



## Passive air sampling of organochlorine pesticides in a northeastern state of India, Manipur

Ningombam Linthoingambi Devi<sup>1</sup>, Shihua Qi<sup>1,\*</sup>, Paromita Chakraborty<sup>2,3</sup>,  
Gan Zhang<sup>2</sup>, Ishwar Chandra Yadav<sup>4</sup>

1. State Key Laboratory of Biogeology and Environmental Geology, School of Environmental Studies,  
China University of Geosciences, Wuhan 430074, China. E-mail: [nldevi.cug@gmail.com](mailto:nldevi.cug@gmail.com)

2. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of sciences, Guangzhou 510640, China

3. State Key Laboratory in Marine Pollution; Department of Biology and Chemistry, City University of Hong Kong, Hong Kong, China

4. Center of Advanced Study in Botany, Banaras Hindu University, Varanasi -221005, Uttarpradesh, India

Received 14 May 2010; revised 24 September 2010; accepted 12 October 2010

### Abstract

Thirty-six polyurethane foam disk passive air samplers (PUF-PAS) were deployed over a year during January to December, 2009 at three locations, i.e., Imphal (urban site), Thoubal (rural site) and Waithou (alpine site) of Manipur, to assess the seasonal local atmospheric emission of selected organochlorine pesticides (OCPs). The average concentration of HCHs monitored at mountain site during hot season (Mar, Apr, and May) and rainy seasons (Jun, Jul, Aug, and Sep) were 403 and 349  $\text{pg}/\text{m}^3$ , respectively. DDTs had a high concentration with 384  $\text{pg}/\text{m}^3$  at rural site and 379  $\text{pg}/\text{m}^3$  at urban site during hot seasons. Endosulfans and chlordane were found high in concentration during hot seasons (260  $\text{pg}/\text{m}^3$ ) and low during retreating monsoon seasons (44  $\text{pg}/\text{m}^3$ ) at rural site. Most of the OCPs concentrations were high during cultivation period. The OCP concentrations of rainy season were highly correlated ( $p < 0.01$ ) with OCPs of hot seasons. Further, positive correlation ( $p < 0.05$ ) was also obtained between cold seasons and retreating monsoon. Principal component analysis showed a significant correlation among the four seasons and distribution pattern of OCPs in air. Back trajectory analysis by using HYPPLIT model showed a long range air transport of OCPs to the present study area. Present OCP levels at Manipur is an outcome of both local emission and also movement of air mass by long range atmospheric transport.

**Key words:** organochlorine pesticides; polyurethane foam; urban; rural; mountain; Manipur

**DOI:** 10.1016/S1001-0742(10)60453-6

**Citation:** Devi N L, Qi S H, Chakraborty P, Zhang G, Yadav I C, 2011. Passive air sampling of organochlorine pesticides in a northeastern state of India, Manipur. *Journal of Environmental Sciences*, 23(5): 808–815

### Introduction

Persistent organic pollutants (POPs) are emitted to the ambient environment either from industrial production as byproducts from combustions, or intentionally as pesticides used in crop field, or for insects control. Organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCH), its isomers and dichlorodiphenyltrichloroethane (DDT), are persistent, toxic, and bio-accumulative in nature (Guo et al., 2009). They are subject to long-range atmospheric transport and can be found within all environmental segments, even in remote areas (Daly and Wania, 2005; Shen and Wania, 2005). Numerous POPs are banned or subject to regulation, under the UNEP Stockholm Convention for POPs. Therefore, an emission of such POPs has decreased during the last decades (Jones and Voogt, 1999), and it shows the effective evaluation of Stockholm Convention (Harner et al., 2006). However, due

to its great persistency, large amounts of POPs are still cycling in the environment. Global Atmospheric Passive Sampling (GAPS) study demonstrated the widely varying concentrations of OCPs across the globe (Poza et al., 2009). The volatility of POPs is temperature dependent, which leads to several consecutive depositions, and re-emission events called multi-hop or grasshopper transport (Wania and Mackay, 1996; Beyer et al., 2003). And higher concentrations of POPs were observed at high elevation due to the mountain cold trapping effect (Chen et al., 2008). It can be transported over long distances in ambient environment, resulting in extensive distribution across the earth, including the regions where they have never been used.

In India, DDT is known to be abstracted for non-public health use and was banned as an agricultural pesticide in 1996 (Battu et al., 2004). Since then no regulation has been put in place to ensure the use of DDT exclusively for disease vector control (Sharma et al., 2003). DDT residues and its metabolites were detected in human blood and

\* Corresponding author. E-mail: [shihuaqi@cug.edu.cn](mailto:shihuaqi@cug.edu.cn)

*www.jesc.ac.cn*

in the indoor residual spraying environment, suggesting distraction of DDT to agriculture (Curtis et al., 2002). HCH was banned in India in 1997 (Gupta, 2004), whereas high concentration of DDT in atmosphere has been reported recently with higher range of  $\gamma$ -HCH (Chakraborty et al., 2010). Lindane is still manufactured and used in India (CAPE, 2005).

Polyurethane foam disk passive air samplers (PUF-PAS) is potentially useful (Bohlin et al., 2010) and cost effective tool for monitoring POPs simultaneously, at numerous sites such as local (Harner et al., 2004), national (Gevao et al., 2006), continental (Jaward et al., 2004), and even on global scale (Poza et al., 2006). High levels of POPs were reported in Indian atmosphere (Baburajendran et al., 1999; Iwata et al., 1994; Ramesh et al., 1990). Elevated level of POPs has been reported along the coastal length of India by a recent PUF-PAS campaign (Zhang et al., 2008). Recently high levels of selected OCPs has been reported in the atmosphere of seven major coastal and inland Indian cities by using PUF-PAS and high volume air sampling concurrently (Chakraborty et al., 2010). However, no data are available on the atmospheric level of OCPs from Manipur, an inland site located at the north-eastern part of India. Therefore, present study aims to elucidate the atmospheric levels and seasonal variation of OCPs in Manipur using PUF-PAS at three sites and over several months to yield seasonal trends and to assess the difference among the three site types of urban, mountain and rural. Back trajectory analysis by HYPPLIT model was used to identify a possible source region of OCPs at Manipur.

## 1 Materials and methods

### 1.1 Study area

Manipur is an inland region located in the north-eastern part of India at latitude of  $23^{\circ}83'N$ – $25^{\circ}68'N$  and longitude of  $93^{\circ}03'E$ – $94^{\circ}78'E$  covering an area of  $22,327 \text{ km}^2$  along the Burma border. The sampling sites of the present study includes Imphal (urban site), Waithou (mountain site) and Thoubal (rural site) (Fig. 1) at an elevation of 779, 820 and 777 m above the sea level, respectively. The urban and mountain sampling sites are 23 and 17 km away from the

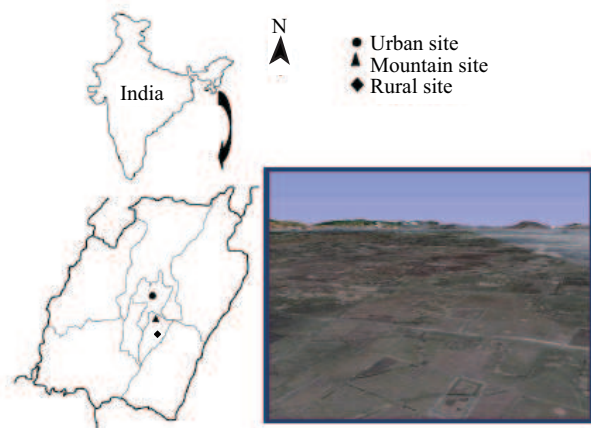


Fig. 1 Study area in Manipur.

rural site, respectively.

### 1.2 Sample collection

The PUF disk sampler consists of two stainless steel domes (approximately 30 cm in diameter), resembling like a flying saucer. A pre-cleaned and weighed PUF disk (14 cm diameter, 1.35 cm thick and  $0.0213 \text{ g/cm}^3$  density) is suspended in the center of the two dishes between washers using solvent-rinsed tweezers. The spacing between the upper and lower chambers allows air to enter the device and flow over the foam disk while providing protection from high winds, direct precipitation, sunlight, and coarse particle deposition. PUF is the same material used in many conventional high-volume, pumped samplers and has a relatively high retention capacity for gas-phase POPs. PUF disks were pre-cleaned by accelerated Solvent extraction before it was transferred to the sampling locations in sealed and solvent cleaned brown glass jars. The samplers were assembled at the deployment sites to avoid contamination during transit. PUF-PASs were deployed at each sampling site over a period of 12 months during January to December, 2009. PUF disks were changed regularly every month. At the end of the deployment period, the PUF disks were retrieved, resealed, and returned to the Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan for analysis. The sample was stored frozen until extraction and analysis.

### 1.3 Extraction and analysis

Before extraction, 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, as has been described elsewhere (Jaward et al., 2004). 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 24 hr. The sample extract was concentrated and solvent-exchanged to hexane and further reduced to 2–3 mL by a rotary evaporator (Heidolph4000, Germany). A 1:2 (V/V) alumina/silica gel column (48 hr extraction with DCM, then 180 and 240°C muffle drying for 12 hr, both 3% deactivated with  $\text{H}_2\text{O}$  before using) was used to clean up the extract and OCPs were eluted with 30 mL of DCM/hexane (2:3). The elute was then concentrated to 0.2 mL under a gentle nitrogen stream. A known quantity (about 20 ng) pentachloronitrobenzene (PCNB) was added as an internal standard prior to gas chromatography electron capture detector (GC-ECD) for analysis of 17 OCPs. This method (8080A) is used by US EPA (1982).

OCPs were analyzed by GC (Agilent 6890 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector and a HP-5 of  $30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$  film thickness fused with silica capillary column). Nitrogen was used as carrier gas at constant flow rate of 2.5 mL/min. Injector and detector temperatures were maintained at 290 and 300°C, respectively. The temperature program used is as follows: oven temperature began at 100°C (equilibrium time 1 min), rose to 200°C at the rate of 4°C/min, then

to 230°C at the rate of 2°C/min, and at last reached 280°C at the rate of 8°C/min, holding for 15 min. A 2- $\mu$ L sample was injected into GC for analysis. A six-point response factor calibration curve was established to quantify the target analyses (according to a series of standard samples with 10, 20, 50, 100, 150 and 200 ng/mL concentrations). Data were acquired and processed with the HP-3365 Chemstation software.

#### 1.4 Quality assurance/Quality control (QA/QC)

Field blanks were treated like samples and taken through the transportation, deployment, storage, and analytical steps. Three field blanks were deployed at each sampling site. There are no significant differences (*t*-test significance, < 95%) between analyte concentration in the laboratory and field blanks. This indicates contamination was negligible during transportation, storage and analysis. Recoveries for TCmX and PCB-209 were above 80%. Data shown in this study were not corrected for recovery.

## 2 Results and discussions

Seventeen OCPs monitored at Imphal (urban), Waithou (mountain) and Thoubal (rural) sites in Manipur are given in Table 1. The selected OCPs concentrations were analyzed over a period of 12 months covering four distinct seasons, i.e., cold season (Dec, Jan, and Feb), hot season (Mar, Apr, and May), rainy season (Jun, Jul, Aug, and Sep) and retreating monsoon season (Oct and Nov).

### 2.1 Hexachlorocyclohexane

The technical HCH and lindane are two formulations of HCHs. The composition of HCH isomers in the present study revealed that:  $\alpha$  = 40%,  $\beta$  = 6%,  $\gamma$  = 36%,  $\delta$  = 17% (Table 1) which is different from the technical grade composition of,  $\alpha$ : 60%–70%,  $\beta$ : 5%–12%,  $\gamma$ : 10%–12%,  $\delta$ : 6%–10% in Asian continents (Kutz et al., 1991; Iwata

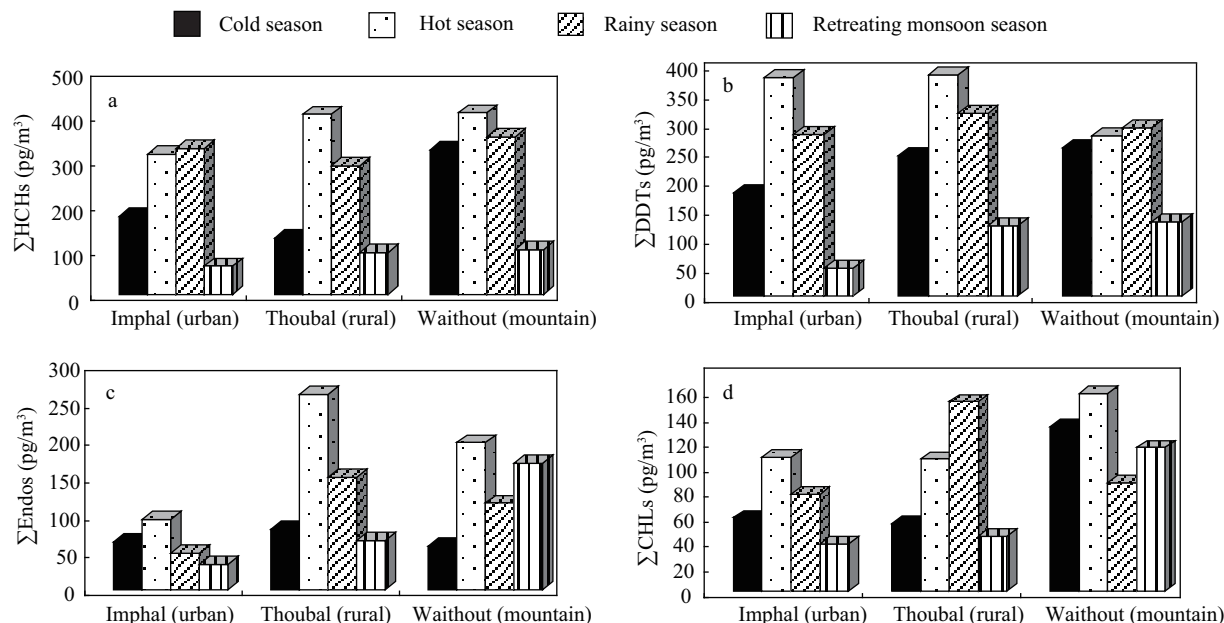
et al., 1994). This is in consistent with recent studies conducted at different parts of India (Zhang et al., 2008; Chakraborty et al., 2010). Majority of  $\alpha$ -HCH concentrations were dominant over other OCPs at the alpine site (176 pg/m<sup>3</sup>) and rural site (165 pg/m<sup>3</sup>) during hot seasons, followed by alpine site (140 pg/m<sup>3</sup>) and urban site (130 pg/m<sup>3</sup>) during rainy seasons (Fig. 2a). Elevated concentration of  $\alpha$ -HCH is highly correlated with atmospheric temperature all through hot and rainy seasons ( $p < 0.01$ ).  $\alpha$ -HCH isomer concentration was higher at the alpine region. This might be due to the mountain cold trapping of the HCH (Wania and Westgate, 2008). Furthermore, the transportation of air mass to the mountains occurs during warmer seasons, hence increases the mobility of persistent compounds at higher temperatures (Beyer et al., 2003).  $\gamma$ -HCH was the second most dominant isomer during hot season (second crop plantation time) at alpine, rural and urban sites with an average concentration 143, 122 and 90 pg/m<sup>3</sup>, respectively. This indicates the fresh use of lindane in agricultural field is closed to the study area. However, use of lindane ( $\gamma$ -HCH) is restricted in India after it was banned for agricultural application in 1999.  $\beta$ -HCH was observed with minimum concentration during entire seasons. Its concentration was the least during the cold and retreating monsoon season and it could persist more in soil rather than in air at lower temperature (Xiao et al., 2004). Ratio of  $\alpha$ -HCH/ $\gamma$ -HCH varied in the range of 0.1–3.2 at urban, 0–4.1 at rural, and 0–1.4 at alpine region. Monthly ratios of  $\alpha$ -HCH to  $\gamma$ -HCH showed regular usage of lindane and technical HCH in all three sampling sites (Fig. 3a).

### 2.2 Dichlorodiphenyltrichloroethane

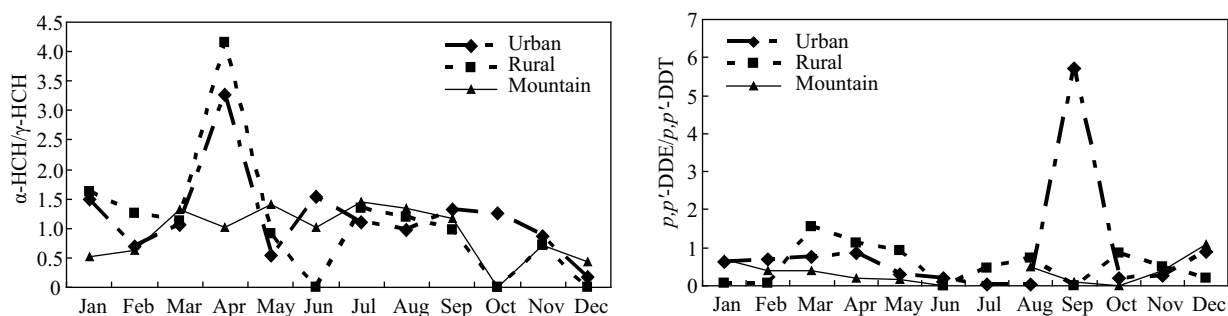
DDT pesticide is restricted for use in India. However, it may still be used in rural and peri-urban areas for residual spraying (Gupta, 2004). In the present study,  $\Sigma$ DDTs (sum of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *o,p'*-DDT and *p,p'*-

**Table 1** Mean concentration of organochlorine pesticides at urban, rural and mountain sites in Manipur (unit: pg/m<sup>3</sup>)

Compounds	Imphal (urban)				Thoubal (rural)				Waithou (mountain)			
	Cold season	Hot season	Rainy season	Retreating monsoon season	Cold season	Hot season	Rainy season	Retreating monsoon season	Cold season	Hot season	Rainy season	Retreating monsoon season
$\alpha$ -HCH	49	111	130	31	78	165	127	42	82	176	140	50
$\beta$ -HCH	18	37	12	0	0	21	5	0	11	32	38	0
$\gamma$ -HCH	71	90	105	30	46	122	106	39	161	143	121	38
$\delta$ -HCH	33	72	76	1	0	91	46	11	68	53	50	9
<i>o,p'</i> -DDE	10	58	45	6	84	23	55	20	15	22	40	13
<i>p,p'</i> -DDE	40	76	19	5	7	151	64	26	49	29	39	15
<i>o,p'</i> -DDD	18	55	34	2	0	18	40	9	16	48	19	11
<i>p,p'</i> -DDD	43	11	14	9	69	22	10	6	60	15	25	9
<i>o,p'</i> -DDT	13	61	66	3	0	38	45	17	49	53	43	26
<i>p,p'</i> -DDT	55	119	102	24	84	132	103	45	68	111	125	55
$\alpha$ -Endosulfan	32	34	31	20	51	155	90	43	28	129	74	96
$\beta$ -Endosulfan	27	45	13	13	24	92	48	18	22	52	18	59
Endosulfan-sulfate	4	14	5	1	6	13	12	5	8	16	24	13
<i>cis</i> -Chlordane	16	17	21	2	0	29	47	4	16	58	22	25
<i>trans</i> -Chlordane	26	19	28	13	0	40	69	13	49	57	36	11
non- <i>trans</i> -Chlordane	12	40	6	20	40	21	9	28	67	10	15	73
non- <i>cis</i> -Chlordane	4	32	31	2	14	15	28	0.3	0	34	15	6



**Fig. 2** Average atmospheric concentration of OCPs at urban, rural and mountain during all the four seasons. (a)  $\Sigma\text{HCHs}$ ; (b)  $\Sigma\text{DDTs}$ ; (c)  $\Sigma\text{Endos}$ ; (d)  $\Sigma\text{CHLs}$ .



**Fig. 3** Ratios of  $\alpha\text{-HCH}/\gamma\text{-HCH}$  (a) and  $p,p'\text{-DDE}/p,p'\text{-DDT}$  (b) during Jan–Dec at urban, rural and mountain location.

DDT) is higher during hot seasons ( $384 \text{ pg}/\text{m}^3$ ) and rainy seasons ( $317 \text{ pg}/\text{m}^3$ ) at rural location compared to urban and alpine sites (Fig. 2b). Higher DDTs concentration were obtained at agricultural site, possibly due to the use for agricultural purposes, which is consistent with GAPS study (Pozo et al., 2009). DDTs can be volatilized to ambient environment in a few days. However,  $p,p'\text{-DDT}$  is the one which was found at urban, rural and alpine locations during both hot seasons and rainy seasons when compared to the metabolites. Parent compound  $o,p'\text{-DDT}$  with elevated concentrations at current site is indicative of recent use of DDTs. However, high concentration of  $p,p'\text{-DDE}$  metabolite showed past use of DDTs for various reasons. One reason behind elevated level of DDE is that it is the only metabolite found in the environment as a result of contamination or breakdown of DDT. The possible source of DDTs at urban site is from vector control or from open waste dumping sites. The lower ratio of  $p,p'\text{-DDE}$  to  $p,p'\text{-DDT}$  indicates the recent usage of DDTs, while  $o,p'\text{-DDT}$  to  $p,p'\text{-DDT}$  ratio helps to establish the usage of dicofol. The  $o,p'\text{-DDT}$  and  $p,p'\text{-DDT}$  ratio of the present study ranged in 0–1 implied the dearth of dicofol. The  $p,p'\text{-DDE}$  to  $p,p'\text{-DDT}$  ratio at urban, rural and mountain ranges in 0–5, 0–2, and 0–1, respectively. These ratio values indicate the fresh uses of DDT in Manipur (Fig. 3b).

### 2.3 Endosulfan

India is the world's largest user and producer of endosulfan (Pathak et al., 2008). Total endosulfans (mixture of  $\alpha$ -endos and  $\beta$ -endos) and its metabolite (endosulfan sulfate) concentration at urban site during whole seasons were lower than rural and mountain sites. However, its concentrations increased significantly at rural site followed by the alpine site (Fig. 2c).  $\alpha$ -Endosulfan was more dominant at rural ( $155 \text{ pg}/\text{m}^3$ ) and mountain site ( $128 \text{ pg}/\text{m}^3$ ) during hot seasons (Table 1). It may attribute to the application of endosulfan in the surrounding cultivable lands. The high concentration of endosulfan at rural (agricultural site) is consistent with GAPS study (Pozo et al., 2009). Because south-west monsoon winds enter Manipur from west and south with an annual rainfall of 1435 mm (MoEF, 2006). During the rainfall time POPs from the atmosphere were washed out and deposited to the soil and water ecosystem, when the ambient temperature raises easily re-volatilized and transported by air to distant regions (Huang et al., 2010).

### 2.4 Chlordanes

Chlordane is banned for manufacture, import and use in India, however, it has been used on a wide variety of crops.

The over all concentration of chlordanes was higher during cold seasons (132 pg/m<sup>3</sup>) and hot seasons (159 pg/m<sup>3</sup>) at mountain site, followed by hot season (106 pg/m<sup>3</sup>) and rainy season (152 pg/m<sup>3</sup>) at rural sampling site (Fig. 2d). Technical chlordane is composed of *trans*-chlordane (TC), *cis*-chlordane (CC), non *trans*-chlordane (non-TC) and non *cis*-chlordane (non-CC) in the proportion of 1.00:0.77:0.62:0.15 respectively (Buchert et al., 1989). The CC and TC were found minimal during the retreating monsoon seasons of urban and rural site while it was absent during the cold seasons at rural site. This may be due to the transition period between rainy season and cold season during which the monsoon winds begin to withdraw TC and CC from Manipur. The ratio of TC/CC is often used to distinguish fresh chlordane, which is close to the technical value of 1.56. TC/CC ratio less than 1 generally indicates of aged chlordane (Bidleman et al., 2002). Therefore, the present study indicates that at urban and rural site ratios ranges from in 0–2 which implied that used of technical chlordane and aged chlordane were present in atmosphere. Further, at the alpine site TC/CC ratios range from 0 to 6 which are higher than other two sites and implied that more fresh input of technical chlordane in this site.

## 2.5 Comparison of PAS in India with regions around the world

The average concentration of  $\alpha$ -HCH at each location of present study is comparable with others parts along the coastal length of India (Zhang et al., 2008), but mostly lower than the major Indian cities (Chakraborty et al., 2010) (Table 2). Similarly, the average concentration of  $\gamma$ -HCH is superior when compared to Toronto and Europe (Harner et al., 2004; Jaward et al., 2004), even though much lower than mega cities in India (Chakraborty et al., 2010). This may be due to unavoidable application of HCHs in developing countries especially in the tropical regions, where the use of chlorinated pesticides such as HCH is considered to be obligatory for agriculture and public health to sustain food supply and to prevent propagation of malaria (Snelson, 1977; Gouin et al., 2008).

*p,p'*-DDE level in the present study is comparable with other parts of India (Zhang et al., 2008; Chakraborty et al., 2010) but lower than China (Jaward et al., 2005). Furthermore, it is much lower than the Pearl River delta of China (120–2300 pg/m<sup>3</sup>) (Wang et al., 2006). Elevated levels of *p,p'*-DDT was observed at Manipur and the observation is similar with the observations at Porto Novo

**Table 2** Comparison of OCPs concentration of Manipur with national and global data (unit: pg/m<sup>3</sup>)

Sampling sites	Year	$\alpha$ -HCH	$\gamma$ -HCH	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	<i>p,p'</i> -DDE	$\alpha$ -ENDO	TC/CC	Reference
India									Present study
Manipur (urban) <sup>a</sup>	2009	89	80	41	82	36	30	0–2	
Manipur (mountain) <sup>a</sup>	2009	119	123	44	96	35	80	0–6	
Manipur (rural) <sup>a</sup>	2009	110	84	27	96	65	89	0–2	
Kolkata (urban)	2008	513	625	262	124	608	372	2	Zhang et al., 2008
Mumbai (urban)	2008	637	912	524	188	925	498	3	
Baroda (urban)	2008	300	1975	135	39	395	317	5	
Chennai (urban)	2008	1691	3562	620	220	2061	680	1	
Bangalore (urban)	2008	42	185	211	11	62	3	2	
Pondicherry (urban)	2008	167	437	129	55	89	369	3	
Cuddalore (rural)	2008	58	231	41	27	48	185	1	
Portonova (rural)	2008	410	686	99	387	161	992	5	
Chennai (urban) <sup>b</sup>	2006–2007	665	2432	117	40	248	155	3	Chakraborty et al., 2010
New Delhi (urban) <sup>b</sup>	2006–2007	298	3104	164	34	261	23	2	
Kolkata (urban) <sup>b</sup>	2006–2007	712	1067	197	61	268	29	1.6	
Downsview, Toronto	2000	41.4	25.6	8	10.5	30	405	1	Harner et al., 2004
Europe	2002	< 14–100	9–390	0.6–190	< 0.4–2.5				Jaward et al., 2004
The Great Lakes Basin	2002–2003	15–73	13–100				40–1090		
Toronto (urban) <sup>b</sup>	2002–2004	60	79				104	1.2	Harner et al., 2006
GAP study <sup>c</sup>	2004–2005								
Australasia		BDL-2	BDL-2		BDL-190	BDL-24	17–66	BDL-2	Pozo et al., 2006
Asia		4–145	10–68		BDL-131	BDL-58	9–101	0.3–1.6	
Europe		0.8–36	2–20		BDL-36.3	BDL-192	21–1760	BDL-2	
Africa		BDL-117	0.4–67		BDL	BDL-2	9–564	BDL-1	
North America		1.3–102	0.6–17		BDL	BDL-232	7–129	0.1–1	
Central America		BDL-1	2–5.5		BDL	BDL	22–39	0.7–0.8	
South America		BDL-2	0.4–9		BDL	BDL-4	29–14,600	BDL-0.7	
Polar region		BDL-48	BDL-9		BDL	BDL-6	BDL-60	BDL-0.6	
Asia	2004								Jaward et al., 2005
China				4.7–472	2–928	2.8–380			
Singapore				1.3–53	<1.9–16	<1.5–10			
Japan				1.4–70	4.4–146	1.62–544			
South Korea				<0.3–14	<1.9–20	<15–25			
Pearl River Delta-Summer	2005	X	X	90–1200	90–2300	50–1700		0.4–1	Wang et al., 2006

<sup>a</sup> Concentration of present study in mean value for one year; <sup>b</sup> mean concentration; <sup>c</sup> mean concentration range of all the sampling sites in each continent.

TC: *trans*-chlordane; CC: *cis*-chlordane; BDL: below detection limit; X: not detected.

jesc.ac.cn



(Zhang et al., 2008; Ramesh et al., 1989). The *o,p'*-DDT and *p,p'*-DDT ratio (0–1) of present study is much lower than that of Porto Novo (0–15) (Zhang et al., 2008) and China where dicofol usage is a major source of DDT (Li et al., 2006).

$\alpha$ -Endosulfan is the dominant isomer throughout present sampling site and is consistent with the observation of several sites located in the southern part of India (Zhang et al., 2008; Chakraborty et al., 2010). However, it is lower than Europe and South America (Poza et al., 2006).

Total chlordane has lower concentration compared to other OCPs compounds. The TC and CC ratios ranged between 0–6 which is comparable with other states of India (1–5) (Zhang et al., 2008) and also comparable with recent study from Indian cities ( $> 1.3$ ) (Chakraborty et al., 2010). However, it is much higher than Toronto ratio (1.2) (Harner et al., 2006) and Pearl River Delta–summer (0.4–1) (Wang et al., 2006).

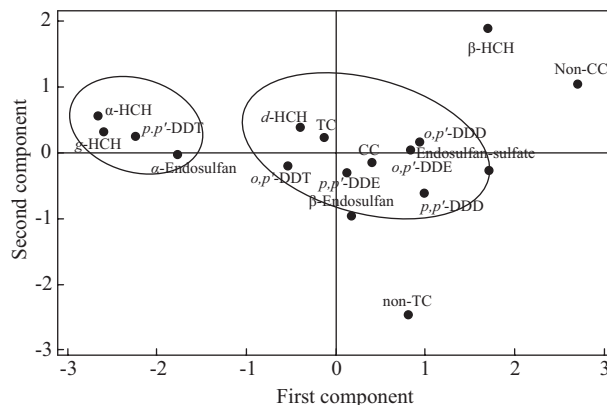
## 2.6 Statistical analysis

Principal component analysis (PCA) is a multivariate statistical method and is frequently employed in environmental science to reduce the dimensionality of data set (Cai et al., 2008). PCA was applied to evaluate the similarities and differences of distribution patterns of OCPs during four seasons of the present study. PCA was performed using Minitab 14 software. Further, SPSS 16.0 software was applied to analyze the Pearson correlation significance. PCA identifies independent factors that explain the maximum amount of mutual correlation. A single PC with Eigen value greater than one was extracted from four principal components such as PC1, PC2, PC3 and PC4. PC1 was negatively correlated with cold seasons, hot seasons, rainy seasons and retreating monsoon seasons with an Eigen value 2.4337. However, PC2 showed positive correlation with hot seasons and rainy seasons with coefficient value of 0.474 and 0.401, respectively. Moreover, PC4 showed positive correlation with cold seasons and retreating monsoon seasons with coefficient value 0.691 and 0.227 respectively. PCA showed positive correlation ( $p < 0.05$ ) between cold seasons and hot seasons. Similarly, cold seasons and rainy seasons were significantly correlated ( $p = 0.007$ ). However, highly correlation ( $p < 0.01$ ) was observed between hot seasons and rainy seasons.

PCA also showed the distributions pattern of OCPs in ambient air (Fig. 4). This demonstrates two clusters while other compounds were scattered. The parent compounds and more volatile compounds such as  $\alpha$ -HCH,  $\alpha$ -endos, *p,p'*-DDT etc. were clustered together. Again, degraded metabolites such as endosulfan-sulfate, *p,p'*-DDE, *o,p'*-DDE, demonstrate cohesive clustering. However, emission of OCPs in ambient environment depends not only on sources during various seasons but also on wide range of temperatures.

## 2.7 Back Trajectory analysis

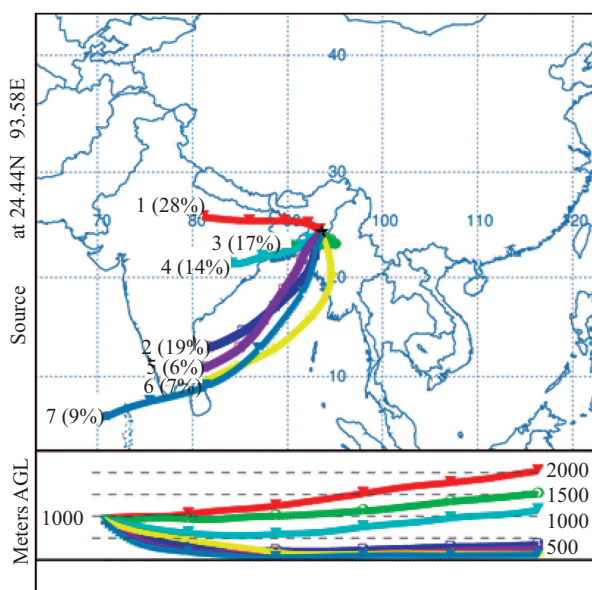
To investigate the possible sources of OCPs, air mass backward trajectories were calculated round the year during the entire sampling period using the HYSPLIT model



**Fig. 4** Distribution pattern of OCP in air as cluster and scatterings of OCP compounds.

(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 (Draxler and Rolph, 2003).

Figure 5 shows back trajectory analysis of air mass movement for whole year. Seven kinds of clusters show air mass with different percentage and originate from different regions. Cluster 1 (28%) contributes major part of the air parcel mass originate from north part of India ending up at Manipur. Clusters 2 (19%), 5 (6%) and 6 (7%) air masses originating from southern part of India crossing through Indian Ocean ending up at present study sites. The coastal length of Indian cities was found to be polluted by OCPs (Zhang et al., 2008), possibly being that air mass originate from coastal area might affect to present study atmosphere. Furthermore, cluster 3 (17%) and cluster 4 (14%) air masses originate from north east India crossing through Kolkata and Bangladesh ending up at Manipur. High levels of OCPs have been reported from north (New Delhi and Agra), south (Chennai and Bangalore) and eastern part of India (Kolkata) (Chakraborty et al., 2010). Hence the elevated level of OCPs at Manipur might have



**Fig. 5** Back trajectory analysis.

been influenced by the long range atmospheric transport of OCPs from varied corners of India apart from local emission due to their use in agriculture or for vector control programs.

### 3 Conclusions

The amount of OCPs monitored at three sampling locations of Manipur (urban, mountain and rural) showed comparable with others parts of India. The potential sources of OCPs might be the local emission mainly from agricultural activities. The study suggests that air is mixed together inside the landlocked site. There is not much variation in OCPs concentrations among urban, alpine and rural sites. Distinct seasonal trends were found in OCPs concentrations at three sites, with high concentration of DDTs during the hot period and low concentration during the cold season. The high levels of those OCPs could be attributed to the seasonal usage of pesticides and long range atmospheric transport Asian monsoon. Very high *p,p'*-DDT levels in hot period at urban, rural and mountain sites were probably related to the seasonal usage of DDT especially to combat vector borne diseases. Likewise high  $\alpha$ -HCH and  $\gamma$ -HCH concentrations were obtained during hot period at rural and alpine sites. Endosulfans were found to be high level during the hot and rainy season from the surrounding cultivable lands. Long range atmospheric transport from southern part of India might be responsible for elevated level of endosulfans because of its use in cotton plantation and tea plantation.

### Acknowledgments

This work was supported by the Government of China and Human Resource Development Ministry, Government of India for financial assistance in the form of Chinese Government fellowship (CSC No. 2008356005). The author would like to thank Mr. Chen Wei for his analytical support.

### References

- Baburajendran R, Venugopalan V K, Ramesh R, 1999. Pesticide residues in air from coastal environment, South India. *Chemosphere*, 39: 699–1706.
- Battu R S, Singh B, Kang B K, 2004. Contamination of liquid milk and butter with pesticide residues in the Ludhiana district of Punjab state, India. *Ecotoxicology and Environmental Safety*, 9: 324–331.
- Beyer A, Wania F, Gouin T, Mackay D, Matthies M, 2003. Temperature dependence of the characteristic travel distance. *Environmental Science and Technology*, 37(4): 766–771.
- Bidleman T, Jantunen L, Helm P, Brorstrom-Lunden E, Junnto S, 2002. Chlordane enantiomers and temporal trends of chlordane isomers in Arctic air. *Environmental Science and Technology*, 36: 539–544.
- Bohlin P, Jones K C, Strandberg B, 2010. Field evaluation of polyurethane foam passive air samplers to assess airborne PAHs in occupational environments. *Environmental Science and Technology*, 44: 749–754.
- Buchert H, Class T, Ballschmiter K, 1989. High-resolution gas chromatography of technical chlordane with electron capture and mass selective detection. *Resinous Journal of Analytical Chemistry*, 61: 211–217.
- Cai Q Y, Mo C H, Wu Q T, Katsoyiannis A, Zeng Q Y, 2008. The status of soil contamination by semi volatile organic chemicals (SVOCs) in China: A review. *The Science of the Total Environment*, 389: 209–224.
- CAPE (Community Action for Pesticide Elimination), 2005. Fact sheet lindane's dirty secret: Indian facilities dump toxic waste. <http://www.panna.org/lindane/resources>.
- Chakraborty P, Zhang G, Li J, Xu Y, Liu X, Tanabe S et al., 2010. Selected organochlorine pesticides in the atmosphere of major Indian cities: levels, regional versus local variations, and sources. *Environmental Science and Technology*, 44: 8038–8043.
- Chen D Z, Liu W J, Liu X D, Westgate J N, Wania F, 2008. Cold trapping of persistent organic pollutants in the mountains of western Sichuan, China. *Environmental Science and Technology*, 42: 9086–9091.
- Curtis C F, 2002. Should the use of DDT be revived for malaria vector control? *Biomedica*, 22(4): 455–461.
- Daly G L, Wania F, 2005. Organic contaminants in mountains. *Environmental Science and Technology*, 39(2): 385–398.
- Draxler R R, Rolph G D, 2003. HYPPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model. Accessed via NOAA ARL READY Website. <http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory.
- Gevao B, Foday M, Jaward S U, Abdul N A G, 2006. Occurrence and concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in coastal marine sediments in Kuwait Baseline. *Marine Pollution Bulletin*, 58: 424–455.
- Gouin T, Wania F, Ruepert C, Castillo L E, 2008. Field testing passive air samplers for current use pesticides in a tropical environment. *Environmental Science and Technology*, 42: 6625–6630.
- Guo Y, Yu H Y, Zeng E Y, 2009. Occurrence, source diagnosis, and biological effect assessment of DDT and its metabolites in various environmental compartments of the Pearl River Delta, South China: A review. *Environmental Pollution*, 157: 1753–1763.
- Gupta P K, 2004. Pesticide exposure–Indian scene. *Toxicology*, 198: 83–90.
- Harner T, Pozo Gallardo K, Gouin T, Macdonald A M, Hung H, Cainey J et al., 2006. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environmental Pollution*, 144: 445–452.
- Harner T, Shoeib M, Diamond M, Stern G, Rosenberg B, 2004. Using passive air sampling to assess urban-rural trends for persistent organic pollutants, polychlorinated biphenyls and organochlorine pesticides. *Environmental Science and Technology*, 38: 4474–4483.
- Huang D Y, Peng P, Xu Y G, Sun C X, Deng H M, Deng Y Y, 2010. Distribution, regional sources and deposition fluxes of organochlorine pesticides in precipitation in Guangzhou, South China. *Atmospheric Research*, 97: 115–123.
- Iwata H, Tanabe S, Sakai N, Nishimura A, Tatukawa R, 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implication for global redistribution from lower altitudes. *Environmental Pollution*, 85: 15–33.
- Jaward F M, Farrar N J, Harner T, Sweetman A J, Jones K C, 2004. Passive air sampling of PCBs, PBDEs and

jesc.org.cn

- organochlorine pesticides across Europe. *Environmental Science and Technology*, 38: 34–41.
- Jaward F M, Zhang G, Nam J J, Sweetman A J, Obbard J P, Kobara Y et al., 2005. Passive air sampling of polychlorinated biphenyls, organochlorine compounds and polybrominated diphenyl ethers across Asia. *Environmental Science and Technology*, 39: 8638–8645.
- Jones K C, Voogt P De, 1999. Persistent organic pollutants (POPs): state of the science. *Environmental Pollution*, 100: 209–221.
- Kutz F W, Wood P H, Bottimore D P, 1991. Organochlorine pesticides and polychlorinated biphenyls in human adipose tissue. *Reviews of Environmental Contamination and Toxicology*, 120: 1–82.
- Li J, Zhu T, Wang F, Qiu X H, Lin W L, 2006. Observation of organochlorine pesticides in the air of the Mt. Everest region. *Ecotoxicology and Environmental Safety*, 63: 33–41.
- MoEF (Ministry of Environment and Forest) Manipur, 2006. Profile on state of environment report of Manipur 2006–07. Government of Manipur, Imphal. 1–16.
- Pathak R, Suke S G, Ahmed R S, Tripathi A K, Guleria K, Sharma C S et al., 2008. Endosulfan and other organochlorine pesticide residues in maternal and cord blood in North Indian population. *Bulletin of Environmental Contamination and Toxicology*, 81: 216–219.
- Pozo K, Harner T, Lee S C, Wania F, Muir D C G, Jones K C, 2009. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. *Environmental Science and Technology*, 43: 796–803.
- Pozo K, Harner T, Wania F, Muir D C G, Jones K C, Barrie L A, 2006. Toward a global network for persistent organic pollutants in air: Results from the GAPS study. *Environmental Science and Technology*, 40: 4867–4873.
- Ramesh A, Tanabe S, Iwata H, Tatsukawa R, Subramanian A N, Mohan D et al., 1990. Seasonal variation of persistent organochlorine insecticide residues in Vellar River waters in Tamil Nadu, South India. *Environmental Pollution*, 67: 289–304.
- Ramesh A, Tanabe S, Tatsukawa R, Subramanian A N, Palanichamy S, Mohan D et al., 1989. Seasonal variations of organochlorine insecticide residues in air from Porto Novo, South India. *Environmental Pollution*, 62: 213–222.
- Sharma V P, 2003. Malaria and poverty in India. *Current Science*, 84: 513–515.
- Shen L, Wania F, 2005. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *Journal of Chemical and Engineering Data*, 50(3): 742–768.
- Snelson J T, 1977. The importance of chlorinated hydrocarbons in world agriculture. *Ecotoxicology and Environmental Safety*, 1(1): 17–30.
- US EPA (United States Environmental Protection Agency), 1982. Environmental monitoring and support laboratory, Cincinnati, OH 45268. EPA-600/4-82-023.
- Wania F, Mackay D, 1996. Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology*, 30(9): 390A–396A.
- Wania F, Westgate J N, 2008. On the mechanism of mountain cold-trapping of organic chemicals. *Environmental Science and Technology*, 42: 9092–9098.
- Wang X P, Yao T D, Cong Z Y, Yan X L, Kang S C, Zhang Y, 2006. Gradient distribution of persistent organic contaminants along northern slope of central-Himalayas, China. *The Science of the Total Environment*, 372: 193–202.
- Xiao H, Li N, Wania F, 2004. Compilation, evaluation, and selection of physical-chemical property data for  $\alpha$ -,  $\beta$ - and  $\gamma$ -Hexachlorocyclohexane. *Journal of Chemical and Engineering Data*, 49: 173–185.
- Zhang G, Chakraborty P, Li J, Sampathkumar P, Balasubramanian T, Kathiresan K et al., 2008. Passive atmospheric sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in urban, rural, and wetland sites along the coastal length of India. *Environmental Science and Technology*, 42: 8218–8223.