

Article

Passive Atmospheric Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Urban, Rural, and Wetland Sites along the Coastal Length of India

Gan Zhang, Paromita Chakraborty, Jun Li, Pichai Sampathkumar, Thangavel Balasubramanian, Kandasamy Kathiresan, Shin Takahashi, Annamalai Subramanian, Shinsuke Tanabe, and Kevin C. Jones

Environ. Sci. Technol., **2008**, 42 (22), 8218-8223 • DOI: 10.1021/es8016667 • Publication Date (Web): 15 October 2008

Downloaded from <http://pubs.acs.org> on November 21, 2008

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Passive Atmospheric Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Urban, Rural, and Wetland Sites along the Coastal Length of India

GAN ZHANG,^{*,†}
 PAROMITA CHAKRABORTY,[†] JUN LI,[†]
 PICHAI SAMPATHKUMAR,[‡]
 THANGAVEL BALASUBRAMANIAN,[‡]
 KANDASAMY KATHIRESAN,[‡]
 SHIN TAKAHASHI,[§]
 ANNAMALAI SUBRAMANIAN,[§]
 SHINSUKE TANABE,[§] AND
 KEVIN C. JONES^{||}

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China, Centre for Advanced Study in Marine Biology, Annamalai University, Tamil Nadu, India, Center for Marine Environmental Studies (CMES), Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan, and Lancaster Environmental Centre, Lancaster University, LA1 4YQ Lancaster, U.K.

Received June 17, 2008. Revised manuscript received August 16, 2008. Accepted August 28, 2008.

India is of prime interest due to the large past and ongoing use of pesticidal persistent organic pollutants (POPs). Rapid dissipation of POPs to the atmosphere in the tropical climate of India infers an atmospheric outflow of these chemicals. Yet data on POPs in the atmosphere of India are sparse. Passive air samplers consisting of polyurethane foam disks were therefore deployed concurrently at 18 locations and exposed for 6 weeks from July 30, 2006, to September 26, 2006, along the coastal length of India to screen for POPs in the atmosphere. The sampling sites were selected to form categories of urban, rural, and background (mangrove/wetlands) locations. Derived air concentrations (pg/m³) ranged as follows: the sum of 28 PCB congeners, 120–1080; DDTs, 16–2950; HCHs, 66–5400; chlordanes, 9–921; endosulfans, 0.45–1120; and the sum of 9 PBDE congeners, 1–181. The highest levels of all the detected POPs (except endosulfan) were observed at the urban sites, indicating the dominant areas of usage and emissions. An urban–rural composition fractionation of PCBs indicates their atmospheric movement. The γ -HCH levels were more than double those of α -HCH, indicating the sporadic use of lindane. DDT concentrations were elevated, at levels comparable to China, but with much higher percentages of *p,p'*-DDE, reflecting a more 'weathered' feature. Although no

dicolol use was recorded in India, the *o,p'*-/*p,p'*-DDT ratios were observed to be even higher than in China. Chlordanes showed high *trans*-/*cis*-chlordane (TC/CC) ratios, indicative of the current use of technical chlordane and a contribution from heptachlor usage.

Introduction

Persistent organic pollutants (POPs) used in the tropical lower latitude regions can be emitted from primary and secondary sources into the atmosphere and undergo long-range atmospheric transport (LRAT) (1–3). However, despite the high usage of POPs in some tropical regions and the relatively high temperatures, comparatively little work has so far been conducted to characterize the levels and potential regional/global contributions of these regions. Passive air samplers (PAS) using polyurethane foam disks (PUF-PAS) are one of the most validated techniques for monitoring of POPs at regional scales. They have been tested as PAS previously and are known to sample POPs at a rate of a few cubic meters of air per day from calibrations with conventional active samplers (4). 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. In previous studies, the feasibility of coordinated sampling using PUF-PAS at regional scales has been demonstrated, e.g., in the remote/background and urban locations of North America, South America (5), and Europe (6), etc. The recent effort of the Global Atmospheric Passive Sampling (GAPS) study has provided information on the global background distribution of POPs (7). A PUF-PAS sampling campaign in Asia including China, Japan, Korea, and Singapore has been also conducted (8). Yet in both the GAPS and the Asian study, no information has been reported for South Asia, in particular India. This is an important omission, because India may be a key country for chemical production and usage.

Annual consumption of pesticides in India is approximately 85 000 t, of which dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane isomers (HCHs), and malathion accounted for 70% (9). India is permitted to use organochlorine pesticides (OCPs) like DDT up to 10 000 t/year under the Stockholm Convention, until an alternative can be found to combat vector borne diseases which may be particularly prevalent in monsoon season. For example, around 10 000 L of concentrated DDT was sprayed over landfill dumps and 1000 L over Mumbai after the serious floods of July 26, 2005, which killed many people, especially on the carcasses to prevent epidemics (10). Again DDT was sprayed in the affected areas during the post-tsunami period (Dec 26, 2004) to prevent vector borne diseases (11, 12). Use of technical HCH in India increased before 1970 and from 1980 to 1990, peaking at 36 000 t/year in 1990, and has remained at ~17 000 t/year since 1991 (13), until it was banned in 1997 (9). Use of γ -HCH (as lindane) in India reached 7700 t/year in 1990, has remained at approximately 600 t/year since 1991 (13). India is the world's largest ship-breaking nation in terms of volume, conducting 38% of the world ship-breaking activities. The ship-breaking industry is mostly confined in the west coast of the country at Gujrat and Mumbai. India is growing at an exponential rate in terms of electronic waste, generating approximately 150 000 t/year, much of which is stockpiled or poorly managed.

Very limited data is available on the atmospheric concentration of POPs in India. But very few studies have stated India as a source region of POPs (14–16). The seasonal

* Corresponding author phone: +86 20 85290178; fax: +86 20 8529 0706; e-mail: zhanggan@gig.ac.cn.

[†] Guangzhou Institute of Geochemistry.

[‡] Annamalai University.

[§] Ehime University.

^{||} Lancaster University.

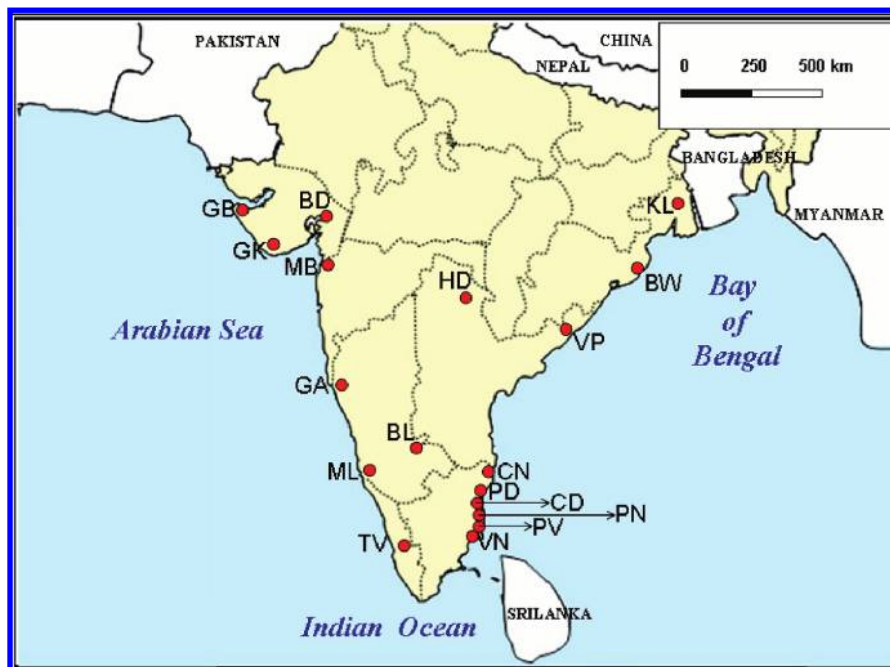


FIGURE 1. Map showing sampling sites. Site description along the west coast: GB = Gujrat Bhuj, GK = Gulf of Kutch, BD = Baroda, MB = Mumbai, GA = Goa, ML = Mangalore, BL = Bangalore, TV = Thiruvanthapuram. Site description along the east coast: KL = Kolkata, BW = Bhubaneshwar, VP = Vishakhapatnam, CN = Chennai, PD = Pondicherry, CD = Cuddalore, PN = Porto Novo, PV = Pitchavaram, VN = Vedaranyam.

variation of HCHs and DDTs at Porto Novo, South India, showed higher levels of HCH and DDTs (15). Previous reports on the atmospheric concentration of POPs in eastern and southern Asia and Oceania revealed very high levels of HCHs, DDTs, chlordane related compounds (CHLs), and polychlorinated biphenyls (PCBs) in most of the major coastal cities of India (16). Pesticide residue levels in the coastal atmosphere of Porto Novo indicated a decline in the levels of DDTs from the previous observation but no significant change in the concentration of HCHs was recorded (14).

The present study focused on the coastal length of India as the coast harbors highly populated cities, agricultural areas, and wetland belts (as background sites). The aim was to elucidate the spatial trends and the degree of contamination of POPs in the atmosphere along the coastal length of India.

Materials and Methods

Sampling. Eighteen locations were selected (Figure 1), with the intention of avoiding point source contamination each at a proximal distance from the coast on the basis of (a) urban sites, including the highly populated industrialized metropolitan cities and commercially growing large cities; (b) rural sites influenced by localized agricultural activities; (c) wetland regions at west and southeast coasts. Wetlands are located in the estuarine regions and chosen as background locations. The design and deployment of the PUF-PAS was described in detail elsewhere (8). Details of each sampling site have been given in the Supporting Information (Table S1). Briefly, PUF disks were precleaned by Accelerated Solvent Extraction (ASE 300, Dionex, U.S.) at State Key Laboratory of Organic Geochemistry in Guangzhou, and then they were 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. PUF-PASs were deployed at each site for about 6 weeks, between July 30 and September 26, 2006. At the end of the deployment period, the PUF disks were retrieved, resealed, and returned to Guangzhou, stored frozen until extraction and analysis.

Extraction and Analysis. A mixture of surrogate standards (2,4,5,6-tetrachloro-*m*-xylene (TCmX), decachlorobiphenyl (PCB209), $^{13}\text{C}_{12}$ -PCB138, and $^{13}\text{C}_{12}$ -PCB180) was added to each of the samples prior to extraction, as has been described elsewhere (6). Activated copper granules were added to the collection flask to remove potential elemental sulfur. POPs adsorbed in the PUF disks were Soxhlet extracted with dichloromethane (DCM) for 18 h. The extract was concentrated and solvent-exchanged to hexane and purified on an 8 mm i.d. alumina/silica column packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% sulfuric acid silica (10 cm), and anhydrous sodium sulfate. The column was eluted with 50 mL of DCM/hexane (4, 6). The fraction was concentrated to 25 μL under a gentle high-purity nitrogen stream after adding 25 μL of dodecane as solvent keeper. A known quantity of pentachloronitrobenzene (PCNB) and PCB-30 was added as internal standards prior to GC-MS analysis.

PCBs and OCPs analysis was carried out on a Finigan-TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μm), operating under single-ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 mL min^{-1} under constant-flow mode. The oven temperature began at 60 $^{\circ}\text{C}$ for 1 min and increased to 290 $^{\circ}\text{C}$ (10 min hold time) at a rate of 4 $^{\circ}\text{C} \text{ min}^{-1}$. Splitless/split injection of a 1 μL sample was performed with a 5 min solvent delay time. Injector temperature was at 250 $^{\circ}\text{C}$. The inlet degradation of DDT was checked daily and controlled within 15% before injecting and analyzing field samples. Polybrominated diphenyl ethers (PBDEs) were analyzed separately on a Shimadzu QP2000 GC MS instrument with a negative chemical ionization (NCI) source in SIM mode using ammonia as the reagent gas. Details of the instruments, GC temperature programs, and monitored ions have been reported elsewhere (6). A total of 28 PCB congeners (PCB-8, -28, -37, -44, -49, -60, -66, -70, -74, -77, -82, -87, -99, -101, -105, -114, -118, -126, -128, -138, -153, -158, -166, -169, -179, -180, -183, -187), nine PBDEs (BDE-28, -47, -66, -85, -99,

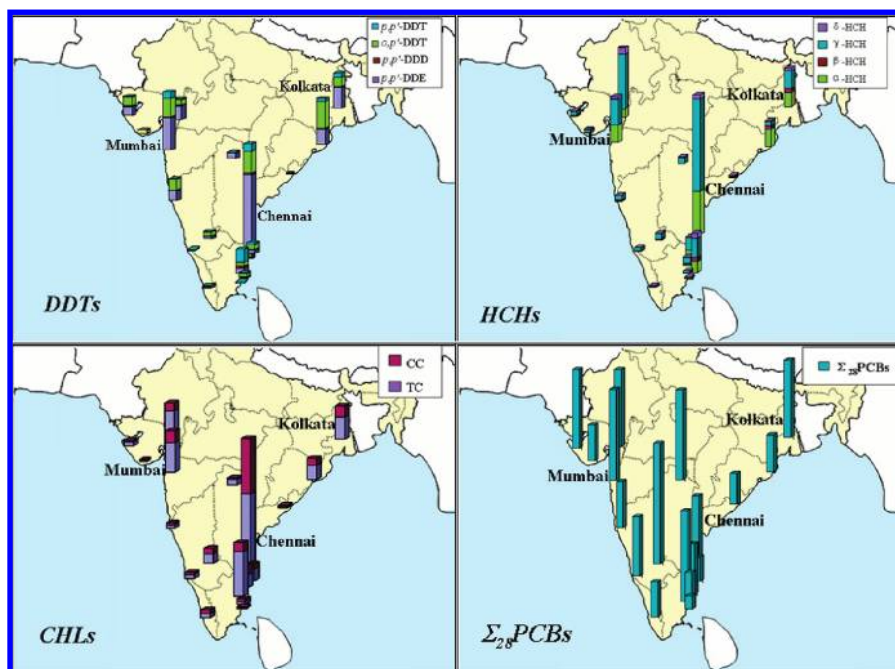


FIGURE 2. Spatial distribution of $\Sigma_{28}\text{PCBs}$, ΣDDTs , ΣHCHs , and CHLs (ng/sample) along the coastal length of India. The bars center on the sample sites. Key: largest bar for $\Sigma_{28}\text{PCBs}$, 177 ng/sample (site BL); for DDTs, 485 ng/sample (site CN, p,p' -DDT = 36, o,p' -DDT = 102, p,p' -DDD = 8, p,p' -DDE = 339); for HCHs, 937 ng/sample (site CN, α = 278, β = 48, γ = 586, and δ = 25); and for CHLs (chlordanes), 94 (site CN, *trans* = 56 and *cis* = 38).

-100, -153, -154, -183), and eight OCP compounds (HCH, o,p' -DDT, p,p' -DDE, p,p' -DDT, and p,p' -DDD, *cis*- and *trans*-chlordanes, and endosulfan) were regularly detected in samples and were quantified.

QA/QC. Chemical standards were purchased from Accustandard Co. U.S. Laboratory and field (i.e., samplers sent to/from field sites unopened) blanks consisting of pre-extracted PUF disks were extracted and analyzed in the same way as the samples. Analytical blanks consisted of 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. Surrogate recoveries were between 67% and 135%. Reported values were recovery and field blank corrected.

Results and Discussion

Amounts of POPs sequestered over the sampling period were converted to estimated air concentrations using typical sampling rates of ca. 3–4 m³ of air per day (in this case using the average value of 3.5 m³/day) (4), as derived from previous calibration studies against active samplers. The measured ambient concentrations in terms of nanograms per sampler are shown in Figure 2. It has been observed that air/sampler partitioning would be altered by a factor of 2–3 for a 10 °C temperature difference, but it can be neglected in the present study as similar temperature conditions prevailed along the coast throughout the sampling period and the conventional ‘flying saucer’ housing of the passive air sampler adequately dampened the wind effect, yielding approximately time-weighted air concentrations (17). Table 1 presents a summary of the data arising from the study. The table also shows the standard deviations and median values for urban, rural, and wetland sites. Detailed data at the sites is provided in the Supporting Information Table S2.

A Perspective on the Data Set. Concentration gradients highlight differences in compound source-sinks and relative transport potential (18).

$\Sigma_{28}\text{PCB}$ and $\Sigma_9\text{PBDE}$ concentrations each varied by ~3 orders of magnitude, with the highest values in urban centers

and the lowest in the remote wetland sites (Supporting Information Figure S1). Electronic waste recycling among informal scrap dealers and ship-breaking activities may be important unregulated activities in the major urban locations. Higher levels of atmospheric concentrations of p,p' -DDE were observed at urban sites CN and MB (2060 pg/m³ and 925 pg/m³, respectively) perhaps resulting from volatilization after the applications to combat vector borne diseases (19) in the coastal flooding areas. Chlordane also had marked urban–rural gradients, with higher levels at urban sites (29–921 pg/m³), followed by rural (15–249 pg/m³), and remote locations (9–28 pg/m³) (Supporting Information Figure S1).

PCBs. The spatial distribution of PAS derived $\Sigma_{28}\text{PCB}$ air concentrations at coastal and inland sites in India ranged from 120 to 1077 pg/m³ (Figure 2, where the length of the bars is proportional to the ng PCB/sampler). These are higher concentrations than obtained in other Asian countries (8) but are comparable to urban locations in Europe (6) and in the GAPS study (7) (Supporting Information Table S2). The highest PCB concentrations were detected at urban sites or sites at close proximity to urban centers (Figure 2) with a predominant gradient in the maximum concentration of $\Sigma_{28}\text{PCB}$. Current global air concentrations of PCBs are mainly the result of emissions from diffusive urban sources (20). A potentially important source of PCBs for developing countries is electronic waste (21). At present, India generates approximately 150 000 t/year of electrical and electronic waste. Mumbai, Delhi, and Bangalore produce ca. 11 000, 9730, and 4650 t of e-waste annually, respectively. Another potentially important source for PCBs is the improper management of ship-breaking activities in India. A typical merchant ship to be dismantled for scrap contains between 250–800 kg of PCBs, principally in the paint and left on the scrap metal in the vessel machinery that is rerolled or remelted (22). Urban PCB sources also include offgassing from closed systems such as older equipments (e.g., transformers that contain large quantities of PCB fluids) (20), and PVC (polyvinylchloride) manufacture. It is noteworthy that the PCB congener profile in the present study showed a higher abundance of the heavier congeners (those with 5–7 chlorine atoms in the

TABLE 1. Derived Concentrations (pg/m³) for the Urban, Rural, and Wetland Areas

	urban (n = 9)			rural (n = 6)			wetlands (n = 3)		
	range	avg ± SD	med	range	"> avg ± SD	med	range	avg ± SD	med
PCB28	18–140	76 ± 43	66	31–175	66 ± 55	44	9–47	22 ± 22	9
PCB52	1–66	31 ± 29	19	0.06–137	27 ± 54	3	2–23	9 ± 12	2
PCB99/101	0–29	11 ± 9	7	BDL-116	44 ± 43	32	3–18	9 ± 8	5
PCB118	0–19	7 ± 7	6	BDL-2	0.37 ± 0.80	0	BDL-1	0.49 ± 0.84	0
PCB153	0.38–16	8 ± 6	7	0.46–3	2 ± 1	2	2–17	7 ± 9	2
PCB138	0.38–77	22 ± 25	13	0.29–9	2 ± 3	1	1–9	7 ± 5	9
PCB180	0.09–8	2 ± 3	1	0.07–1	1 ± 1	1	BDL-15	6 ± 8	1
Σ ₂₈ PCBs	216–1077	662 ± 257	689	279–805	464 ± 190	429	120–320	238 ± 104	274
α-HCH	22–1691	451 ± 528	300	12–167	53 ± 59	34	20–31	25 ± 6	23
β-HCH	0–149	36 ± 56	8	1–28	16 ± 10	15	11–27	17 ± 9	12
γ-HCH	135–3562	909 ± 1156	437	31–437	174 ± 150	151	34–100	61 ± 34	50
δ-HCH	8–214	75 ± 69	42	4–42	16 ± 14	9	BDL-7	3 ± 3	2
o,p'-DDT	23–620	268 ± 238	135	0–307	88 ± 116	39	BDL-78	52 ± 45	77
p,p'-DDT	2–249	110 ± 91	87	3–387	79 ± 152	13	9–45	25 ± 18	21
p,p'-DDE	26–2061	554 ± 628	395	15–282	81 ± 102	39	6–19	13 ± 6	14
p,p'-DDD	2–56	33 ± 16	32	3–39	18 ± 13	14	BDL-19	9 ± 10	9
TC	7–340	62 ± 105	28	3–39	15 ± 13	11	3–12	7 ± 5	5
CC	16–230	89 ± 72	61	9–55	28 ± 20	19	3–11	7 ± 4	7
α-ENDO	3–680	264 ± 243	317	1–992	262 ± 388	103	BDL-12	5 ± 6	4
β-ENDO	19–143	76 ± 51	80	BDL-160	53 ± 63	30	BDL-10	6 ± 5	8
BDE-28	0.08–6	1 ± 2	0.21	0.06–0.43	0.22 ± 0.18	0.17	0.02–0.08	0.04 ± 0.03	0.03
BDE-47	0.44–72	12 ± 24	1	0.36–3	1 ± 1	1	0.05–1	1 ± 1	0.3
BDE-66	0.03–3	1 ± 1	0.18	0.02–1	0.2 ± 0.17	0.14	0.02–0.16	0.08 ± 0.07	0.07
BDE-100	0.04–7	1 ± 2	0.09	0.02–0.17	0.11 ± 0.06	0.12	0.01–0.17	0.07 ± 0.09	0.02
BDE-99	0.15–27	4 ± 9	0.36	0.14–1	0.42 ± 0.36	0.24	0.02–0.57	0.23 ± 0.29	0.11
BDE-85	2–61	13 ± 19	5	2–8	5 ± 2	5	1–4	2 ± 2	2
BDE-154	0.04–4	1 ± 1	0.1	0.04–0.79	0.23 ± 0.28	0.15	0.01–0.11	0.05 ± 0.05	0.05
BDE-153	0.02–1	0.22 ± 0.37	0.06	0.01–0.17	0.04 ± 0.02	0.03	0–0.03	0.01 ± 0.01	0.01
BDE-183	0.01–1	0.20 ± 0.23	0.06	0.02–0.20	0.08 ± 0.06	0.06	0.01–0.05	0.02 ± 0.02	0.01
Σ ₉ PBDE	2–181	34 ± 59	8	3–13	8 ± 4	8	1–6	3 ± 3	3

molecules) in the urban locations, compared to more remote locations (Supporting Information Figure S2). For example 5-Cl contributed almost 60% to the total PCB in the urban sites, 25% in the rural sites, and 15% in the remote locations; heavier congeners decline and the lighter congeners increase proportionally (23).

DDTs. Total DDT concentrations (sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD) varied substantially (16–2952 pg/m³) along the coastal length of India (Figure 2), much higher than in Europe (6) and several other Asian countries (8) but comparable to mainland China and Hong Kong (24). However, the pattern was very different, with a higher concentration of the metabolites in most of the urban sites compared to a high level of parent compounds (*o,p'*-DDT and *p,p'*-DDT) in the rural and remote locations. This implies an ongoing usage in the agricultural areas although the previously recorded total DDT concentration range at most of the coastal sites (16) seems to have declined due to the ban on DDT in agricultural practice except for the purpose of malaria control. The *p,p'*-DDT values ranged between 2–387 pg/m³ contributing 12% of the total DDT concentration. The range of *p,p'* DDT in India is lower than that in China (8) but higher than that in Europe (0.6–190 pg/m³) (6). Again the concentration is much lower when compared to the Pearl River Delta of China (120–2300 pg/m³) and Hong Kong (90–1400 pg/m³) (24). The highest level of *p,p'*-DDT was observed at Porto Novo and is consistent with previous observations (25). The *o,p'*-DDT values ranged from below the level of detection to 620 pg/m³ contributing about 31% of the total DDT concentration. The *p,p'*-DDE (a metabolite of *p,p'*-DDT) values ranged between 6–2061 pg/m³, high than in other PUF-PAS data across the globe (Supporting Information Table S2).

The elevated *p,p'*-DDE + *p,p'*-DDD/*p,p'*-DDT ratio (1–72) mostly in the urban and rural sites has been found to be much higher in comparison to a typical south China region, the Pearl River Delta, and Hong Kong (0.2–4) (24). This range is possibly due to aged DDT sources emitted to the atmosphere from

previously treated agricultural soils or DDT application (19) to prevent vector borne diseases revealing the depletion of *p,p'*-DDT to its metabolites. When comparing the average *o,p'*-DDT/*p,p'*-DDT ratio of other parts of Asia with the present study (Figure 3), rural sites in India have the highest ratio. This is unusual, as no dicofol use has so far been recorded in India. The *o,p'*-DDT/*p,p'*-DDT ratio (0–15) is also much higher than in China where dicofol usage is a major source of DDT (26). The vapor pressure of *o,p'*-DDT is 7.5 times greater than *p,p'*-DDT (27), and *p,p'*-DDT metabolizes much faster in subtropical soils (28). So the amounts of *p,p'*-DDT volatilized from the soil surface may be relatively small compared to the amounts of *o,p'*-DDT although some *p,p'*-DDT must have been volatilized from the surface, especially for a short time following application. After DDT applications were discontinued, much of the DDT may be converted to *p,p'*-DDE. Higher concentrations of *p,p'*-DDE have been interpreted as a result of its conversion to *p,p'*-DDE by UV radiation after prolonged exposure in the environment during atmospheric transport (29). Thus with the lower concentration of *p,p'*-DDT, concurrently higher levels of *p,p'*-DDE have been observed in all the sites except Porto Nova, where recent use of the technical DDT is suspected. The higher

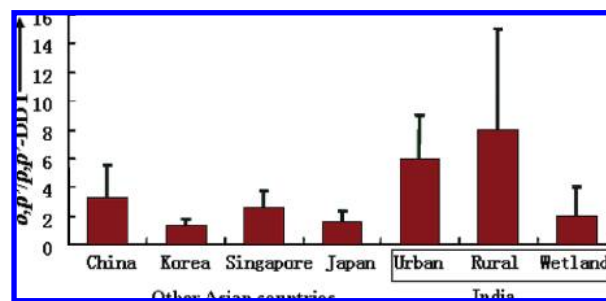


FIGURE 3. A comparison of *o,p'*-DDT/*p,p'*-DDT ratios of urban, rural, and wetland sites of India with other parts of Asia. Data of China, Korea, Japan, and Singapore are from Jaward et al., 2005 (8).

o,p'-DDT/*p,p'*-DDT ratio at the other sites is possibly due to the faster degradation of the parent compound in the tropical atmosphere. The large cities along the coast face possible monsoon and flood damage, thereby leading to the use of DDT to combat vector borne diseases. High concentrations of DDTs have been observed in mothers milk samples collected from Chennai city (site CN) and Kolkata (site KL) (30, 31), but low concentrations were found in recent (surface) sediment samples from the Hugly estuary and Sunderban (32, 33). In summary, total DDT trends are the combined effect of past and ongoing use.

HCHs. Technical HCH and lindane are two formulations of HCH. The composition of HCH isomers in the present study reveals $\alpha = 30\%$; $\beta = 4\%$; $\gamma = 60\%$; $\delta = 6\%$ (Table 1) in contrast to the technical grade composition $\alpha = 60-70\%$; $\beta = 5-12\%$; $\gamma = 10-12\%$; $\delta = 6-10\%$; $\epsilon = 3-4\%$ (34, 35). The Σ HCH concentrations ranged between 66–5404 pg/m³, which seem to be lower than previous reports (16) at most of the sites, presumably following the ban on technical HCH. The urban sites showed high concentrations of both α - and γ -HCH. The isomeric composition of HCH at site BW ($\alpha = 636$ pg/m³; $\beta = 117$ pg/m³; $\gamma = 146$ pg/m³; $\delta = 31$ pg/m³) along the east coast probably reflects the use of technical mixture in the area, while the high levels of all four isomers at sites KL and PV suggests fresh use, despite the ban on the technical mixture, along with the ongoing usage of lindane (Figure 2). In India, lindane formulations are registered for use in pharmaceutical products for control of head lice and scabies on people and fly, flea, cockroach, and mosquito populations. In agriculture, it is registered for use to control pests in cotton, sugar cane, and some vegetables. HCH technical mixtures were produced and used in India until it was banned in 1997 (9), and thereafter the government of India has been encouraging the use of lindane (γ -HCH). In the present study the isomeric composition of HCH has changed substantially from what was recorded in the past (16) with the increasing use of lindane in the recent years after the ban on technical HCH. Increased residue levels of HCHs has been observed in mothers milk samples of Chennai (site CN) compared to Porto Novo (site PN), which may be due to the current use of HCHs in Chennai city for vector control by the health department or in home gardens (30).

The ratio of the α - to the γ -isomer in the present study (0.11–4) can be used to identify the source of HCH contaminations and may also be used as an indicator of long-range atmospheric transport. The range is comparable to Toronto (1, 2) (23) and GAPS data (1–10) (7). Iwata et al. (34) reported α/γ -HCH ratios of 4.8–9.6 in the Bay of Bengal and Arabian Sea, and 0.65–2.4 for the Eastern Indian Ocean. In contrast, the α/γ HCH values in the present study were higher than the technical HCH ratio (3–7) only at site BW (4). At all the other sites, the ratio was close to or below unity. Such a low ratio in the present study indicates the presence of a possible sporadic source of lindane.

Endosulfan. India is one of the major producers of endosulfan. Since 1996–97 it produces an average of 8206 t/year totaling 41033 t in 1995–2000. Endosulfan consists of two isomers, α and β , in the ratio of 7:3. In this study, the sum of endosulfan isomers and its metabolite (endosulfan sulfate) ranged from 0.45–1122 pg/m³ (Supporting Information Figure S4), with the highest concentration of α -isomer at Porto Nova. Such an elevated level may be attributed to the use of endosulfan in the surrounding cultivated lands. Except for South America (29–14600 pg/m³) the level is comparable to Europe (21–1760 pg/m³) and higher than the rest of the world (7). The range detected is also consistent with the GAPS study (40–1090 pg/m³) (36). Endosulfan alone accounts for over 10% of the total insecticide consumption in India, although the aerial spraying

of endosulfan has been banned recently after adverse effects in cashew plantations at Kasargod, south India. The average isomeric ratio (3) of endosulfan in the present study is close to the technical grade and the concentration of the metabolite endosulfan sulfate was very low, thereby indicating ongoing application of technical endosulfan, especially in the cotton fields and tea plantations.

Chlordanes. Chlordane isomers (*trans*- and *cis*-) were detected at all the sites (Figure 2). The total chlordane concentrations (*trans*-, *cis*-, *trans*-, and *cis*-nonachlor) derived from this study (Table 1) ranged from 9–921 pg/m³. Urban sites had higher values than rural and wetland sites. This range is higher than the previous study in Europe (6), Asia (8), and the global background locations (0.7–338 pg/m³) (7). However, it is lower than the Pearl River Delta and Hong Kong of China (24). Previous studies (16) showed much higher concentrations of chlordane in the coastal cities of India. The TC/CC ratios in the present study sites ranged from 1–5 (Supporting Information Figure S2). This is much higher than what has been reported in China (37) and other parts of Asia (8), implying that India may use/have used chlordane of domestic formulation (5). The higher chlordane concentrations in most of the sampling sites indicate fresher chlordane input to the atmosphere. The fresher pattern for chlordane observed at urban sites suggests that the urban burden might be due to the nondegraded *trans*-chlordane present in heptachlor (38).

PBDEs. Polybrominated diphenyl ethers are a class of recalcitrant and bioaccumulative halogenated compounds that have emerged as POPs of interest. PBDE production and use has been a relatively recent phenomenon as POPs (39). Figure 2 shows the congener specific spatial distribution pattern for the Σ_9 PBDEs in the atmosphere along the coastal length of India. The derived concentrations for Σ_9 PBDEs varied from 1–181 pg/m³, and the maximum level is next to China among the Asian countries (8) and close to the range in Europe (6). The spatial distribution showed low concentrations in the rural and remote wetland sites and higher levels in the urban sites (Supporting Information Figure S5). The highest concentration was observed in Chennai, the third largest commercial and industrial center and the automobile capital of the country. Industries using PBDEs in their production (i.e., car, textile, and electronic industries) are the potential sources (40). BDE-47 (tetra BDE) and BDE-85 (penta BDE) dominated the congener pattern, contributing ca. 77% to the overall Σ_9 PBDE burden. The deca-product mostly composed of BDE 209 (>97%) (41) is widely used to protect the plastic components of electronic devices from the risks of fire. Higher levels of DE-85 (penta BDE) than BDE-47 in all the sites except at Chennai (site CN) may perhaps be due to photolysis of deca-BDE in the tropical atmosphere. It has been previously reported that a degradation of deca-BDE as a solid film by sunlight produced no PBDE congeners with less than five bromine atoms (42). Recent studies also report the photochemical decomposition of BDE-209 into lower molecular weight congeners under laboratory conditions (43) and highlight similar reactions in the subtropical/tropical environment. The usage of Bromkal 70-5DE seems to dominate the congener profile at Chennai.

Acknowledgments

The study was partly funded by National Natural Scientific Foundation of China (NSFC 40590391, 40673076, 40821003) and Global COE Program awarded to CMES Ehime University. The authors thank the students in Annamalai University for their help in field sampling.

Supporting Information Available

Figures as described in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Beyer, A.; Mackay, D.; Matthies, M.; Wania, F.; Webster, E. Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.* **2000**, *34*, 699–703.
- (2) Wania, F. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. *Environ. Sci. Technol.* **2003**, *37*, 1344–1351.
- (3) Klecka, G.; Boethling, B.; Franklin, J.; Graham, G.; Grady, L.; Howard, P.; Kannan, K.; Larson, R.; Mackay, D.; Muir, D.; vandeMeent, D. Evaluation of persistence and long-range transport of organic chemicals in the environment. SETAC Special Publication Series; Society of Environmental Toxicology and Chemistry: Pensacola, FL, 2000; Vol. 1, p 5.
- (4) Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4142–4151.
- (5) Pozo, K.; Harner, T.; Shoeib, M.; Urrutia, R.; Barra, R.; Parra, O.; Focardi, S. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environ. Sci. Technol.* **2004**, *38*, 6529–6537.
- (6) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* **2004**, *38*, 34–41.
- (7) Pozo, K.; Harner, T.; Wania, F.; Muir, D. C. G.; Jones, K. C.; Barrie, L. A. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environ. Sci. Technol.* **2006**, *40*, 4867–4873.
- (8) Jaward, F. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* **2005**, *39*, 8638–8645.
- (9) Gupta, P. K. Pesticide exposure—Indian scene. *Toxicology* **2004**, *198*, 83–90.
- (10) Black rain claims 2,500 buffaloes. Available at www.rediff.com/news/2005/jul/29/jcm.htm, 2005.
- (11) Krishnamoorthy, K.; Jambulingam, P.; Natarajan, R.; Shriram, A. N.; Das, P.; Sehgal, S. C. Altered environment and risk of malaria outbreak in South Andaman, Andaman & Nicobar Islands, India affected by tsunami disaster. *Malar. J.* **2005**, *4*, 32.
- (12) Murty, C. V. R.; Jain, S. K.; Sheth, A. R.; Jaiswal, A.; Dash, S. R. Response and recovery in India after the December 2004 great Sumatra earthquake and Indian Ocean tsunami. *Earthquake Spectra* **2006**, *22*, S731–S758.
- (13) Macdonald, R. W.; Barrie, L. A.; Bidleman, T. F.; Diamond, M. L.; Gregor, D. J.; Semkin, R. G.; Strachan, W. M. J.; Li, Y. F.; Wania, F.; Alae, M.; et al. Contaminants in the Canadian arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci. Total Environ.* **2000**, *254*, 93–234.
- (14) Baburajendran, R.; Venugopalan, V. K.; Ramesh, R. Pesticide residues in air from coastal environment, South India. *Chemosphere* **1999**, *39*, 1699–1706.
- (15) Ramesh, A.; Tanabe, S.; Iwata, H.; Tatsukawa, R.; Subramanian, A. N.; Mohan, D.; Venugopalan, V. K. Seasonal variation of persistent organochlorine insecticide residues in Vellar River waters in Tamil Nadu, South India. *Environ. Pollut.* **1990**, *67*, 289–304.
- (16) Iwata, H.; Tanabe, S.; Sakai, N.; Nishimura, A.; Tatsukawa, R. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. *Environ. Pollut.* **1994**, *85*, 15–33.
- (17) Tuduri, L.; Harner, T.; Hung, H. Polyurethane foam (PUF) disks passive air samplers: Wind effect on sampling rates. *Environ. Pollut.* **2006**, *144*, 377–383.
- (18) Jaward, F. M.; DiGuardo, A.; Nizzetto, L.; Cassani, C.; Raffaele, F.; Ferretti, R.; Jones, K. C. PCBs and selected organochlorine compounds in Italian mountain air: the influence of altitude and forest ecosystem type. *Environ. Sci. Technol.* **2005**, *39*, 3455–3463.
- (19) Harner, T.; Bidleman, T. F.; Jantunen, L. M. M.; Mackay, D. Soil-air exchange model of persistent pesticides in the US cotton belt. *Environ. Toxicol. Chem.* **2001**, *20*, 1612–1621.
- (20) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. Towards a global historical emission inventory for selected PCB congeners—A mass balance approach: 2. Emissions. *Sci. Total Environ.* **2002**, *290*, 199–224.
- (21) Wong, M. H.; Wu, S. C.; Deng, W. J.; Yu, X. Z.; Luo, Q.; Leung, A. O. W.; Wong, C. S. C.; Luksemburg, W. J.; Wong, A. S. Export of toxic chemicals - A review of the case of uncontrolled electronic-waste recycling. *Environ. Pollut.* **2007**, *149*, 131–140.
- (22) Hess, R.; Rushworth, D.; Hynes, M. V.; E., P. J. *Disposal Options for Ships*; Rand: Santa Monica, CA, 2001.
- (23) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.* **2004**, *38*, 4474–4483.
- (24) Wang, J.; Guo, L. L.; Li, J.; Zhang, G.; Lee, C. S. L.; Li, X.; Jones, K. C.; Xiang, Y. R.; Zhong, L. Passive air sampling of DDT, chlordane and HCB in the Pearl River Delta, South China: implications to regional sources. *J. Environ. Monit.* **2007**, *9*, 582–588; DOI: 10.1039/b700798a 2007.
- (25) Ramesh, A.; Tanabe, S.; Tatsukawa, R.; Subramanian, A. N.; Palanichamy, S.; Mohan, D.; Venugopalan, V. K. Seasonal variations of organochlorine insecticide residues in air from Porto Novo, South India. *Environ. Pollut.* **1989**, *62*, 213–222.
- (26) Li, J.; Zhu, T.; Wang, F.; Qiu, X. H.; Lin, W. L. Observation of organochlorine pesticides in the air of the Mt. Everest region. *Ecotoxicol. Environ. Saf.* **2006**, *63*, 33–41.
- (27) Spencer, W.; Cliath, M. M. Volatility of DDT and related compounds. *J. Agric. Food Chem.* **1972**, *20*, 645–649.
- (28) Talekar, N. S.; Sun, L. T.; Lee, E. M.; Chen, J. S. Persistence of some insecticides in subtropical soil. *J. Agric. Food Chem.* **1977**, *25*, 348–352.
- (29) Atlas, E.; Giam, C. S. Ambient concentration and precipitation scavenging of atmospheric organic pollutants. *Water, Air, Soil Pollut.* **1988**, *38*, 19–36.
- (30) Subramanian, A.; Ohtake, M.; Kunisue, T.; Tanabe, S. High levels of organochlorines in mothers' milk from Chennai (Madras) city, India. *Chemosphere* **2007**, *68*, 928–939.
- (31) Gnanasekaran, D.; Subramanian, A.; Someya, M.; Sudaryanto, A.; Kunisue, T.; Takahashi, S.; Chakraborty, P.; Tanabe, S. Persistent organochlorines in human breast milk from major metropolitan cities in India. *Environ. Pollut.* **2008**, doi: 10.1016/j.envpol.2008.07.011.
- (32) Bhattacharya, B.; Sarkar, S. K.; Mukherjee, N. Organochlorine pesticide residues in sediments of a tropical mangrove estuary, India: implications for monitoring. *Environ. Int.* **2003**, *29*, 587–592.
- (33) Guzzella, L.; Roscioli, C.; Viganò, L.; Saha, M.; Sarkar, S. K.; Bhattacharya, A. Evaluation of the concentration of HCH, DDT, HCB, PCB and PAH in the sediments along the lower stretch of Hugli estuary, West Bengal, northeast India. *Environ. Int.* **2005**, *31*, 523–534.
- (34) Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.* **1993**, *27*, 1080–1098.
- (35) Kutz, F. W.; Wood, P. H.; Bottimore, D. P. Organochlorine pesticides and polychlorinated biphenyls in human adipose tissue. *Rev. Environ. Contam. Toxicol.* **1991**, *120*, 1–82.
- (36) Harner, T.; Pozo, K.; Guoin, T.; Macdonald, A. M.; Hung, H.; Caine, J.; Peters, A. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environ. Pollut.* **2006**, *144*, 445–452.
- (37) Li, J.; Zhang, G.; Guo, L. L.; Xu, W.; Li, X. D.; Lee, C. S. L.; Ding, A.; Wang, T. Organochlorine pesticides in the atmosphere of Guangzhou and Hong Kong: Regional sources and long-range atmospheric transport. *Atmos. Environ.* **2007**, *41*, 3889–3903.
- (38) Bidleman, T. F.; Jantunen, L. M. M.; Helm, P. A.; Brorstrom-Lunden, E.; Juntto, S. Chlordane enantiomers and temporal trends of chlordane isomers in arctic air. *Environ. Sci. Technol.* **2002**, *36*, 539–544.
- (39) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583–624.
- (40) ter Schure, A. Describing the flows of synthetic musks and brominated flame retardants in the environment: A new ecotoxicological problem? Introductory Paper No. 120; Department of Ecology, Lund University: Sweden, 2000.
- (41) Hale, R. C.; Alae, M.; Manchester-Neesvig, J. B.; Stapleton, H. M.; Ikonomou, M. G. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ. Int.* **2003**, *29*, 771–779.
- (42) Minh, N. H.; Minh, T. B.; Watanabe, M.; Kunisue, T.; Monirith, I.; Tanabe, S.; Sakai, S.; Subramanian, A.; Sasikumar, K.; Viet, P. H.; Tuyen, B. C.; Tana, T. S.; Prudente, M. S. Open dumping site in Asian developing countries: A potential source of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **2003**, *37*, 1493–1502.
- (43) Bezares-Cruz, J.; Jafvert, C. T.; Hua, I. Solar photodecomposition of decabromodiphenyl ether: Products and quantum yield. *Environ. Sci. Technol.* **2004**, *38*, 4149–4156.

ES8016667