REGIONAL MONITORING AND ASSESSMENT NETWORK OF POPS POLLUTION IN ASIAN COUNTRIES

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Abstract

In order to develop a regional monitoring and assessment network of environmental pollutants, the United Nation University (UNU) has been implementing a capacity development project on analysis and monitoring of environmental pollutants since 1996. The project has undertaken monitoring of various organic pollutants in the environment in ten participating countries in Asia using gas chromatography/mass spectrometry (GC/MS). Various pollutants in various environmental media were detected. Some of results of the project activities were presented. This UNU project, as one of the existing regional networks engaged in POPs monitoring, could be an important data source on the regional POPs levels which will help the effectiveness assessment of the implementation of Stockholm Convention.

Introduction

Due to the properties of POPs and the geographical conditions, the emissions of POPs from one country or region can potentially result in heavy pollution and exposure in another country or region. Therefore, collaborative research should be conducted on a regional/global scale. But few such works have been done in Asia. Environmental data are needed in Asian countries, especially developing countries, to better understand regional/global sources of POPs and the key processes that control their regional/global distribution. To develop a regional monitoring and assessment network of POPs is a very important issue. Therefore, United Nations

University (UNU) has been implementing a capacity development project on monitoring of environmental pollutants in Asia since 1996. The project has monitored various organic pollutants in the environment in 10 Asian countries (China, India, Indonesia, Korea, Malaysia, Pakistan, Philippines, Singapore, Thailand, and Viet Nam) using gas chromatography/mass spectrometry (GC/MS). Here, some monitoring results in a selection of Asian countries are presented and discussed.

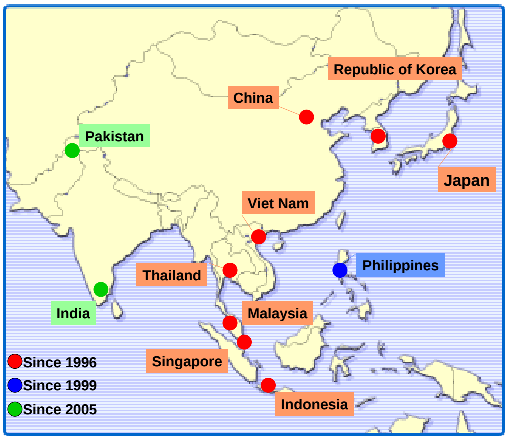

Fig 1 Project partner countries

Materials and Methods

From its beginning in 1996, the project is now in its 13th year and has completed its fourth phase. In total, more than 80 researchers from participating governmental institutions and universities in ten Asian countries have been trained on sample pretreatment and instrumental analysis using GC/MS for a wide variety of samples (water, biota, sediment, rice, fish and air). Shimadzu Corporation has verified and provided the sample pretreatment and analytical procedures that have been customized to meet capacities and resources available at the participating institutes [1,2]. Organic pollutants were determined in various environmental samples in 10 Asian countries using Shimadzu GC/MS systems.

In the first two phases (1996~1998 and 1999~2001) of the project, various target organic pollutants, mainly Volatile Organic Compounds (VOCs) and EDCs, in rice, air and water were analyzed using Shimadzu GCMS-QP5050A. In the third phase (200~2004) and fourth phase (2005~2008), Organochlorine Pesticide (OCPs) POPs (including Hexachlorobenzene, Heptachor, Aldrin, *trans*-Chlordane, *cis*-Chlordane, Dieldrin, Endrin, *p,p*'-DDT etc.) in water, sediment, shrimp, fish and squid were analyzed using GCMS-QP2010.

To ensure the quality of the analytical activities, quality control indicators such as blank tests, injection repeatability tests and standard addition recovery tests were conducted by all project partners as necessary, and DDT-$^{13}C_{12}$ cleanup spike recovery ratios have been checked with 70-130% as its acceptable range. One of the two internal standards, phenanthrene-d_{10} and chrysene-d_{12}, were chosen for the quantification of each POPs depending on its GC elution time. To determine instrument detection limit (IDL), five to eight times injections for the injection repeatability test were recommended. More details are described in the UNU Project Quality Assurance Document [3].

Results and Discussion

In the past 12 years, more than 50 compounds were measured in the 10 participating Asian countries and more than eight POPs, mainly those used as insecticides, were analyzed. The project has monitored POPs in water, sediment, soil and organisms since the start of the third phase. Samples were collected at more than 600 sites in rivers, lakes, coastal waters and sediments throughout the 10 participating Asian countries, which provide a general overview of the POP levels in the region.

POPs in water and sediment

Among all the samples, the most commonly detected compounds were *p,p'*-DDT and its metabolites, *p,p'*-DDD and *p,p*'-DDE, followed by HCB, Lindane and *cis*- and *trans*-Chlordane. Specifically, in limnic sediment samples, *p,p*'-DDD, *p,p*'-DDE and HCB, have a detection frequency exceeding 70%. In marine sediment, Lindane, HCB and *p,p*'-DDD were detected in more than 70% of the samples. In seawater, detection frequencies for cis-Chlordane, Heptachlor, Lindane, Dieldrin and *p,p*'-DDT were above 50%; whereas in freshwater samples, the most common compounds, *p,p*'-DDT, Lindane, trans-Chlordane, and HCB, exceeded a detection frequency of only 30%.

In Thailand, *p,p'*-DDT was found up to 8.5 ng/L in water and 40 ng/g in sediment, while *trans*-Chlordane was found up to 8.9 ng/L in water and 0.96 ng/g in sediment collected from coastal areas and river basins between 2004-2005. Fig. 2 shows POPs concentrations in water bodies measured in Thailand in 2002-2005. The detection ratios of these POPs have been found to be comparatively low and do not vary remarkably (0-24%). Fig. 3 shows POPs detected in river water samples in China, 2003. Among 11 compounds detected, *α*-HCH was the most frequently detected one throughout the sampling sites, and the highest concentration of *α*-HCH was 98 ng/L. The environmental level is not statistically dependent on seasons but on water bodies. The samples from Haihe River showed higher concentrations than those in the Chaobai River and Miyun Reservoir.

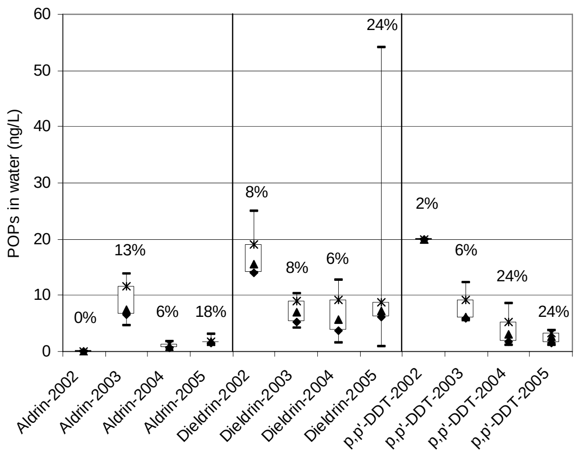

Fig.2 POPs levels in river/sea water sampled in Thailand (2002-2005) with the detection ratios indicated in %

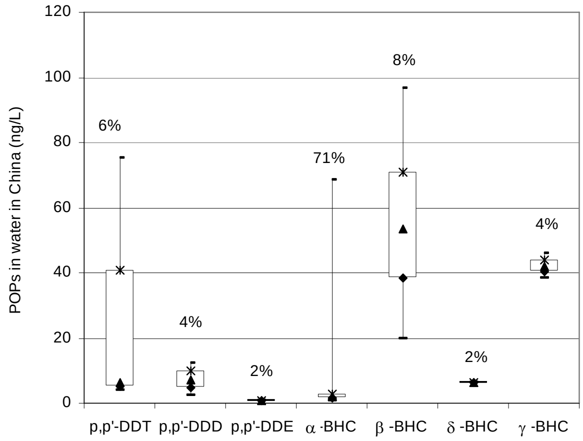

Fig.3 POPs levels in river water sampled in China, 2003, with the detection ratios indicated in %

POPs in Organisms

Shrimp

In 2005 and 2006, some POPs were detected in wild shrimps by some project participants. In the Philippines, Chlordanes and *p,p'*-DDT were detected from a substantial number of the samples originating from Bay Laguna. In Singapore, a wide range of OCPs was detected in shrimp samples. The total OCPs concentrations ranged from nd to 0.673 ng/g, with means of individual OCP concentrations between 0.007 and 0.038 ng/g. The highest concentrations of Endrin and Aldrin detected were 0.131 ng/g and 0.091 ng/g. In Vietnam, HCB, Heptachlor, Aldrin, and trans-chlordance, DDTs were detected widely in shrimp samples from Ha Long Bay and Hai Phong Port. Interestingly, it is recognized that in general the levels of OCPs (especially DDTs) in the rainy season are lower than those in the dry season. In China, Hexachlorobenzene and DDTs were widely detected from all samples taken from Donting and Tai Lakes. The mean concentration of HCB and DDTs in shrimp were 1.475 mg/kg and 2.21 mg/kg, respectively. The distribution of OCPs in shrimp samples are as follows: HCB: ND~13.2 mg/kg; *p,p*'-DDE: 0.79~5.82 mg/kg; DDD: ND~0.599 mg/kg. The levels of HCB and DDE in head of shrimps were 15.4 times and 53.4 times higher than those in the body, respectively.

Fish

In 2007, Ha Long Bay, Hai Phong Port, and Ba Lat Estuary were selected as fish sampling locations in Vietnam. Fish species sampled in Vietnam were *Sparus macrocephalus*, *Sparus latus* and *Psammoperca*. Mirex and *cis*-, *trans*-Chlordane were not detected in fish samples. Recent inputs of *p,p*'-DDT to the water bodies may be indicated by the ratios of DDT/DDE higher than 0.5. Different DDT/DDE profiles were found in fish tissues obtained in the Republic of Korea. While in both sampling locations of Tongyeong and Gadukdo which are about 60km apart, DDT and its metabolites were the dominant compounds among the detected OCPs, *p,p*'-DDT was detected only in Gadukdo, which implied the recent inputs of p,p'-DDT to the environment.

Squid

In 2008, Squid samples (*Loliolus japonica*) were taken from Dalian, Yantai, Qingdao in China, and various OCPs in the body and liver were analyzed. But, only HCB and DDTs were detected. In Korea, common squid (Todarodes pacificus) was collected from South Sea (Chilchun-do, CP) and East Sea (Ulleung-do, UP). DDTs, HCHs, HCB and CHLs are detected in the liver tissue. Among these compounds, DDTs were the highest in both the regions, followed by HCHs and others. The highest DDTs concentration in Ulleung-do (UP) was nearly 5 times higher than their levels in Chilchun-do (CP). On the other hand, the levels of HCHs were nearly equal in these regions. Fig. 4 compares the DDTs levels in four regions around Korea. The highest levels were recorded for *p,p'*-DDD and *p,p'*-DDE in the Yellow Sea, indicating weathering and metabolism from the DDT input over a period of time. The *p,p*-DDT levels was the highest in Ulleung-do (UP) indicating a recent input of these pesticides in that region. In Philippines, sampling was performed during the dry season (May-June, 2008) and the rainy season (September, 2008). In general, OCPs were detected in liver and muscle tissues in all the squid samples collected during the dry season. *β*-HCH was detected in all liver and muscle samples. Other OCPs were detected in squid samples depending on the sampling site. OCPs were detected in most of the squid samples collected during the rainy season. *β*-HCH was detected in most liver samples and in all muscle samples. The liver samples from Cavite showed the highest detection ratios of OCPs, including *cis*-chlordane, dieldrin, endrin, *cis*-, *trans*-nonachlor and methoxychlor.

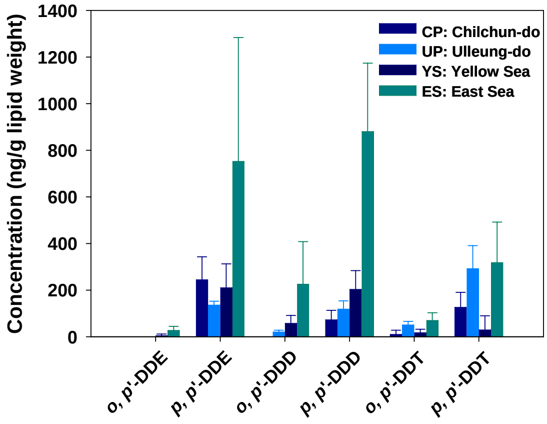

Fig.4 Concentration of DDTs in the liver in squid along Korean coastline.

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