Morita, NIES, Japan
14:10 - 14:40	Environmental Standards in China Dr Yeru Huang and Li Zhou, SJFC, China-Japan Friendship Center for Environmental Protection
14:40 - 15:10	Coffee break
15:10 - 15:40	Environmental Standards in Thailand Ruchaya Boonyatumanond, Sukanya Boonchalermkit, EMC
15:40 - 16:10	The status of aquatic environment monitoring in Malaysia Dr Mustafa Ali Mohd. Univ. of Malaya
16:10 - 17:00	Discussion Session
17:00 - 17:30	Formulation of Recommendations



## January 27, 2003

- Session 3: Environmental Monitoring and Analytical Techniques  
Chairs: Dr Masatoshi Morita, NIES and Prof. Man-Bock Gu, KJIST
- 9:00 - 9:15 Introduction to the UNU Project in Nine East Asian Laboratories: Comparative Monitoring Activities and Standardized Methods  
Prof. Keichiro Fuwa, Senior Project Adviser, UNU
- 9:15 – 9:45 Internal Validation of Analytical Methods for OCPs, Phenols and Phthalates in Water  
Dr Evangeline Santiago, Univ. of Philippines
- 9:45 – 10:15 The Development of Advanced Analytical Techniques for POPs Monitoring  
Prof. Hian Kee Lee, NUS, Singapore
- 10:15 – 10:45 Direct Extraction of Phenolic Compounds from Acid-Digested Sediment for Simultaneous GC/MS Analysis  
Jae Ryoung Oh, Donghao Li, and Jongman Park, KORDI
- 10:45 - 11:15 Coffee break
- Session 4: Discussion Session
- 11:15 – 11:45 Introduction to the Inter-laboratory Calibration Concept and Possible Approaches  
Dr Zafar Adeel, Project Manager, UNU
- 11:45 - 12:45 Discussion
- 12:45 – 14:15 Lunch
- Session 5: EDC's Research in Korea  
Chairs: Dr Zafar Adeel, UNU and Prof. Kyoung-Woong Kim, K-JIST
- 14:15 – 14:45 Monitoring of organic pollutants in the coastal environment of Korea  
Won Joon Shim, Sang Hee Hong, Un Hyuk Yim and Jae Ryoung Oh, KORDI
- 14:45 – 15:15 Strategies and Perspectives on EDCs Research in Korea  
Dr. Kyunghee Choi, National Institute of Environmental Research
- 15:15 – 15:45 Monitoring of POPS level in human breast milk and its risk analysis: Korean perspective  
Dr. Park (President of Lab Frontier, former Director of Korea Food and Drug Administration)
- 15:45 – 16:15 Coffee break and Poster Session
- 16:15 – 16:45 Toxicity Monitoring and Classification of EDCs Including Dioxins Using Recombinant Bioluminescent Bacterial Biosensors  
Prof. Man-Bock Gu, K-JIST
- 16:45 – 17:15 Electroenzymatic Degradation of Persisting Organic Pollutants  
Prof. Seung-Hyeon Moon, K-JIST
- 17:15 – 17:30 Closing Remarks  
Prof. Keiichiro Fuwa, Senior Adviser, UNU

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# Workshop Presentations

