LINGKUNGAN HIDUP

UNITED NATIONS UNIVERSITY

UNU International Symposium on "POPs: Global Transport, Best Environmental Practice, and Risk Perception"

14 November 2007
Istana Ballroom, Sari Pan Pacific Hotel
Jakarta, Indonesia

Organized by
Pusarpedal-KNLH Indonesia
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The UNU Project Management Meeting and International Symposium Schedule
13-15 November 2007, Sari Pan Pacific Hotel, Jakarta - Indonesia

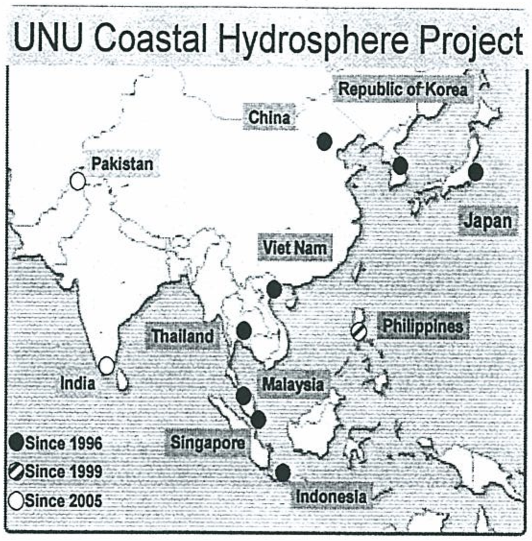
Day 1, November 13, 2007
Project Management Meeting (Closed Meeting)
Venue : Sari Pan Pacific Hotel, Jakarta (Phone: +62-21-3902707)

9:00 - 9:10	Opening	UNU - Dr. Fukuya Iino
9:10 - 9:20	Selection of Chair and Agenda Setting	
9:20 - 11:00	5 Country Reports	China India Indonesia Korea Malaysia
11:00 - 11:10	Coffe Break	
11:10 - 12:50	5 Country Reports	Pakistan Philippines Singapore Thailand Vietnam
13:00 - 14:30	Lunch Break	
14:30 - 15:00	Presentation from AIT on Viet Nam's NIP	Prof. Henning Schroll
15:00 - 15:40	Evaluation of Analytical Method	Dr. Morita
15:30 - 15:40	Coffe Break	
15:40 - 18:00	Project Management Issues	Dr. Fukuya Iino
18.00 - 20.00	Welcome Dinner	

Day 2, November 14, 2007
International symposium on POPs
Symposium title: **POPs: Global Transport, BEP, and Risk Perception**
Venue : Sari Pan Pacific Hotel, Jakarta (Phone: +62-21-3902707)

8:00 - 9.00	Registration	
9.00 - 9.10	Organizing Comitee Report	Dra. Halimah Syafrul, Msi - MoE
9.10 - 9.20	Welcom Speech from the GOI	Ir. Isa Karmisa A. - Deputy VII MoE
9.20 - 9.30	Opening address	Dr. Masatoshi Morita UNU Programme Advisor
9:30 - 10.30	**Low risk and high public concern!? The cases of persistant organic pollutants (POPs), heavy metals, and nanotech particles**	Prof. Dr. W. Roland Scholz Institutefor Env. Decisions (IED) Natural and Social Interface (NSSI), Zurich, Switzerland
10.30 - 10.45	Coffe Break	
10.45 - 11.15	Indonesia Government NIP	GOI, Deputy IV MoE
11.15 - 11.45	UNU Project report 1 INDONESIA	Dra. Halimah Syafrul, MSi. Pusarpedal KLH
11.45 - 12.15	Presentation	Yasuyuki Shibata Director Env. Chem. Div., National Institute for Env. Studies, Japan
12.15 -12.45	Panel discussion	Moderator: Dr Sri Nuegrohati
12.45 - 14.00	Lunch Break	
14.00 - 15.00	**Measurement of dioxin emissions from bushfires in Australia**	Dr. C.P (Mick) Meyer CSIRO, Marine and Atmospheric
15.00 - 15.30	UNU Project report 2 (Republic of Korea)	Dr. Sang Hee Hong
15.30 - 16.00	UNU Project report 3 (India)	Prof. Babu Rajendran
16.00 - 16.30	**Organochlorine dynamics in Indonesian Tropical Climate: a study in Segara Anakan Estuarine Ecosystem**	Dr. Sri Noegrohati Indonesia: The Gadjah Mada University- Yogyakarta
16.30 - 17.00	Panel discussion	Moderator: Dr. Mustafa Ali Mohd
17.00 - 17.15	Closing remarks	
17.15	Coffe Break	
17.30	Close	

Message from UNU



Persistent Organic Pollutants (POPs) have become an international agenda since the Stockholm Convention entered into force in 2004. The Convention is designed to reduce global concentration levels of 12 POPs which have been found in animals in higher food chain living in a remote place as far as the polar zones. Some of the POPs were used as pesticides or industrial chemicals. The others are unintentionally emitted mainly from various incineration processes. These chemicals have been also identified in human blood and breast milk.

This UNU symposium, "POPs: Global Transport, Best Environmental Practice, and Risk Perception" is aimed to introduce two important concepts in raising awareness among the general public to reduce POPs emission; Best Environmental Practice (BEP) and Risk Perception. Open burning still prevails in many parts of the world because "open burning is the cheapest, easiest, most sanitary means of volume reduction and disposal of combustible materials" as found in the latest draft of guidance of BEP published by the Stockholm Convention. While the guidance clearly states that its provision should not be considered as acceptance of the practice, it provides practical guidance to reduce POPs emissions from open burning.

The success of the POPs reduction, therefore, is now in the hands of the general public. What policy makers need to understand is the concept of risk perception. Risk perception has been extensively studied since the publication of the original paper (Slovic, Science, 236, 280-285, 1987.) The paper found that unknown and dread risks are perceived as higher risks than they really are by the general public.

Risk communication and monitoring results play significant roles to help the general public raise their appropriate awareness and take voluntary actions to reduce risks in their daily life.

The UNU's project, "Environment Monitoring and Governance in the Asian Coastal Hydrosphere", has been supporting chemical analysis capacity building efforts of 10 Asian countries since 1996. The chemical analysis capacity is indispensable to monitoring POPs and assessing its risks and successfully implementing the Stockholm Convention's mandates. This symposium is one of the UNU's project efforts to disseminate the project results and offer opportunities for Asian countries to share the latest status of the global issues.

In addition to presentations given by our project partners, this symposium will invite three international researchers who will share their latest research results on regional transport of POPs, risk perception and open burning research results as well as representatives from the Government of the Indonesia. I believe this symposium will provide a discussion platform for experts, policy makers, industrial stakeholders and general audience to further deepen their scientific understanding on POPs, exchange their concerns, and identify shared views and future needs.

Finally, I would like to thank the organizers, Environmental Impact Control Facility (SARPEDAL), and the Government of Indonesia for organizing this symposium as well as all other participants and audience who joined us today. I also look forward to receiving your comments and opinions.

Itaru Yasui
Vice Rector, UNU

Study on Residues of Organic Chlorinated Pesticides in Bohai Sea

Yeru HUANG, Liang DONG, Ting ZHANG, Shuangxin SHI, Dingding SHAO, Li ZHOU, China-Japan Friendship Centre for Environmental Protection, P.R.China

Abstract

In September, 2007, after China's fishing-closed period(from 14th June to first September every year), China-Japan Friendship Center for Environmental Protection has collected some samples from 10 cities and town in Bohai Region, including sea water, Chinese prawns and sea bass to study the residues of organic chlorinated pesticides there. According to *Manual for Sample Collection and Analysis*, we have analyzed the 14 organic chlorinated pesticides(OCPs) in labs and finally obtained detailed data. In this report, we will first give an introduction to Bohai Region and then give a brief introduction to our analysis.

Bohai Sea, shallow northwestern arm of the Yellow Sea, off the North China coast, is enclosed by the Liaodong Peninsula (northeast) and the Shandong Peninsula (south). The gulf's maximum dimensions are 480 kilometres from northeast to southwest and 306 kilometres from east to west. The strait leading to the gulf is about 105 kilometres in width. The mean depth of Bohai Sea is about 18 meters. The Yellow River, China's second longest river, discharges into the gulf. Two other major rivers draining into Bohai Sea include Hai River System and Liao River System, which constitute two of the five river systems in China. The gulf has long been used as a source of prawns and salt. There are both onshore and offshore petroleum deposits, and several oil refineries are located there. Bo Hai region is one of the most important economic zones with its GDP growing by more than 10 folds in the past 12 years. Bohai Region has covered some major cities from 3 provinces and 2 municipalities, such as Dalian(in Liaoning Province), Tangshan(in Hebei Province), Dongying (in Shandong province), Tianjin and Beijing. Bohai Sea is relative closed bay, interchange of sea water with ocean outside is weak, so the water quality of this area are influenced seriously by the activity of human.

We decided 6 sampling locations around Bohai Sea and also selected 3 sampling locations in South Huanghai Sea as a contrast. South Huanghai Sea is belongs to the fringe sea of Pacific Ocean. The depth of which is deeper than Bohai Sea. The area is about 300 thousand square kilometer. In addition, South Huanghai Sea is influenced by Black Current coming from Pacific Ocean further. Black Current is a famous warm current, the temperature of the water here is higher than that in Bohai Sea. The Black Current can agitate the seawater and abundant pabulum in the bottom will be moved up to the surface layer, then many fishes are bloom here. These situations are very different from Bohai Sea.

Sea basses which we collected varied widely in size, from 25 centimetres to a maximum, about 90 centimetres. The weight varied from 200 grams to 6500 grams. Significantly, the bigger ones have grown for much more years than the younger ones. So the residues of OCPs in them are quite different. It is reasonable to analyze them individually. Chinese prawns which we collected are in similar size. The average length is 20 centimetres, the average weight is 53 grams. So we analyzed them according to the sampling locations. The hexachlorobenzene, Chlordane, p,p'-DDD, p,p'-DDT and p,p'-DDE were detected widely in all samples. Aldrin, Dieldrin, Endrin, Heptachlor and Mirex were less than the quantification limit. We also analyzed the OCPs in livers of sea bass individually. The results showed that the concentration of OCPs in livers of sea fish was much higher than the mussels.

Key Words: Bohai Sea, organic chlorinated pesticides, prawn, sea bass

Monitoring on POPs and OCs Compounds in Aquatic Environment at Main Cities in Java Island

Erini Yuwatini, C.H Netty Widayati, Arum Prajanti, Dewi Ratnaningsih, Ety Sumiati, Adriantoro

Environmental Managenent Center, Indonesia

Abstract

Since 2001, some Persistent Organic Pollutant (POPs) and Organochlorine (OCs) compounds at aquatic environment in Java Island were annually monitored in river water, seawater, sediment and since 2006, biota was included. Previous monitoring showed that some POPs compounds were detected on sediment and biota due to long usage in the past, strong affinity to organic sediment and fat. Even in very small concentration, it was also detected in river and seawater by desorption from sediment into water and or probably contamination from new application of POPs compounds.

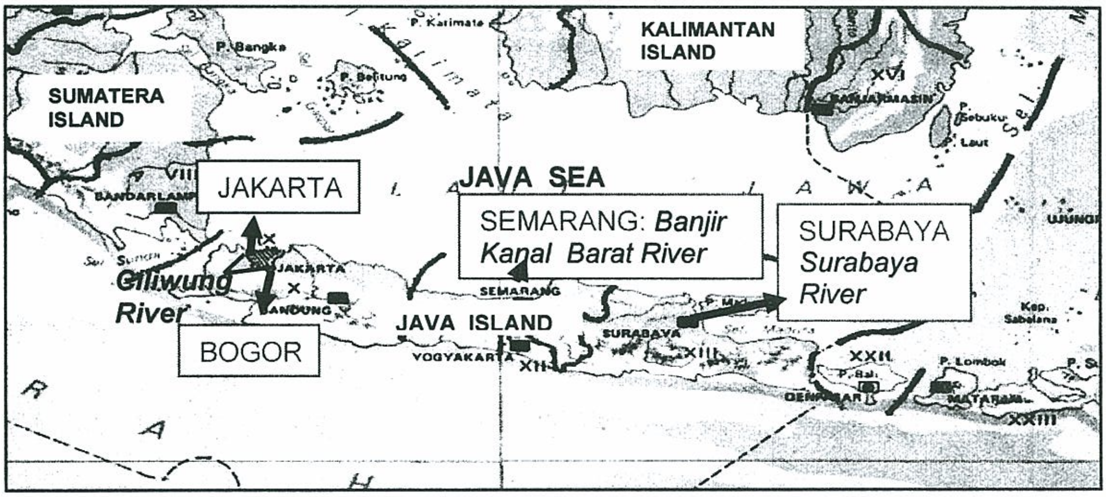


Fig.1 Sampling location

Three main cities (Jakarta, Semarang and Surabaya) in Java Island were chosen as the sampling location (fig.1) due to their high density of population and high frequency of pesticides application on both agriculture area and urban area. Those cities are located at northen part of Java Island. The sampling points were selected at the river passing through the city from the upper reaches of river to the estuary at Java Sea. The main river selected for sampling point as follows:1. Ciliwung River that the upper reaches is located in Bogor, West Java. The down stream flows through the north of Jakarta City and last at the Jakarta Bay. 2. Banjir Kanal Barat River is located at Semarang City, Central Java. 3. Surabaya River is located at Surabaya City, East Java, flows to Madura Strait. Those rivers are running into the Java Sea that has known as busy pathway of Java Strait connecting Java Island and Kalimantan Island. Main activity of the strait is transportation followed by fishery.

River water and sediment were collected at 5-6 points between up stream of river to the estuary. Seawater was sampled at location where sea bass selected as biota sample was also collected (2 km from the land). The activities were conducted in wet season (April) and dry season (September) in order to see the season effect to the season towards the POPs and OCs concentration in the aquatic environment.

Through the analytical method recommended by UNU, The POPs compounds (hexachlorobenzene, heptachlor, aldrin, heptachlor epoxide, trans-chlordane, DDT-isomers, dieldrin, endrin, mirex) and OCs (lindan and metoxychlor) were examined in sample of water, wet sediment and sea bass muscle tissue.

As result, DDT and its metabolites were detected in water. More various kinds of POPs compound were detected in sediment. A few DDT and its metabolites also were detected in sea bass muscle tissue. Its concentrations were about tens ppt in water, tens ppb in sediment, some ppb in sea bass muscle tissue respectively. OCs (lindan and methoxychlor) were not detected in almost all sample except in sediment at one sampling point.

As far, the monitoring showed that POPs and OCs were detected in aquatic environment at the interest locations in Java Island. It probably could represent the POPs and OCs contamination status of some other locations in Indonesia.

Contamination Status of Persistent Organic Pollutants in Fish from the Han River Estuary, Korea

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Abstract

Persistent organic pollutants such as PCBs, DDTs, and chlordanes accumulated in marine organisms through body surface or respiratory organs by diffusion and food intake. Organic pollutants accumulate in the human body over a lifetime, mainly through a diet. According to total diet study by Tsutsumi *et al.* (2001), mean daily intake of dioxin like compounds were highest from fish and shellfish. Since fish generally contain higher levels of organochlorines than any other food category, human's diets containing higher amounts of fish may be expected to lead to higher OCs intake. Consequently, determination of organochlorine concentration in fish is useful to understand the extent of aquatic contamination and to evaluate the possible risk for human. Fish and shellfish tissue monitoring serves as an important indicator of contaminated sediments and water quality as well, and many countries routinely conduct chemical contaminant analyses of fish and shellfish tissues as part of their comprehensive water quality monitoring program.

In order to assess the status of OCs contamination in fish inhabiting the coastal zone of Korea, we collected fish samples from Han River estuary from May 2005 to February 2007. The fish collected consists of several species because sampling of same species was difficult at all sites and seasons. Dorsal muscle tissue of fish was dissected from the whole body for analysis. Sampling location and fish species were presented in Fig. 1.

Polychlorinated biphenyls and organochlorine pesticides such as DDTs, HCHs, CHLs and HCB were detected in muscle homogenates of all the fish samples. The overall summary of OCs concentrations is presented in Figure 2. Polychlorinated biphenyls were the predominant contaminants with concentrations ranging from 8.46 to 1710 ng/g lipid weight (lw) and DDT compounds recorded the second highest concentrations with the range of 5.76 - 1170 ng/g lw. HCHs, CHLs and HCB concentration in fish were relatively low ranging 1.14 - 133 ng/g lw, 0.28 – 89.7 ng/g lw, and 0.09 – 61.0 ng/g lw, respectively. The OC levels are relatively lower than those found in harbor regions of Korea (Yim et al., 2004). Among DDT compounds, DDE is dominant with the average composition of 60±12% and followed by DDD (35±11%) and DDT (5±3%). Same signature was also observed in sediment collected from this region before, which indicating that the degradation of DDT is in progress in the coastal environment. Regarding the HCH isomers, high proportion of β-HCH (33±17%) and γ-HCH (46±19%) was observed in fish samples followed by α-HCH (15±6%), and δ-HCH (5±3%).

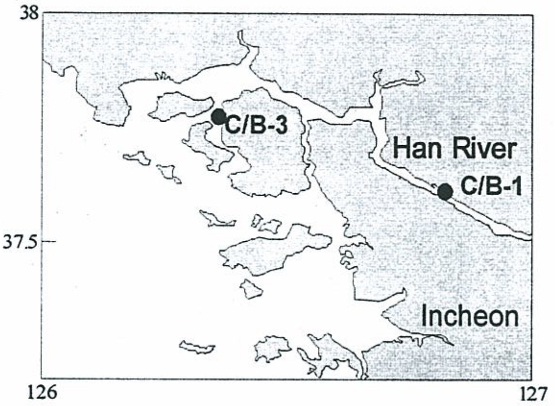

Figure 1. Sampling location of fish from Han River estuary

Risk-based screening value (SV) based on EPA method was calculated using the EPA approach to identify the primary chemicals of concern (Figure 2). About 90% of the fish samples showed the PCB concentrations exceeding the SV (5.04 ng/g). The concentrations of DDTs and dieldrin in fish exceeded their SVs at 47% and 20% of the samples, respectively, but the other compounds were mostly below SV values. Based on the estimated screening values, PCB, DDT, and dieldrin compounds were identified as potential chemicals of concern in this region.

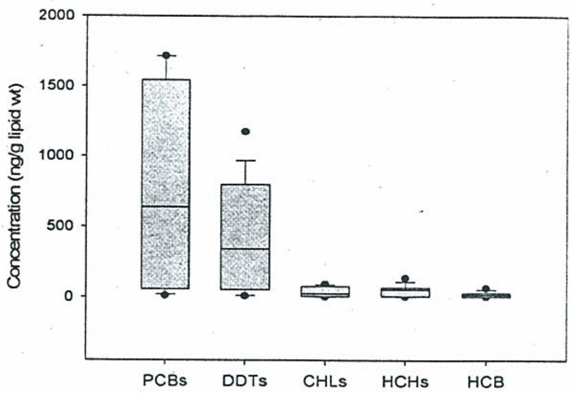

Figure 2. Concentration of organochlorine compounds if fish muscle samples from the Han River estuary.

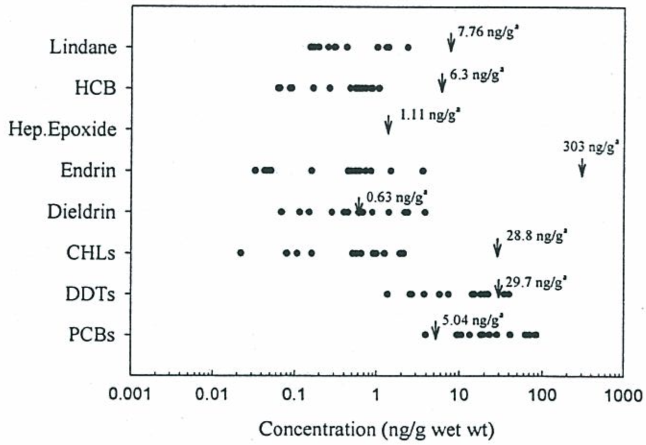

Figure 3. Comparison of organochlorine concentrations in fish muscle from the Han River estuary with estimated screening values for fish consumption risk.

Keywords: PCBs, organochlorine pesticide, Contamination, Fish, Screening value, Korea

Analysis of Selected POPs in Water from Selangor River, Malaysia and in Selected Sea Bass Samples.

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Abstract

The presence of POPs in Malaysian aquatic environment resulted from human activities has raised concerns on the water quality and safety of aquatic organism for domestic use. Although often present at trace levels, the ability of POPs to bio-accumulate is a concern owing to the possible adverse reactions from pesticides exposure to life beings. Due to the chemical nature of pesticides which rendered them persistent, monitoring programmes are conducted to assess the levels of pesticides in water and aquatic organisms. The present work is carried out with aim to assess the water quality of Selangor River for the selected pesticides (OC group) contamination. In addition to the river water monitoring, pesticides levels evaluation was also conducted in 'siakap' fish (sea bass). Selangor River is chosen as the sampling location as this river is not only providing fresh water supply to Selangor and Kuala Lumpur residents, it also flows through heavily developed area. Therefore, this river is exposed to many human activities from agricultural to tourism industries. Hence, this river is highly susceptible to chemical pollutions. This project is conducted as part of UNU hydrosphere monitoring program.

The river water samples were collected in two cycles, in June and August 2006. Ease of sampling allowed our sampling team to collect duplicate river water samples from nine stations along the Selangor River. Five fish samples were collected where four samples were purchased from the local market and one sample was caught by the local fisherman. One fish sample was a product of organic fish farming whereas the other four were wild fish origin. The water samples were transferred to the SUCXeS laboratory at the University of Malaya in chilled boxes and in ice packs. All samples

undergo thorough clean up process prior to GCMS analysis. The water samples were processed and extracted within 24-48-hour upon received. Liquid-liquid extraction method with ethyl acetate and dichloromethane was used in sample clean up. Preparations for fish sample require liquid-liquid extraction with hexane and ethyl acetate followed by further clean-up using amino and silica SPE cartridges. The GCMS method used were developed by UNU and Shimadzu corporations.

The river water analysis results showed pesticides residues at ng/L level found in four samples from the two sampling cycles. The residues detected were DDT, DDD and mirex (summarized in Table 1). The residues were detected at sampling stations where the surrounding activities are predominantly agriculture based. HCB and DDT were detected in the fish samples, products of organic farming and local market respectively (Table 2). Information on the surroundings of the fish sampling sites was not known. However we could suggest the controlled environment in organic fish farming could expose the fish to many chemicals, pesticides alike, as disease preventive measures. This could result in the possibility of pesticides traces to be found in the fish. On the other hand, dilution factor of chemical entities in the water from point source to open sea could hint almost zero pesticides detection in the wild fish. Nevertheless, these results showed persistent characteristic of OC pesticides as the use of OC based pesticides have been limited in Malaysia. In fact, DDT has been banned by Malaysian Board of Pesticides since 1995. Leaching from the agricultural sites and continuous land development has caused the pesticides to find their way into the water system and aqua life.

In order to ensure the reliability of the analysis data, control measures were taken not only during sample collection but also during analysis. For the sample collection, samples were transferred in chilled boxes to prevent degradation of chemicals in the samples and processed immediately. Quality control for analysis was fulfilled by including the internal standards and surrogate standard in sample analysis (Tables 3 and 4).

Table 1: Summary of pesticides detected in the river water samples

Sample Number	Compound	Observed Value	Unit	MDL (ng/L)	Sample Date	Temperature Deg C	Use/Surroundings
1SR01A	p,p'-DDD	0.0428	ng/L	0.0079	6/18/06	28.22	Agricultural, residential and land development
1SR01A	p,p'-DDT	0.1236	ng/L	0.0215	6/18/06	28.22	Agricultural, residential and land development
1SR05A	p,p'-DDD	0.0438	ng/L	0.0079	6/18/06	28.00	Agricultural and land development
1SR01B	p,p'-DDD	0.0388	ng/L	0.0079	8/21/06	29.24	Agricultural, residential and land development
1SR03B	Mirex	0.0478	ng/L	0.0158	8/21/06	26.46	Agricultural, residential and land development

Table 2: Summary of pesticides detected in the fish samples

Sample Number	Compound	Observed Value	Unit	MDL (ng/g)	Sample Date	Length (cm) / weight (kg)	Use/Surroundings
F1A	HCB	0.8360	ng/g	0.63	7/11/07	30.0 / 0.55	Fish farming (obtained from market)
F1B	HCB	0.7968	ng/g	0.63	7/11/07	30.0 / 0.55	Fish farming (obtained from market)
F3A	p,p'-DDT	2.6278	ng/g	1.94	7/15/07	28.0 / 8.99	Obtained from Giant Supermarket (wild fish)
F3B	p,p'-DDT	2.0622	ng/g	1.94	7/15/07	28.0 / 8.99	Obtained from Giant Supermarket (wild fish)

Table 3: Recovery and repeatability check for pesticides in deionized water at 5ppb (n=5)

Compound	Recovery (%)			Repeatability (ng/ml)				
	Average	Deviation	CV	Average	Deviation	CV (%)	3s	10s
HCB	93.33	3.482	3.73	4.67	0.174	3.74	0.52	1.74
Heptachlor	94.14	5.045	5.36	4.71	0.252	5.36	0.76	2.52
Aldrin	84.80	1.192	1.41	4.24	0.062	1.45	0.18	0.62
trans-chlordane	96.15	5.177	5.38	4.81	0.259	5.38	0.78	2.59
o,p'-DDE	97.49	2.918	2.99	4.88	0.145	2.98	0.44	1.45
cis-chlordane	94.37	2.429	2.57	4.72	0.122	2.58	0.36	1.22
Dieldrin	93.83	3.796	4.05	4.69	0.190	4.05	0.57	1.90
p,p'-DDE	94.68	3.320	3.51	4.74	0.166	3.51	0.50	1.66
o,p'-DDD	96.99	2.245	2.31	4.85	0.112	2.32	0.34	1.12
Endrin	84.64	1.917	2.27	4.23	0.098	2.32	0.29	0.98
p,p'-DDD	95.57	1.557	1.63	4.78	0.079	1.65	0.24	0.79
o,p'-DDT	91.97	2.401	2.61	4.60	0.122	2.66	0.37	1.22
p,p'-DDT	97.45	4.250	4.36	4.87	0.215	4.42	0.65	2.15
Mirex	92.89	3.172	3.41	4.64	0.158	3.40	0.47	1.58
p,p'-DDT-13C (%)	101.65	1.143	1.12	101.65	1.143	1.12		

Table 4: Recovery and repeatability check for pesticides in fish (n=5)

Compound	Recovery 50ppb (%)			Repeatability (10ppb)				
	Average	Deviation	CV	Average	Deviation	CV (%)	3s	10s
HCB	99.81	0.985	0.99	10.58	0.063	0.60	0.19	0.63
Heptachlor	101.06	0.860	0.85	11.09	0.055	0.49	0.16	0.55
Aldrin	99.62	1.274	1.28	10.17	0.098	0.97	0.30	0.98
trans-chlordane	99.20	0.836	0.84	10.32	0.097	0.94	0.29	0.97
o,p'-DDE	99.28	1.359	1.37	10.23	0.102	1.00	0.31	1.02
cis-chlordane	99.54	0.941	0.94	11.48	0.060	0.52	0.18	0.60
Dieldrin	102.10	1.582	1.55	10.26	0.081	0.79	0.24	0.81
p,p'-DDE	99.83	1.145	1.15	10.31	0.125	1.21	0.37	1.25
o,p'-DDD	96.72	0.885	0.91	10.97	0.044	0.40	0.13	0.44
Endrin	94.07	1.657	1.76	11.42	0.338	2.96	1.02	3.38
p,p'-DDD	96.14	0.878	0.91	11.15	0.030	0.27	0.09	0.30
o,p'-DDT	96.04	0.674	0.70	11.05	0.140	1.27	0.42	1.40
p,p'-DDT	94.71	1.166	1.23	11.21	0.194	1.73	0.58	1.94
Mirex	99.01	1.188	1.20	11.28	0.115	1.02	0.35	1.15
p,p'-DDT-13C (%)	96.70	3.347	3.46	103.70	4.118	3.97		

Monitoring of POPs' In Pakistan –River Water Bodies and Shrimps

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Abstract

Total 19 samples were collected from five rivers and Arabian Sea in two seasons i.e. pre monsoon and post monsoon to know the level of POPs' pollution in Pakistan. The collected samples were analyzed for fourteen compounds i.e. Heptachlor, Aldrin, trans-chlordane, cis-chlordane, Dieldrin, Endrin, p,p'-DDT, HCB, o,p'-DDT, o,p'-DDE, p,p'-DDE, p,p'-DDD, o,p'-DDD & Mirex, by using GSMS QP 2010 Shimadzu-Japan. Aldrin and Dieldrin were identified in the samples collected from Sutlaj River located at Islam Reservoir in dry and wet seasons. Heptachlor and o,p'-DDD were identified in samples collected from Ravi River located at Balloki Reservoir and Lahore near the Indian border in pre monsoon season. p,p'-DDT and o,p'-DDT were determined in the sample collected from Chenab River located at Marala Barrage in dry and wet seasons respectively. Aldrin was identified in the samples collected from Indus River located at Guddu Reservoir in dry and rainy seasons. 10 Shrimps samples were analyzed for the determination of POPs' in the ecosystem, o,p'-DDE was identified in three shrimps samples and p,p'-DDE was found in only one sample.

Keywords: Water bodies, POPs', Ecosystem, Shrimps, Impacts of POPs'

Organochlorine Pesticides in Water and Sea Bass in Selected Coastal Sites in the Philippines

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Objective:

To determine the concentration of organochlorine pesticides in sea bass (*Lates Calcarifer*) and water from selected coastal areas in the Philippines.

Methodology:

A. Sampling Plan:

1. Identify (in coordination with the Fisheries Aquatic Resources Management Council (FARMC) of the Bureau of Fisheries and Aquatic Resources (BFAR) some coastal areas where wild sea bass (*Lates Calcarifer*) can be caught. Select two coastal sites in Luzon and two in the Visayas
2. For each site, purchase 3 sizes of fish (small, medium and large) from a fisherman. Collect 3 pieces of fish for each size. Store in the freezer the whole fish when analysis cannot be started immediately. Thaw before sample preparation.
3. Collect one liter water sample from the area where the sea bass is caught (0.5 km -2 kms from the shoreline). Collect one water sample (2-1 liter bottles) from each site per sampling period as recommended in the standard methods for analysis of organochlorine pesticides in water (APHA)

Rational for selection of the sites:

Only two sites in Luzon were identified by FARMC where wild sea bass can be caught. These sites are in Naic, Cavite in Manila Bay and in Tagkawayan in Quezon Province.

Several sites in Bohol island and in Cebu Province in the Central Visayas were identified by FARMC. Sampling in these areas would entail considerable expense because we have to take air transportation to get to these areas. Considering the limited budget for this year's project, we decided to get samples from one area in Bohol and one area in Cebu.

B. Actual Sampling

In Luzon, sampling was done only at Tagkawayan, Quezon in Ragay Gulf as no sea bass could be caught in Naic, Cavite. Water sample was collected about ½ kilometer from the shore in Tagkawayan. Nine fish samples of varying sizes were collected. These were classified according to size and weight as small, medium and large corresponding to three composite samples for analysis.

In the Visayas, sampling was done in Barra, Roxas City and in Estancia, Ilo-ilo. One water sample was collected about ½ kilometer from each coastal shore. One fish sample was collected in Roxas City and 7 fishes were collected in Estancia, Ilo-ilo. The fishes from Estancia were classified into 2 groups by length and size. The number and the size of fishes collected in Luzon and Visayas were limited by the availability of the fish caught in the wild.

The locations of the planned and actual sampling sites are shown in Figure 1. The details of the sampling sites, sampling conditions and the samples collected from each site are listed in Table 1.Photos of the fish samples are shown in Fig 2.

Interaction with people who cooperate with the sampling team has always been an enjoyable experience with the UNU researchers. During sampling, the researchers get a chance to explain to the fishermen cooperators what the UNU project is about. In most cases, many of the fishermen are enthusiastic to help and are very interested to know the outcome of the sampling from their localities. Figure 2 shows some photographs of the sampling sites and the people who cooperated with the sampling team for this project.

C. Quality Control:

Reagent Blank

One reagent blank was analyzed per batch of analysis. There were 2 batches of 1 to 2 samples per batch of analysis for water samples and 2 batches of 9-12 samples per batch of analysis for the fish samples.

Recovery Test

Table 2 shows the results of recovery of 25 ng spike for 2 batches for water samples and 100 ng spike for 2 batches for fish samples

Quantitation Limit

Table 3 shows the results of the repeated injections of 10 ppb standard solution and the calculation for the quantitation limits for water and fish analysis

Recovery of Surrogate

The recovery of p,p'-DDT-$^{13}C_{12}$ with nominal concentration of 100 ng for water samples and with nominal concentration of 20 ng for fish samples are shown together with the result of OCPs analysis in Tables 4 and 5

D. Analysis Procedure:

The analysis method for water contained in the UNU Manual for Water and the method for fish in the UNU Manual for Aqua Organisms were applied in water and fish samples respectively.

Results of Analysis

The results of analysis of duplicate water samples from the three selected coastal sites in Table 4 showed that organochlorine pesticides were not detected based on the quantitation limit of the UNU method.

The results of analysis of three trials of composite samples of fishes collected from Tagkawayan, Quezon in Luzon and in Roxas City and in Estancia in Ilo-ilo in the Visayas in Table 5 showed that organochlorine pesticides were not detected based on the quantitation limit of the UNU Method. The differences in the length and weight of the groups of fish samples did not indicate a difference in the OCPs contamination in the fish.

Table 1. Details of sampling sites, sampling conditions and samples collected for the UNU 2007 Monitoring Project

Location	Coordinates		Date and time of sampling	Weather Conditions	Water Samples		Sea Bass Samples	
	latitude	longitude			Sampling condition	Sample Code	Sampling Condition	Sample Code
Tagkawayan, Quezon Coastal Area in Ragay Gulf	13°57'30N	122°32'10E	July 18, 2007, 2:30 P.M	Sunny	Collected at surface Depth of water, 3m	TQFS-W	Wild 9 samples (165-205grams) collected within several days	TQFS-S1 TQFS-S2, TQFS-S3
Barra, Roxas City Coastal Area: Mouth of Panay River in Visayan Sea	11°35'09N	122°43'08E	September 19, 2007 9:15 A.M	Cloudy, Drizzling	Collected at surface Depth of water, 2m	RCFS-W	Wild One sample (921 grams) collected over one week monitoring of catch	RCFS-S
Estancia, Ilo-ilo Coastal Area Visayan Sea	11°27'12N	123°09'21E	September 19, 2007 1:15 P.M	Cloudy, Raining	Collected at surface Depth of water, 3m	EIFS-W	Wild 7 samples (106-194 grams) collected in one day	EIFS-S1 EIFS-S2

Table 2a. Recovery of spiked OCPs in water samples

Batch 1	Spike Soln.	Spk TQ FS W	NET of TQ FS W	% Recovery	Batch 2	Spike Soln.	Spk EI FS W	NET of EI FS W	% Recovery
		Concentration., ppb					Concentratiom., ppb		
alpha BHC	22.206	23.383	23.383	105	alpha BHC	23.2549	23.7602	23.7602	102
beta BHC	17.389	21.4739	21.4739	123	beta BHC	22.7896	23.6046	23.6046	104
gamma BHC	20.5422	21.6323	21.6323	105	gamma BHC	23.5695	21.4449	19.0941	81
delta BHC	18.6519	16.9342	16.9342	91	delta BHC	23.376	17.0678	17.0678	73
HCB	22.726	13.6238	13.6238	60	HCB	21.8082	14.5102	14.5102	67
Heptachlor	23.5163	17.8734	17.8734	76	Heptachlor	20.1426	17.5967	17.5967	87
Aldrin	21.4697	17.0719	17.0719	80	Aldrin	23.4227	16.2043	18.2344	78
Heptachlor epoxide	20.0453	22.867	22.867	114	Heptachlor epoxide	22.1155	21.0159	21.0159	95
gamma chlordane	20.9404	22.1911	22.1911	106	gamma chlordane	20.6309	20.7917	20.5	99
o,p' DDE	22.6827	24.8969	24.8969	110	o,p' DDE	21.2462	21.0043	21.0043	99
Endosulfan I	21.337	23.9209	23.9209	112	Endosulfan I	23.797	21.8703	21.8703	92
alpha chlordane	21.3498	22.9484	23.9484	112	alpha chlordane	19.3485	20.2802	20.3602	105
trans nonachlor	22.0951	22.8449	22.6449	102	trans nonachlor	19.8003	20.1259	20.1259	102
Dieldrin	19.3817	21.9241	21.9241	113	Dieldrin	21.1879	20.7247	20.9937	99
p,p' DDE	22.4559	24.6479	24.6479	110	p,p' DDE	21.0338	20.7943	20.7943	99
o, p' DDD	20.6742	22.8447	22.8447	110	o, p' DDD	21.0722	22.0777	22.0777	105
Endrin	20.8132	21.9345	20.5345	99	Endrin	20.7378	20.5303	20.5303	99
Endosulfan II	16.2592	14.9953	14.9953	92	Endosulfan II	20.7515	3.9228	3.9228	19
p, p' DDD	17.7242	18.8874	18.8874	107	p, p' DDD	21.8337	21.1048	21.1048	97
cis nonachlor	20.228	20.776	20.776	103	cis nonachlor	21.0703	20.5376	20.5376	97
o, p' DDT	20.5054	20.4246	20.5246	100	o, p' DDT	19.8019	21.7113	21.4008	108
p, p' DDT	20.466	22.154	22.154	108	p, p' DDT	20.533	20.6367	20.6367	101
Methoxychlor	18.9728	10.596	11.596	61	Methoxychlor	20.7529	6.8885	6.8885	33
Mirex	21.8739	19.6585	19.6585	90	Mirex	22.5805	20.6945	20.6945	92
p,p' DDT 13C12	85.1195	85.4024			p,p' DDT 13C12	87.8635	85.2738		
% Recovery		100			% Recovery		97		

Table 2b. Recovery of spiked OCPs in fish samples

Batch 1 Concentration Weight of fish sample	Spk Soln. ng/ml	Spk (ng/g ww.) 5.0938	Net Spk TQFS S3 (ng/g ww.)	% Recovery	OCPs Batch2 Concentration Weight of fish sample	Spk Soln. ng/ml	Spk (ng/g ww.) 5.0701	Net Spk RCFS S ng/g ww	% Recovery
OCPs					OCPs				
HCB	88.1383	17.30305	8.842965959	51	HCB	89.1463	17.58275	13.3109012	76
Heptachlor	92.3119	18.1224	12.89793474	71	Heptachlor	92.2644	18.19775	16.6231633	91
Aldrin	92.2625	18.11271	14.6914288	81	Aldrin	91.951	18.13593	19.9714404	110
trans-chlordane	92.964	18.25042	17.92084495	98	trans-chlordane	96.0642	18.9472	19.3855945	102
o,p'-DDE	92.3964	18.13899	17.09792297	94	o,p'-DDE	93.3314	18.4082	18.4488077	100
cis-chlordane	91.6063	17.98388	17.73100632	99	cis-chlordane	88.5452	17.46419	18.4875051	106
Dieldrin	95.1756	18.6846	17.59601869	94	Dieldrin	101.549	20.02899	19.2748325	96
p,p'-DDE	91.4724	17.9576	16.92693078	94	p,p'-DDE	92.3981	18.22412	18.2643143	100
o,p'-DDD	99.6412	19.56127	19.44652322	99	o,p'-DDD	100.1738	19.75776	20.7432595	105
Endrin	94.4493	18.54201	17.71834387	96	Endrin	94.5181	18.64226	23.7746198	128
p,p'-DDD	101.7301	19.97136	20.49593447	103	p,p'-DDD	100.394	19.80119	22.7779609	115
o,p'- DDT	91.6527	17.99299	19.71940429	110	o,p'- DDT	90.2016	17.79089	20.8777379	117
p,p'-DDT	95.333	18.7155	19.78151871	106	p,p'-DDT	97.7109	19.27199	21.4959665	112
Mirex	92.6843	18.19551	19.07852684	105	Mirex	91.7801	18.10223	19.2259522	106
Other OCPs					Other OCPs				
alpha-BHC	90.1924	17.70631	0	0	alpha-BHC	91.9116	18.12816	0	0
beta-BHC	117.0444	22.97782	0	0	beta-BHC	119.9585	23.65999	20.7429439	88
gamma-BHC	98.9811	19.43168	17.45873415	90	gamma-BHC	99.4115	19.6074	21.4314708	109
delta-BHC	102.8066	20.18269	0	0	delta-BHC	104.3244	20.5764	0	0
Heptachlor epoxide	95.7454	18.79646	18.4304803	98	Heptachlor epoxide	95.2158	18.77987	18.5812114	99
Endosulfan I	97.8713	19.21381	20.53653461	107	Endosulfan I	98.4025	19.40839	17.4699537	90
trans-nonachlor	93.8148	18.41745	17.73228238	96	trans-nonachlor	95.153	18.76748	19.9120833	106
Endosulfan II	97.4692	19.13487	0	0	Endosulfan II	103.7696	20.46697	0	0
cis-nonachlor	92.4895	18.15727	19.4194511	107	cis-nonachlor	96.8946	19.11098	20.0568036	105
Methoxychlor	98.0242	19.24383	19.55817458	102	Methoxychlor	101.547	20.0286	22.3811945	112
p,p'-DDT-13C12	20.0484		18.8876		p,p'-DDT-13C12	20.6168		19.3628	
% Recovery			94		% Recovery			94	

Table 3. Quantitative Limit for water and fish analysis

OCPs	Concentration, ng/ml 1	2	3	4	5	Mean	s	3s	10s	QL 10s D.F=1ml/1000ml	QL Water µg/L	QL 10S D.F. = 1mL/5g	QL Fish ng/g
HCB	10.4712	10.9376	10.7026	10.8664	10.5484	10.70524	0.19959	0.598769	1.995897	0.001996	**0.002**	0.399179	**0.4**
Heptachlor	11.2431	11.174	11.5194	11.2405	10.9848	11.23236	0.191876	0.575628	1.918759	0.001919	**0.002**	0.383752	**0.4**
Aldrin	10.3267	10.5934	10.4247	9.8237	10.2997	10.29364	0.286795	0.860386	2.867953	0.002868	**0.003**	0.573591	**0.6**
trans-Chlordane	12.2404	12.1796	11.5789	12.7039	10.9025	11.92106	0.695737	2.08721	6.957365	0.006957	**0.007**	1.391473	**1**
o,p'-DDE	11.5518	10.6802	11.1401	11.2835	10.4091	11.01294	0.462353	1.387059	4.62353	0.004624	**0.005**	0.924706	**0.9**
cis-Chlordane	9.1713	9.9413	10.5949	10.4923	9.9359	10.02714	0.567204	1.701611	5.672038	0.005672	**0.006**	1.134408	**1**
Dieldrin	11.7506	10.7	11.6986	12.7363	10.7534	11.52778	0.840273	2.520818	8.402727	0.008403	**0.008**	1.680545	**2**
p,p'-DDE	11.0287	10.5734	10.5088	11.1706	10.305	10.7173	0.366272	1.098817	3.662723	0.003663	**0.004**	0.732545	**0.7**
o,p'-DDD	11.0813	10.7577	11.4021	10.8219	10.8381	10.98022	0.265979	0.797936	2.659786	0.00266	**0.003**	0.531957	**0.5**
Endrin	8.8344	9.1919	8.4644	8.2399	9.5277	8.85166	0.523763	1.57129	5.237633	0.005238	**0.005**	1.047527	**1**
p,p'-DDD	10.6122	9.9475	9.6587	9.8508	10.4394	10.10172	0.405472	1.216415	4.054716	0.004055	**0.004**	0.810943	**0.8**
o,p'-DDT	9.2118	9.5873	10.1948	9.1636	9.6988	9.57126	0.418546	1.255639	4.185463	0.004185	**0.004**	0.837093	**0.8**
p,p'-DDT	10.4461	10.2997	10.0144	10.3849	10.7542	10.37986	0.266707	0.800121	2.667069	0.002667	**0.003**	0.533414	**0.5**
Mirex	11.1348	11.0459	11.0176	10.7403	11.2906	11.04584	0.20123	0.603689	2.012297	0.002012	**0.002**	0.402459	**0.4**
Other OCPs													
alpha BHC	10.7331	11.4038	11.523	11.363	11.9887	11.40232	0.449391	1.348173	4.493909	0.004494	**0.004**	0.898782	**0.9**
beta BHC	11.4739	12.2798	12.0837	13.6534	12.3349	12.36514	0.797077	2.391232	7.970772	0.007971	**0.008**	1.594154	**2**
gamma BHC	11.3529	10.1557	10.9363	10.148	10.571	10.63278	0.518925	1.556774	5.189246	0.005189	**0.005**	1.037849	**1**
delta BHC	9.8073	11.6817	10.8503	11.0604	11.515	10.98294	0.737746	2.213238	7.377459	0.007377	**0.007**	1.475492	**1**
Heptachlor epoxide	10.658	9.5393	9.5299	11.7042	10.4251	10.3713	0.903035	2.709106	9.030354	0.00903	**0.009**	1.806071	**2**
Endosulfan I			12.7898	8.6642	9.796					0			
trans nonachlor	10.084	10.0473	11.0688	12.0315	10.3921	10.72474	0.837574	2.512722	8.37574	0.008376	**0.008**	1.675148	**2**
Endosulfan II										0			
cis nonachlor	8.939	10.6215	10.5672	10.5918	10.8457	10.31304	0.776074	2.328223	7.760742	0.007761	**0.008**	1.552148	**2**
Methoxychlor	10.2384	11.6314	11.2678	10.9907	11.2244	11.07054	0.518647	1.555942	5.186472	0.005186	**0.005**	1.037294	**1**

Table 4. Concentration of OCPs in water samples

OCPs	Ragay Gulf Tagkawayan, Quezon		Visayan Sea Estancia, Iloilo		Mouth of Panay River / Visayan Sea Barra, Roxas City		MDL, NSRI	UNU,QL
	TQFS-WA	TQFS-WB	EIFS-WA	EIFS-WB	RCFS-WA	RCFS-WB		
	Concentration, ug/L based on NSRI MDL Limit							
HCB	ND	ND	ND	ND	ND	ND	0.009	0.002
Heptachlor	ND	ND	ND	ND	ND	ND	0.002	0.002
Aldrin	ND	ND	ND	<MDL	<MDL	ND	0.001	0.003
trans-Chlordane	<MDL	<MDL	ND	ND	ND	ND	0.004	0.007
o,p'-DDE	ND	ND	<MDL	ND	<MDL	<MDL	0.002	0.005
cis-Chlordane	<MDL	<MDL	ND	ND	<MDL	ND	0.002	0.006
Dieldrin	ND	ND	ND	ND	ND	ND	0.001	0.008
p,p'-DDE	ND	ND	<MDL	ND	<MDL	<MDL	0.001	0.004
o,p'-DDD	ND	ND	ND	<MDL	<MDL	ND	0.002	0.003
Endrin	ND	ND	0.0045	ND	ND	ND	0.002	0.005
p,p'-DDD	ND	ND	<MDL	ND	<MDL	ND	0.0009	0.004
o,p'-DDT	<MDL	ND	ND	ND	ND	ND	0.002	0.004
p,p'-DDT	ND	<MDL	ND	ND	<MDL	<MDL	0.002	0.003
Mirex	ND	ND	ND	ND	ND	ND	0.002	0.002
Other OCPs								
alpha BHC	ND	ND	ND	ND	ND	ND	0.002	0.004
beta BHC	ND	ND	ND	ND	ND	ND	0.02	0.008
gamma BHC	ND	ND	<MDL	ND	ND	<MDL	0.002	0.005
delta BHC	ND	ND	ND	ND	ND	ND	0.02	0.007
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	0.002	0.009
Endosulfan I	ND	ND	ND	ND	<MDL	<MDL	0.02	
trans nonachlor	ND	ND	<MDL	ND	ND	<MDL	0.002	0.008
Endosulfan II	ND	ND	ND	ND	ND	ND	0.009	
cis nonachlor	ND	ND	<MDL	ND	<MDL	ND	0.0008	0.008
Methoxychlor	ND	ND	ND	ND	ND	ND	0.0004	0.005
% Rec.: p,p'-DDT-$^{13}C_{12}$	100.2	99.6	97.9	92.8	93.0	97.0		

NSRI limit is based on 3s of repeated (n=8) analysis of 3-25 ppb spiked sample.
UNU limit is based on 10s of repeated injection of 10 ppb standard solution in the GCMS
All samples are ND based on UNU QL

Table 5. Concentration of OCPs in fish samples

	TQ FS1			TQ FS2			TQ FS3			EI FS1			EI FS2			RC FS1			QL, UNU
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	
% Moisture, ave		80.20			81.90			81.20			76.50			77.60			76.00		
Wax, mg/g		3.59			2.92			4.30			3.93			3.75			4.52		
OCPs	Concentration, ng/g wet weight																		
HCB	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.40
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.38
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.57
trans-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.39
o,p'-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.92
cis-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.13
Dieldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.68
p,p'-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.73
o,p'-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.53
Endrin	ND	2.20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.05
p,p'-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.81
o,p'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.84
p,p'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.53
Mirex	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.40
Other OCPs																			
alpha BHC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.90
beta BHC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.59
gamma BHC	ND	ND	3.40	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.04
delta BHC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.48
Heptachlor –epox.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.81
Endosulfan I	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.20	ND	ND	ND	1.70	ND	2.20	
trans nonachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.68
Endosulfan II	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
cis nonachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.55
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.04
% Rec.: p,p'-DDT-13C12,	92.20	91.32	98.10	99.10	84.50	82.80	87.60	89.40	98.50	97.40	82.40	87.80	61.90	89.90	99.80	97.40	97.80	102.60	

Persistent Organic Pollutants in Singapore's Environment

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Introduction

Over the years, widespread contamination of persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) have caused great harm to human beings and the environment. These xenobiotic pollutants are toxic and ubiquitous in the global environment [1-3]. As these pollutants are lipophilic and persistent in nature, they can readily undergo bioaccumulation and biomagnification in the food chain [4,5]. Certain POPs such as lindane have already been identified to be possible carcinogens and there is growing evidence that these chlorinated compounds have the potential to cause endocrine disruption in biota by impacting upon reproductive and hormonal functions [6,7]. POPs are introduced into the environment via atmospheric deposition, oil spillages, sewage discharges, and the food chain through the consumption of seafood [8]. In consideration of the health hazards posed by these chlorinated compounds, production of POPs has been banned in many countries. Nonetheless, OCPs has continued to be routinely detected in marine life, wildlife, human adipose tissues, serum, breast milk, soils and sediments because of their former use, accidental spills, high persistence and low biodegradability [9-11]. Analysis of pesticides at trace levels in the environmental and food samples poses special challenges for analytical chemists, since the pesticides are present at low level concentrations.

The objective of the present investigation was to determine the concentrations of POP residues in the coastal waters, seafood samples and human tissue samples in order to attempt the determination of the status and trends of contamination by POPs in the Singapore environment.

Monitoring of Seawater, Shrimps and Human Tissue

Selection of locations and sampling conditions

Surface seawater samples (from 13 locations) were collected along the Singapore coastline from 2002 to 2006 (Figure 1) Surface seawater samples were collected in precleaned glass bottles and seawater samples were stored at -4°C until analysis. There are no seasons in Singapore. Weather conditions are generally constant, usually warm, humid and abundant rainfall can be experienced throughout the year.

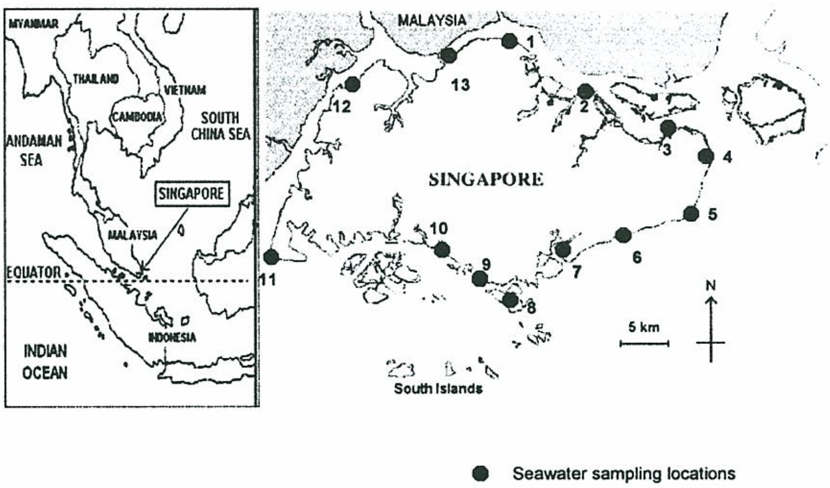

Figure 1. Baseline monitoring locations 2002-2006

Shrimp samples were purchased local supermarket and extracted and analysed for the presence of POPs. Specific sources of the shrimp sample were not known, however (it is believed that most were imported from (a) foreign country or countries).

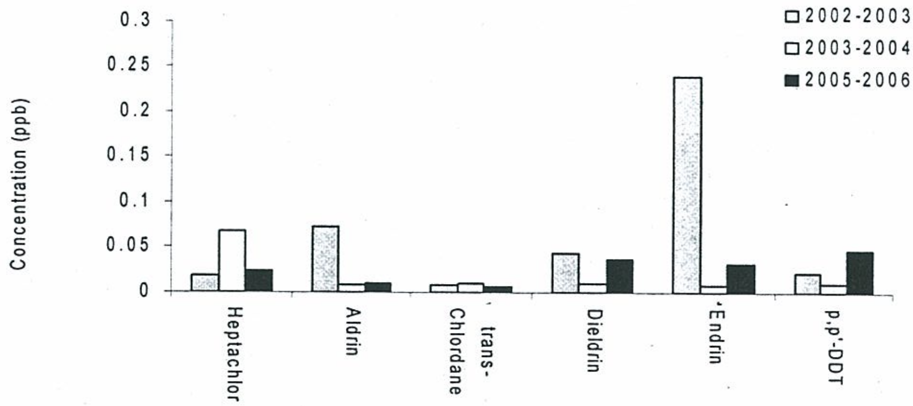

Figure 2. Concentration of selected pesticides monitored in Singapore's coastal waters from 2002 to 2006

POPs in seawater samples

Figure 2 shows the concentration data of selected pesticides from the 2002 to 2006 monitoring programmes. Pesticides were detected in all 13 sampling locations. Results from this study illustrate the extent of pollution of these compounds and despite the relatively small size of the overall sampling area, there was considerable variation in the concentration levels from the sites. The overall mean concentration of OCPs varied from 0.01 to 0.23 μg/L and the highest amounts of endrin was detected at year 2002-2003 sampling period. However, the overall concentrations were within the limits of 0.04 μg/L in recent years. Surprisingly, *p-p'*-DDT concentration has increased slightly over the years. This could be due to its longer half-life time (over 5 years) and regular inputs derived, perhaps, from agriculture runoff from foreign countries (these may also include industrial, manufacturing discharge and municipal sewage disposal).

Analysis of shrimp samples and comparison with water samples

Human exposure to POPs can occur by various routes, with food being the primary source. A number of studies have shown that the major food sources for these organic pollutants are fat-containing animal products, including shrimp and other seafood samples [25]. We have collected shrimp samples from different supermarkets around Singapore and analysed them for POP contamination.

Twenty-five shrimp samples were sampled. The concentrations of pesticides in the samples were in the range of between 0.01 and 0.04 ng/g. In comparison with seawater samples, for obvious reasons (since the shrimps were all imported), there is no distinct trend observed in terms of the link to bioaccumulation.

Determination of pesticides in human ovarian cancer tissue samples

All human ovarian samples used in this study were collected following approval from the Domain Specific Review Board, National Health Group, Singapore. Samples were collected from patients post-operatively and immediately stored at −80°C. Since the amount of each cancer tissue sample was too small to use the United Nations University/Shimadzu Corporation method, we have developed a novel microextraction technique to quantify pesticides and chlorinated biphenyl (CB) congeners concentrations [12] in these samples. The concentrations of these compounds present in the ovarian cancer tissues are reported in Figure 4. Two compounds, *p,p'*-DDD (P=0.009) and *p,p'*-DDT (P=0.045) showed statistically significant differences in the accumulation patterns in benign cases compared to cancer cases.

Hexachlorobenzene and chlorobiphenyl-28 (CB-28) showed higher accumulation in cancer tissue (10 cancer cases). However, the p values (0.094 and 0.117 respectively) were not statistically significant. The study has to be carried out on a larger sample set to get more meaningful results. Nevertheless, this preliminary study [12] is highly promising insofar that microextraction is a feasible technique for extracting low concentrations of POPs from small amounts of biological tissue.

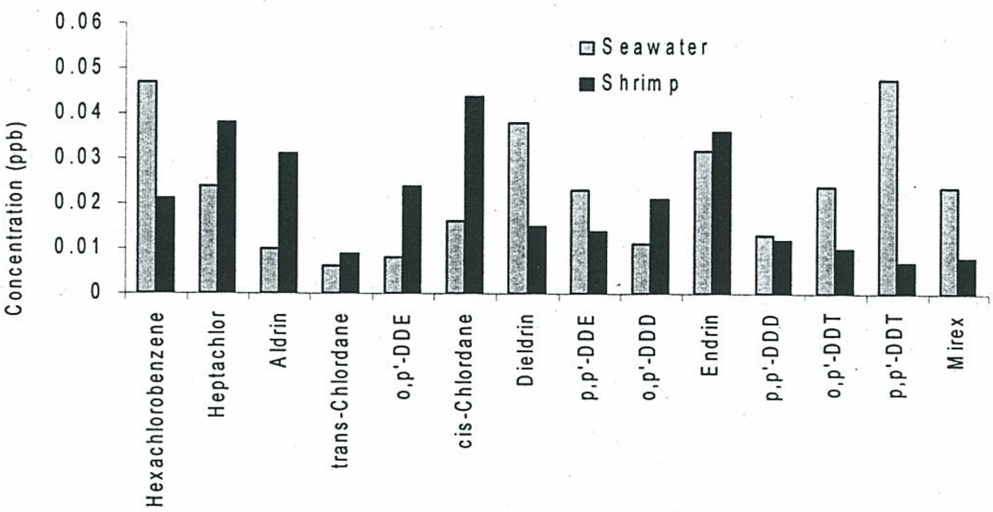

Figure 3. Concentrations of pesticides in shrimp and seawater samples

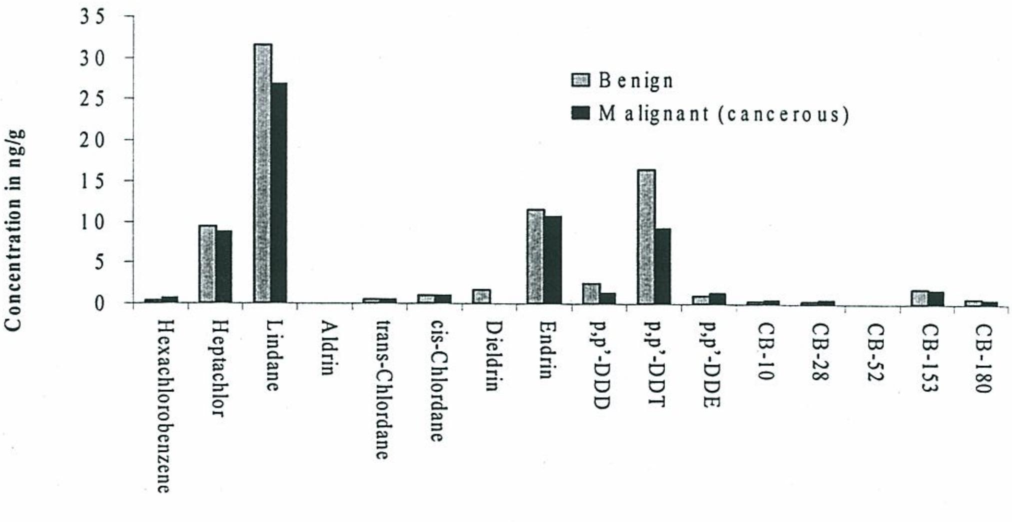

Figure 4. Concentrations of POPs in ovarian tissue samples

Conclusion

Current study shows the distribution of persistent organic compounds present in Singapore's environment and human tissue samples. The levels of POPs measured can be said to be in the moderate range. This is not surprising, as extensive agricultural activities in Singapore have been phased out for more than two decades. However, these POPs are persistent and atmospheric deposition could be the source of entry to our environment. Conventional extractions such as liquid-liquid extraction and Soxhlet extraction are not selective enough to meet the needs for environmental monitoring, food safety and food regulatory requirements. Pesticide detection methods are becoming more specific and sensitive; yet, to achieve the desired specificity and sensitivity there is still a need for careful sample preparation. Trace level determination of the target compounds in a complex samples such as milk, blood or other biological matrices is particularly important as it can account for a significant amount of the variability of the extraction method.. More desirable are selective, simple and miniaturized sample preparation methods that are also environmentally-benign that can be applied to routine pesticide analysis. It is expected that a great deal of effort will continue to be expanded along this line in the foreseeable future.

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Reflections on the USEPAM Curriculum Development Activities.

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The purpose of the presentation is to give an account of the USEPAM (University Support for Environmental Planning And Management) curriculum development experience as a practice of capacity building.

Involved universities are National university of Laos; Royal University of Phnom Penh, Cambodia; Hanoi Agricultural University, Vietnam; Copenhagen University and Roskilde University, Denmark; and Asian Institute of Technology, Thailand.

The points covered are:
The Background of the project, philosophy & objectives
Problem based learning within the environmental field
Necessary conditions & challenges at the outset
Highlighting some significant outcomes
Reflections on delivery of Technical Assistance
Outreach activities
Applied research
Some general lessons learned & challenges for the future

Monitoring and Policy of Persistent Organic Pollutants (POPs) in Thailand

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Abstract

The demand of agricultural productivity and the expansion of industry caused a rapid increase in the use of chemicals. In particular, during 1950-1970, most of the pesticides imported were organochlorines, which include such POPs as DDT, endrin, heptachlor and so on as shown in Table 1. Thailand has recognized the problem of chemical hazards, and considers the health and environmental concerns that they pose as apriority for action. Under the Stockholm Convention activities on Persistent Organic Pollutants (POPs), Thailand has developed a National Implementation Plan (NIP) to demonstrate how the obligation contained in Article 7 of Convention will be implemented. Most of POPs pesticides under the Stockholm Convention have been banned for importation since 1980. There are numerous chemicals considered as severely restrict or banned for agricultural and public health use as shown in Table 2. The use of POPs pesticides has been banned in Thailand for a long period of time. However, there are some stockpiles of obsolete and POPs pesticides scattered around the country. There are no specific measures for eliminating these stockpiles.

The survey and monitoring of organochlorine residues in the environment was first initiated in 1976 and had continued for ten year till 1985. The work was emphasized mainly on water, sediment, soil, fish and shellfish collected from various site in our country. In addition to share the data among the Asian countries, the cooperative monitoring program between Environmental Research and Training Center and the United Nations University was established under Environmental Monitoring and Governance in the Asian Coastal Hydrosphere Monitoring of POPs in the Asian Region in 2007.

Table 1 Import of pesticides during 1977-2003

Year	Insecticides	Fungicides	Herbicides	Other
	Quality (Ton/ai)	Quality (Ton/ai)	Quality (Ton/ai)	Quality (Ton/ai)
1977	2,806	1,131	2,874	44
1987	5,881	4,530	3,967	247
1997	7,526	4,588	14,403	610
2000	6,608	4,375	17,809	1,859
2001	21,255	5,369	20,662	1,569
2002	10,116	5,681	22,670	1,234
2003	10,622	6,732	31,879	1,353

Source: Department of Agriculture

Table 2 Organochlorine pesticides banned and/or restricted under the Ministry of Agriculture and Cooperatives, Thailand

chemicals	Date of Ban
HCHs	1980
dieldrin	1988
DDTs	1983 (AG) 1994 (PH)
aldrin	1988
endrin	1981
toxaphene	1983
heptachlor	1988
Mirex	1995
chlordane	1995 (PH) 2000 (AG)

Source: Department of Agriculture, AG: agricultural use, PH: public health use

The monitoring program was focused on fish samples from the Gulf of Thailand. The sampling locations were showed in Figure 1. The fish was collected 20 samples and analyzed for POPs such as heptachlor, endrin, aldrin, dieldrin, DDT-isomers. The objectives are to assess the status of POPs accumulation in fish samples and to know the relationship of POPs chemicals in biota and sediment samples.

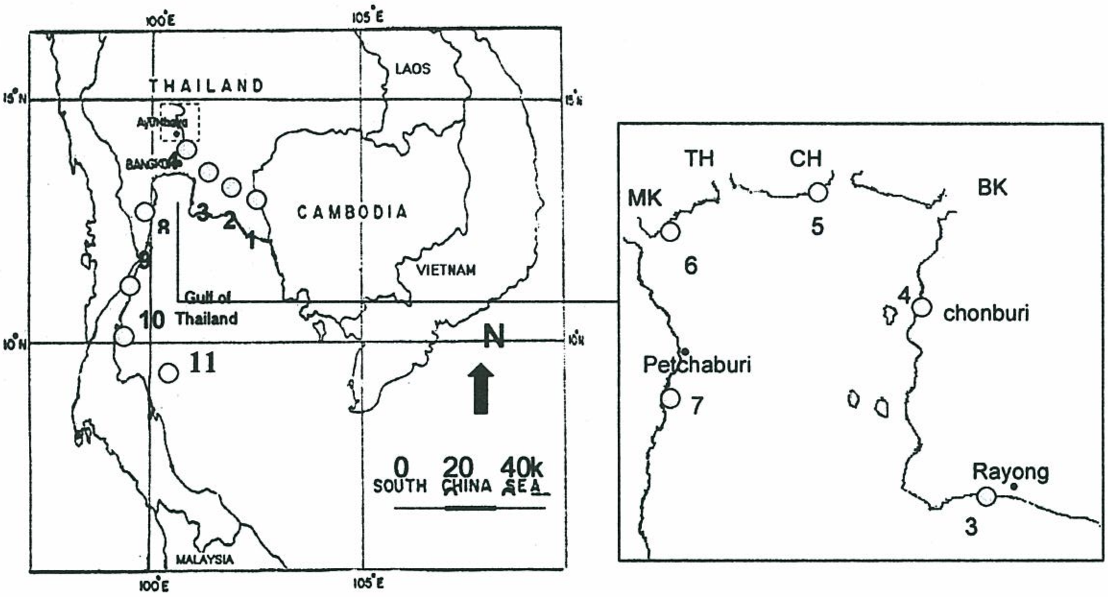

Figure 1 Sampling locations of fish samples from the Gulf of Thailand

Keywords: monitoring, UNU, POPs, fish, Gulf of Thailand

Low Risks, High Public Concern? The Cases of Persistant Organic Pollutants (POPs), Heavy Metals, and Nanotech Particles

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Swiss Federal Institute of Technology Zurich

Abstract: *Risk is an ancient, historic concept .It is a primitive in the sense that almost everybody has some subjective understanding of what is meant by risk. There are, however, different definitions and notions of risk. For instance, the notion of pure risk only considers negative events or losses. The term speculative risk, on the other hand, incorporates the evaluation of both benefit and harm. Furthermore, it is important to distinguish between science-based risk assessment and subjective, individual and public risk perception.. Scientific risk assessment consists of well-defined procedures and methods for assessing the likelihood of future negative events. Individual and public risk perceptions are affected by what is officially stated about the effects of certain pollutants, technologies or instances. Risk assessment and risk perception are to some extent interrelated. We will introduce some fundamentals of risk assessment and risk perception and report what is known about these in the significant cases of heavy metals, POPs and nanotechnology. Up to date the three cases do not represent stigmatized risks, as is the case with nuclear material or genetic modified organisms. But all three cases embody significant environmental risks. We will report on possible risks and on the research examining public risk perception..*

INTRODUCION

Where does the concept of risk come from?

Historically, the first pre-concepts of risk were already known by the Mesopotamians about 3,000 years before Christ (Oppenheim 1977; Mumpower, Menkes et al. 1986). It is interesting to see that the *Mesopotamians* had a profession of risk experts. This was a group of wise men called the *Ashipu* and they were responsible for risk management. The *Ashipu* were elected as they could read signs from the gods and thus were supposed to provide an excellent service of aiding in decisions to their clients. In order to assess the likelihood of positive and negative outcomes regarding different matters (e.g. of starting a war or not), they simply noted advantageous or disadvantageous signs associated with each matter on clay disks. After recording the data they recommended a solution which was simply made by taking the alternative which had more positive signs.

The term risk became common in the 15th century in North Italian merchandising. Etymologically risk refers to the Latin *ricare* that originates from the Greek concept ριζα, which, in turn, means root as well as cliff. A Hellenistic sailor took ριζα if he chose a route close to the cliffs, which increased the peril of shipwrecking but also shortened the distance travelled.

The scientific concept risk was introduced by Laplace when dealing with "*the probability of the events linked to the hope but also the anxiety of tomorrow*" (Laplace 1816, 1921). In this context, *hope* is defined as the expectation of an uncertain but likely benefit. Note that Laplace already defined risk as the product of all harms and benefits multiplied with the probability of their occurrence.

The notion of risk became accented with the rise of the industrial age. Harm, at that time, was merely considered opportunity costs for gaining access to the benefits tied to new technologies. Here, the simple definitions of *risk as the probability of loss* have dominated literature and practice for a long time. In Europe, for instance, the discussions on technological risks in the 1970s were almost exclusively characterized by definitions of risk in which only the losses were considered. These conceptions are also denoted as *pure risk*. The historical context also reveals why the concept of risk was narrowed down to the probability of losses. However, as Paustenbach (Paustenbach 1989) pointed out, the environmental and health risk assessment methodologies, which were developed in 1970, were a major change compared to what existed before. Instead of a "black and white", "yes or no" answer on the existence of hazard or peril, a gradual, mostly numerically differentiated assessment was provided which evaluates the likelihood of becoming exposed to certain unwanted, negative events.

Today, risk assessment, risk perception, and risk management have become very important. Risk became universal in that all sciences, ranging from natural through to technical, medical, and social sciences and on to the humanities, deal with this concept. Risk – and in particular environmental risk – was given a new dimensionality with the mastering of nuclear fission (Krohn and Weingart 1987) because the human species was able to cause damage worldwide to microcosmic systems. In principle, this phenomenon is of importance for many new technological aspects. Sociologists, such as Ulrich Beck, speak about a new age called World Risk Society (Beck 1986; Beck and Sznaider 2006). The issue here is that some scientists and other concerned people are afraid that we cannot fully exclude new technological inventions (e.g., a specific genetic manipulation in a plant or animal, a new organic compound, or a specific nanotech particle) and that these could pose considerable risks for humans and for the environment.

Variants of risk

As we can see from the aforementioned historic example, risk has different meanings. Therefore we speak about a *concept field of risk* rather than a clear and unambiguously defined concept (such as a natural number). First, it is important to know that many scientists distinguish *risk* from *danger* or *hazard*. If we speak about risk, there must be the option of deciding between different alternatives or strategies, which may lead to different outcomes (including at least one unwanted one). This is the case with technologies or man made chemical compounds as society or industry can, in principle, decide whether to produce them. This is not the case with natural hazards as the path of an asteroid does not depend on human action.

Second, an important distinction to be made is that between *pure* and *speculative* risk. If we speak about pure risk only the negative and unwanted outcomes of certain alternatives or strategies are considered. This is done by the traditional basic definition of *the risk of a decision or technical alternatives* (A_i) as the sum of all losses that may result from negatively evaluated events ($u_i(E_{i,j}) < 0$) related to an alternative ($E_{i,j}$) that may result multiplied by the probability of occurrences ($p(E_{i,j})$). Formally the definition of this variant of pure risk reads:

$$r(A_i) = \sum_{j \text{ with } u_i(E_{i,j})<0} p_i(E_{i,j}) * u(E_{i,j})$$

This simple definition dominates the financial world or health risk assessment. A typical occurance would be if one would count only the number of lethal events. In this case, the risk – say of an energy plant – would be the expected number of deaths resulting from the building, operation, and destruction of a power plant.

Another variant is speculative risk. In this concept of risk not only the losses but also the potential benefits that may result from one alternative are incorporated in a risk judgment or risk assessment (Fishburn 1982; Brachinger and Weber 1997). We can see from this that there are different definitions of risks for a certain event, but the uncertain outcome of an uncertain negative event is an indispensable feature of risk perception and risk assessment. However, we should also emphasize that what is considered to be a negative outcome may not only differ across situations, but also in one and the same judge. This has been elaborated in the so called prospect theory (Kahneman and Tversky 1979; Kahneman and Tversky 2000).

RISK ASSESSMENT AND RISK PERCEPTION

There are various conceptualizations of risk, such as mathematically defined variants of financial risk from banks, statistically assessed health risks or simulation model based risk assessments on climate change impacts (e.g. the probability of a rise of the sea level). But many risk judgments are not based on analytic, scientific judgments but based on intuition, life experience, or holistic judgments. This holds true for experts and for laypersons. In the context of environmental risks, which will be discussed in this paper, we will thus distinguish between

1. Science based *risk assessment* procedures. These procedures provide evaluations of the likelihood of diverse future events focusing, or at least including, the negative, unwanted events. Risk assessments are based on certain transparent, well-defined procedures and methods and includes both the description of the unwanted events and a characterization of the uncertainties *inherent in the process of inferring risks. Risk assessment is essentially a modeling approach for evaluating risks.*
2. *The risk* perception of people, which is based on individual experience and the mental processing of consequences of certain actions or events.

Risk management should be considered a different activity to risk assessment. By risk management we understand the process of "evaluating alternative regulatory actions and selecting among them. Risk management, which is carried out by regulatory agencies under various legislative mandates, is a agency decision-making process that entails considerations of political, social, economic, and engineering information ..." (NAS 1987). It is interesting to see that environmental risk management can be traced back to the early Medieval age. The negative impacts of air pollution, at that time caused primarily by soft coal, was noticed in London in the 13th century. In 1285, King Edward I of England initiated a process of reducing coal smoke in London and in 1298 the smiths in London voluntary declared that they would not "... work at night on account of the unhealthiness of coal and damage to their neighbors." (Hughes 1975) As these voluntary efforts were not sufficient, Edward issued a proclamation prohibiting the use of soft coal in ovens (Mumpower, Menkes et al. 1986). We will not deal with risk management but briefly introduce the essentials of risk assessment and risk perception for environmental risks

Risk assessment

In principle, risk assessment has to include the following stages (compare e.g. (Paustenbach 1989):

(a) *Defining the risk situation*: This includes the *definition of the alternatives underlying risk assessment.* Examples are the definition and the prevalence of a certain endangering toxic element including the level of contamination or the existence of a certain technology or organism (e.g. of a certain genetically modified crops). Furthermore, the safeguard object (e.g., fish, birds, humans, biodiversity etc.) and the system boundaries (e.g. a family, village, nation etc.) have to be defined.

(b) *The negative effects have to be defined*: As mentioned above, different aspects can be considered a negative effect. For instance, if we look at potential negative effects of airborne heavy metals, we have to define whether we look at the acute or chronic effect and on what safeguard object (e.g. the gastrointestinal system, kidney, liver etc. on psychological effects, or on whole health). It is apparent that the assessment of an effect can be done by different technical or medical procedures.

(c) *Assessing the dose-response relationship*. This assessment deals with the relation between the dose (e.g. concentration or absolute load) of an agent (e.g. toxic chemical) received or administered and the consecutive incidence of an adverse health effect or negative impact on the safeguard object.

(d) *Assessing the exposure*. This step includes the measuring or the estimating of the intensity, frequency, and duration of human, animal, plant, ecosystem etc. due to the exposure to a chemical compound (or – technical speaking – to an Alternative A_i).

(e) *Characterizing the risk*. This step includes the estimation occurrence of an negative effect (e.g. a health effect) under the various conditions of exposure described and with respect to the safeguard object of interest.

If we look at the history of environmental risk assessment, we can trace back a long history starting from Agricola's (Agricola 1565) study on occupational risks in mining and ending with the Harvard industrial hygiene program of identifying which diseases are due to exposure at the workplace. According to Paustenbach (Paustenbach 1989), what we call risk assessment started around 1930. We can discriminate between different risk assessment methods which are based on different scientific roots and data and acknowledged the uncertainties and the issues of the above points (a) to (e) in a different way. In particular, we can distinguish between

- *Epidemiological studies*: These studies investigate the distribution of diseases within a population and possible factors causing them. Often these studies are post hoc studies, and historical data is used: A critical issue is that it is extremely difficult to identify the specifities of the context factors and the generic of exposure (Rothman and S. 1998).

- *Animal experiments*: As it is mostly ethically not feasible to expose human samples to environmental toxicants, certain animals serve as "model observations" (animal bioassays), critical issues is in what way the dose-response relationships observed in animals can be used to make statements for human species; further often the dose are unrealistic high and the question is what conclusions can be made for humans.

Further there are other methods such as simulation based on literature data, low-dose human experiments with volunteers or expert judgments for cases

Risk perception

By risk perception of an individual we understand all mental, emotional (affective) and psychophysical processes (e.g. the change of hormone level) which are linked to risk in a risk situation. In this context we consider risk as a primitive (Sokolowska 2006) or as cognitions and emotions which are saliently associated with the semantics of risk (Scholz and Tietje 2002), p. 181).

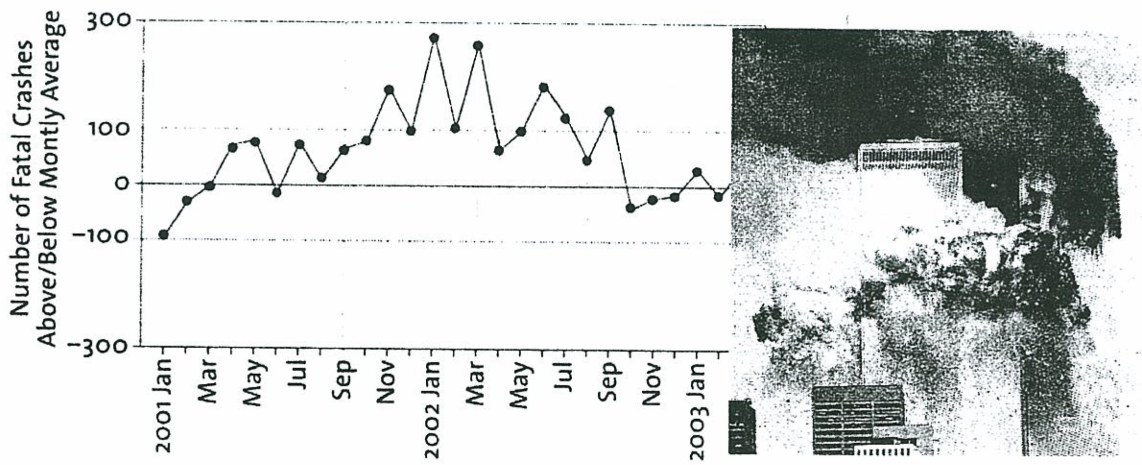


Figure: Single events can change behavior. The fear and high risk judgments of becoming a victim by an aircraft after September 11, 2001 led many U.S. citizens to driving by car instead of flying . In 2002 this caused about an additional 1,500 fatalities due to car crashes compared to previous years.

Risk perception is not only a matter of numbers. According to the seminal work of Slovic, Fischhoff et al. (Slovic, Fischhoff et al. 1979), *risk* has a kind of personality. Obviously, decision makers are not only taking the statistical (actuarial) data into account, but are rather strongly influenced by their own interpretation of the situational characteristics. Judgments of riskiness rely on many other aspects than statistical frequencies. In studies examining risk perception, participants assess, for example, how dreadful the hazards are, whether the risks are known to science, and whether people have control over their exposure to the hazard. Results of this research suggest that qualitative dimensions are more important than actual fatalities for lay people's risk perception. Lay people tend, for example, to assess commercial aviation as more dreadful than cars. The reason for this perception is, that in the case of aviation a large number of people can be killed in an accident. Car accidents are more common, of course, but few people are killed in each accident. Results suggest, therefore, that in this example not the mean value of fatalities is important for lay people's risk perception, but rather the maximum of possible fatalities. The fact that people perceive low-probability, high-damage events as dreadful may have undesirable consequences. Americans reacted to the terrorist attacks on September 11, 2001 by reducing their air travel after the attack. Many people decided not to fly but rather to drive to their destination. However, flying would have been safer than driving a car. Gigerenzer (2006) estimated that 1,500 Americans died on the road in the attempt to avoid the unlikely event of being killed in an airplane by terrorists.

According to Slovic et al. (Slovic, Fischhoff et al. 1979), the most influential factors in risk judgments are the perception of *dread* and *voluntariness* with respect to the outcomes/events, the conviction of having *personal control* over the likelihood or the magnitude of the outcomes, and whether the risk is *known or unknown*, i.e. the *familiarity with the risk* (sometimes split into *novelty and knowledge*). Naturally, the very situational characteristics such as the *expected number of fatalities or losses* (i.e. the *catastrophic potential*) are decisive factors (Renn 1992). However, although the perceived average number of fatalities correlates with the judged riskiness of a situation, the relationship is weak and generally explains less than 20 percent of the declared variance (Renn 1983); (Jungermann and Slovic 1993). Finally, risk is rated greater if it violates common *equity principles* (see Figure 32).

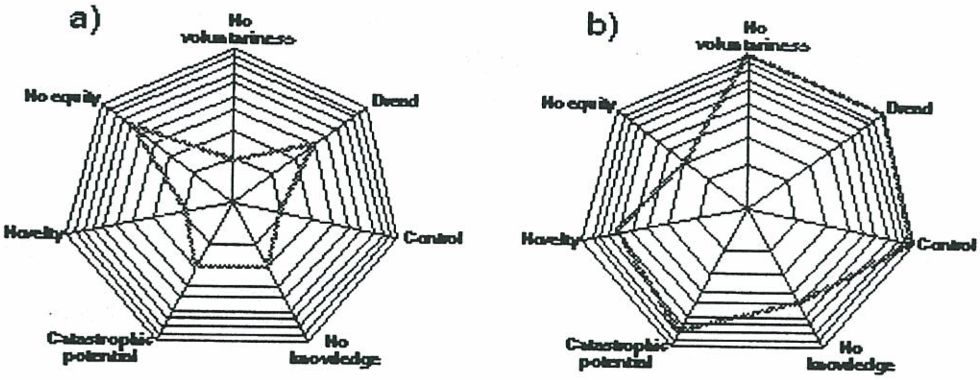


Figure 32 *Egg graphic of risks as investigated by Slovic and his group. The aspects of risk are rated on a 10-point scale (the outer circle means highest rating). Risk situations show certain profiles and are thus also judged to have a kind of personality. We present two profiles of risk perception of an individual: a) the risk of car travel, b) the risk of a nuclear power plant.*

THE CASES OF PERSISTANT ORGANIC COMPOUNDS (POPS), HEAVY METALS, AND NANOTOTECH PARTICLES

Heavy Metals

From the periodic table, 80 out of 105 elements are considered metals. About thirty of them are considered toxic, 23 of them are heavy metals (Steven 2007). Lead, cadmium, mercury, arsenic, but also aluminums (as dust or as additives in water) are harmful. These metals are well explored as through human occupational exposure significant poisonings became visible very early. Hippocrates described a man and the impact on his health due to smelting arsenic and mercury, called metal fume fever, which was known in ancient Greece. The dissemination of heavy metals was linked to most industrial processes and was a characteristic to the industrial age, in particular the heavy metal industry and allied combustion processes. Various measures were used in order to have the use of leaded gas phased out, such as filtering techniques as well as documented studies on the environmental and health damages caused by lead. As a result, in the U.S., the Clean Air Act for road vehicles was passed in 1996.

There is a manifold of human health impacts of heavy metals ranging from the ingesting organs (lung, gastrointestinal system, etc.), through organs (such as kidney, liver, etc.) and the central and peripheral nerve system to the bones. However, one should note that many nutrients and all environmental compartments include heavy metals, which are – in general – part of the universal material flow. Therefore, one has to discriminate between a basic natural exposure and additional exposure to humans made by contaminated soil, air and subsequently increased loads. Thus, an environmental risk assessment requires not only assessing the (a) risk situation, (b) the existence of negative effects and (c) the dose-response relationship, but also (d) the multiple exposure. This is essential as some of these metals, such as Cadmium, come from smoking or natural sources (such as ingesting something containing heavy metal soil dust; (Scholz, May et al. 1991)). It should be emphasized that both assessing the exact exposure, i.e. the uptake from different sources, as well as the dose-response functions, are difficult processes which include the modeling of uncertainties in the data and the knowledge by means of probabilistic models (Wallsten and Whitfield 1986; Scholz, May et al. 1992; Nothbaum 1997; Scholz, Heitzer et al. 1997; Cullen and Frey 1999). If a certain uptake has been (probabilistically) assessed, the (probabilistic) dose-response relationships can often only be quantitatively specified for certain physiological parameters, which are responsible for certain physical or mental harm. So, characterizing the effects of exposure to environmental contamination asks for expert-based judgments (e) and thus includes uncertainty.

Related to risk perception of heavy metals in the environment, there are several studies, which investigated people's risk perception (Krogmann, Gibson et al. 2001; Weber, Scholz et al. 2001; Grasmuck and Scholz 2005; Scholz and Schnabel 2006). The study of Weber et al. (Weber, Scholz et al. 2001) included people who actually lived on contaminated soil and compared their risk judgments with people not living on a contaminated site. One should note that the maximum contamination level is typically rather low (i.e. investigated sites in the inquired area in Switzerland are rather low, in the contaminated area e.g. below < 5 ppm Cd).

A factor analysis showed that the factors dread, control, and catastrophic potential were relevant to the perception and evaluation of low-dose environmental risks such as the contamination of the investigated area, whereas the catastrophic potential was realistically judged as low.

A cluster analysis showed that the people perceived the heavy metal soil contamination similar to that of oil contamination, ozone layer, preservatives and genetic technology. It was perceived indifferently with regard to dread.

Sustainability or precautionary issues, such as the prevention of harm for future generations, were highly correlated with the acceptance of the use of bioremediation methods in people's residential areas.

The study of Grasmuck and Scholz (Grasmuck and Scholz 2005) compared people on more and less contaminated sites. Both groups judged the risk for themselves similarly. Quite surprisingly the low-exposure group, when compared to the high-exposure group, judged perceived risk for other affected people living in their community to be higher. Unfortunately the survey does not answer whether this is an impact of illusionary control or whether this is an impact of (believed) behavioral change of the inquired people.

A main finding was that risk perception was not so much determined by the factual exposition to heavy metals but to emotional concerns. So the emotional and highly concerned people had a higher desire for additional knowledge, provided lower scores in self-estimated knowledge, and showed a lower risk acceptance. Factually, the question on the knowledge about contaminated soil did not differ between the people with high and low emotional concern.

Judgments on the need for decontamination are determined by risk perception, less application of dissonance-reducing heuristics and commitment to sustainability. The desire for additional information is not affected by missing knowledge but is affected by emotional concerns.

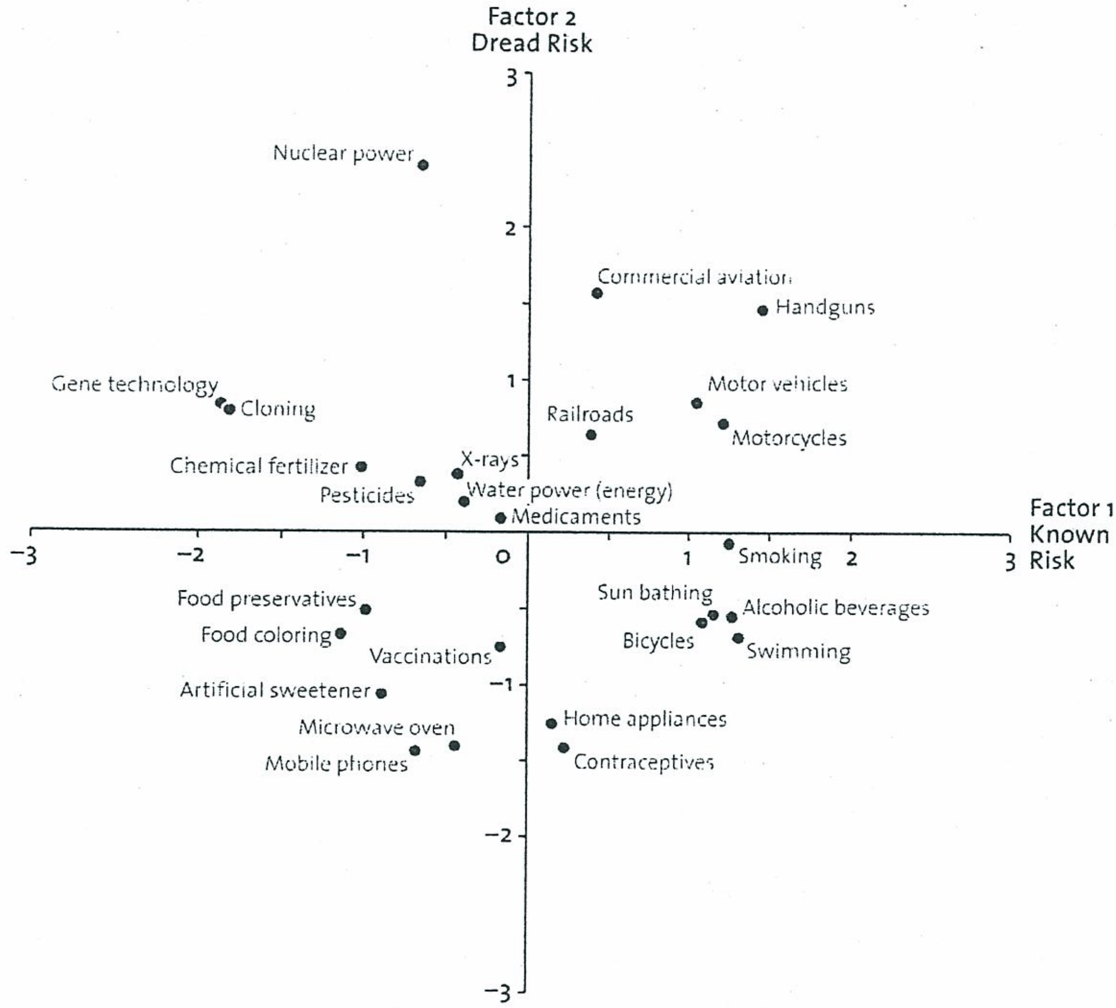
Persistant Organic Pollutants (POPs)

The environmental decision-making community is now facing the adverse health and ecological effects of POPs. The situation regarding POPs is much more complex than with heavy metals. In the domain of the European Union alone there are 100,000 registered industrial manufactured chemicals and most of these are in daily use (EINECS, (Allanou 2007)). Critical POPS are frequently chlorine compounds. Well-known examples are DDT, PCDDs (polychlorinated dibenzo-pdioxines) PCDFs, (polychlorinated dibenzofurans), lindane (beta HCH) or PCB (coplanar polychlorinated biphenyls). Also carcinogenic polycyclic hydrocarbons (PAHs) are considered POPs. POPs are caused by many human activities including combustion for energy production and transportation, industrial processes, and agricultural uses of pesticides. POPs can be found in all environmental compartments and are accumulated particularly in fat tissues.

As the attribute *persistant* indicates, POPs have a very long life-time and are characterized by long distance travel in water and (due to their semi-volitility) in the air. This allows for long-range transportation and multiple environmental interactions. Because they travel long distances POPs cannot be regarded as a local problem as they also cross local regulatory boundaries. One can say that the "scientific or regulatory community has not adequately addressed human exposure to POPs through multiregional, multimedia exposure scenarios." (Bennet, E. et al. 2002) For instance, to date, an effective and sustainable global strategy against unseen contamination of aquatic environments barely exists (Schwarzenbach, Escher et al. 2006).

Historically, organoclorine insecticides and the food chain were the primary sources of human uptake. "It is now clear that the group of chemicals included in the term "persistant organic pollutants" generally are present in humans as a result of their presence in diet. More than 90 percent of the intake of these 15 to 50 chemicals occur through ingestion of fish, meat, and dairy products." ((Fries 2002), p. 890) A strong dose-response relationship between serum concentration of POPs and diabetes indicates one of the health effects (Lee, Lee et al. 2006).

Figure 2: The location of chemical risks such as Chemical fertilizers or Pesticides that are related to POPs



Though there have been sophisticated so called 'multi-compartment models'(Hertwich, Pease et al. 1998; Lee, Lee et al. 2006), from the perspective of environmental risk assessment the issue regarding POPs is more difficult than with heavy metals. First, we have to acknowledge the magnitude anthropogenic fluxes of synthetic chemical production of 300 million tons per year, which is huge compared with the 0.4 million tons of average oil spill (in the time frame of 1980-2000; (FAO 2006; Schwarzenbach, Escher et al. 2006)). We would like to mention that due to the complexity of ecosystems, the ubiquitousness of organic chemical cocktails and due to biological processes which are starting at bacterial and micro level including enzymatic and surface related reactions (Schwarzenbach, Escher et al. 2006), also the sketched risk assessment approach above (separating exposure and effects) can come to its limits if systemic risks are considered.

> The mutual interaction of thousands of chemicals in the environment with millions of biological species will ultimately determine whether a given pollutant (mixture) leads to marginal or catastrophic ecological consequences. ((Schwarzenbach, Escher et al. 2006), p. 1075)

There have been many studies investigating the risk perception of chemicals (Mertz, Slovic et al. 1998; Tucker and Napier 1998; Beehler, McGuinness et al. 2001; Slovic 2001; Tucker and Napier 2001) but factually none, which specialized on POPs. However, DDT and chlorides were sometimes included in the so called 'psychometric approach'. They consistently show that these chemicals are not at the extremes of the subjective factors such as dread and known (Slovic 1987; Siegrist, Keller et al. 2007) though the missing knowledge seems to be essential (see Figure 2).

Also other studies show that sport fishers (Beehler, McGuinness et al. 2001) or farmers (Tucker and Napier 2001) who are more exposed to POPs than the average person do not show considerable concern. There are, however, differences of chemical risk judgments between the senior managers of the chemical industry and the public. Those who benefit, i.e. the senior managers, show less concern than the public (Mertz, Slovic et al. 1998). This difference might be due to the fact that the managers refer to the concept of speculative risk and incorporate the benefits (both for themselves and for the public) which emerge from producing and applying the POPs. But also toxicolologists intuitive judgments of chemical risks are lower than those of laypersons (Slovic, Malmfors et al. 1995).

These studies might reveal that value judgments and other issues such as social justice (who benefits from a risk) are essential factors of risk perception. This also holds true for the environmentalist movement. One should note that the cradle of the environmentalist movement is Rachel Carson's book 'Silent Spring'(Carson 1962). The book describes the subtle but dramatic impacts of POPs were and the term biocide was first coined here. If symbolic values are included then public risk judgments are seriously affected.

Nanotechnology

Nanotechnology is perceived as one of tl : key technologies of the 21st century. This technology will generate new products with various benefits. At the moment we do not fully understand potential health risks or environmental risks from engineered nanoparticles (Morgan 2005). Since nanotechnology allows the introduction of new properties to materials it could potentially lead to huge benefits. The use of such materials may also mean that these products may be associated with some risks (Pusztai and Bardocz 2006). Recent studies suggest, that at least some nanomaterials may be problematic for humans or for the environment (Oberdörster, Oberdörster et al. 2005). Results of these risk assessment studies do not allow, at present, to definitely quantify the risks associated with nanotechnology to humans and the environment . In addition to these risks, the development of nanotechnology faces risks in terms of unintended economic and societal impacts. Various stakeholders seem to agree that public perception and public acceptance of nanotechnology will be crucial for the realization of technological advances (Royal Society and Royal Academy of Engineering 2004). It is remarkable that the Royal society addressed both risk assessment issues and risk perception issues. It is hoped that in addressing public perception at an early stage that acceptance problems, which were observed for genetically modified foods in Europe, can be avoided.

Recent surveys suggest that the public does not know very much about nanotechnology (Cobb and Macoubrie 2004). In a recent study we examined how lay people perceived various nanotechnology applications (Siegrist, Keller et al. 2007). In order to assess public perception of this new technology participants have to be informed about possible risks and possible benefits associated with nanotechnology. Based on this information participants were asked to evaluate various nanotechnology-applications in regard to several qualitative dimensions. Results suggested that perceived dreadfulness of applications and trust in governmental agencies are important factors for lay people's risk perception. It should be added that similar results were observed for experts and laypeople, but the latter perceived greater risks than the former. Results of this study suggest that public concerns about nanotechnology may diminish if measures are taken to enhance public trust in governmental agencies regulating nanotechnology.

Nanotechnology is increasingly being employed in the areas of food production and food packaging (Sanguansri and Augustin 2006). Food and nutrition products containing nanoscale additives are already commercially available. It is expected that nanotechnology will become increasingly important in the near future. The public showed low levels for stated willingness to buy nanotechnology foods or food with nanotechnology packaging (Siegrist, Cousin et al. 2007). Furthermore, results of this study suggest that nanotechnology packaging is perceived as being more beneficial than nanotechnology foods. As suggested by the affect, heuristic (Slovic, Finucane et al. 2002) affect had an impact on perceived benefits and perceived risks. In the absence of sufficient knowledge, trust and affect are important heuristics that guide our decisions.

Public discussions in the fields of gene technology and nuclear power show that public perception may have a strong impact on the development, funding and acceptance of a technology. In the field of nanotechnology there seems, to some agreement, that in addition to risk assessments there should also be concern assessments (Renn and Roco 2006). In our view, nanotechnology is a good example of a new technology, for which technological assessment and examination of public concerns started at an early stage (Royal Society and Royal Academy of Engineering 2004). It is hoped that addressing public concerns during the development of new products may facilitate public acceptance. It remains to be seen whether the mistakes made in the GM debate can be avoided and whether the introduction of nanotechnology will be more sustainable.

CONCLUSIONS

We have introduced different concepts of risks (pure and speculative), introduced the fundamentals of risk assessment and risk perception and analyzed the state of the art research on three cases. These cases differ with respect to their history, the knowledge gained on negative impacts on human and environmental health and other issues. The impact of heavy metals is known for a long time and the classical procedures of risk assessment, including the relation of differing between exposure of a safeguard object and dose-response relationships can be ideally applied to this case. This is different for POPs for which the interaction with other chemical compounds (i.e. the impact of unknown cocktails) and unknown effects on the micro-level appear to be more important. Nanotechnology is an issue of the 21st century and though there is a consensus about a potential of these entities, no comprehensive risk assessment procedure has been developed for these particles yet. From an environmental and natural science point of view, all these cases deserve high attention with respect to national and international risk management. As history has shown, particulary in regards to heavy metal contamination, there have been large environmental risks and subsequent financial losses emerging from these types of chemicals and particles.

From a psychological perspective, these cases have something in common--they do not belong to the stigmatized hazards by the public, such as nuclear technologies or genetic modified organisms. However, when POPs and nanotech (and also heavy metals in principal) are seen in the contexts of food or as harmful to highly appreciated issues such as valued species (e.g. eagles) which also have a symbolic value, these issues might change.

Risk perceptions differ across countries and cultures. However, personal characteristics such as gender, age, family status (e.g. having children), education, and class level seem at least as important as the cultural issue. This is shown by the empirical findings that different stakeholders provide different risk judgments. As we have argued, one reason for the confusion among the stakeholders can be seen in that they utilize different concepts of risk. For instance, some can apply the concept of speculative risk, which provides an integrated view on the benefits and the negative consequences. Others may only focus on pure risks, which combine the evaluation of negative events and their probability. We should note that the application of different concepts of risks by different stakeholders in different situations is a well-known issue. For instance, concerned people under stress (e.g. when worrying about their own new-born child) tend to focus their risk judgment only on the largest thinkable damage (e.g. that their own child may die). On the contrary, people from national environmental protection agencies may think about risks in statistical terms (e.g. considering the chance that the child may die [for instance 1: 100,000]) as neglectibly small.

Looking at risk assessment and at risk perception we recommend that both should be considered from a realist stance. The biophysical effects as well as what people think are both real. The natural scientists assessment and the perception of the public have their own rationale. Both can be more or less appropriate though by different reasons. Based on this statement, we think that it is important to appropriately relate risk assessments and risk perception at an early stage of technological developments. This, in particular, relates to nanotech and to some extent to POPs, as they embody the risk to become stigmatized and also to incorporate some significant risk with respect to health and ecosystems.

Clearly, risk perception should not replace risk assessment. However, as safeguard objects and risk judgments include values, lay people's risk perception should be considered as one factor which determines what research questions should be primarily addressed. Thus, as the issue presented case studies demonstrate, risk assessment is not only an issue of purely natural science but an issue of risk perception as a purely psychological or sociological matter. Both issues ask to be appropriately related.

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PERSISTENT ORGANIC POLLUTANTS (POPs) MANAGEMENT IN INDONESIA

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Stockholm Convention on Persistent Organic Pollutants (POPs)

- The purpose of Stockholm Convention is to protect environment and human health from POPs;
- The concerns on problems and POPs' impact leads countries to sign the SC (Indonesia signed on 21 May 2001)

National Policy on POPs

- To reduce and eliminate the use and production of POPs in order to protect human health and environment from POPs.
- To encourage the cooperatioan among relevant sectors and other stakeholders including community in dealing with POPs problems.

REGULATIONS (1)

- **GR No. 74/2001 concerning hazardous and toxic substance management** – banned 10 POPs
- **GR No. 18/1999 jo GR No. 85/1999 concerning hazardous and toxic waste management** – standard emission of aldrin, dieldrin, chlordane, endrin, heptachlor, hexachlorobenzene/ HCB, Polychlorinated Biphenyl/ PCB, Toxaphene in TCLP test, DRE for incinerator
- **Ministerial Regulation of Agriculture No. 7/2007** concerning pesticide registration

REGULATIONS (2)

- **GR No 82/2001 concerning water pollution control –** water quality criteria: standard for POPs pesticide (Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Toxaphene).
- **Head of BAPEDAL Decree No: Kep-03/BAPEDAL/09/1995** concerning technical criteria for hazardous and toxic treatment.
- **Head of BAPEDAL Decree No: Kep-04/BAPEDAL/09/1995** concerning guideline of criteria for the disposal of treatment product, criteria for used treatment location, and used disposal hazardous waste location.

NATIONAL IMPLEMENTATION PLAN (NIP)

- NIP is framework for developing and implementing policies, regulations, capacity building, dan investment programs on POPs;
- The development of NIP involved relevant stakeholders through several meetings and workshops;
- The development of NIP is based on the priority setting

Priority Setting

- POPs pesticide management
- PCB and equipment containing PCB management
- Unintentionally POPs management

NATIONAL IMPLEMENTATION PLAN (NIP)

NIP consist of:

- The result of POPs inventory and UPOPs estimation;
- The action plan, its budget and financial sources;
- The technical and financial assistance to implement NIP;
- Participation of relevant government institutions.

POPs in Indonesia

- There is no production data on POPs pesticides except DDT;
- There was only importation data on HCB from 1994 to 2002, up to 92,569 kg;
- There were no stockpile of POPs pesticides in 9 ex warehouses in 9 cities;
- There were some equipments (capacitor and transformer) contaminated with PCBs;
- The estimated releases from unintentational production of PCDD/PCDFF was 20,977 g TEQ

(Source: Draft National Implementation Plan, April 2007)

ACTION PLAN (1)

There is 86 action plans in NIP, including:

- Strengthening the capacity of institutional and human resources in POPs management
- Strengthening policy and regulation framework for facilitating environmentally sound POPs management
- A comprehensive POPs invetory
- The management of POPs stockpiles, equipment containing POPs, POPs waste and its disposal
- Inventory of contaminated sites and strategies for remediate contaminated sites

ACTION PLAN (2)

- The development of environmentally sound destruction technology and increase the number of such facilities
- Inventory and implementation of BAT/BEP for sources in Annex C
- The development of UPOPs laboratory
- Monitoring of POPS, UPOPs dan the impact of POPs on human health and environment
- Raising awareness on POPs
- Looking for alternative POPs
- Controlling illegal trade

CURRENT STATUS

RATIFICATION

- The ratification of SC is included in National Legislation Program (PROLEGNAS) tahun 2007-2008
- The harmonization process has finished. Indonesia is currently in the last steps of ratification process

NIP

- The draft NIP has circulated to other relevant sectors and some comments are given
- The endorsement of NIP is in progress

THANK YOU

New POPs - Candidate Chemicals for Stockholm Convention

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Abstract

Environmental pollution by chemicals, particularly of persistent, bioaccumulative and toxic nature (so-called "Persistent Organic Pollutants" or "POPs"), has been of major concern. After four decades since publication of the famous "Silent Spring" written by Rachel Carson, an international treaty to protect environment and human health from POPs pollution, Stockholm Convention, was adopted and was entered into force in May 2004, in which 12 chemicals, i.e., dioxins, furans, PCB, HCB, DDT, chlordane, heptachlor, aldrin, dieldrin, endrin, mirex and toxaphene, are banned / regulated.

An important aspect of the Convention is the mechanism to add new chemicals to the target POPs list (Article 8). An expert committee, POPs Review Committee (POPRC), was established at the 1st Conference of Parties (COP-1; May 2005) to review the proposal of Parties for listing new chemicals. The reviewing process proceeds;

1) Apply screening criteria and judge whether the criteria is fulfilled or not
2) Evaluate a developed risk profile and judge whether the proposed chemicals have enough risk to be regulated under Stockholm Convention or not
3) Develop a risk management evaluation based on the information provided by the Parties

The result of each step will be reported to the next COP, and if approved, the process will move to the next step.

So far 10 compounds have been proposed as additional chemicals to the Annex A – C of the Convention[1)];

1st POPRC (2005)	pentabromodiphenyl ether (PeBDE), hexabromobiphenyl (HxBB), chlordecone, Lindane (γ-HCH), PFOS and derivatives
2nd POPRC (2006)	octabromodiphenyl ethers (OcBDE), pentachlorobenzene (PeCB), short-chained chlorinated paraffin (SCCP), α-HCH, β-HCH

All the chemicals have passed the 1st step and the 1st five passed the 2nd step. This year the 3rd POPRC meeting will be held during 19-23 Nov in Geneva, where 3rd step of the first five, and the 2nd step of the second five chemicals will be done in addition to the 1st step of the new proposal on endosulfan.

The 10(+1) chemicals may be categorized into several groups;

(A) organochlorine pesticides used extensively in the past; α-, β-, γ-HCHs, chlordecone, (+ endosulfan)

(B) brominated fire retardants; PeBDE, OcBDE, HxBB

(C) industrial organochlorine chemicals used for fire retardants and other purposes; SCCP, PeCB

(D) fluorinated surfactants; PFOS

Among them, five (Chlordecone, HxBB and three HCHs) have already been banned or regulated as POPs in the Convention on Long-Range Transboundary Air Pollution (LRTAP) in European Commission[2)]. In addition, the remaining five (PeBDE, PFOS, OcBDE, PeCB and SCCP) are being reviewed as candidates for POPs in LRTAP. Another group of chemicals, polycyclic aromatic hydrocarbons (PAH), is a target of LRTAP but not yet included/reviewed in Stockholm Convention. Two more chemicals not included/reviewed in Stockholm Convention, i.e., polychlorinated naphthalenes (PCN) and hexachlorobutadiene (HCBD), are being reviewed now in LRTAP. Endosulfan, the newest proposed candidate to the Stockholm Convention, is now reviewed by Chemicals Review Committee of Rotterdam Convention as an addition to the Annex III[3)].

Among the "new POPs", organochlorine pesticides (A) are, in fact, rather 'old' chemicals, used extensively in the past but banned in many countries now. The analytical methods for these chemicals have been established and many reports have been published. Brominated fire retardants (B), especially PeBDE and OcBDE, on the other hand, have been used until recently or even now. PeBDE and OcBDE are complex mixtures of chemicals and are rather difficult to analyze. SCCP is another example of continued production and complex mixtures with difficult analytical procedure. PFOS (D) is in a different category; it is non-volatile and is analyzed by LCMS instead of GCMS. PFOS is again a mixture of different compounds, with many branched isomers and derivatives, and its quantification method needs standardization. Also PFOS is different from other POPs in its unique property to be accumulated in livers, a target organ of its toxicity, and blood, a transport media within the body, rather than in lipids.

PBDE (polybrominated diphenyl ether including PeBDE and OcBDE) as well as PFOS and other fluorinated surfactants have been studied extensively in recent several years. For example, 104 and 54 presentations among 762 presentations in Dioxin 2007 meeting held in Tokyo, Japan, in Sept 2007, dealt with PBDE and fluorinated surfactants, respectively. Reports of their analysis in Asian environment have been increasing, too. In this presentation, brief outlines of usage, chemical and environmental properties, and environmental levels of these candidate POPs chemicals will be summarized with special reference to the two emerging chemicals, brominated fire retardants, especially PBDE, and fluorinated surfactants, especially PFOS..

References:

1) POPs Review Committee activities in Stockholm Convention homepage:
http://www.pops.int/documents/meetings/poprc/poprc.htm
see meeting reports of POPRC for detailed information on the proposed candidate POPs chemicals
2) Convention of Long-range Transboudary Air Pollutants homepage:
http://www.unece.org/env/lrtap/welcome.html
3) Rotterdam Convention homepage:
http://www.pic.int/home.php?type=t&id=5&sid=16

Measurement of Dioxin Emissions in Australia.

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Introduction

Emissions from biomass burning are a major component of the global carbon cycle. Estimates of the global area of forest burned range from 170 Mha to 320 Mha from which between 1400 Tg and 1800 Tg of carbon are emitted (Kasischke and Penner, 2004). Australia contributes approximately 10% of this emission. The proportion of the carbon emitted in the form of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF), collectively known as dioxins, remains a topic of concern and investigation.

That fires are a major source of dioxins is not in dispute. In Australia, a desktop study on dioxin emissions carried out in 1998 estimated that more than 80% of dioxin-like chemicals expressed as TEQ found in Australia are emitted from biomass burning such as bushfires (EA, 2002). This inventory, however, relied on emission factors (EFs) such as those provided by the UNEP toolkit (UNEP, 2001), in which the recommended emission factors were sourced from measurements from experiments using combustion chambers and combustion rooms. These EFs varied by a factor of more than 20, and consequently the total dioxin emissions were highly uncertain. Taking the upper and lower end of the range EA (2002) reported that bushfires emit between 70g TEQ and 1700 g TEQ.

There are some indications that emission factors for Australian forests could fall at the lower end of the range. In experiments that measured PCDD/F levels in fuel, soil and smoke of open chamber forest fire simulations Prange et al. (2003) found no increase in the mass of dioxin following combustion. This group also measured the dioxin content of bushfire smoke sampled in the field and found the concentrations to be low, and dominated by the higher chlorinated congeners, particularly OCDD (Prange et al, 2002). The comprehensive studies of (Gullett and Touati, 2003a, 2003b) also report low emission factors for wheat and rice stubble combustion of 0.5 µg TEQ (t fuel)$^{-1}$ however EFs for pine litter ranged from 1 to 56 µg TEQ (t fuel)$^{-1}$. The congener patterns of the latter were also different from the patterns, observed by Prange et al. (2003) with the less chlorinated furans forming a significant fraction of the emissions.

These issues led to a more comprehensive measurement campaign in Australia. The measurement programme concentrated on sampling in the field at a range of low intensity prescribed fires conducted for fuel reduction in forests, and some high intensity forest wildfires, and savanna grassland fires. The focus on field measurements was based on the difficulty in defining and implementing in a laboratory environment the combustion patterns observed in the field, and the possibility that factors such as soil heating may also influence the nature of the emissions. Nevertheless some laboratory studies were undertaken focusing on crop residues which are generally difficult to sample in the field.

Fires in Australia

Biomass burning in Australia has been classified for National inventory purposes by activity and by State. The four fire classes are wildfire, prescribed fires (generally for fuel reduction, but also slash removal following logging, and some other minor cases), savanna fires, which include fires of all classes in the savanna woodlands of tropical Australia, the arid zone woodlands and grasslands, and the temperate zone grasslands, and agricultural residue burning, principally cereal stubble and sugar cane). On average approximately 10% of the land area of Australia is exposed to fire each year. The distribution of the fires greater than 400 ha in area is shown in Figure 1.

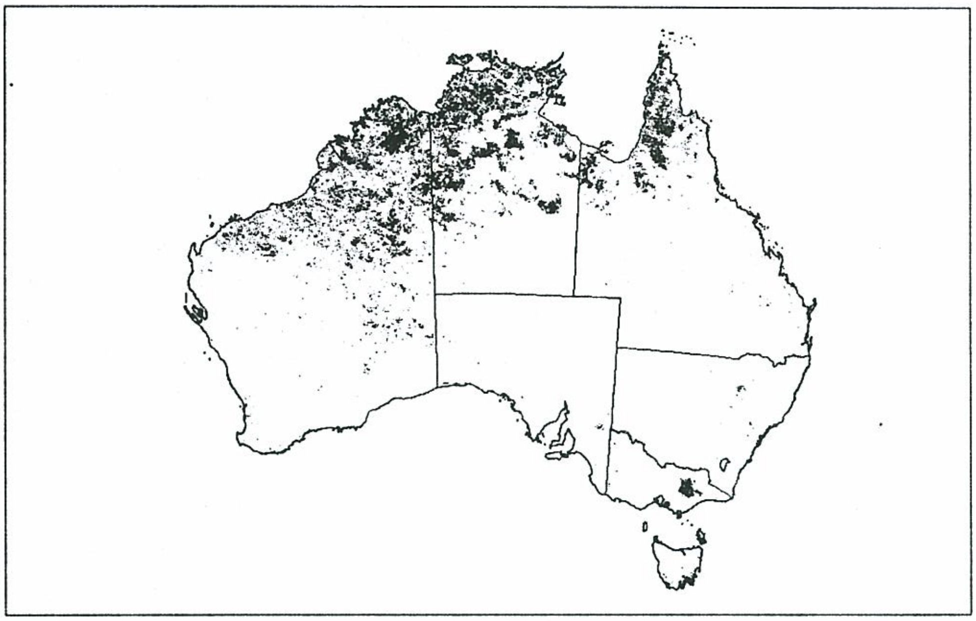

Figure 1 Distribution of fires in Australia for the inventory year 2007

Most of the area (approximately 95%) and most of the carbon emissions (77%) are due to savanna burning. While wildfires are more intense and destructive, their contribution to emissions is relatively minor (14%). Low intensity prescribed fires contribute 3% and crop residue burning accounts for the remaining 6%. This distribution poses a major challenge for comprehensive sampling. Most of the burning occurs in extremely remote regions where access is difficult and expensive. Wildfires pose a major safety risk, and access to the fire front is generally restricted by the incident controllers. Crop residue fires, like grassfires, are rapid and intense and in many cases the plume rises beyond the reach of ground-based sampling. Prescribed fires, however, are tractable because they are closely managed by fire crews. Nevertheless, the objective was to measure emissions from all these classes of fires, and to the extent practicable and possible a sampling strategy was designed to measure emissions from all these classes.

Measurement methodologies

Emission factors of trace gases are usually measured using a dual tracer method. This is described in detail in Andreae and Merlet (2001). In brief, the ratio of emissions of the chemical species of interest (Ei) to the emission of a quantifiable trace (in our case fuel carbon, Ec) is equal to the ratio of the increase in their concentrations above background in the smoke plume, i.e.

$$E_i / E_C = ([i]-[i]_{amb})/([c]-[c]_{amb})$$

The atmospheric concentration of pyrolised fuel carbon is the total of $\Sigma C=CO_2$ + CO + CH_4 + volatile organic compounds + particulate C. In most cases more than 90% of the emission is CO_2 and therefore CO_2 is a good surrogate for ΣC. The emission ratio is equivalent to the EF expressed relative to fuel carbon. The carbon content of biomass fuels ranges from 0.4 to 0.55, averaging approximately 0.5, therefore the EF on a fuel carbon basis is approximately two times the EF relative to fuel mass.

High-volume smoke sampling units were designed and constructed by CSIRO to sample a sufficient volume of the smoke plume to collect an analyzable mass of dioxins. These units could be mounted on the tray of a utility vehicle and located within the smoke plume as close to the fire front as was safe. Air was drawn through a 1 - 4 m long snorkel at 0.5 to 1 m^3/min. The PCDD/PCDF sampling head comprised an open face filter for particulate phase followed by a 130 mm diameter gas trap with polyurethane foam plugs (PUF) surrounding an XAD-2 layer containing 40 g resin. Flow rate and CO_2 concentration of the sampled smoke passing through the trap were measured and logged continuously and integrated throughout each sampling period, to determine when sufficient sample had been trapped prior to analysis. Analysis of the 29 PCDD/PCDF and dioxin-like PCB congeners (WHO 1998), and the PCDD/PCDF homologue groups collected on the filter and adsorbent (combined) was carried out at National Measurement Institute

Laboratories in Sydney using isotope dilution technique and high resolution mass spectrometry based on US- EPA methods 1613B, 1668A and T09A.
The sampler was deployed in the field campaign covering 3 savanna fires, 2 wildfires, 13 prescribed fires and 2 cane fires in the locations shown in Figure 2.

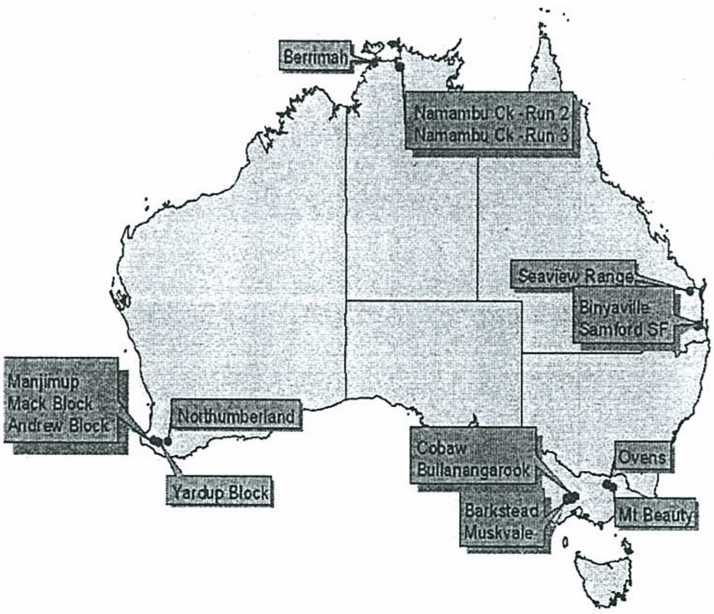

Figure 2 Location of the field measurement sites.

The sampler was also deployed in laboratory tests. These were conducted in a test facility designed for measuring fire behaviour in buildings, but which was easily adapted for burning biomass fuels in a manner approximating the field situation in which a fire front propagates across a bed of fuel. The combustion chamber was an open ended corridor, 10m long, 1m wide and 2m high lined with fibro-cement sheeting. The smoke vented into an exhaust hood where the dioxin sample was collected. Nineteen laboratory tests were conducted using cereal straw, a native grass fuel from the savanna woodlands near Darwin, NT, sugar cane residue and fine fuel collected from the floor of a forest near Barkstead, 100km west of Melbourne.

Results

Field measurements

Dioxin-like chemicals were detected in smoke from all field burns and the calculated emission factors (EF) expressed on a carbon basis ranged from 0.39 pg TEQ/g C to about 5.8 pg TEQ/g C. The data are summarized in Table 1. The mean EF was 1± 0.5 pg TEQ/g C which translates to approximately 0.5ug TEQ t^{-1} and for 90 % of all measured burns the EF was < 3 pg TEQ/g C. PCDDs contributed on average 70% of the emissions (expressed as TEQ), with PCDFs and PCBs contributing a further 20 and 10% respectively. The measured emission factors for our forest fires (prescribed and wildfires) and savanna fires fall at the lower end of the range suggested by the review (EA, 2002). These data were consistent across 20 measurements at different sites across Australia and emissions are much lower than expected based on literature values.

Table 1. Emission factors for dioxins (PCDD), Furans (PCDF) and coplanar PCB expressed relative to emitted fuel carbon

	Emission Factor, (pg TEQ)/(g C)			
	Cane	PF	WF	SF
PCDD	1.8	1.2	0.65	2.0
PCDF	0.14	0.36	0.13	0.16
PCB	0.07	0.18	0.13	0.07
Total	2.0	1.8	0.9	2.3
Stdev	1.3	1.3	1.0	3.1

[1] PF: Prescribed fires; WF: wildfire; SF: Savanna woodland fire.

Total emission factors ranged from 0.05 to 2.9 pg TEQ (g fuel)$^{-1}$ as observed in the field burns for total PCDD/PCDF and (PCBs) with means of 0.9, 1.2, and 0.5 TEQ (g fuel)$^{-1}$ for total PCDD/PCDF for prescribed fires, savanna fires, wildfires, respectively. Emission factors observed for the two wild fires tested were very low, and at variance with previous speculation that high temperature fires might be large emitters of dioxins (EA, 2002). There is additional evidence supporting these wildfire data. In a companion study, ambient measurements were made in the dense smoke plume 100 km downwind of 2003 wildfires in NE Victoria (Gras and Mueller, 2004). In these, the two integrated weekly samples of particulate matter peaked at 700 µg m^{-3}, confirming the protracted impact of a concentrated smoke plume with a corresponding peak in non-salt potassium concentration confirming that the particulate matter was predominantly from biomass combustion. However the ambient dioxin concentration measured during this period of 0.3 fg TEQ m^{-3} was less than the background air concentration observed in the preceding months. Therefore the wildfire smoke plume was extremely low in dioxin content.

The emission profiles of all classes for fires were dominated by PCDD which contributed between 75% and 92% of total mass emissions. The fully substituted dioxin, OCDD, accounted for 32%, 43% and 80% of the total PCDD/PCDF mass emitted from prescribed fires, savanna fires and cane fires, respectively, but was a less significant component of wildfire emissions. The other dioxin groups TCDD, PeCDD, HxCDD and HpCDD comprised 11%, 4% 10% and 11%, respectively, of total emissions averaged across all fire classes. In contrast, the only significant furan group observed in the smoke was TCDF, which accounted for approximately 19% of PCDD/PCDF mass emissions.

While OCDD is the dominant toxic congener in terms of mass, its TEF is very low (0.0001) and, consequently, in terms of toxicity the PCDD/PCDF emissions are dominated by 1,2,3,7,8-PeCDD. This congener accounts for 50%, 38%, 40% and 38% of total emitted TEQ from cane fires, prescribed fires, wildfires and savanna fires, respectively. Of the other toxic PCDDs congeners, 2,3,7,8-TCDD contributed approximately 13%, 1,2,3,4,6,7,8-HpCDD contributed 11% and the HxCDD isomers each contributed approximately 5% of total toxic emissions. The only significant furan was 2,3,4,7,8-PeCDF, which contributed between 2% and 12% depending on fire class. Overall, PCDD accounted for 93%, 83%, 86% and 79% of toxic emissions from cane fires, prescribed fires, wildfires and savanna fires, respectively.

Laboratory measurements

In contrast to the field measurements, emissions measured in the laboratory tests were dominated by the lower chlorinated furans. While total mass emission were similar for most of the laboratory and field results, the higher fraction of toxic furans resulted in significantly higher emission factors for all the grass fuels. The forest litter emission factors measured in the laboratory, in contrast, were lower than in the field. The differences between the two sets of measurements appeared to be associated with a long residence time at temperatures above 200 °C (Figure 3). In the field, rapid entrainment of ambient air cools the pyrolysed gases below the temperature required for heterogeneous dioxin formation chemistry (Stanmore, 2004). In our laboratory tests, when the smoke plume was confined within the tunnel at temperatures above 200 °C significant furan formation occurred. Consequently the laboratory measurements are most likely strongly affected by sampling artifacts and therefore do not describe the real world. Only the field measurements were used in subsequent inventory accounting.

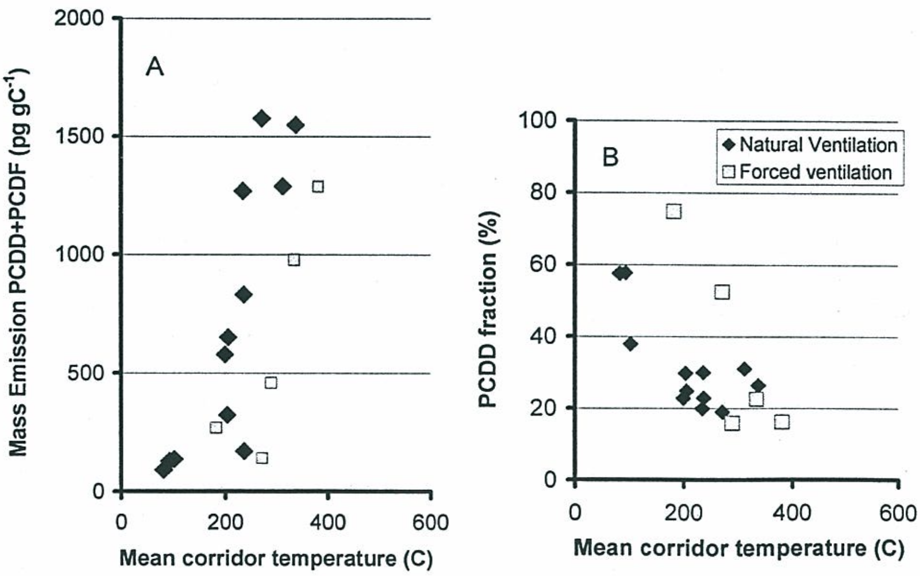

Figure 3 Relation between mean corridor temperature above the fuel bed and emission factor (A) and the fraction PCDD in emitted mass (B)

National Emissions

The field-measured emission factors were used to estimate the National emissions from bushfires in Australia. The methodology is modified from Australia's National Greenhouse Gas Inventory (NGGI) Methodology (AGO, 2003) with activity and parameter values replaced by appropriate probability density functions and the emissions calculated by a Monte Carlo simulation. This allows the uncertainties to be aggregated correctly though the inventory calculations and produces uncertainty ranges for the total emission estimates. All factors other than the PCDD/PCDF and PCB emission factors were sourced from the National Greenhouse Gas Inventory (NGGI, 1998).

The 2002 dioxin and furan inventory (EA, 2002) was calculated using activity data for the 1994 inventory year. Using the measured field emission factors from Table 1 in our uncertainty analysis we estimate the total emission of dioxins, furans and dioxin-like PCBs in 1994 was 142 g TEQ with a 95% confidence range of 31 to 494 g TEQ (Table 2). This overlaps the previous inventory range of 72 to 1708 g TEQ however, because the latter is essentially a uniform distribution with no central estimate, comparison between the two inventories can only be made at the extremes of their ranges. On this basis the impact of the field measured emission factors is to reduce the emission estimates by 56% at the lower limit and by 72% at the upper limit. Almost 84% of the emission occurs in the savanna woodlands of tropical northern Australia and arid zone grasslands of central Australia; wildfires and prescribed fires in the southern temperate forests account for 9% and 4% respectively with the remainder produced from the burning of crop residues in the field. This distribution is similar to the lower bound of the 2002 estimate but is a major shift from the upper estimate in which savanna fire emissions comprise only 72% of the total. The difference in the distribution of emissions between fire classes resides in the relatively low emissions factors for the southern Australian forest, particularly wildfires in comparison to the savanna emission factors.

There was a substantial increase in emission between 1990 and 2001, primarily due to increased savanna burning. In 1990, total annual emissions of PCCD/F and PCBs were approximately 46.5 kg. By 2001, these emissions increased 67% to 76.1 kg In terms of mass, emissions in the savanna woodlands are dominated by OCDD, however despite relatively low toxicity of OCDD, total TEQ emissions also increased by 67% between 1990 and 2001 from 140 g TEQ to 233 g TEQ. Emissions from forest fires and crop residues fires decreased slightly over this period therefore the increase in emissions were largely confined to the unpopulated regions of northern and central Australia.

Table 2. Total emissions (g TEQ) of PCDD/PCDF and coplanar PCB from bushfires in Australia in 1994.

Source	Emission (g TEQ)		
	This study		EA, 2002
Crop residue	3.2	(1.8 – 5.6)	3-260
Prescribed fires	3.6	(1.4-7.9)	
Wildfire	4.9	(1.2 – 15)	7-400
Savanna	130	(20 – 476)	62 – 1240
All	**142**	**(31 – 494)**	**72 – 1700**

Emerging areas

The study produced several unexpected findings; the emission factors from all classes of fires when measured in the field, were low. For wildfires, this was unexpected because it was assumed that their high temperatures would support greater rates of PCDD and PCDF production sources than would the cooler prescribed fires. However, the finding is consistent with the hypothesis raised by Prange et al (2003) and others, that PCDD, PCDF and PCB present in smoke may have been released by volatilization from the soil pool rather than produced *de novo* during combustion. Intense wildfires, particularly crown fires, spread quickly producing less heating of the surface soil than the lower intensity but slow moving prescribed fires which are confined to the fuel load on the forest floor.

Additional work, which will be presented, also indicates that the soil may be a source of dioxin emissions, however whether this is a physical process of revolatilization is not clear. Apart from its importance for emissions accounting, the involvement of precombustion sources in emissions from fires could have implications for the way fires are classified in inventories. Currently they are classified primarily by fire class. If the dioxin content of soil and fuel are significant determinants of emissions, then the classification should instead primarily be a regional one based on soil chemistry.

The laboratory tests are difficult to interpret as other than artifacts of the sampling system. While it is not the case that all laboratory tests will be similarly affected, it does suggest that particular attention should be given to minimising the length of time the combustion products remain at dioxin formation temperature.

Conclusions

The studies indicate that, in Australia at least, EFs from bushfires fall at the lower end of the published range. From this, it is estimated that Australia produced approximately 230 g TEQ dioxins annually from bushfires in 2001, a test year that has been comparable in fire activity to the subsequent years. This falls within the range of the EA (2002) estimate, however the 95% uncertainty range is now considerably smaller, 41 g to 840 g. Clearly there is considerable scope for future work to further refine these emissions estimates.

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Organochlorines Dynamics in Indonesian Tropical Climate A Study in Segara Anakan Estuary

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Abstract

Segara Anakan Estuary, a semi-enclosed coastal area in south coast of Central Java, continuously receive dicharges from rivers of west java and central Java, and seawater from the Indian Ocean by tidal actions. The POPs reach Segara Anakan estuary by waterways and atmospheric transportation, which is governed by physicochemical characteristics of POPs and climate condition.

The POPs studied in Segara Anakan estuary are HCB, Heptachlor, Hepox, Endosulfan, Endrin, p.p'-DDE, p.p'-DDD, and p.p'-DDT. p,p' DDT dissipation and degradation pattern in soil under Indonesian tropical climate was influenced by rainy season and dry season. The dissipation pattern was biphasic with faster rate in rainy season, while the degradation product, p,p' DDE and p,p' DDD was formed in rainy season, but in dry season, only p,p' DDD was formed.

Rainy and dry season also influence the transportation, bioavailability and fate of POPs in the environment, which is determined by complex equilibrium, such as sorption-desorption between particles and the overlying or interstitial waters, and evaporation-precipitation. In rainy season, Segara Anakan receives more rivers discharges from inland, including the deposited POPs in the washed off surface runoff and suspended particles. Upon meeting with saline water, they are sedimented in the estuary. However, the water velocity in rivers increases from 0.3 m/sec in dry season to 0.7 m/sec, causing POPs washed out off from the estuarine environment. Therefore the ΣDDT of estuarine sediment in rainy season was 3.2 μg/kg, lower than in dry season 4.2 μg/kg. The ratio of DDT/DDE+DDD were 0.4 in dry season and 0.2

in rainy season, indicating of no fresh input of DDT in inland, surrounding the estuary and in estuary itself. Comparing with the level of p,p'-DDE in estuarine water of 1994, 0.31 μg/L, which is much higher than determined in this study 0.01 μg/L.

In dry season, the salinity of estuarine water increases from 2.2‰ in rainy season to 25.7‰, and salting out effect prevails. The POPs level in estuarine water is lower and in sediment is higher than in rainy season. The ratios of POPs concentrations in sediment to water for POPs transported more through waterways in dry season were 2.0 to 3.4 times of those in rainy season, confirmed the salting out effect to the sorption-desorption equilibrium. The ratios of POPs transported more through atmospheric pathway were 1.1 to 1.2, indicating of more input from precipitation.

This study confirms that estuarine sediment act as scavenger and also as source of POPs to the organisms. In this semi-enclosed coastal area, the determined POPs level were higher than in the river, causing the organisms in estuarine at higher risk then in the river. The ratio of POPs concentrations in soft mass of *Geloina* spp. to estuarine water were in the range of 4 to 75, fillet of *Mugil* spp. to water were 15 to 350, and human milk to estuarine water were 175 to 2976. The daily consumption rate limit (CR_{lim}) for fishmeal consumer calculated based on their DDT carcinogenicity is 0.9 kg/day, and for breast fed babies is 0.015 L/day human milk. Therefore risk management on POPs is still required, especially for p,p'-DDT.

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