Passive Air Sampling Of Pcbs, Organochlorine Compounds

Kevin C. Jones, Foday Jaward[1], Jae Jak Nam, Gan Zhang, Jeff Obbard, Yuso Kobara

[1]Lancaster University

.

Introduction and Context

Atmospheric transport is the primary distribution pathway moving POPs from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems. They may be transported long distances prior to subsequent deposition. During their transport in the atmosphere, they can be removed by reactions, which will ultimately alter ('weather') their atmospheric profile. Due to this long-range atmospheric transport (LRAT) from source regions to more remote locations, POPs have been detected in remote regions where they were neither used nor produced. The toxicity coupled with the ubiquity of these compounds has prompted international organisations to put more effort in understanding their global presence and to control their use and disposal. This has focussed international regulation on reducing emissions to air [(1, 2)], and risk assessment/modelling efforts on their ambient distribution.

To assess the relative importance of such processes, to assess sources, and validate models, it is desirable to make simultaneous regional measurements of air concentrations. This can only be achieved with the desired resolution with passive air samplers; they are simple to use, cheap and versatile[1]. A range of different passive sampling devices has been utilised. These include polyurethane foam (PUF) disks, polymer-coated glass slides and vegetation. PUF disks are a particularly attractive sampler; they are cheap, easy to handle and can be used to sample over periods of several weeks. PUF disks of 14 cm diameter and 1.2 cm thickness have been tested as passive samplers previously; they sample at a rate of a few m^3 of air/day[(3)]. In this study we report the first attempt to monitor the regional distribution of PCBs, PBDEs and selected organochlorine pesticides in the atmosphere of four Asian countries – China, Japan, South Korea and Singapore.

Materials and Methods

The PUF disk samplers have been described previously[(3, 4)]. The PUF disks were transferred to the sampling locations in sealed, solvent cleaned brown glass jars. The samplers were only assembled at the deployment sites to avoid contamination during transit. The sampling involved four Asian countries (China, Japan, South Korea and Singapore). These countries have different production and use patterns for the compounds studied. To be able to compare sequestered amounts between the sampling campaigns, care was taken to deploy, store and extract the PUF disks in exactly the same way. All samples were deployed for 56 days from 21 September 2004 to 16 November 2004 in rural and urban settings. Rural sampling sites were chosen on the condition that they were away from direct exposure to local sources or human activity. In China, a total of 32 samplers were successfully deployed in13 rural and 19 urban sites; 20 samplers were deployed in Japan; 15 in South Korea and 10 in Singapore. The PCB distribution is shown in Figure 1. Samplers were deployed in replicates at certain sites. Concentrations for replicate samples are not significantly different from each other. At the end of the deployment period, the PUF disks were retrieved, re-sealed in their original solvent cleaned brown glass jars at the sampling locations and returned by courier to Lancaster University. On receipt in Lancaster, they were stored frozen until extraction. The extraction, cleanup methods and GC/MS analyses have been described elsewhere[(4)]. A total of 29 PCB congeners (PCB-18, 22, 28, 31, 44, 49, 52, *60/56,* 70, 74, 87, 90/101, 95, 99, 105, 110, 118, 132, 138, 141, 149, 151, 153, 158, 170, 174, 180, 183 and 187), 8 PBDEs (17, 28,32, 47, 49, 75, 99 and 100)and 5 OC compounds (HCB, o,p'-DDT, o,p'-DDE, p,p'-DDT and p,p'-DDE) regularly detected in samples were quantified using an internal standard method. Data presented focus on the ICES congeners (PCB-28, 52, 90/101, 118, 138, 153/132 and 180), $å_{29}$PCBs, HCB, o,p'-DDT, o,p'-DDE, p,p'-DDT and p,p'-DDE.

Results and Discussions: Regional comparison of compounds

Levels of PCBs, HCB and sum of DDT and DDE were significantly higher in China than the other countries (see Fig 2). In China, very high levels of PCBs and DDT were measured in the three most developed and populated zones along the east coast, that is, Tianjing-Tsingtao, the Yangtze River Delta, and the Pearl River Delta. The high DDT levels in these regions are a reflection of widespread agricultural use. High HCB levels were observed in both rural and urban sites in China suggesting that the sources of HCB to the atmosphere could be due various factors, for example, in agriculture as pesticide, manufacturing or combustion. Estimated air concentrations (pg m^{-3}) in China for HCB (10-460), p,p'- DDE (3-380) and p,p'-DDT (2-900) are higher than the recent results from a European passive air sampling network where the ranges for HCB, p,p'- DDE and p,p'- DDT were 11-50, <0.4-25 and 0.6-190 pg m^{-3} respectively[(4)]. Levels of PCBs, HCB and sum of DDT and DDE in Japan, South Korea and Singapore were generally low. On the other hand, PBDE levels were also generally low (and most times below the detection limit) across the region.

A ratio of highest/lowest (H/L) for HCB, and DDT in Europe has been determined to be ~6 and 400 respectively[(4)]. The HCB ratio is similar to those of Japan and South Korea while it is 45 for China. This suggests that HCB is not uniformly distributed in the Chinese atmosphere. This may suggest that there are continuing primary emissions of this compound class, presumably largely from pesticide applications, manufacturing or combustion. In Japan, South Korea and Singapore, HCB appears not to have been used as pesticide, although it has been included as impurity of PCP and PCNB. Other sources are manufacturing and combustion. The DDT ratio for Europe is similar to that of China (see Table 1), suggesting that DDT is still being used in China as it is in Eastern Europe[(5)]. The ratio is 32 for Japan, suggesting no/minimal usage (note that ratio has been calculated for compounds where ~ 100% of samples gave detectable levels).

References

1. UNECE. 1998. *Protocol on persistent organic pollutants under the 1979 Convention on Long-Range Transboundary Air Pollution*, United Nations Economic Commission for Europe (ECE/EB.Air/60).

2. UNEP. 1998. *Preparation of an internationally legally binding instrument for implementing international action on certain persistent organic*

pollutants, United Nations Environment Programme, UNEP/POPs/Inc.1/6.

3. Shoeib M, Harner T. 2002. Characterisation and comparison of three passive air samplers for persistent organic pollutants. *Environ Sci Technol* 36: 4142-4151.

4. Jaward FM, Farrar NJ, Harner T, Sweetman AJ, Jones KC. 2004. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ Sci Technol* 38: 34-41.

5. Di Guardo A, Zaccara S, Cerabolini B, Acciarri M, Terzaghi G, Calamari D. 2003. Conifer needles as passive biomonitors of the spatial and temporal distribution of DDT from a point source. *Chemosphere* 52: 789-797.

Table 1. Summary data: Measured (ng/sample), air concentration (pg/m3) and Highest/Lowest (H/L) ratio.

		China			Singapore			Japan			South Korea	
Compounds	**Measured**	**Air conc**	**H/L ratio***	**Measured**	**Air conc**	**H/L ratio***	**Measured**	**Air conc**	**H/L ratio***	**Measured**	**Air conc**	**H/L ratio***
28	0.5-13	2.7-68	25	0.2-0.8	1.0-4	4	0.4-3.7	2.0-19	9	0.2-2.3	1.0-11.6	11
52	0.3-6	1.4-29	20	<0.12-0.5	<0.6-2.7		0.12-4	0.63-21	33	0.2-1.8	1.0-9	9
90/101	0.13-2	0.7-10	15	<0.07-0.34	<0.3-1.7		0.12-3	0.6-16	25	0.1-1.5	0.5-7.5	15
118	0.08-1.4	0.4-7	14	<0.03-0.12	<0.13-0.6		0.03-1.5	0.14-7.6	50	0.03-0.5	0.17-2.7	16
138	<0.1	<0.5-7.3		<0.1-0.8	<0.55-4		0.13-1.3	0.7-7	10	<0.1-0.5	<0.55-2.7	
153	<0.05	<0.2-5.5		<0.05-0.9	<0.24-4.4		0.08-1.2	0.4-6	15	0.06-0.4	0.3-2.3	7
180	<0.05	<0.2-5.8		<0.05-0.6	<0.23-3		<0.05-0.2	<0.23-1		<0.05-0.7	<0.23-3.6	
$å_7$ PCBs	1.4-23	7.0-117	16	0.3-2.7	1.5-14	9	0.3-15	1.6-76	50	0.8-6	4.0-29	7
$å_{29}$ PCBs	4.2-66	21-336	16	1.0-6	5.0-31	6	1.4-48	7.0-247	35	2.3-16	12.0-84	7
HCB	2.0-90	10.4-462	45	2.0-5	9.5-24.5	2.5	3.0-19	14-95	7	5.0-27	26.0-136	5
o,p' DDT	0.9-92	4.7-472	100	0.26-10.4	1.3-53	40	0.3-14	1.4-70	50	<0.05-2.7	<0.3-14	
o,p' DDE	0.24-15	1.2-75	60	<0.05-0.8	<0.3-4		0.07-2	0.4-10.4	28	0.08-0.35	0.4-1.8	4
p,p' DDE	0.56-74	2.8-380	130	<0.3-1.9	<1.5-10		0.32-106	1.62-544	330	<0.3-4.9	<1.5-25	
p,'p DDT	0.39-182	2.0-928	460	<0.4-3.2	<1.9-16		0.9-28.6	4.4-146	32	<0.4-4	<1.9-20	
PBDE-17	<0.03-7	<0.13-35		<0.03-0.2	<0.13-1		<0.03-0.2	<0.13-0.8		<0.03-0.34	<0.13-1.7	
PBDE-28	<0.03-25	<0.13-130		0.2-1.2	1.0-6	6	0.3-10	1.4-52	35	<0.03-0.5	<0.13-2.6	
PBDE-32	<0.03-2.6	<0.13-13		<0.03-0.1	<0.13-0.5		<0.03-0.12	<0.13-0.6		<0.03-0.23	<0.13-1.2	
PBDE-47	<0.03-15	<0.13-78		0.5-2	2.8-10	4	<0.03-0.2	<0.13-1		<0.03-1.8	<0.13-9	
PBDE-49	<0.03-9.5	<0.13-48		<0.03-0.6	<0.13-3		<0.03-0.3	<0.13-1.3		<0.03-0.3	<0.13-1.3	
PBDE-75	<0.03-2.5	<0.13-13		0.45-2.4	2.3-12	5	0.44-3.7	2.2-19	8	<0.03-0.34	<0.13-1.7	
PBDE-99	<0.03-9.7	<0.13-50		0.5-1	2.8-5	2	0.08-0.26	0.4-1.3	3	<0.03-2	<0.13-10	
PBDE-100	<0.03-1	<0.13-5.5		0.2-0.3	1.0-1.5	1.5	<0.03-0.05	<0.13-0.3		<0.03-0.44	<0.13-2.3	
$å_8$ PBDEs	<0.03-67	<0.13-340		2.0-6	10.0-29	3	1.0-14	5.0-71	14	0.4-5.2	2.0-27	13

*this ratio has been calculated for compounds where ~ 100% of samples gave detectable levels.

+derived as described in Jaward et al [(4)].

Figure 1. $å_7$PCB and $å_{29}$PCB

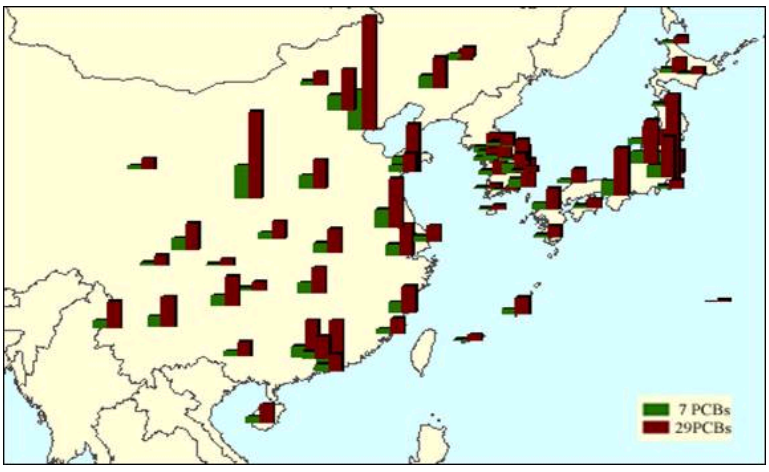

Figure 2. Geometric mean concentrations of sum PCBs, DDT/DDE, PBDE and HCB in China, Japan and South Korea