

REGIONAL VERSUS LOCAL VARIATIONS OF DDTs, HCHs, HCB, CHLORDANES AND ENDOSULFANS IN THE ATMOSPHERE OF COASTAL AND INLAND CITIES OF INDIA

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Abstract

India is an agrarian country with massive production and ongoing use of organochlorine pesticides (OCPs) for both agriculture and vector control. But data on regional variations and local distributions are exiguous. Concurrently active (diurnal) and passive air sampling (PAS) was therefore conducted between Dec'3rd 2006-Mar'24th 2007 in four metropolitan cities located in the north (New Delhi), east (Kolkata), west (Mumbai) and south (Chennai) of India. Active air sampling (diurnal) was also conducted in Bangalore, Agra, and Goa. The average AAS data and the PAS data at the similar sampling site for individual OCPs were within a factor of 1-3. Paired T-test analysis shows significantly pronounced regional variation compared to minor local variation of OCPs. The dominance of γ -HCH reflects the substantial use of lindane except in Kolkata where high α -HCH might be due to technical HCH usage. Significant correlation between TC and CC ($p < 0.0001$) in AAS/PAS datasets suggests the ongoing usage of chlordane in India. Elevated α/β -endosulfan ratio in AAS/PAS data from southern India suggests recent use of endosulfan. Higher p,p' -DDE+ p,p' -DDD/ p,p' -DDT ratio and decreasing TC/CC ratio from southern to northern India reflects substantial weathering of DDT and degradation of *cis*-chlordane with the decreasing latitude.

Introduction

The developing countries in the lower latitude regions have been the point sources of persistent organochlorines¹ and tropical climate initiates their global redistribution. India is of prime interest since organochlorine pesticides (OCPs) have been largely used in the history and some of them like lindane and DDT are still in use for agriculture and health purposes. The high temperature and the south-west monsoon may initiate the atmospheric efflux of organochlorine compounds (OCs) at both regional and global scales. In terms of global context there is a data gap from India since there has been no thorough information of organochlorines especially in terms of regional/local atmospheric distribution of these chemicals. Due to the diverse climatic zones extending from the 8th to the 35th degree of North Latitude multifarious agricultural activities are practiced in India. In 1990s more than 70% of the gross tonnage of pesticides used in agricultural applications in India consisted of formulations which are banned or severely restricted in other countries². Recently various PUF disk passive air sampler has been used in large scale for spatial distribution of atmospheric POPs globally³, at regional scale e.g., in the Great Lakes region of North America, South America⁴, at continental scale in Europe⁵ and Asia⁶ and at national level in China⁷. Similar study was conducted along the coastal length of India in 2006⁸. This study reports a detailed follow-up of the previous work with the objectives to: 1. elucidate the atmospheric concentration of organochlorine pesticides in seven major cities of India by active air sampling (AAS); 2. interpret the feasibility

of passive air sampler by comparing the data obtained from AAS from the similar site. 3. statistically deduce the regional versus local variations of OCs.

Materials and Methods

Sampling. All together 86 active air samples was obtained from the seven major cities of India on diurnal basis by running the active air sampler for two days each in Bangalore, Agra and Goa and for 8 days in Chennai and 10 days each in New Delhi, Mumbai (7 days in the urban site at Nerul, Navi Mumbai and 3 days at rural site, Vasai), and Kolkata between Dec 3rd 2006 to Mar 24th 2007. Concurrently passive air samplers were successfully deployed at 17 locations in Chennai, 15 in New Delhi, 17 in Mumbai, and 20 in Kolkata (Figure 1).

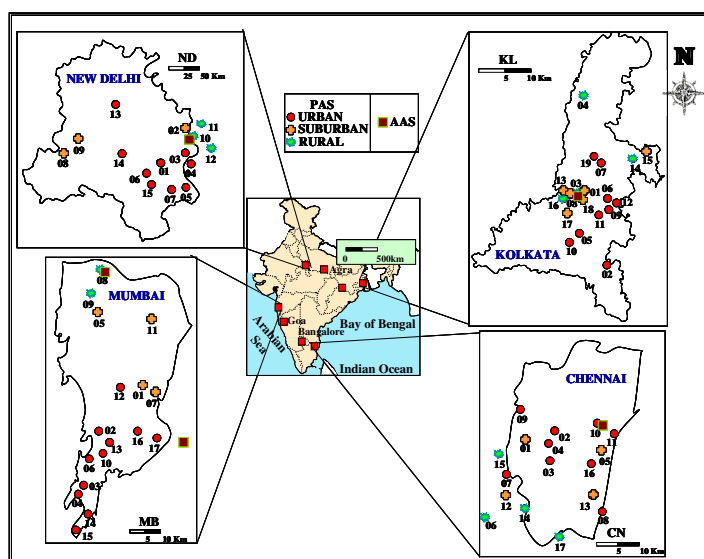


Figure 1: AAS and PAS sampling sites in the coastal and inland cities of India

In each site active sampling was conducted at a height of ~4m identical to the passive samplers to provide a time integrated concentration of the target compounds that could be used to calibrate the passive samplers.

For active air sampling air volumes of 72 m³ in 12 hr (diurnally 8:00-20:00 and 20:00-8:00) was drawn through circular quartz microfibre filter (QFF) (Grade GF/A, 8.9cm diameter, Whatman, Maidstone, England), and subsequently through 6.5 cm in diameter-7.5 cm in thickness (a density of 0.030 gm⁻³) polyurethane foam (PUF) plugs using a high-volume sampler (of the Anderson type) at a flow rate of 0.1m³ min⁻¹. Passive samplers were deployed in each city on urban-suburban and rural transect. At the common sampling site the PAS was deployed at the same time with the onset of AAS. Prior to sampling, QFFs were baked at 450°C for 12 h to remove any organic contaminant, and PUF plugs were Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two overnight extractions using dichloromethane (DCM). PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon lined lids before use. Samplers were then transferred to the sampling locations in airtight containers to avoid contamination. During the sample collection, gloves were worn, and QFFs and PUFs were handled using acetone-rinsed stainless steel tongs. Meteorological data, such as temperature, relative humidity, wind speed/direction, and precipitation were recorded at each sampling station. At the end of the deployment period, the PUF-PAS samples and the QFFs and PUF-AAS

samples were re-sealed in their original transport containers, and returned to Guangzhou Institute of organic geochemistry and all the samples 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 DCM. Prior to extraction a mixture of surrogate standards (2,4,5,6-tetrachloro-m-xylene (TCmX), decachlorobiphenyl (PCB209), ¹³C₁₂-PCB138 and ¹³C₁₂-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 15mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5mL and cleaned on a 8 mm i.d. chromatography column with 6 cm alumina (BDH neutral Alumina 3% deactivated), 10cm of silica gel (Merck Silica 60 3% deactivated), 10 cm of 50% sulfuric acid silica and 1 cm of baked sodium sulfate (all baked at 450°C overnight) and the column was eluted with 10 ml mixture of 50:50 hexane: DCM (v/v). The samples were reduced to a final volume of 25µl after adding 25 µl of dodecane as solvent keeper and a known quantity of pentachloronitrobenzene (PCNB) and PCB54 was added as an internal standard prior to GC-MSD analysis. The samples were analyzed for OC pesticides by Finigan-TRACE GC-MS system with a CP-Sil 8 CB capillary column (50m, 0.25mm, 0.25mm) operating in electron ionization mode using selected ion monitoring. GC temperature program and monitored ions are given elsewhere⁹. 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. Laboratory and field blanks carried to and from each of the sampling sites consisted of pre-extracted PUF disks and filters extracted and analyzed in the same way as samples. 24 PAS (6 from each city carried to and fro from different urban, suburban and rural locations), 14 AAS PUF (two from each city) and 7 filter field blanks (one from each city) and 10, 14 and 12 laboratory blanks respectively were used. Field and lab blanks were <3% of sample values for OCPs. There was no difference (t-test significance, <95%) between concentrations of analytes in the laboratory and field blanks, indicating contamination was minimal during transport, storage, and analysis. Field blanks and method blanks were below the instrument quantification limit. Surrogate recoveries were 85-125% (average 94%) for PCB209 and 69-74% (average 72 %) for TCmX. The reported values were corrected by the recovery rates of the standards.

Results and Discussion

OCPs in the AAS data set. The Box and whisker plot (Figure 2) shows the entire range of distribution of each of the detected and estimated organochlorine compound in the entire AAS dataset. The overall range of OCPs air concentration by AAS in pg·m⁻³(average): HCHs, 895-17057 (5427); DDTs, 249-6109 (1466); CHLs=288-5257 (1530); ENDOs, 238-4654 (1038); HCB, 121-2892 (794).

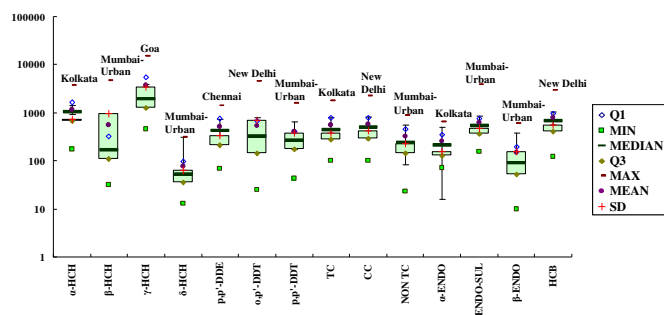


Figure 2: Box plot of organochlorine compounds by active air sampling

With regard of time trends, except at Bangalore and Chennai the level of HCHs, DDTs and chlordanes has decreased in New Delhi, Mumbai, Kolkata and Goa from the past^{1,10} perhaps due to strict ban on agricultural usage. The highest average *p,p'*-DDE+ *p,p'*-DDD/ *p,p'*-DDT ratio of six has been observed in tropical Chennai, with elevated average *p,p'*-DDE level (927 $\text{pg}\cdot\text{m}^{-3}$) whereas subtropical New Delhi shows the lowest average ratio of 1.6 with very low average *p,p'*-DDE level (391 $\text{pg}\cdot\text{m}^{-3}$). The increasing levels of *p,p'*-DDE from subtropical regions of northern India (New Delhi) to tropical regions of southern India (Chennai) indicate the faster rate of *p,p'*-DDT degradation with decreasing latitude¹¹. The highest *o,p'*-DDT/ *p,p'*-DDT ratio has been observed in northern India at Agra (average 7) followed by New Delhi (average 5). Since the vapor pressure of *o,p'*-DDT is 7.5 times greater than *p,p'*-DDT¹² such a high ratio plus elevated *o,p'*-DDT levels indicate some recent DDT usage. The highly elevated TC/CC ratio in southern India at Bangalore and Chennai suggests the faster photodegradation of *cis*-chlordane due to higher temperature in the tropical atmosphere¹³.

PAS and AAS data set. The PAS value and mean AAS value of each of the organochlorine compound at the same site are within a factor of 1-3 (Figure 3) which is consistent with other study⁹. The estimated γ -HCH obtained from PAS and mean AAS corresponding to the similar deployment sites is within a factor of 1-3. Considering the spatial variability (error bars) in the average PAS data of γ -HCH levels and temporal variability (error bars) in the average AAS data of γ -HCH levels for individual city were also within a factor of 1-2. The higher level of γ -HCH in the PAS in New Delhi than AAS can be very well explained with the 5 days hourly air parcel back trajectory using the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7). New Delhi PAS and AAS samples were affected by the 46% cluster crossing the state of Uttar Pradesh (U.P) where lindane is manufactured and also used for agriculture. Due to longer exposure and proximity to the lindane source regions the PAS sample showed larger concentration than the similar AAS site bordering U.P.

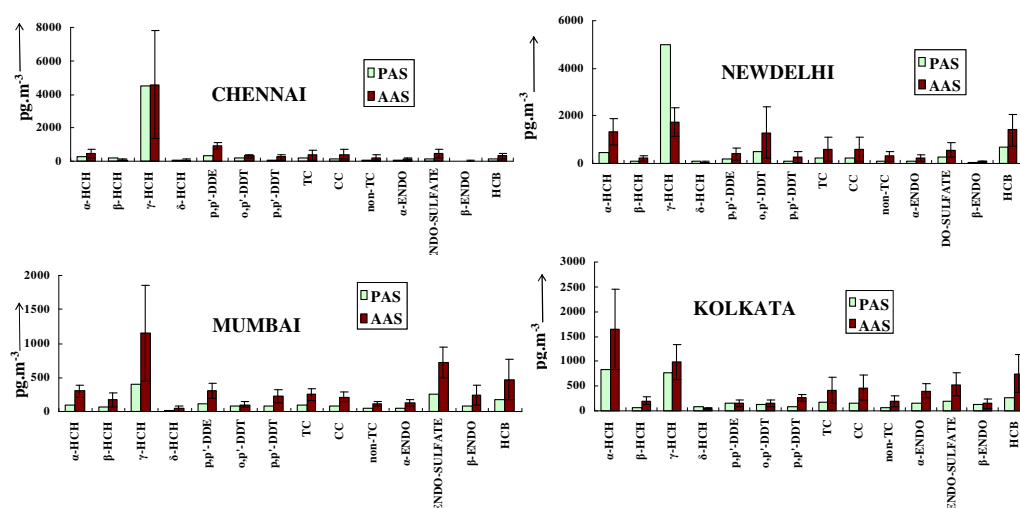


Figure 3: Comparison between the mean concentration of AAS and PAS at similar site.

Regional versus local variation-conjunction of AAS and PAS dataset

PUF-PAS is a very useful device to study the broad scale spatial distribution in terms of regional and local variation of organochlorine contamination. The regional variation is mainly the outcome of varied region specific pesticide usage coupled with the effect of environmental processes on the pollutant's chemical make up. Local variation is primarily influenced by the distance from the local emission sources. In order to compare the regional and local variation, the paired T-test analysis was carried out in SPSS (Table 1) and the results shows significantly pronounced regional variation of each of the OCPs compared to minimum local variation.

Like the AAS data set, in the PAS data set the average p,p' -DDE/ p,p' -DDD/ p,p' -DDT ratio is high in all the four cities. p,p' -DDE contributing 47% of Σ DDT dominated the overall congener pattern. This weathered feature of p,p' -DDT in India is consistent with our previous observation⁸. Similarly the predominance of γ -HCH in the PAS data is similar to AAS data and is consistent with our previous observation⁸. But in Kolkata the average isomeric composition of HCH ($\alpha=37\%,\beta=2\%,\gamma=55\%,\delta=7\%$) reflects ongoing use of technical HCH at certain regions apart from lindane application.

In the PAS data high TC/CC ratio (1-23) with significant correlation between TC and CC ($p<0.0001$) indicates the ongoing usage of the chlordane in India. In technical chlordane and the *trans*-Nonachlor/*trans*-Chlordane ratio is

0.15-0.45¹⁴ and for heptachlor 0.2-0.36. In this study this ratio varied 0.05-0.59 (average 0.30) for 60% of the PAS samples thereby reflecting heptachlor contamination in conjunction with the ongoing use of chlordane.

The higher range of HCB concentration in the PAS data set has been found particularly in the industrial belts of New Delhi and Kolkata where lower range of temperature prevailed during the entire passive sampling period. Recently HCB levels due to industrial combustion in the regions of lower atmospheric temperature has been observed in China⁷. In this study the highest level of HCB obtained from active air sampling has been observed in New Delhi. Since New Delhi had the lowest average temperature during sampling the elevated atmospheric concentration of HCB might have resulted as byproduct from industries¹⁵.

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OCPs	Regional variation	Site specification	p-value	Local Variation	Site specification	p-value
HCHs	Mumbai and Kolkata	Urban	<0.05			
	NewDelhi and Kolkata	Urban	<0.05			
	Chennai and Kolkata	Overall data	<0.05			
	NewDelhi and Kolkata	Overall data	<0.001			
DDTs	Chennai and Kolkata	Suburban	<0.05	Chennai	Urban-suburban	<0.05
				Mumbai	Urban-suburban	<0.05
CHLs	Chennai and Mumbai	Rural	<0.05	Chennai	Urban-suburban	<0.05
				Chennai	Suburban-rural	<0.05
ENDOs	Chennai and NewDelhi	Suburban	<0.01	Chennai	Urban-suburban	<0.01
	Chennai and Mumbai	Suburban	<0.05		Suburban-rural	<0.01
	Chennai and Kolkata	Suburban	<0.01			
	Chennai and NewDelhi	Overall data	<0.05			
	Kolkata and NewDelhi	Overall data	<0.05			
HCB	Chennai and NewDelhi	Urban	<0.05	Chennai	Urban-rural	<0.05
	Mumbai and NewDelhi	Urban	<0.01	Mumbai	Urban-rural	<0.05
	Chennai and Mumbai	Suburban	<0.05			
	Chennai and NewDelhi	Rural	<0.05			
	Kolkata and NewDelhi	Rural	<0.05			
	Chennai and NewDelhi	Overall data	<0.001			
	Chennai and Kolkata	Overall data	<0.05			
	NewDelhi and Kolkata	Overall data	<0.05			
	Mumbai and Kolkata	Overall data	<0.05			
	Mumbai and NewDelhi	Overall data	<0.0001			

Table 1: T-test analysis in SPSS showing pronounced regional compared to minimum local variation

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