PASSIVE AIR SAMPLING OF POPs ACROSS ASIA: ORGANOCHLORINE PESTICIDES AND PCBs

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Introduction

Persistent organic pollutants (POPs) are a group of synthetic organic chemicals that persist in the environment for a longer period, subsequentlybioaccumulate through the food web and pose a significant hazard to humans and wildlife. By virtue of their semi-volatility, they can travel through long distances in the air and water, leading to them being widespread globally, and hence detected in remote regions where they are not, or never have been used[1].

Most of the air monitoring studies relies on active air samplers such as high volume air samplers (HVAS) used for the collection of POPs in both gaseous and particulate phases. Nowadays,thepassive-sampling in the environmental research is getting an increasing attention as an alternative to the expensive and more laborious active- sampling[2]. It can provide time-integrated samples for air and water. Moreover, during the exposure of passive sampler by a contaminant, the total concentration reflects only the integral amount of analyte and, thus, reduces problems arising from its short time concentration peaks. Passive air samplers (PAS) are cheaper and smaller than that of conventional active samplers, and they do not require the electricity. For this reason, they can be used for the environmental monitoring with a wide range of spatial coverage[3,4].

Air pollution is a heavy price that many of the Asian nations paying for the rapid development seen in the past few decades. AMETEC is an APEC Marine Environmental Training and Education Center in KIOST, South Korea with the aim to transfer the current knowledge on the environmental sustenance to developing nations in Asia Pacific region. AMETEC has organized the three training workshops on the title “Passive Air Sampling: Long range transport of pollutants" from 2010 to 2012. Ten participants from 8 Asian countries including China, India, Indonesia, Malaysia, Micronesia, Philippines, Sri Lanka, Thailand and Vietnam participated. In order to understand air pollution in Asia, polyurethane foam (PUF)-type passive air samplers developed by Dr. Tom Harnerwere deployed and maintained by AMETEC trainees[3]. Participants exposed the PAS for one to three months at the rural and urban surrounding in their countries (Fig. 1), then brought the PUF disks to KIOST to attend the workshop, and analyzed themselves with the assistance of KIOST staffs. The samples were used to measure PAHs and organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominateddiphenyl ethers (PBDEs). In this paper, the contamination status and characteristics of OCPs and PCBs in the Asian atmosphere are discussed.

Materials and methods

PUF disk sampler

The PUF disk sampler (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}) was placed inside a stainless steel chamber consisting of two stainless steel domes (“flying saucer” design) that protect the foam disks from rain, sunlight, and coarse particle deposition. Air was allowed to flow over the disk surface, and entered the chamber through a ~2.5 cm gap between the two domes[5].

Sampler deployment

Prior to deployment, PUF disks were cleaned by Soxhlet extraction using acetone and then petroleum ether. After cleaning, the PUF disks were desiccated under vacuum to remove the excess solvent. Prior to and after sample collection and during shipping, PUF disks were stored in solvent-rinsed, stainless steel (round) box

having Teflon-lined lids. A total of 68 samplers were deployed successfully for 28-95 days (every year from June to October, 2010-2012) at 11locations from 9 countries (Fig. 1). Participants installed PASs in both urban and rural areas at each location. At the end of the deployment period, the disks were retrieved by the participants and stored at -20°C until the extraction.

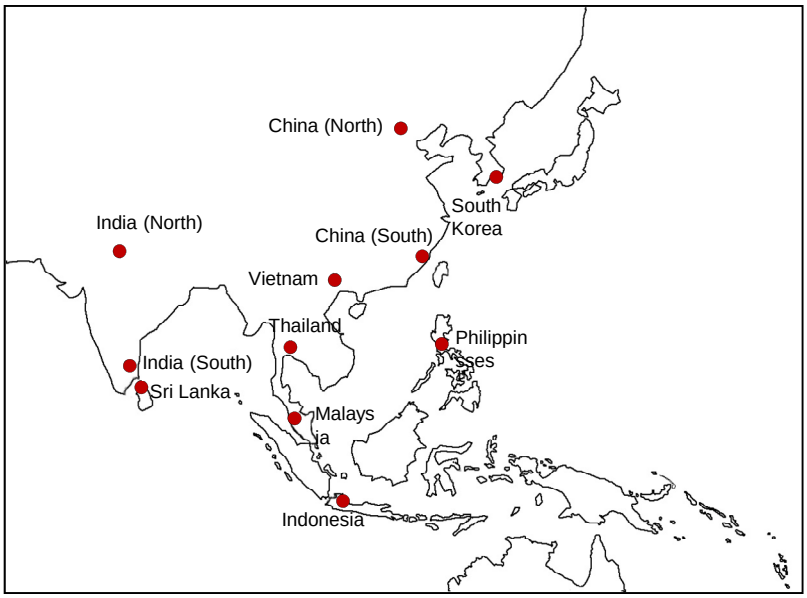

Figure 1. PAS sampling locations in Asia: each location has two sampling sites, rural and urban

Chemical analysis

The PUF disks were soxhlet extracted for 18 h with 240 ml of dichloromethane:hexane (v:v, 1:1). The extracts were cleaned first using silica gel and alumina (5% and 1% deactivated, respectively) multilayer column chromatography. The eluate was then fractionated using a size-exclusion high pressure liquid chromatography (HPLC, 250 22.5-mm I.D. size-exclusion column packed with Phenogel 100 Å, Phenomenex Co.). Samples were spiked with a surrogate mixture containing PCB103, PCB198, prior to extraction, and recovery was measured in each sample. As an instrumental recovery standard, tetrachloro-m-xylene (TCMX) was spiked into each sample prior to the instrumental analysis. A procedural blank was run with every set of 12 samples to check for secondary contamination. Identification and quantification were performed using a Thermo trace ultra gas chromatograph (GC) coupled to a Thermo Fisher Scientific DFS mass spectrometer (MS) in an electron impact ionisation (EI) mode for organochlorines (OCPs and PCBs). The analytical column used was a DB-5 column (30-m x 0.25-mm i.d. x 0.25 µm film thickness, J & W Scientific). The GC oven temperatures were as follows: 100°C for 1 min, 5°C min^{-1} to 140°C, 140°C for 1 min, 1.5°C min^{-1} to 250°C, 250°C for 1 min, 10°C min^{-1} to 300 °C, and 300°C for 5 min. The analyzer mode was used as the selected ion monitoring (SIM) with a resolving power of 10,000. The electron energy and source temperature were specified at 35 eV and 260 °C, respectively. The mean recoveries for the added surrogates were 78±17%, and 88±17% for PCB103 and PCB198, respectively. Total PCB concentrations (PCBs) were presented by summing the 22 individual congeners (IUPAC nos. 8, 18, 28, 29, 44, 52, 66, 87, 101, 105, 110, 118, 128, 138, 153, 170, 180, 187, 195, 200, 206, and 209) in the text. Total DDT concentrations (DDTs) are the sum of p,p'-DDE, p,p'-DDD, o,p-DDT, and p,p'-DDT. Total HCH concentrations (HCHs) are the sum of α-HCH, β-HCH, γ-HCH and δ-HCH. Total chlordane concentrations (CHLs) are the sum of α-chlordane(CC), γ-chlordane(TC), oxychlordane, heptachlor, *cis*-nonachlor and *trans*-nonachlor(TN).

Previous studies by Harner et al. have shown that the value of linear phase sampling rate, R, is about 4 m^3 d^{-1} for most non-polar hydrophobic chemicals[3,6,7,10]. In the present study the same value of R is applied for calculating the concentration of target compounds in air.

Results and discussion

Concentrations of OCPs and PCBs inthe Asian atmosphere

The overall concentration of POPs intheAsian air were in the range of 7.32 - 579 (median value: 21.4) pg m^{-3} for HCB, 1.03 - 1029 (26.5) pg m^{-3} for HCHs, 0.08 - 476 (8.85) pg $m^{-3}$for CHLs, 0.22 – 125 (2.68) pg $m^{-3}$for Dieldrin, 3.33 – 1237 (42.7)pg $m^{-3}$for DDTs, and 2.44 – 932 (41.4) pg $m^{-3}$for PCBs(Fig. 2).Among the target analytes, DDT showed the highest concentration and followed by PCBs and HCHs. Dieldrin and CHLs showed the lowest level. The concentration levels of HCHs, HCBs and DDT in Asia are higher thanthosein Europe (23 – 490 pg m^{-3} for HCHs, 11 – 50 pg m^{-3} for HCB and 1.0 – 215 pg m^{-3} for DDTs)[4]. On the other hand,low value of concentration was found for PCBs as the reported levels of PCBs in the European air (20 – 1700 pg m^{-3})[4]. All the POPs were detected abundantly at the urban site in comparison to rural area, indicating the dominant areas of usage and emissions (Fig. 3).

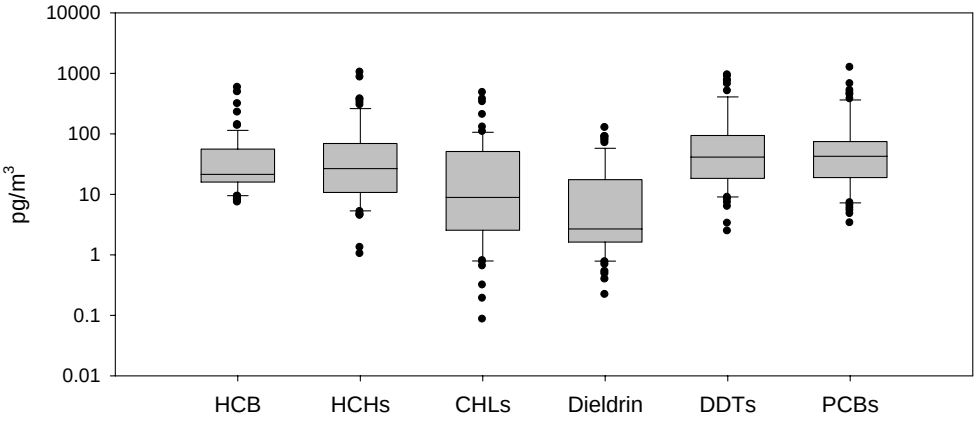

Figure 2.Overall concentration of OCPs and PCBs in the air from Asia.

Hexachlorocyclohexanes (HCHs)

Among the nine countries, India (both northern and southern parts) and China (north) showed the highest HCH concentrations at both rural and urban areas (Fig. 3). Air concentration (pg m^{-3}) of HCHs in urban and rural areas was in the range of 12.3 – 526 and 5.48 - 407, respectively. In general, urban sites had higher values for HCHs than rural sites. This concentration range is even higher than other reported studies in Europe and GAPs study, but lower than that in India (66 – 5400 pg m^{-3})[1,4,8].

HCH was used as a commercial insecticide in two formulations: technical HCH, which includes multiple stereoisomers and is dominated by α-HCH (60-70%), β-HCH (5-12%) and γ-HCH (10-15%), and lindane, which is the purified form of γ-isomer[7].In the air samples from Thailand, Philippines, Malaysia and Indonesia, γ--HCH was determined to be the predominant HCH isomer, accounting for 76-93% to total HCHs. This result indicates the recent usage of lindane in those countries. At the other countries, α-HCH, isomer having the highest atmospheric transportability, was abundant.

Chlordane compounds (CHLs)

Chlordanes are another pesticide group that was once widely used and now persists in the environment. Chlordane in urban areas has been associated with use on lawns and for termite control in house foundations and construction materials[3]. Air concentration (pg m^{-3}) of CHLs in urban and rural areas wasin the range of 1.47 – 394 and 0.34 – 68.1, respectively (Fig. 3).The ratio TC/CC is often used to distinguish fresh Chlordane (TC/CC: the technical value of 1.56) from material that has undergone aging (TC/CC less than 1 is caused by greater reactivity of TC in the environment)[11]. The high ratios (more than 1) of TC/CC to the countries such as Philippines (1.39), Malaysia (1.43), and Thailand (1.41)weeindicating the recent use of these persistent chemicals. The low value (approximately 0.71 and 0.63) was calculated for the rural and urban sites of South

Korea.

Dichlorodiphenyltrichloroethanes (DDTs)
DDT,an insecticide of long past, continues to have limited use in the control of the malaria vector.The highest concentrations were detected at India, and followed by China (south), Thailand and Vietnam (Fig. 3). This range is higher than other study in Europe, but lower than in GAP's study and India[4,7,8]. Similar to HCHs, urban area showed higher level of DDTs than rural area. The ratio of p,p'-DDT to its degradation produces (p,p'-DDD and p,p'-DDE) was above 1 in the air from Vietnam, Malaysia and India (both north and south), implying recent use of technical DDT.

Polychlorinated Biphenyls (PCBs)
Total PCB air concentrations(pg m^{-3}) in urban and rural were in the range of 19.8 – 673 and 7.32 – 138, respectively. As expected, the highest PCB levels were detected at urban sites (Fig. 3). The environmental burden of PCBs is believed to be mainly associated with emissions from existing and disposed electrical equipments. Low-chlorinated congeners were dominant such as tri-, tetra-, penta- and di-CBs accounting for approximately 80 – 90% of total PCB concentration.

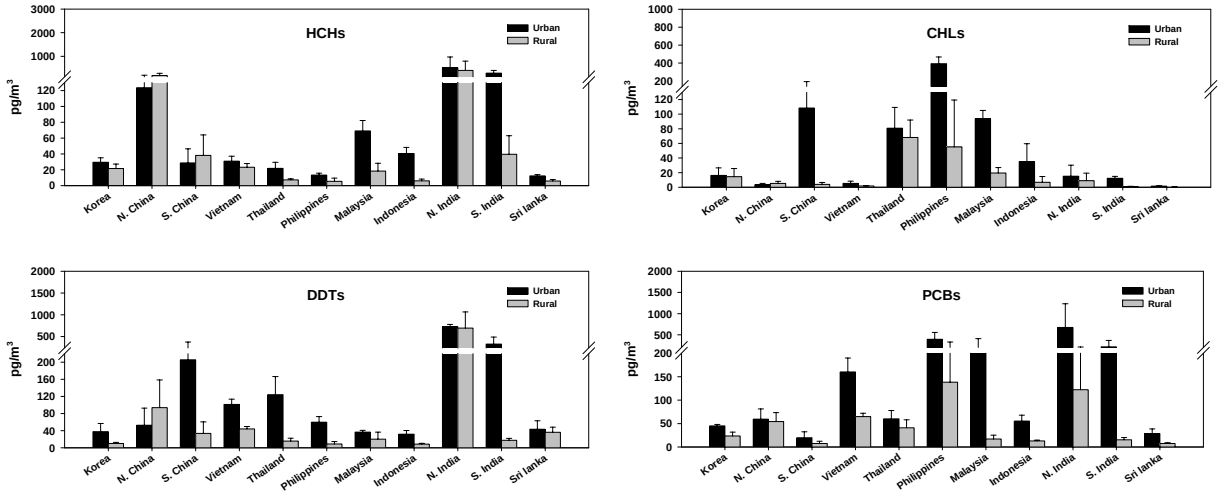

Figure 3.The spatial distribution of OCPs and PCBsinthe air of Asia

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