

# Passive Air Sampling of Polychlorinated Biphenyls, Organochlorine Compounds, and Polybrominated Diphenyl Ethers Across Asia

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Asia is of global importance economically, yet data on ambient persistent organic pollutant levels are still sparse for the region, despite international efforts under the Stockholm Convention to identify and reduce emissions. A large-scale passive air sampling survey was therefore conducted in Asia, specifically in China, Japan, South Korea, and Singapore. Polyurethane foam disks were deployed simultaneously at 77 sites, between Sept 21 and Nov 16, 2004, and analyzed for polychlorinated biphenyls (PCBs), organochlorine compounds (hexachlorobenzene (HCB), dichlorodiphenyltrichloroethanes (DDTs), chlordane), and polybrominated diphenyl ethers (PBDEs). The meteorological conditions prevailing in the region at this time facilitated the assessment of local/regional differences in atmospheric emissions, because large-scale advection effects due to monsoons or dust storms did not occur. Air concentrations estimated assuming an average sampler uptake rate of 3.5 m<sup>3</sup>/day ranged as follows (pg m<sup>-3</sup>): PCBs, 5–340; HCB, 10–460; DDTs, 0.4–1800; chlordanes, 1–660; PBDEs, <0.13–340. South Korea and Singapore generally had regionally low concentrations. Elevated concentrations of PCBs, DDTs, and HCB occurred at sites in China, higher than reported in a similar recent sampling campaign in Europe. Chlordane was highest in samples from Japan (which also had elevated levels of PCBs and DDTs) and was also elevated in some Chinese locations. PBDE levels were generally low in the region.

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## Introduction

Atmospheric transport is the primary distribution pathway moving persistent organic pollutants (POPs) from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems. POPs are transboundary pollutants and undergo long-range atmospheric transport (LRAT) from sources to remote regions (1, 2). Indeed, the reduction of atmospheric emissions of POPs is now the focus of a coordinated international regulatory framework (3, 4). Direct quantification of sources is often difficult, because of poor information on past chemical usage and inventories. Consequently, environmental data are needed from all regions of the globe to better understand regional/global sources of POPs and the key processes that control their global distribution. At present there is a paucity of reliable environmental data on the levels of most POP chemicals in Asia from which to assess the effectiveness of international efforts to minimize the release of these chemicals to the environment. Current research on POPs focuses on uncertainties over their ambient sources, atmospheric transport and fate, and air–surface exchange, to improve understanding of the complex array of factors controlling atmospheric concentrations. To assess the relative importance of such processes, to assess sources, and to validate models, it is desirable to make simultaneous regional measurements of prevailing concentrations of POPs in air. This can only be achieved with the desired resolution by the deployment of passive air samplers (PASs) as they are simple and cheap to use.

A range of different PASs have been utilized in recent years. To date, most work on PASs has focused on integrating measured concentrations of POPs over a period of weeks/months, using samplers with a high “capacity” to retain POPs, such as semipermeable membrane devices (SPMDs) (5–7), polyurethane foam (PUF) disks (8–11), and Amberlite XAD adsorbent resins (12–14). These generally operate as “kinetic samplers” where it is necessary to know the sampling/uptake rate of contaminants, rather than as equilibrium samplers (15). PUF disks are particularly attractive as sampling devices, because they are cheap and easy to handle and can be used to sample air over periods of several weeks. PUF is the sampling medium routinely deployed in conventional (active) high-volume air samplers, so there is key information already available on how POPs partition to PUF, its capacity to absorb POPs, etc. (16). PUF disks of 14 cm diameter and 1.2 cm thickness have been tested as passive samplers previously and are known to sample POPs at a rate of a few cubic meters of air per day when calibrated against an active sampler (8). With appropriate instrumental detection limits and low blank values, this allows the detection of many classes of POPs, after several weeks of exposure in ambient air. The sampling period used in this study was 8 weeks, so it can be assumed that the PUF disk was operating in the “kinetic” phase (8) over the study period, although uptake of the lighter polychlorinated biphenyls (PCBs) (e.g., PCB-28) and hexachlorobenzene (HCB) during the 8 week sampling period is expected to have left linearity and their distribution between the PUF and air approached/reached equilibrium (8). Given their *K<sub>OA</sub>* values, uptake of heavier PCBs and polybrominated diphenyl ethers (PBDEs) was assumed to still be in the linear portion of the uptake curve (17). POPs existing on particles may also be trapped in the PUF disk, but this is less easy to characterize (11, 17).

In previous studies, the utility of PASs has been demonstrated at the local scale (6, 8) and for conducting urban–rural (9) and latitudinal (7) transects. The feasibility of coordinated sampling at the continental/regional scale has



**FIGURE 1.** Map showing sampling sites. Note: Singapore is a relatively small country, and all sites would overlay each other on this scale. It is therefore not shown on this map.

also been demonstrated by studies in Europe and North America, where data from PAS surveys have confirmed their efficacy in defining known source/background areas of POP contamination (7, 10, 11, 14). In this study, we report data from the first study undertaken to profile the regional distribution of PCBs, selected organochlorine (OC), compounds and PBDEs in the atmosphere of four Asian countries—China, Japan, South Korea, and Singapore. Asia is a major global industrial center with some of the fastest economic growth rates in the world, so it is important to redress the imbalance in data availability among this region, Europe, and North America.

PCBs, OC pesticides, and PBDEs enter the environment via different routes. PCBs are associated with industrialized countries and urban source areas (18, 19). Current atmospheric levels of PCBs in the environment are a result of either primary anthropogenic emissions (e.g., intentional production and disposal or accidental releases of products or materials containing PCBs), volatilization from environmental reservoirs (e.g., sea, soil), or incidental/unwanted formation of some congeners (e.g., via combustion processes) (19). OC pesticides are released into the atmosphere by agricultural spray drift, postapplication volatilization, and wind erosion of soil. These emissions are influenced by numerous physical and chemical factors (20, 21). For example, a substantial portion of HCB measured in the atmosphere is derived from the volatilization of HCB applied to soils in the past, together with combustion and other poorly quantified sources (20, 21). PBDEs have been extensively used in Europe and North America as flame retardants in various products, such as furnishing foam, plastics, textiles, wire and cable insulation, electrical and electronic connectors, etc. (22, 23). Entry into the environment may also occur via volatilization from products containing PBDEs (22, 23). Products containing PBDEs are also frequently disposed of to landfills and incinerators. In China, for example, extensive PBDE contamination is associated with the handling, disposal, and recovery of electronic waste (24). It is estimated that between 50% and 80% of the electronic waste collected for recycling in the western United States is not recycled domestically, but exported to destinations in China and other developing nations in Asia (24). In addition, China is the world's largest producer of many electrical appliances, the

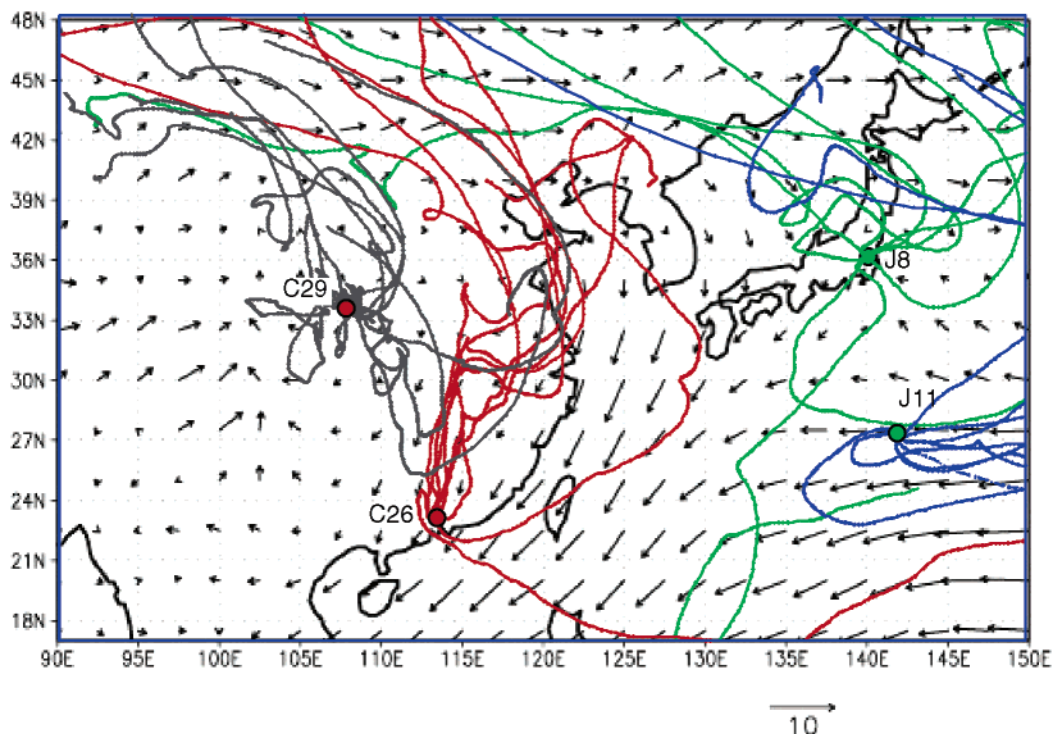
production rate having generally increased exponentially between 1978 and 2003 (25).

## Materials and Methods

**Air Sampling, Extraction, and Analysis.** The PUF disk samplers used in this study have been described previously (8, 10). Disks were precleaned by extraction at Lancaster University, U.K., and then transferred to the sampling locations in sealed, solvent-cleaned brown glass jars. The samplers were assembled at the deployment sites to avoid contamination during transit. To be able to compare sequestered amounts of target POPs between the sampling episodes, care was taken to deploy, store, and transport the PUF disks according to a prescribed protocol. Samples were deployed for 56 days from Sept 21, 2004, to Nov 16, 2004, in both rural and urban settings in the countries selected. Rural sampling sites were chosen on the condition that they were distant from local sources or significant human activity. In China, a total of 32 samplers were successfully deployed in 13 rural and 19 urban sites, 20 in Japan (13 rural, 7 urban), 15 in South Korea, and 10 in Singapore (see Figure 1). Samplers were deployed in replicate at eight sites in China, Japan, and Korea. The calculated relative deviations for PCBs (20 congeners; see the description below), dichlorodiphenyltrichloroethanes (DDTs), and PBDEs (8 congeners; see the below) were 13% (3–26%), 19% (10–30%), and 21% (5–33%), respectively. At the end of the deployment period, the PUF disks were retrieved, resealed 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.

In the laboratory, the PUF disks were Soxhlet extracted using DCM. Prior to extraction, each sample was spiked with a range of  $^{13}\text{C}_{12}$ -labeled PCB congeners ( $^{13}\text{C}_{12}$ PCB-28, -52, -101, -138, -153, and -180) to quality ensure the extraction and cleanup procedures which have been described elsewhere (10). Samples were reduced to a final volume of 25  $\mu\text{L}$  under a gentle stream of nitrogen and solvent exchanged to 25  $\mu\text{L}$  of dodecane containing PCB-30 and  $^{13}\text{C}_{12}$ PCB-141 as internal standards.

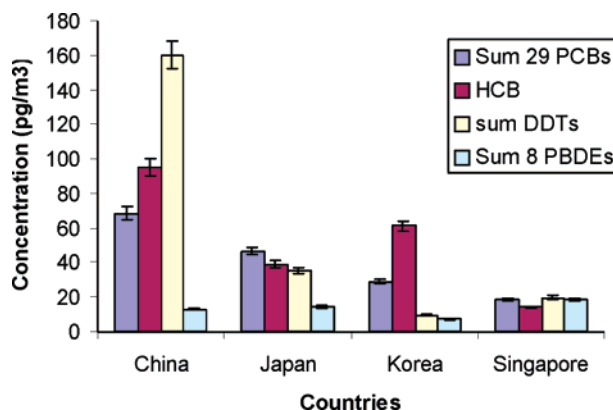
The samples were analyzed for PCBs and OC compounds on a Thermo Trace GC–MS instrument operated in electron



**FIGURE 2.** Average wind speed and direction between September and November 2004. Representative back-trajectories are also shown for three sites (see the text for details). Key arrows represent 10 m/s windspeed.

ionization mode using selected ion monitoring (SIM) (see refs 5 and 24 for details). PBDEs were analyzed separately on a Fisons MD800 GC–MS instrument with a negative chemical ionization source in SIM mode using ammonia as the reagent gas. Details of the instruments, GC temperature programs, and monitored ions have been reported elsewhere (10). 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 (PBDE-17, -28, -32, -47, -49, -75, -99, and -100), and 7 OC compounds (HCB,  $\alpha$ -chlordane,  $\gamma$ -chlordane, *o,p'*-DDT, *o,p'*-DDE (DDE = dichlorodiphenylethylene), *p,p'*-DDT, and *p,p'*-DDE) regularly detected in samples were quantified using an internal standard method. Data presented focus on the International Council for the Exploration of the Seas (ICES) congeners (PCB-28, -52, -90/101, -118, -138, -153/132, and -180),  $\Sigma_{29}$ PCBs, HCB, *o,p'*-DDT, *o,p'*-DDE, *p,p'*-DDT, *p,p'*-DDE, and  $\Sigma_8$ PBDEs.

**Quality Control/Quality Assurance (QA/QC).** All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field (i.e., samplers sent to/from field sites unopened) blanks consisting of preextracted PUF disks were not extracted and analyzed in the same way as the samples. Analytical blanks consisted of at least six field and three laboratory blanks. There was no significant difference (*t* test significance <95%) between analyte concentrations in the laboratory and field blanks, indicating contamination was negligible during transport, storage, and analysis. Method detection limits (MDLs) were derived from the blanks and quantified as 3 times the standard deviation of the mean blank concentrations. MDLs ranged between 0.03 and 0.14 ng/sample for PCBs and PBDEs (depending on the congener) and between 0.05 and 1.2 ng/sample for OC compounds. In addition, peaks were only integrated when the signal-to-noise ratio was  $\geq 3$ ; otherwise, they were considered nondetects. Recoveries were between 70% and 107% for all the compounds studied. Reported values are not recovery corrected. Instrument performance was



**FIGURE 3.** Geometric mean concentrations of sum PCBs, DDTs, and PBDEs and HCB in China, Japan, South Korea, and Singapore.

monitored using quality control standards after every six samples analyzed on the instrument.

**Back-Trajectories/Wind Direction.** The wind direction during the sampling period (September to November 2004) was determined by analyzing meteorological data from the National Center for Environmental Prediction (NCEP), the National Centre for Atmospheric Research (NCAR), and the Centre for Global Environmental Research (CGER). Figure 2 shows the average back-trajectories/wind direction and wind speed at 10 m height. These lines show the 10 day back-trajectories over C26—Guangzhou (red lines), C29—Xi'an (gray lines), J8—Tsukuba (green lines), and J11—Ogasawara (blue lines), every week from Sept 21 to Nov 16, 2004. Monsoon conditions prevail in Asia during the months of June and August, while air moves out of central Asia/Russia/Siberia during January and April, often causing dust storms. Obviously, this did not apply during this deployment period. Backward trajectory analysis therefore shows that the POPs detected were unlikely to have been influenced by large,



**TABLE 1. Summary Data for the Passive Air Sampling Program (ng/sampler; Air Concentration, pg/m<sup>3</sup>)**

compd	China			Singapore			Japan			South Korea		
	measd	air concn <sup>a</sup>	H/L ratio <sup>b</sup>	measd	air concn <sup>a</sup>	H/L ratio <sup>b</sup>	measd	air concn <sup>a</sup>	H/L ratio <sup>b</sup>	measd	air concn <sup>a</sup>	H/L ratio <sup>b</sup>
PCB-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
PCB-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
PCB-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
PCB-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
PCB-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	
PCB-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
PCB-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	
sum 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
sum 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
<i>o,p'</i> - 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	
<i>o,p'</i> - DDE	0.24–15	1.2–75	62	<0.05–0.8	<0.3–4		0.07–2	0.4–10.4	28	0.08–0.35	0.4–1.8	4
<i>p,p'</i> - DDE	0.56–74	2.8–380	132	<0.3–1.9	<1.5–10		0.32–106	1.62–544	330	<0.3–4.9	<1.5–25	
<i>p,p'</i> - DDT	0.39–182	2.0–9 28	464	<0.4–3.2	<1.9–16		0.9–28.6	4.4–146	32	<0.4–4	<1.9–20	
$\alpha$ -chlordane	0.27–21	1.4–109	77	<0.05–3.6	<0.26–19		0.34–60	1.8–305	175	0.1–0.3	0.6–1.7	3
$\gamma$ -chlordane	0.22–31	1.14–159	140	0.07–4.7	0.4–24	60	0.3–70	1.3–360	270	0.07–0.6	0.35–3	9
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	
sum 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

<sup>a</sup> Derived as described in the text. “<” values utilize the % < dl data. <sup>b</sup> This ratio has been calculated for compounds where ~100% of the samples gave detectable levels.

regional-scale meteorological conditions at the time of sampling.

## Results and Discussion

**Introductory Remarks.** Table 1 presents a summary of the data arising from the study. Data on the measured range in samples are given as nanograms of compound per sample. Also shown in Table 1 is the ratio of the highest to lowest measured values (H/L ratio), as calculated for those compounds that were routinely above the respective detection limit, and the estimated range of air concentrations (pg/m<sup>3</sup>) (see below). Further details of sampling sites and compounds detected in individual samples are available in the Supporting Information (Tables S1 and S2).

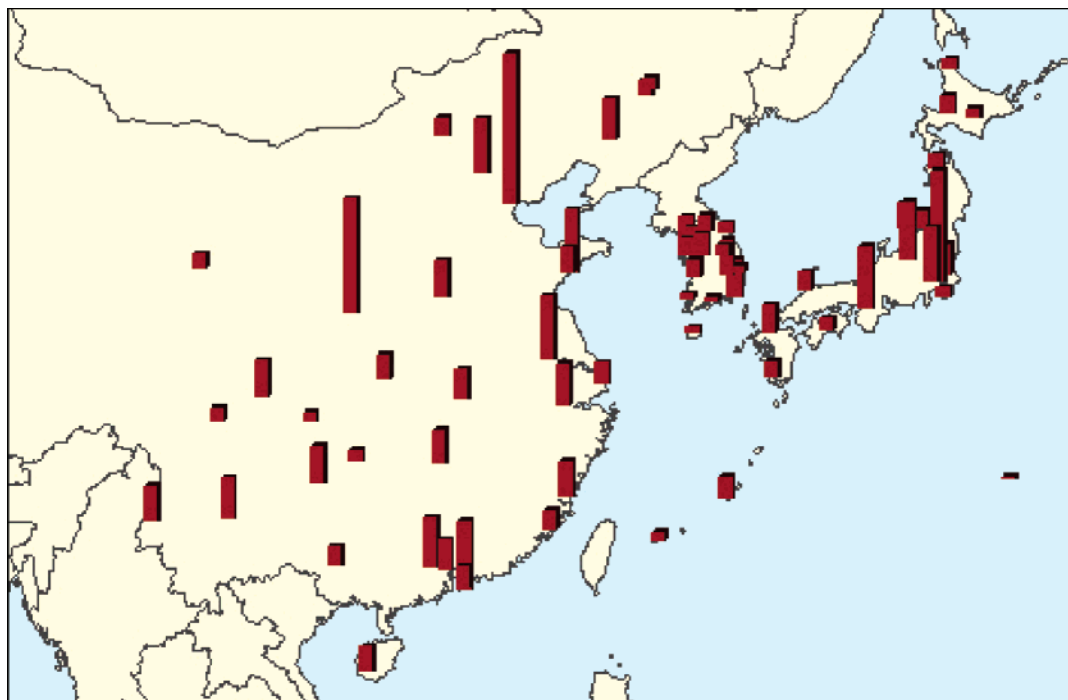
**Conversion of Sequestered Amounts of POPs to Air Concentrations and Introductory Remarks on Levels/Distribution.** Amounts of POPs sequestered over the sampling period were converted to estimated air concentrations using typical sampling rates of ca. 3–4 m<sup>3</sup> (average 3.5 m<sup>3</sup>) of air per day (8), as derived from calibration studies against an active sampler. An 8 week deployment period therefore “samples” ca. 200 m<sup>3</sup> of air. However, for those compounds which were estimated to approach equilibrium during the exposure time (i.e., HCB, PCB-28), eq 9B derived in ref 8 was used. A complication in the field is that equilibrium conditions are affected by temperature. Without detailed information on this, no correction could be applied. However, it is believed that air/sampler partitioning would be altered by a factor of 2–3 for a 10 °C temperature difference.

In summary, the data indicate that Asian  $\Sigma_{29}$ PCB concentrations are broadly in the range of tens to a few hundreds of picograms per cubic meter, with values ranging from ~20 to 340, from ~5 to 30, from 7 to 250, and from 12 to 80 pg/m<sup>3</sup> for China, Singapore, Japan, and Korea, respectively. Values of  $\Sigma_{29}$ PCB obtained in the recent European PAS survey ranged between 20 and 1700 pg/m<sup>3</sup> (10), meaning that the current Asian survey tended to indicate lower atmospheric concentrations of PCBs.

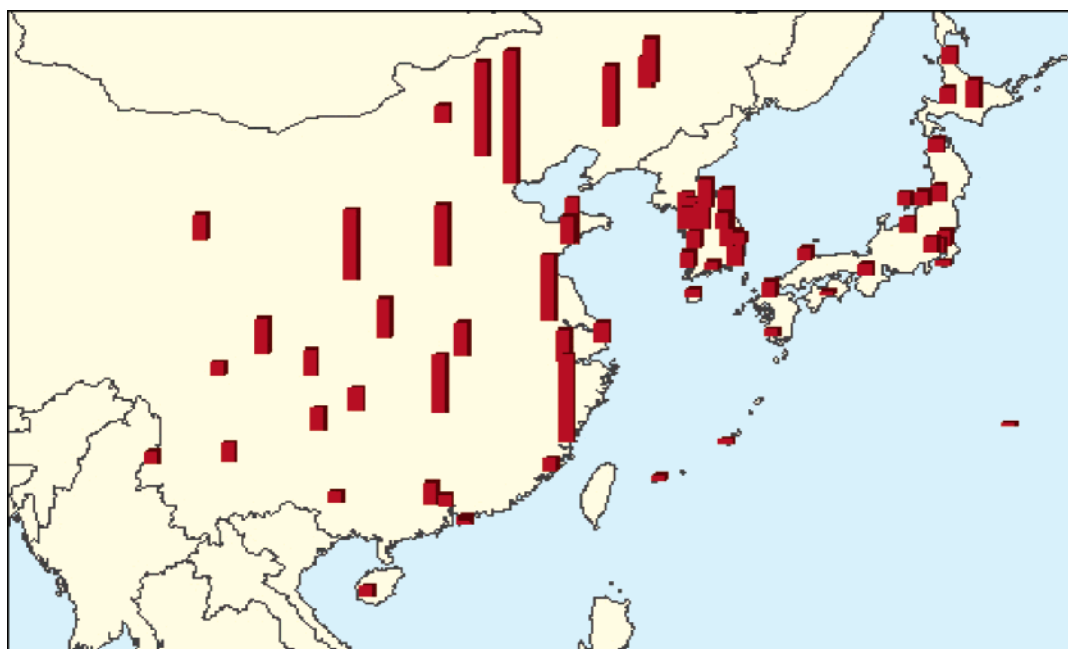
Average ambient HCB concentrations in the atmosphere of the temperate northern hemisphere have been estimated to be ~50 pg/m<sup>3</sup> (20, 21). HCB concentrations (pg/m<sup>3</sup>) derived from this study ranged from 10 to 460, from 10 to 24, from 14 to 95, and from 25 to 140 in China, Singapore, Japan, and Korea, respectively. HCB concentrations in the European atmosphere were also quite uniform with the H/L value, ~6 (10). This was interpreted as evidence of the extreme atmospheric persistence of HCB (1, 10) and a general lack of significant primary sources. A similar profile of uniformity was also noted for data from Japan and South Korea. However, HCB values in China varied by a factor of ~45. This indicates some continuing primary emissions of this compound. HCB sources include pesticide applications, chemical manufacturing processes, and combustion (20, 21). HCB appears not to have been used as a pesticide in Japan (HCB has never been registered as a pesticide in Japan), South Korea, and Singapore, although it can occur as an impurity in pentachlorophenol (PCP), pentachloronitrobenzene (PCNB), chloral dimethyl (TCTP), chlorothalonil (TPN) (20), and breakdown products (26, 27).

DDT data are also summarized in Table 1. The range of *p,p'*-DDT values in Asia (~1–930 pg/m<sup>3</sup>) was greater than that reported for Europe (0.6–190 pg/m<sup>3</sup>), with the highest values in China. Data from the analysis of sediment cores suggest ongoing DDT inputs in parts of China (28). Indeed, DDT is still being produced in China for use in malaria control and is also present in dicofol (29–33). In contrast, prevailing atmospheric concentrations outside China were low, with the exception of one sample in Japan.

Chlordane values were highest in Japan and parts of China. In Japan, 240 t of chlordane was used as an agricultural insecticide up to 1968 (34) and 17000 t was used as a termite pesticide for housing and wood preservatives by 1986. Chlordane concentrations in the Japanese atmosphere varied widely, with the H/L ratio being 175 for  $\alpha$ -chlordane and 270 for  $\gamma$ -chlordane. Generally, urban areas were highest and rural areas lowest, consistent with other studies (34, 35) and



**FIGURE 4. Spatial distribution of  $\Sigma_{29}\text{PCB}$  (ng/sample).** Note: The bars center on the sample sites. Key: largest bar  $\Sigma_7$  ICES PCBs, 23 ng/sample (site C17); largest bar  $\Sigma_{29}\text{PCB}$ , 66 ng/sample (site C17).



**FIGURE 5. Spatial distribution of HCB (ng/sample)** Note: The bars center on the sample sites. Key: largest bar, 90 ng/sample (site C17).

the usage pattern just noted. Chlordane has been widely used as a termiticide in China; there are still nine manufacturers located in eastern China (Shanghai area), with an estimated recent annual production of 500–800 t.  $\Sigma_6\text{PBDE}$  values were also generally low, ranging from  $\sim 0.1$  to tens of picograms per cubic meter in Japan, Korea, Singapore, and most of China (Table 1). These values are similar to those reported for the remote west coast of Ireland (ca.  $0.1\text{--}5\text{ pg/m}^3$ ) and in rural/semirural England (up to tens of picograms per cubic meter) (10, 36). However, some anomalously high values were found in some samples from China (up to  $340\text{ pg/m}^3$ ), and were similar to values reported by Jaward et al. from urban centers in the United Kingdom where PBDE usage is known to have been high (10).

**Spatial Distribution of PCBs, Selected OC Compounds, and PBDEs.** *PCBs.* The spatial variation in air concentrations of PCBs across the Asian sampling region is shown in Figure 4, where the length of the bars is proportional to the nanograms of PCB per sampler. The full dataset is given in Table S2. As expected, the predominant declining gradient was among urban, rural, and remote locations. In China, the highest levels were measured in the three most developed and populated zones sampled along the east coast, i.e., Tianjing–Tsingtao, the Yangtze River Delta, and the Pearl River Delta (sites C2, C13, C17, C19, C29, and C32). In Japan, the highest levels were measured in the most developed and populated zone from the Kanto region to the Kansai region (sites J9, J10, and J14). The lowest levels were measured in

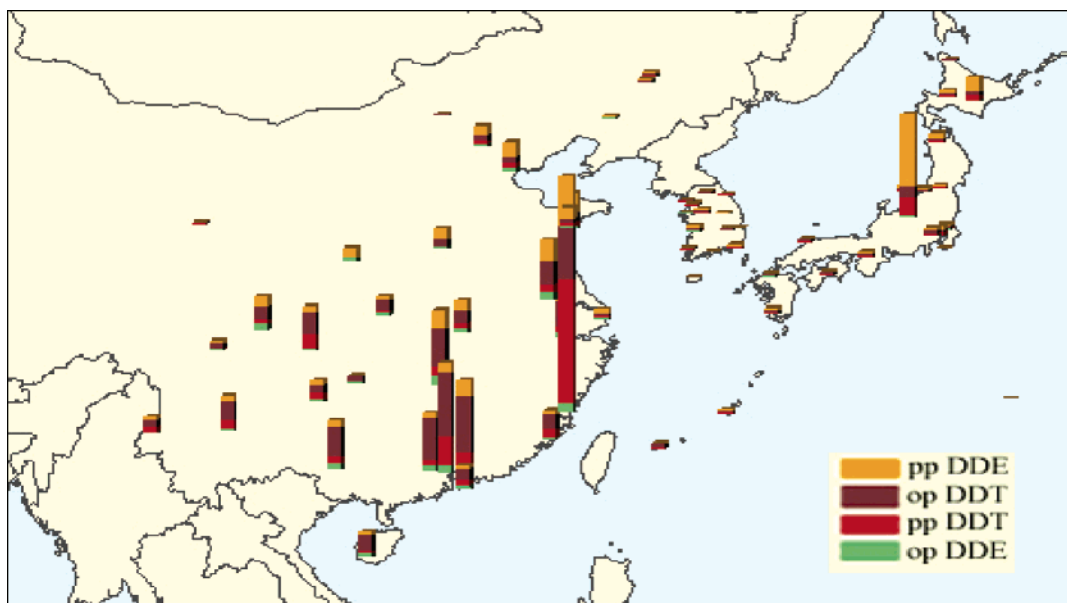


FIGURE 6. Spatial distribution of *o,p'*-DDT/E and *p,p'*-DDT/E (ng/sample). Note: The bars center on the sample sites. Key: largest bar *o,p'*-DDT, 93 ng/sample (site C26); largest bar *p,p'*-DDT, 182 ng/sample (site C15).

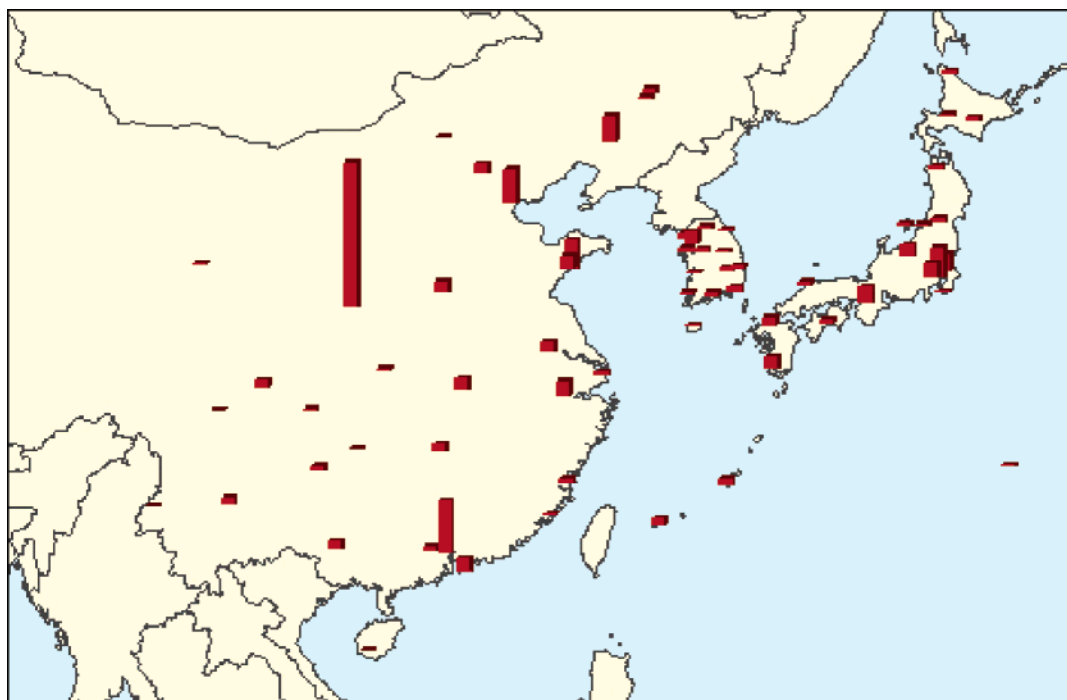


FIGURE 7. Spatial distribution of  $\Sigma$  PBDE (ng/sample). Note: The bars center on the sample sites. Key: largest bar, 67 ng/sample (site C29).

rural/remote sites in Korea and Singapore. As noted earlier, the urban–rural gradient in PCB concentrations extended over at least 2 orders of magnitude, emphasizing that diffuse atmospheric emissions from urban locations continue to contaminate the regional atmosphere three decades after international restrictions on PCB usage were initially introduced.

**OC Compounds.** Due to their historically high rate of use, with only a recent production ban or restriction on the use of OC pesticides, tropical regions in developing countries are considered to be major sources of these pesticides. Concentrations of DDT in air are still very high, even though the use of technical DDT has been banned in China since 1983 (31).

**HCB.** Recent studies have yielded a profile of global HCB emissions (20, 21) and indicate that no single source type dominates in air, where (largely past) pesticide applications to soil, manufacturing, and combustion processes all influence ambient levels. As noted earlier, HCB levels in Japan, Korea, and Singapore were consistent (Table 1), reflective of low contemporary inputs and the atmospheric persistence of HCB (1, 10). In contrast, in China, high levels were measured in Tianjing, Beijing, and Fuzhou (sites C17, C19, and C15, respectively). HCB is currently used as a precursor in the manufacture of sodium pentachlorophenol for schistosomiasis control in southern and eastern China. Recent annual HCB production in China has been ca. 2000 t by a current manufacturer located in Tianjing (close to site C17 and the

adjacent C19). This therefore suggests that primary emissions during HCB production may be an important source for HCB in North China.

*o,p'*-DDT and *p,p'*-DDT. The spatial distributions of *o,p'*-DDT and *p,p'*-DDT levels in air are shown in Figure 6. In China, very high levels of DDT were measured in the three most developed and populated zones along the southeast coast, that is, Tianjing–Tsingtao, the Yangtze River Delta, and the Pearl River Delta. Higher *o,p'*-DDT levels were mostly found in sampling sites in the southeast (C26, Ghangzhou; C13, Hok Tsui (Hong Kong); C15, Fuzhou; C10, Dinghushan). Higher *o,p'*-DDT concentrations have also been measured in the air over the East China Sea (37) and in Hong Kong (33), suggesting an atmospheric contribution of DDT derived from dicofol. Dicofol is one of the major acaricides manufactured from technical DDT and is used extensively in the southern and eastern provinces of China to eradicate cotton mites (29, 31). The high *p,p'*-DDT level measured in Fuzhou, C15, is probably due to widespread agricultural activity in this region and suggests some DDT usage continues. Recent studies on pine needles (30), sediments of a river/estuary system (32), and mussels in coastal waters (38) suggest that the DDT levels are higher in the south of China than the north. Levels were generally low and sometimes below the detection limit in samples from Korea, Singapore, and Japan.

*PBDEs.* Figure 7 shows the spatial distribution data for the  $\Sigma_8$ PBDEs in air. PBDE production and use has been a relatively recent phenomenon, with the resultant environmental emissions peaking much later than for the organochlorine compounds discussed earlier (22, 23). In Asia, the use of PBDEs is limited and the levels found are very low or below the detection limit in most sampling sites. However, in China, an extremely high concentration was measured in an urban station in Xi'an, which is the city with the largest electronics industry in northwestern China (site C29). As expected from previous studies, PBDE-47 and -99 dominated the congener pattern, contributing ca. 75% to the overall  $\Sigma_8$ PBDE burden.

**Comparison between Countries.** *China.* Levels of PCBs, HCB, and sums of DDT and DDE were significantly higher in China than the other countries (see Figure 3). Previous estimates suggested that global production/usage of PCBs has been minor in China (18, 19). However, the data presented here imply that this estimate needs to be reevaluated. Improper management/disposal of decommissioned capacitors and electronic wastes may also contribute to the levels observed. China is the second-largest producer and consumer of pesticides, accounting for 14% of the world total (25). High HCB levels were observed in both rural and urban sites in China, suggesting that the sources could be agricultural (following evaporation from HCB-bearing sodium pentachlorophenol for schistosomiasis control in South China rural areas), manufacturing, and/or combustion derived. Estimated air concentrations ( $\text{pg}/\text{m}^3$ ) in China for HCB (10–460), *p,p'*-DDE (3–380), and *p,p'*-DDT (2–930) are higher than the data recently reported for Europe, where the ranges for HCB, *p,p'*-DDE, and *p,p'*-DDT were 11–50, <0.4–25, and 0.6–190, respectively (10). In China, PBDE levels were generally low, except for a limited number of sites (for example, C29, 67 ng/sample). Further work is needed to assess the regional transport of POPs in Asia and their contribution to global cycles and budgets.

*South Korea.* Levels of PCBs, HCB, DDT, and DDE in South Korea were generally low. PBDE levels were also generally low (and most times below the detection limit) across the region. These results are expected, with large-scale industrial development in Korea occurring relatively recently (post-1970). In addition, there are strict regulations for the usage of chemicals such as PCBs, DDTs, and PBDEs in Korea. Levels of HCB in the region are strongly influenced by regional

background values. It has been estimated that a relatively small amount (77 kg) of HCB is introduced into the environment every year as an impurity of chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile), which is widely used as a fungicide in Korea (27).

*Japan.* Levels of PCBs, HCB, DDT, and DDE in Japan were generally low. PBDE levels were also generally low (and most times below the detection limit) across the region. Back-trajectories indicate that the amounts detected at the Japanese sites generally reflected local site differences and were little influenced by LRAT during this campaign. The site at Ogasawara (J11) provided important background data for the Pacific Ocean.

*Singapore.* Levels of PCBs, HCB, DDT, DDE, and PBDE in Singapore were generally low. Singapore has no agricultural base, and pesticide usage is restricted to limited application for malaria-vector control. Usage of PCBs has been phased out, although PBDEs have been detected in both environmental and human tissue samples (39, 40). Due to its small land area (approximately 700  $\text{km}^2$ ) and the prevailing wind direction, the atmosphere of Singapore is mostly impacted by regional emission sources from elsewhere in Asia.

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## Supporting Information Available

Sampling information and mean concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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