Selected Organochlorine Pesticides in the Atmosphere of Major Indian Cities: Levels, Regional versus Local Variations, and Sources

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India has extensive production and usage of organochlorine pesticides (OCPs) for agriculture and vector control. Despite this, few data are available on the levels and distribution of OCPs in the urban atmosphere of India. Passive and active air sampling was therefore conducted between Dec 2006 and March 2007 in 7 metropolitan cities: New Delhi, Kolkata, Mumbai, Chennai, Bangalore, Goa, and Agra. Concentrations (pg·m^{-3}) were as follows: HCHs 890–17000 (mean: 5400 ± 4110); DDTs 250–6110 (1470 ± 1010); chlordanes 290–5260 (1530 ± 790); endosulfans 240–4650 (1040 ± 610); and hexachlorobenzene 120–2890 (790 ± 510). HCHs observed in India appear to be the highest reported across the globe. Chlordanes and endosulfans are lower than levels reported from southern China. Passive sampling enabled within- and between-city variations to be assessed. As expected, paired-sample *t*-test analysis revealed higher regional than local variation. Comparisons with the limited data available from studies conducted in 1989 suggest general declines of HCHs and DDTs for most regions. γ-HCH dominated the HCH signal, reflecting widespread use of Lindane in India, although the isomeric composition in Kolkata suggests potential technical HCH use. High *o,p'-/p,p'*-DDT ratios in northern India indicate recent DDT usage. High HCB levels in the industrial areas of New Delhi and Kolkata indicate ongoing sources. Correlation between *trans*- and *cis*-chlordane implies ongoing usage. Endosulfan sulfate generally dominated the endosulfan signal, but high values of α/β-endosulfan at Chennai, Mumbai and Goa suggest ongoing usage. Backward trajectories were computed using the NOAA HYSPLIT model to trace the air mass history. Result shows local/regional sources of OCPs within India.

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Introduction

Some developing countries in the lower latitude regions have attracted attention as potentially important regional and global sources of organochlorine pesticides (OCPs), because of past and/or continued use (*1*), with the environmental conditions in tropical regions potentially enhancing emissions and subsequent atmospheric transport. The Stockholm Convention requires national monitoring of persistent organic pollutants (POPs) (*2*). India is a large and important tropical country where OCPs have been widely used in the past; usage of some compounds continues (e.g., Lindane, DDT, endosulfan) because of their low cost and versatility against various pests. Many agricultural activities are practiced in India across diverse climatic zones, extending from 8–35°N. During the 1990s more than 70% of the gross tonnage of pesticides used in Indian agriculture consisted of formulations which are banned or severely restricted in many other countries (*3*). Despite this, there is still very little data available to assess regional differences, estimate usage, and provide input to atmospheric transport models.

Several recent studies on biotic (*4–6*) and abiotic compartments (*7–10*) have highlighted POPs in India. High but limited ambient air concentrations were reported in 1989 for HCHs, DDTs, and chlordanes, from major Indian cities including Mumbai, Goa, and Kolkata (*1*), together with limited data from the late 1980s for DDTs and HCHs from New Delhi (*11*). Urban and coastal locations are important because they are source areas of POPs (*12*). Recently passive air sampling (PAS) campaigns have been organized to assess the regional and global scale distribution of POPs (*13–17*). A similar study was conducted along the coastal length of India in 2006 (*18*). This paper reports a more comprehensive follow-up to assess current levels and distribution in different highly populated regions and to assess within-city and between-city variations. The implications for sources are discussed. Being a tropical country, India experiences higher year-round temperatures, but comparatively the winter samples as in this study can reflect the association of OCPs in particulate phase. Furthermore the OCPs detected seem to be unlikely affected by large regional-scale meteorological conditions at the time of sampling especially events associated with the southwest monsoon.

Materials and Methods

Air Sampling. Active and passive air sampling (AAS and PAS) approaches were both used. Active sampling was undertaken in each of the 7 cities. For logistical reasons and to give data which may be suitable for subsequent modeling work, these were short-term high resolution samples of 12 h duration (8 a.m.-8 p.m. and 8 p.m.-8 a.m.). A total of 91 samples were taken (see Supporting Information Table SI1 for details). PAS was deployed to give time integrated data (28 day deployment periods) to assess within and between city variations, selecting a major city in the north (New Delhi), east (Kolkata), west (Mumbai), and south (Chennai) of India (Figure 1). Table SI-X1a,b provides details of the PAS and AAS sampling sites, respectively. Details of the sampling procedures are given in the SI text. Meteorological data (temperature, relative humidity, wind speed/direction, and precipitation) were recorded at each active sampling station. At the end of the deployment period, the PAS-PUF samples and the QFFs and AAS-PUF samples were resealed in their original transport containers and returned to the GIGCAS laboratory in China where they were stored in sealed, solvent-cleaned brown glass jars at −20 °C until extraction.

Extraction and Analysis. The samples were Soxhlet extracted for 18 h with dichloromethane (DCM). Prior to
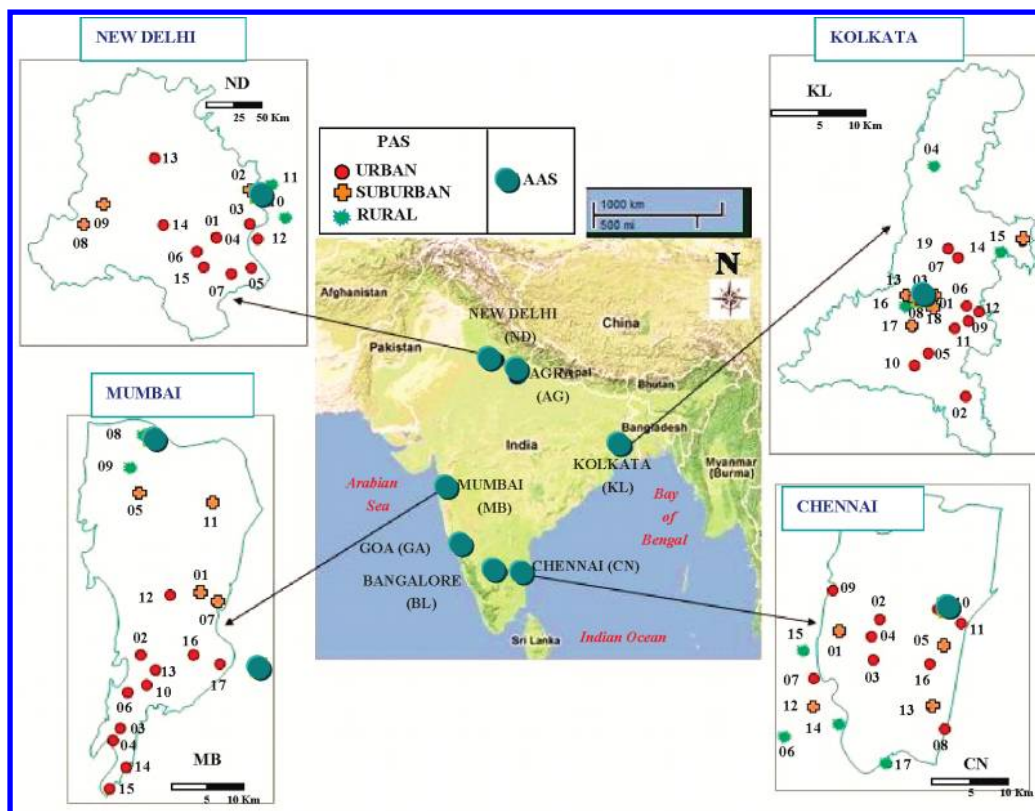
FIGURE 1. Sketch map showing the sampling sites for active and passive air sampling in seven major cities of India.

extraction a mixture of surrogate standards (2,4,5,6-tetra-chloro-*m*-xylene (TC*m*X), decachlorobiphenyl (PCB209), $^{13}C_{12}$–PCB138 and $^{13}C_{12}$–PCB180) was added to each of the samples. Activated copper granules were added to the collection flask to remove potential elemental sulfur. The extract was rotary evaporated and transferred with hexane to a 15 mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 mL and cleaned on a 8 mm *i.d.* chromatography column with 6 cm alumina (BDH neutral alumina 3% deactivated), 10 cm of silica gel (Merck Silica 60 3% deactivated), 10 cm of 50% (W/W) sulfuric acid silica, and 1 cm of baked sodium sulfate (all baked at 450 °C overnight before use), and the column was eluted with a 40 mL mixture of 1:1 hexane:DCM (v/v). The samples were reduced to a final volume of 25 μL after adding 25 μL of dodecane as solvent keeper. A known quantity of pentachlo-ronitrobenzene (PCNB) and PCB54 was added as an internal standard prior to GC-MSD analysis. The samples were analyzed for OC pesticides by an Agilent-5975C GC-MSD system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μm thickness) operating in electron ionization mode using selected ion monitoring. GC temperature program and monitored ions are given elsewhere (*19*). The pesticides (*o,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, α-, β-, γ-, and δ-HCH, HCB, chlordanes, endosulfan) regularly detected in samples were quantified using an internal standard method.

Quality Control/Quality Assurance (QA/QC). All analytical procedures were monitored using strict quality assurance and control measures. Field blanks (consisting of pre-extracted PUF disk and filters) were taken to and from each sampling site, extracted, and analyzed in the same way as samples. Procedural blanks were obtained by following the extraction and cleanup procedure without the PUF plug. A total of 24 PAS-PUF (6 from each city carried to and from urban, suburban, and rural locations), 14 AAS-PUF (2 from each city), 7 filter field blanks (1 from each city), and 10, 14, and 12 laboratory blanks were used for PAS-PUF, AAS-PUF, and filter, respectively. Field and procedural blanks were

<1% of sample values for OCPs. There was no difference (*t*-test significance, <95%) between concentrations of analytes in the procedural and field blanks, indicating contamination was minimal during transport, storage, and analysis. Field blanks and procedural blanks were below the instrument quantification limit. The limit of detection defined as the average blank + 3 × standard deviation, estimated from a signal-to-noise ratio of 3, were typically ∼0.3−1 pg·m^{-3} for AAS and ∼0.2−1 pg per sample for PAS. Surrogate recoveries were 85−125% (mean 94%) for PCB209 and 69−74% (mean 72%) for TC*m*X. Concentrations of the samples were corrected based on those results. The recoveries are comparable to a previous study in the same lab (*18*).

Results and Discussion

First, the general ambient levels obtained by short-term active sampling and inferred from longer-term passive sampling are presented and discussed. This focuses on placing the current Indian levels in context with other regions of the world and the limited past data on India. Observations are also made on the within-city and between-city comparisons (based on paired-sample *t*-test analysis) to highlight implications for sources and usage within India. Finally, diurnal variations of OCPs are discussed.

Observations on the General Levels in Indian Air. The passive sampling results were converted from the mass per sample after 28 days exposure to estimated air concentrations using an uptake rate of 3.6 m^3 day^{-1}. This value is consistent with previously published measurements obtained where this design of passive sampler has been calibrated against active samplers (*12, 20*). It was also supported by uptake rate estimates made as part of this project. Uptake was assumed to be linear in the 28 day deployment period (*21*), and no correction was made for wind speed or temperature on sampling rate (SI Table SX1). Figure 2 presents the data range for both active and passive sampling and the levels observed in the past (*1*).

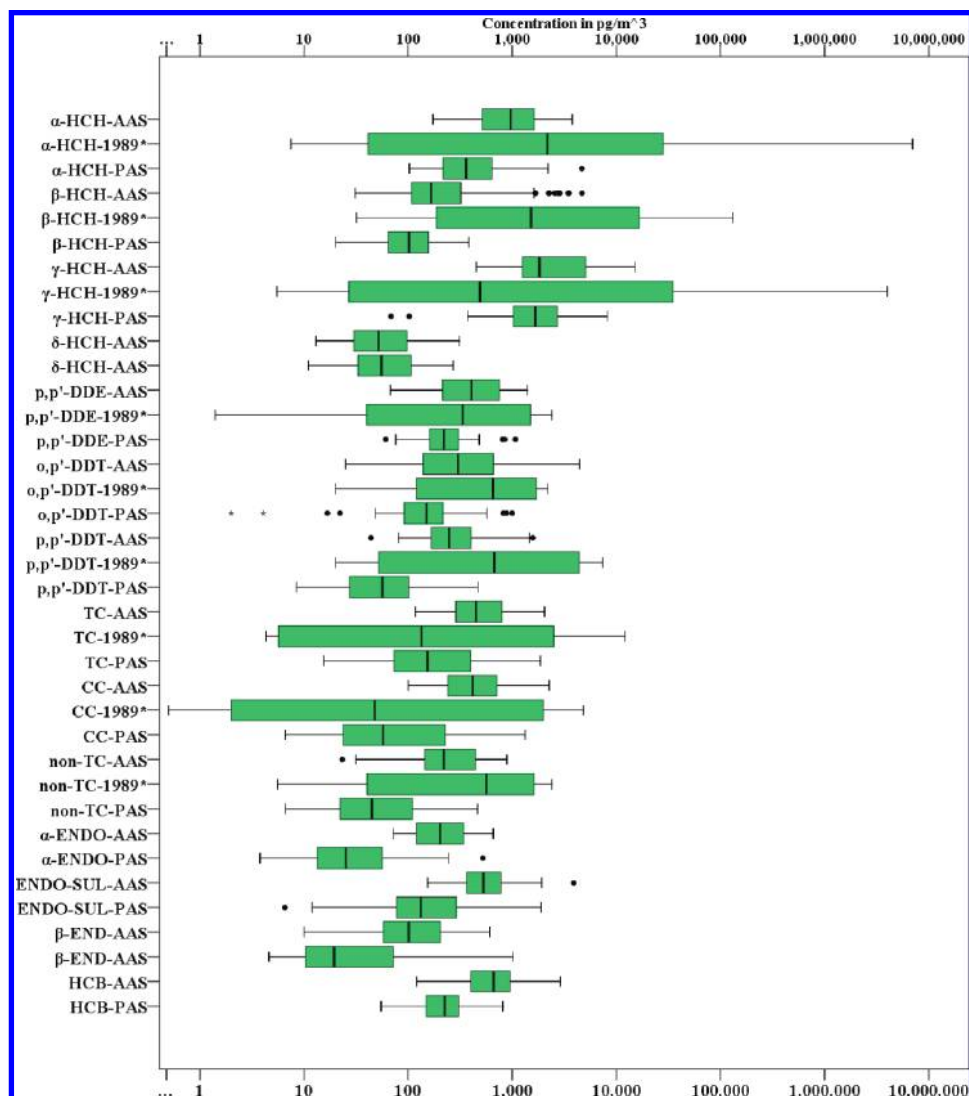**HCHs.** Annual technical HCH use in India in 1990 was estimated to be 28400 t/yr or approximately 98% of the

FIGURE 2. Box whisker plot in log scale showing the concentration range in air (pg·m⁻³) of each organochlorine pesticides by AAS. The central box represents the concentration values from the 25 to 75%ile. The bold line represents the median. The horizontal line extends from the minimum to the maximum value, excluding the outliers which display the high/low concentrations values. 1989* values taken from Iwata et al., 1994 (1).

worldwide use at that time (22). It was banned in India in 1997 (3). The technical grade composition of HCH is $\alpha = 60-70\%$; $\beta = 5-12\%$; $\gamma = 10-12\%$; $\delta = 6-10\%$; and $\varepsilon = 3-4\%$ (23), whereas Lindane is nearly 99% γ-HCH. Lindane is still manufactured in India (24) and used for agricultural purposes, pharmaceutical products, and health care programs (3). Between 1995 and 2005, 6200 t of Lindane was produced in India (24). Values of total HCHs by AAS (i.e., sum of α, β, γ, and δ isomers) determined here ranged between 890−17000 pg·m⁻³ (5400 ± 4110) (see SI Table 1). The present atmospheric levels of α- and γ-HCH are much higher than reported in recent campaigns in other parts of the world (SI Table 1). However, compared to data obtained in India in the winter of 1989 (1), concentrations of HCHs appear to have decreased (Figure 2).

γ-HCH constitutes 67% of the total HCHs concentration, about three times higher than α-HCH (21%). α/γ-HCH ratio range between 0.02−3 and the overall average (0.67) is below unity, thereby signifying a dominant contribution from Lindane applications. The dominance of γ-HCH in India is consistent with our previous observation (18) and also with the GAPs site at New Delhi (15). But in Kolkata alone, the α/γ-HCH ratio varied between 1 and 3 (average 2) with higher relative contents of α-HCH ($\alpha = 57\%$, $\beta = 7\%$, $\gamma = 34\%$, $\delta = 2\%$). Likewise in certain PAS sites the α-HCH level is one to two folds higher than γ-HCH (PAS samples KL-01, 03, 04, 07, 08, 18) (Figure SI

1a). This can be explained by the effect possibly arising out of the technical formulation usage apart from Lindane.

The highest contribution of β-HCH by AAS is seen in Goa and Mumbai, consistent with past observations (1), and in a recent study, the distribution of β-HCH in the coastal marine environment of Mumbai was found to be quite constant (10). India was found to be a major source of global β-HCH emissions in 2000 (25). Goa and Mumbai are located in the western part of India where cotton cultivation is prevalent. β-HCHs could be present due to the past use of technical HCH on cotton fields. Coincidently, human milk samples collected from the areas having intensive cotton cultivation in Punjab, a state in western India, reported the abundance of the β-isomer over other residues (26).

DDTs. DDT is registered and currently produced in India. Use of DDT in agriculture was banned in 1989 with a mandate to use a maximum of 10,000 t/yr for the control of vector borne diseases. In 2001 the national malaria program (NAMP) used 3750 tons of DDT, in rural and peri-urban areas for residual spraying (3). A total of 14,976 t of DDT was produced in India during 1997−2001. Nearly 20% of global consumption is used for control of visceral leishmaniasis which is restricted to India - thereby making India the largest consumer of DDT. However use in 2007 was down one-fourth from the 2005 level (27).

The total DDT concentrations (ΣDDTs, sum of p,p'-DDT, o,p'-DDT, p,p'-DDE, and p,p'-DDD) by AAS ranged between 250−6110 pg·m^{-3} (1470 ± 1010). This indicates that present DDTs levels in India have radically decreased [11], presumably due to the phasing out of technical DDT after the strict ban on agricultural use. Generally, the concentrations in India are similar to those measured recently in mainland China [28], Hong Kong [28], Korea [29], and Belize [30] but are considerably higher than in Japan [31], southern Mexico [32], and other parts of North America [33] and Europe [34]. The greatest range was found in New Delhi, but mean levels were highest from Goa followed by the urban site of Mumbai (Figure SI 1b). High levels of p,p'-DDT were found in parts of Mumbai (PAS samples MB-02, 08, 14, 15, and 17), located close to the coast and possibly resulting from applications for vector control purposes [10]. Kolkata and Bangalore had lower levels. p,p'-DDE dominated the overall congener pattern, contributing ~50% of ΣDDTs. This result is consistent with our previous observation [18].

High p,p'-DDE/p,p'-DDT ratios (~6) in AAS samples were seen in Chennai, while in Bangalore, Goa, Mumbai, and Kolkata the average ratio was between 1−2. In New Delhi the ratio was 1.6, with a very low average p,p'-DDE level (390 pg·m^{-3}). Similar dominance of the parent compound over degradation products has been reported in soils from northern India, close to New Delhi [35]. Elevated o,p'-DDT levels and the highest o,p'-DDT/p,p'-DDT ratio was observed at Agra (average 7) followed by New Delhi (average 5). In Chennai the average o,p'-DDT/p,p'-DDT ratio is 2, whereas in other cities this ratio is below unity. The vapor pressure of o,p'-DDT is 7.5 times greater than p,p'-DDT [36] leading to greater volatilization of o,p'-DDT to the atmosphere, suggesting the recent use of DDT and degradation of older DDT. Recent studies on human milk samples reported highest levels of DDTs in New Delhi and Chennai [5]. Significant correlation for p,p'-(DDE+DDTs) was observed ($R^2 = 0.7366$, $p < 0.05$) (Figure SI2) between six PAS sites in India with human milk data from similar sites [4−6].

Chlordanes. Chlordane has been used on a wide variety of crops in India, especially wheat. It has also been used extensively in the control of termites. As such, it was intentionally applied to soils both in agricultural and urban settings. The total concentration of chlordanes (ΣCHLs, *trans*-, *cis*-, *trans*-nonachlor) by AAS detected at all the sites ranged between 290−5260 (1530 ± 790) pg·m^{-3}. The overall atmospheric concentration of CHLs has reduced from past levels in India [1], although the concentration of *trans*-chlordane (TC) and *cis*-chlordane (CC) is still generally higher than other studies across the world (SI Table 1). Higher levels were recently reported in mainland China [28] but are comparable in Hong Kong [28]. The most abundant components in the technical chlordane mixture are TC and CC with TC/CC ratios of 1.2 [37]. TC/CC ratio can give an indication of the chlordane age. TC is less stable in the environment than CC, resulting in TC/CC ratios lower than 1.2 for aged chlordane. TC/CC ratios across all the sites were >1.3, except for New Delhi (1.1) and Agra (0.96). The low TC/CC at these sites may be due to the re-emission from "weathered" chlordane sources.

However, relatively high TC/CC ratios (average 2−4) have been observed in the PAS data set. Spearman's rank correlation coefficients (R_S) showed a strong correlation between TC and CC both by AAS ($R^2 = 0.449$, $p < 0.01$) (SI Figure 3a) and PAS ($R^2 = 0.9331$, $p < 0.0001$) (SI Figure 3b) reflecting the ongoing usage of chlordane in India. In an environment of continuous usage of chlordane, the *trans*-nonachlor/*trans*-chlordane ratio would be 0.15−0.45, and in the PAS samples the ratio varied between 0.05−0.59 (average 0.30).

Endosulfans. India is one of the major producers of endosulfan, with an average annual consumption of 3600 t from 1995 to 2000 [38]. The overall concentration range

observed in the present study by AAS was 240−4650 (1040 ± 610) pg·m^{-3}. The levels of the α-endosulfan isomer is comparable to the urban site of Guangzhou in China [28] and Tapachula, Chiapas in Mexico [32]. Endosulfan sulfate (a breakdown product) contributed an average of 61% of the total endosulfan concentration, reflecting breakdown from past usage. Technical grade endosulfan comprises of two stereo isomers, α- and β-endosulfan in a ratio of 7:3. The overall average α/β endosulfan in the present study is 4. Higher level of α-endosulfan suggests ongoing use of technical endosulfan in India.

In the PAS samples of Chennai elevated α/β-endosulfan ratios (average 2) possibly resulted from the extensive application of endosulfan in cotton and paddy fields in the surrounding state of Tamil Nadu [7]. Kolkata has a higher range of endosulfans especially in the urban sites with the β-isomer being dominant. Kolkata is the capital city of West Bengal where technical endosulfan had been used for a longer period for an important winter season pulse crop, Bengal gram [39]. β-Endosulfan has been found to be more persistent in Kolkata than α-isomer attributable to higher conversion of the latter to endosulfan sulfate in soil and plant [40]. The highest levels of endosulfan sulfate were detected in Mumbai (SI Figure 1d). Cotton cultivation is widespread in central and western India. Endosulfan is the single largest selling insecticide in Central India, with an estimated 85% of it used on cotton [41]. Hence the probable reason for the high range of α/β-endosulfan ratios from Mumbai (0.3−3, mean 1) and Goa (1−6, mean 3) and the highest level of endosulfan sulfate may be due to the past application as well as ongoing use of endosulfan in the surrounding cotton growing fields.

HCB. HCB concentrations by AAS were 120−2890 pg·m^{-3}(790 ± 510), much higher than levels typically found in developed countries (typically 50 pg·m^{-3}) [42, 43]. HCB has 3 source categories globally - use as a fungicide, as a product for the chemical industry, and as a byproduct from combustion processes [42, 43]. HCB has never been registered as a pesticide in India, but 42612 t of technical grade HCB was produced during 1995−1997 [44]. HCB in India is believed to originate primarily from chemical industries [45]. The highest level of HCB in New Delhi has been detected at the rural PAS sites (samples ND-10−12) (Figure SI 1e) bordering the industrialized city of Ghaziabad with large scale automobile manufacturing units. The higher concentration of HCB has been observed mostly in the rural and suburban PAS sites of north Howrah region (PAS samples KL-01, 07, 13−17) where many heavy scale industries and factories are located. Current sources for ambient air concentration of HCB may be also due to the use of chlorinated solvents and pesticides containing HCB as a byproduct [46].

Regional versus Local Variation. Regional variation is mainly the outcome of varied region specific pesticide usage in India. Local variation is primarily influenced by proximity to emission sources. The intercity (regional) and intracity (local) variations were derived from the PAS data set on the basis of urban, suburban, and rural transects (Figure SI6). A paired-sample *t*-test analysis in SPSS 17 was used to ascertain differences between regional and local variations. The results showed significantly pronounced regional variation of most of the compounds, compared to local variation (Table SI3). For example, all the isomers of HCHs showed significant intercity variation, but no significant variation was found within each city. DDT isomers showed a higher level of intracity variation, presumably due to local usage for vector control programs.

In order to assess the possible sources of OCPs in the air samples, the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.9), a comprehensive modeling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory [47], was used. The emphasis placed on the application of

back trajectory here was to broadly identify source sectors and origins of the air masses by computing 5-days hourly isentropic backward air mass trajectories. Further details are given in the SI text.

Figures SI7 and SI8 illustrate how all the daily trajectories for the entire period of study were assigned to the three clusters identified by the clustering algorithm. These plots give a qualitative impression of the variability of the trajectories within each cluster. Although considerable variability within each individual cluster is evident, there is ample evidence that the clustering procedure grouped the trajectories into three clearly distinct cluster types. The three mean cluster types represent the three general air mass pathways to each site in terms of direction of flow, wind speed, and the preferential transport height. The majority of cluster types for each site mostly originated from different parts of India, and the air masses spent most time within India before reaching the sampling site implying the source areas are local or regional. The level of γ-HCH shows one of the strongest relationships with air mass origin in New Delhi. Level of γ-HCH in New Delhi (ND) is higher by PAS than AAS (Figure SI4). ND AAS samples were affected mostly by cluster type 1 and 2, altogether contributing 87% (Figure SI7) of the total trajectory. The dominant cluster type 2 (53%, blue lines) encircles within a range of 500 km during the last 4 days of active sampling period and the air mass traverse near to the lindane manufacturing unit located at Uttar Pradesh (U.P, 24.2N and 83.1E) in India (*24*). Due to longer exposure and proximity to the lindane source region (bordering U.P. in northern India), the PAS sample influenced by air mass movement near the same source as the AAS (Figure SI7e), showed higher concentrations of γ-HCH than the similar AAS site. Furthermore other than γ-HCH, higher levels of α-, β-, and δ-isomers of HCHs were also detected in the PAS sites from the suburban areas in the eastern part of ND (PAS sample ND-02) and in the nearby rural sites (PAS samples ND-10−12) (Figure SI1a) located at a close proximity from U.P. where α-, β-, and δ-HCH are generated as byproducts in lindane producing units and the wastes are openly discarded (*24*). HCH isomers were also high in the active air samples collected from Agra (site-AG), located within UP. More than 80% of air mass originated within a 500 km grid before ending to AG (Figure SI7f) (slightly more close to the lindane manufacturing unit than New Delhi). High levels of residues of all the isomers of HCHs were detected in agricultural soils of New Delhi on account of the run-offs from the dumping sites of U.P. and other adjoining states (*48*). The high atmospheric burden of HCH isomers in northern India is possibly due to the re-emission from contaminated soil (*49*) within ND and the adjoining state (U.P.). Endosulfan sulfate also showed strong relationships with air mass origin in Mumbai (site-MB) and Goa (site-GA). Figure SI8a shows that 37% of the air mass (green lines line) arriving from central India and 23% from the western part of India (blue line) before ending at an urban site of Mumbai during AAS. Maximum cluster (40%, red line) circulated within a 100 km grid in the state of Maharashtra where Mumbai is the capital city. Again 100% air mass cluster originated within a 300−400 km grid from the western belt of India before ending at GA (Figure SI8f). Cotton cultivation is well practiced in central India and in the state of Gujrat and Maharashtra located at the western coast of India. Hence the highest range of endosulfan sulfate has been detected in the urban AAS samples coinciding with the dates when more than 77% air mass arrived from western and central India. Similarly the highest level of β-HCH in urban sites of MB and GA is due to similar influence of the air mass clusters at these sites. Technical HCH was used in the past for cotton cultivation in western regions of India (*26*). Due to the higher persistence nature of β-HCH, the present atmospheric source of β-HCH is attributed to the past use of technical HCH formulation (*25*), hence higher levels of β-HCH from the western part of India in this study probably reflect the similar phenomenon.

Diurnal Variation. December and January are typically the coldest months in India, and the mean temperature increases from east to south. Temperature ranges between day time high temperatures and night time low temperatures at each city. An almost cloudless sky, lack of dust, and weak winds (SI Table 1) lead to a high diurnal range of temperatures during the sampling period. Hence the air temperature was fitted to a sine wave for the sampling time at each site as a function of time of day t hours (24 h basis). The equation may be given as

$$y(T°C) = A \sin[2\pi(t\text{-}8)/24] + D \qquad (1)$$

The equation for each site and the cyclic pattern of the concentration of HCH isomers is given in Figure SI6. The fit had r^2 ranging between 0.73−0.99; the implication is that the maxima and minima for each OC is at 8 a.m. and 8 p.m., respectively.

Average air temperatures in subtropical northern India (New Delhi and Agra) were relatively low ($\sim$10−13 °C) during winter when sampling occurred. The other locations lie in the tropics and averaged $\sim$23−25.5 °C during sampling. The highest levels of OCPs in the particulate phase were detected in the samples from Agra and New Delhi. The average fraction on the filters was as follows: HCHs, DDTs, ENDOs, CHLs, HCB 0.1−3%, 3−11%, 2−12%, 0.2−7%, and $\sim$0.2%, respectively, of the gaseous phase. β-HCH and p,p'-DDT dominated the $\sum$HCHs and $\sum$DDTs pattern, and endosulfan sulfate was the dominant OC in the particulate phase.

Supporting Information Available

Word file display the figures of PAS data at each site, correlation between TC and CC in AAS and PAS data set, comparison between the mean concentration of AAS (with temporal error bars) and PAS at similar site, mean atmospheric concentrations of the organochlorine compounds in each of the metropolitan city on urban-suburban and rural basis, 5-day hourly basis back trajectory at New Delhi, Agra, Mumbai, and Goa, and tables including the range of OCPs in AAS data set, comparison of AAS data with other works across the globe, results of paired sample t test. Excel files contain the sampling details and PAS data at each site. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) 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* (1), 15−33.

(2) Fiedler, H. Stockholm Convention on Pops: Obligations and Implementation. In *The Fate of Persistent Organic Pollutants in the Environment*; 2007; pp 3−12.

(3) Gupta, P. K. Pesticide exposure--Indian scene. *Toxicology* **2004**, *198* (1−3), 83−90.

(4) Subramanian, A.; Ohtake, M.; Kunisue, T.; Tanabe, S. High levels of organochlorines in mothers' milk from Chennai (Madras) city, India. *Chemosphere* **2007**, *68* (5), 928−939.

(5) Devanathan, G.; Subramanian, A.; Someya, M.; Sudaryanto, A.; Isobe, T.; Takahashi, S.; Chakraborty, P.; Tanabe, S. Persistent organochlorines in human breast milk from major metropolitan cities in India. *Environ. Pollut.* **2009**, *157* (1), 148–154.

(6) Someya, M.; Ohtake, M.; Kunisue, T.; Subramanian, A.; Takahashi, S.; Chakraborty, P.; Ramachandran, R.; Tanabe, S. Persistent organic pollutants in breast milk of mothers residing around an open dumping site in Kolkata, India: Specific dioxin-like PCB levels and fish as a potential source. *Environ. Int.* **2009**, *36* (1), 27–35.

(7) Jayashree, R.; Vasudevan, N. Organochlorine pesticide residues in ground water of Thiruvallur district, India. *Environ. Monitor. Assess.* **2007**, *128* (1), 209–215.

(8) Rajendran, R. B.; Imagawa, T.; Tao, H.; Ramesh, R. Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. *Environ. Int.* **2005**, *31* (4), 503–512.

(9) Guzzella, L.; Roscioli, C.; Vigano, 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* (4), 523–534.

(10) Pandit, G. G.; Sahu, S. K.; Sharma, S.; Puranik, V. D. Distribution and fate of persistent organochlorine pesticides in coastal marine environment of Mumbai. *Environ. Int.* **2006**, *32* (2), 240–243.

(11) Kaushik, C. P.; Pillai, M. K. K.; Raman, A.; Agarwal, H. C. Organochloride insecticide residues in air in Delhi, India. *Water, Air, Soil Pollut.* **1987**, *32* (1), 63–76.

(12) 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* (17), 4474–4483.

(13) 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* (1), 34–41.

(14) Liu, X.; Zhang, G.; Li, J.; Yu, L.-L.; Xu, Y.; Li, X.-D.; Kobara, Y.; Jones, K. C. Seasonal Patterns and Current Sources of DDTs, Chlordanes, Hexachlorobenzene, and Endosulfan in the Atmosphere of 37 Chinese Cities. *Environ. Sci. Technol.* **2009**, *43* (5), 1316–1321.

(15) Pozo, K.; Harner, T.; Lee, S. C.; Wania, F.; Muir, D. C. G.; Jones, K. C. Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study. *Environ. Sci. Technol.* **2008**, *43* (3), 796–803.

(16) 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* (22), 8638–8645.

(17) 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* (16), 4867–4873.

(18) Zhang, G.; Chakraborty, P.; Li, J.; Sampathkumar, P.; Balasubramanian, T.; Kathiresan, K.; Takahashi, S.; Subramanian, A.; Tanabe, S.; Jones, K. C. Passive Atmospheric Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Urban, Rural, and Wetland Sites along the Coastal Length of India. *Environ. Sci. Technol.* **2008**, *42* (22), 8218–8223.

(19) Shoeib, M.; Harner, T. Characterization and Comparison of Three Passive Air Samplers for Persistent Organic Pollutants. *Environ. Sci. Technol.* **2002**, *36* (19), 4142–4151.

(20) Gouin, T.; Wania, F.; Ruepert, C.; E. Castillo, L. Field Testing Passive Air Samplers for Current Use Pesticides in a Tropical Environment. *Environ. Sci. Technol.* **2008**.

(21) Klanova, J.; Eupr, P.; Kohoutek, J.; Harner, T. Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. *Environ. Sci. Technol.* **2008**, *42*, 550–555.

(22) Li, Y.-F.; McMillan, A.; Scholtz, M. T. Global HCH Usage with 1° × 1° Longitude/Latitude Resolution. *Environ. Sci. Technol.* **1996**, *30* (12), 3525–3533.

(23) 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. **1991**, xxxx.

(24) CAPE (Community Action for Pesticide Elimination): Factsheet Lindane's Dirty Secret: Indian facilities dump toxic waste 2005. http://www.panna.org/lindane/resources (accessed month day, year).

(25) Li, Y.-F.; Scholtz, M. T.; Van Heyst, B. J. Global Gridded Emission Inventories of β-Hexachlorocyclohexane. *Environ. Sci. Technol.* **2003**, *37* (16), 3493–3498.

(26) Kalra, R. L.; Singh, B.; Battu, R. S. Organochlorine pesticide residues in human milk in Punjab, India. *Environ. Pollut.* **1994**, *85* (2), 147–151.

(27) van den Berg, H. Global Status of DDT and Its Alternatives for Use in Vector Control to Prevent Disease. *Environ. Health Perspect.* **2009**, *117* (11), .

(28) 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* (18), 3889–3903.

(29) Yeo, H.-G.; Choi, M.; Sunwoo, Y. Seasonal variations in atmospheric concentrations of organochlorine pesticides in urban and rural areas of Korea. *Atmos. Environ.* **2004**, *38* (28), 4779–4788.

(30) Alegria, H. A.; Bidleman, T. F.; Shaw, T. J. Organochlorine Pesticides in Ambient Air of Belize, Central America. *Environ. Sci. Technol.* **2000**, *34* (10), 1953–1958.

(31) Murayama, H.; Takase, Y.; Mitobe, H.; Mukai, H.; Ohzeki, T.; Shimizu, K.; Kitayama, Y. Seasonal change of persistent organic pollutant concentrations in air at Niigata area, Japan. *Chemosphere* **2003**, *52* (4), 683–694.

(32) Alegria, H. A.; Wong, F.; Jantunen, L. M.; Bidleman, T. F.; Figueroa, M. S.; Bouchot, G. G.; Moreno, V. C.; Waliszewski, S. M.; Infanzon, R. Organochlorine pesticides and PCBs in air of southern Mexico (2002−2004). *Atmos. Environ.* **2008**, *42* (38), 8810–8818.

(33) Hoh, E.; Hites, R. A. Sources of Toxaphene and Other Organochlorine Pesticides in North America As Determined by Air Measurements and Potential Source Contribution Function Analyses. *Environ. Sci. Technol.* **2004**, *38* (15), 4187–4194.

(34) Harrad, S.; Mao, H. Atmospheric PCBs and organochlorine pesticides in Birmingham, UK: concentrations, sources, temporal and seasonal trends. *Atmos. Environ.* **2004**, *38* (10), 1437–1445.

(35) Singh, K.; Malik, A.; Sinha, S. Persistent Organochlorine Pesticide Residues in Soil and Surface Water of Northern Indo-Gangetic Alluvial Plains. *Environ. Monit. Assess.* **2007**, *125* (1), 147–155.

(36) Spencer, W.; Cliath, M. M. Volatility of DDT and related compounds. *J. Agric. Food Chem.* **1972**, *20* (3), 645–649.

(37) Jantunen, L. M. M.; Bidleman, T. F.; Harner, T.; Parkhurst, W. J. Toxaphene, Chlordane, and Other Organochlorine Pesticides in Alabama Air. *Environ. Sci. Technol.* **2000**, *34* (24), 5097–5105.

(38) Usha, S.; Harikrishnan, V. R. Endosulfan - Fact sheet and Answers to Common Questions 2005. www.thanal.org (accessed month day, year).

(39) Chowdhury, A.; Das, C.; Kole, R.; Banerjee, H.; Bhattacharyya, A. Residual fate and persistence of endosulfan (50 WDG) in Bengal gram (*Cicer arietinum*). *Environ. Monitor. Assess.* **2007**, *132* (1), 467–473.

(40) Kole, R. K.; Banerjee, H.; Bhattacharyya, A. Monitoring of Market Fish Samples for Endosulfan and Hexachlorocyclohexane Residues in and Around Calcutta. *Bull. Environ. Contam. Toxicol.* **2001**, *67* (4), 554–559.

(41) Kranthi, K. R.; Jadhav, D. R.; Kranthi, S.; Wanjari, R. R.; Ali, S. S.; Russell, D. A. Insecticide resistance in five major insect pests of cotton in India. *Crop Prot.* **2002**, *21* (6), 449–460.

(42) Bailey, R. E. Global hexachlorobenzene emissions. *Chemosphere* **2001**, *43* (2), 167–182.

(43) Barber, J. L.; Sweetman, A. J.; van Wijk, D.; Jones, K. C. Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Sci. Total Environ.* **2005**, *349* (1−3), 1–44.

(44) Indian Ministry of Chemicals & Fertilisers (MC and F). *Information compiled by Plant Protection, A., Department of Agriculture & Corporation, Ministry of Agriculture and Corporation, New Delhi*, 2000.

(45) Nair, A.; Pillai, M. K. K. Monitoring of Hexachlorobenzene Residues in Delhi and Faridabad, India. *Bull. Environ. Contam. Toxicol.* **1989**, *42* (5), 682–686.

(46) Breivik, K.; Alcock, R.; Li, Y.; Bailey, R. E.; Fiedler, H.; Pacyna, J. M. Primary sources of selected POPs: regional and global scale emission. *Environ. Pollut.* 2004;128:3−16, **2004**, xxxx.

(47) Draxler, R. R.; Rolph, G. D. *NOAA Air Resources Laboratory*, Silver Spring, MD, 2003. http://www.arl.noaa.gov/ready/hysplit4.html (accessed month day, year).

(48) Prakash, O.; Suar, M.; Raina, V.; Dogra, C.; Pal, R.; Lal, R. Residues of hexachlorocyclohexane isomers in soil and water samples from Delhi and adjoining areas. *Curr. Sci.* **2004**, *87* (1), 73–77.

(49) Finizio, A.; Bidleman, T. F.; Szeto, S. Y. Emission of chiral pesticides from an agricultural soil in the Fraser Valley, British Columbia. *Chemosphere* **1998**, *36* (2), 345–355.

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