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PII: S0048-9697(18)32902-4
DOI: doi:10.1016/j.scitotenv.2018.07.414
Reference: STOTEN 28008

To appear in: *Science of the Total Environment*

Received date: 2 June 2018
Revised date: 28 July 2018
Accepted date: 29 July 2018

Please cite this article as: Paromita Chakraborty, Gan Zhang, Jun Li, P. Sampathkumar, Thangavel Balasubramanian, Kandasamy Kathiresan, Shin Takahashi, Annamalai Subramanian, Shinsuke Tanabe, Kevin C. Jones , Seasonal variation of atmospheric organochlorine pesticides and polybrominated diphenyl ethers in Parangipettai, Tamil Nadu, India: Implication for atmospheric transport. Stoten (2018), doi:10.1016/j.scitotenv.2018.07.414

Seasonal variation of atmospheric organochlorine pesticides and polybrominated diphenyl ethers in Parangipettai, Tamil Nadu, India:Implication for atmospheric transport

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Abstract

During 1990s, residues of several persistent organic pollutants (POPs) in different environmental matrices have been reported from a tropical coastal site, Parangipettai (PI), located along the bank of the Vellar River in Tamil Nadu. Hence to fill the existing datagap after the strict ban on several POPs, high volume air sampling was conducted in PI to study the variability of atmospheric pesticidal POPs and polybrominated diphenyl ethers (PBDEs) during summer, pre-monsoon and monsoon. Emission source regions were tracked by using five days back trajectory analysis. Derived range of air concentrations in pg/m^3 were: DDTs; BDL - 1976; HCHs, 260-1135, HCB; 52- 135, chlordanes; 36-135, endosulfans; 66-1013. $\sum_6$PBDE ranged between 25-155 with highest concentration in summer followed by pre-monsoon and monsoon. Atmospheric DDT and HCH in PI has drastically reduced by several thousand folds from the past report thereby showing the strict ban on agricultural use of these compouds. During monsoon fresh source of *o,p'*-DDT, *trans*-chlordane and *α*-endosulfan was evident. Unually higher level of endosulphan sulfate in PI seems to be likely effected by the air mass originating from a neighbouring state Kerela, where endosulfan has been extensively used for cashew plantations. Similarly in summer, the day showing the highest level of PBDEs, the sample was concurrently impacted by air parcel comprised of two major clusters, 1 (25%) and 2 (49%) that traversed through the the metropolitan cities like Bangalore and Chennai. Dominance of BDE-99 over BDE-47 in Parangipettai is in line with the PBDE profile reported from Chennai city during the similar time frame. Average concentration of tetra and penta BDE congeners in summer samples were nearly 2-3 folds higher than pre-monsoon or monoon. Given the fact that strong localised source for heavier BDE congeners are lacking in PI, regional atmospheric transport from the strong emission source regions in Chennai.

Keywords: Parangipettai; OCPs; PBDEs; High Volume air sampling; Back Trajectory

1. Introduction

Being predominantly an agricultural country, for nearly five decades the pesticidal persistent organic pollutants (POPs) have been manufactured and widely used for agriculture in India until they were banned in 1997 (Aktar et al., 2009). During 1990s, about 70 % of pesticides used in India was comprised of hexachlorocyclohexane (HCH), *p,p'*-dichlorodiphenyltricholoethane (DDT) and malathion (Gupta et al., 2004). Ongoing use of OCPs like DDT for vector control programs resulted in the atmospheric outflow from the urban centers of India (Chakraborty et al ., 2010). Even after the strict ban on agricultural use of OCPs in India, due to the extensive usage in the past, soil is now acting as a secondary source for atmospheric OCPs (Chakraborty et al., 2015).

Production and usage of polybrominated diphenyl ethers (PBDEs) as brominated flame retardants is a relatively recent phenomenon than that of OCPs (De Wit and Cynthia, 2002). PBDEs are a class halogenated compounds having physico-chemical properties similar to a number of other POPs, which are known to persist and undergo bioaccumulation.Since PBDEs do not bind chemically to the products (open system applications), the chemicals may continuously leak to the environment. Industries using PBDEs in their production (i.e., car producers, textile and electronic industries) are the major sources (Ter Schure, 2000). PBDEs added as additives to various commercial products owing to their flame retarding property, may end up in the solid waste stream. In a developing country like India where open burning of dumped waste is a regular practice, PBDEscan easily volatilize in the atmosphere (Chakraborty et al., 2017).Three major commercial formulations of PBDEs are: penta (is comprised of about 74%BDEs-47 and 99, along with smaller quantity of other tetra-, penta-, and hexa-BDEs); octa (amixture of hexa (10-12 %), hepta- (44-46 %), octa- (33-35 %), nona- (10-11 %); and deca (98 % decabromodiphenyl ether (BDE 209) and 2% various nona-BDEs)

(McDonald, 2002; Alcock et al., 2003) .

Persistence and toxic impacts of OCPs and PBDEs are of serious concern due to the carcinogenic and endocrine disrupting effects. Being semi-volatile in nature, these organic pollutants are likely to be emitted from various primary and secondary sources, and the atmosphere often plays a key role in their transport within the immediate vicinity of POPs sources as well as in their widespread distribution to those regions where these compounds have never been used (Wania, 2003).

The stateTamil Nadu where Parangipettai (PI) is located, tops the three highest consumers of technical grade pesticides in India (NASTEC,2003). High levels of OCPs and PBDEs in Chennai, Cuddalore and Parangipettai in the state of Tamil Nadu, were reported along the coastal length of India (Zhang et al., 2008). Among the coastal cities, the urban transect of Chennai was found with relatively highlevel of atmospheric OCPs (Chakraborty et al., 2010) and PBDEs (Chakraborty et al., 2017). Relatively high level of POPs have been reported in different environmental matrices ofPI compared withother parts of the world (Ramesh et al., 1989; Kannan et al., 1992; BabuRajendran et al., 1999; Subramanian et al., 2007; Tanabe and Kunisue, 2007).

After the ban on OCPs there is paucity of data on atmospheric POPs from PI. Therefore this study aims to elucidate the atmospheric levels of OCPs and PBDEs in PI and seasonal variability during summer, pre-monsoonal and monsoonal events by using high volume sampling events. Finally, the emission source region was tracked using multivariate principal component analysis and back trajectory analysis.

2. Materials and Methods:

2.1.Study area:

In the state of Tamil Nadu, Parangipettai(Lat. 11°26´30´´N;Long. 79° 45´48´´E), is mainly a

coastal fishing village situated on the north bank of the mouth of the Vellar river in the Cuddalore district. Agriculture is practiced in the areas surrounding the Vellar River. State Industries Promotion Corporation of Tamil Nadu (SIPCOT) Chemical Industrial Estate located on the seaward side of the Cuddalore-Chidambaram Road, stretching from Pachaiyankuppam in the North to Semmankuppam in the South is 8 km from Cuddalore.

2.2.Sampling

Weekly gaseous phase samples were collected using a high volume sampler, covering summer, pre-monsoon and monsoonal seasons ofParangipettai during May to November in 2006 (Fig 1). Air volumes of nearly 430 m^3 in 24h was drawn through a quartz microfiber filter (QFF) (QMA, 20.3×25.4 cm, Whatman, Maidstone, England) and polyurethane foam (PUF) plugs of 6.5 cm in diameter-7.5 cm in thickness (a density of 0.030 gm/cm^3) using a high-volume sampler (of the Anderson type) at an average flow rate of $0.3m^3min^{-1}$. Prior to sampling, the QFFs were baked in a muffle furnace at 450 °C for 4 h 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. During the sample collection, gloves were worn, and PUF plugs were handled using acetone-rinsed stainless steel tongs. After sampling, all the samples were wrapped in aluminium foil, sealed in Teflon bags and then transported to the laboratory and stored at-20°C until extraction. Meteorologicaldata, such as temperature, relative humidity, wind speed/direction, and precipitation were recorded at each sampling event.

2.3 Extraction and analysis

PUF plugs were spiked with 20 ng of 2,4,5,6-tetrachloro-m-xylene (TCmX), BDE 181as

surrogates, and Soxhlet-extracted with dichloromethane for 18 h. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract was concentrated and solvent exchanged to n-hexane and purified on an 8mm i.d. alumina/silica column packed, from the bottom to top, with neutral alumina (6 cm, 3 % deactivated), neutral silica gel (10 cm, 3 % deactivated), 50 % (on a weight basis) sulfuric acid silica (10 cm), and anhydrous sodium sulfate (1 cm). Before use, neutral alumina, neutral silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 18 h with DCM, and then baked for 12 h in 250, 180, and 450 ºC, respectively. The column was eluted with 50 ml of DCM/hexane (4:6). The fraction was concentrated to 25 µl under a gentle high purity nitrogen stream. OCPs analysis were carried out on a Finigan-TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m×0.25 mm×0.25 mm), operating under single ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 ml min^{-1} under constant-flow mode. Details of the method have been given elsewhere (Chakraborty et al 2010). PBDEs were analyzed separately on a Shimadzu QP2000 GCMS with a negative chemical ionization (NCI) source in SIM mode using ammonia as the reagent gas. Details of the instruments, GC temperature programs, and monitored ions have been reported elsewhere(Gouin et al., 2005).

A total of 8 non-deca PBDEs (BDE-28, -35, -47, -99, -100, -153, -154, -183) were analysed but only 6 PBDEs (BDE-28, -35, -47, -99, -100, -154), and 14 organochlorine pesticides viz., *α*, *β*, *γ*, *δ*-isomers of hexachlorocyclohexane (HCH), *o,p′* -dichlorodiphenyltrichloroethane (DDT), *p,p′* -DDT, and *p,p′* -dichlorodiphenyldichloroethylene (DDE), *cis*-(CC) and *trans*-chlordane (TC) and trans-nonachlor (TN); *α* and *β*-isomers of endosulfan, endosulfan sulfate and hexachlorocyclobenzene (HCB) were regularly detected in PUF samples and were quantified.

2.4 QA/QC

Chemical standards were purchased from Accustandard Co. US. Laboratory and field (i.e., samplers sent to/from field sites unopened) blanks consisting of pre-extracted PUF disks were extracted and analyzed in the same way as the samples. Analytical blanks consisted of nine field and three laboratory blanks. There was no significant difference (t-test significance, <95%) between analyte concentrations in the laboratory and field blanks, indicating contamination was negligible during transport, storage, and analysis. In addition for all the samples, peaks were only integrated when the signal-to-noise ratio was≥3; otherwise, they were considered not detects. The limit of detection (LOD) defined as: average blank+ 3 × standard deviation for OCPs in pg/m^3 for PUF plugs were as follows: 0.97 for α-HCH, 0.2 for β-HCH, 1.1 for γ-HCH, 0.3 for δ-HCH, 0.7 for TC and CC, 0.5 for *p,p'*-DDE, 1.3 for *o,p'*-DDT, 1.6 for *p,p'*-DDT, and 0.97 for α-endosulfan and 0.9 for β-endosulfan. Concentrations lower than LOD was considered non-detectable for quantified OCPs.LOD for PBDEs increased with the level of bromination and varied between 0.1-3.7 pg/m^3. In QFFs the target analytes were below detection limit. Surrogate recoveries were between 72-94 % for TCmX (average 81 %) and 83-113 % for BDE-181 (average 89 %).

2.5. Back Trajectory Analysis

In order to assess the possible sources of OCPsusing the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7), a comprehensive modelling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler, 2003) was used. For each of the sampling date,five days back trajectories ending at 0600 UTC in PI, i.e. 11:30 local time were plotted. In order to classify the air masses, the trajectories at a level of 500m was considered which is about half the height of the mean day time atmospheric boundary layer (ABL) and represents general transport conditions in the

ABL.

Fig. 1 represents the four major clusters of air mass backward trajectories at the sampling site, PI.The corresponding trajectories could be divided into four types according to the direction and the passed area.

Cluster 1 (25 %): The air mass of this cluster originated from Arabian Sea crossing the southern state particularly Karnataka and enters Tamil Nadu from west coast before ending atPI.

Cluster 2 (49 %): This air mass originated from the Indian Ocean and after traveling through the southern state of Karnatakasimilar to Cluster 1, after crossing Chennai, the capital city of Tamil Nadu,ultimately ends at PI.

Cluster 3 (10 %): This parcel of air orginated from land inKerala and from south-west it entered Tamil Nadu from the deep south and finally ends in the south east coast of Tamil Nadu at PI.

Cluster 4 (16 %): This air mass originated from the Bay of Bengal and enters ends at PI from the south-east coast.

2.6. Statistical analysis

Principal component analysis (PCA) and other statistical analysis were performed using SPSS version 22.0 software.

3. Results and Discussion

3.1.1 Occurrence and seasonal variability

3.1.1.1 Organochlorine pesticides

In Parangipettai the sum of all the quantified OCPs ranged from 869 to 3537 pg/m^3 with an average of 1779 pg/m^3. Overall range of OCPs in PIduring summer, pre-monsoon and monsoonal phases have been given in Table 1. Among OCPs *p,p'*-DDT were higher during

summer followed by pre-monsoon and monsoon (Fig 2). Comparison of atmospheric OCPs in PI with other parts of India and other studies across the world have been given in Table S1. The levels of α- HCH, γ-HCH, *p,p'*-DDE, *p,p'*-DDT, *o,p'*-DDT, TC, CC and α-endosulfan were lesser than Indian metropolitan cities viz. Bangalore, Delhi, Kolkata, Chennai and Mumbai (Chakraborty et al., 2010). HCH isomers in this study are higher compared with other Asian cities like Guangzhou and Hong Kong (Li et al., 2007) and north American cities like Veracruz City Tapachula (Alegria et al., 2008).

HCHs

Range of ∑HCHs (sum of α, β, γ and δ isomers of HCH) in pg/m^3 varied between 480-603, 260-1135 and 279-636 during summer, pre-monsoon and monsoon respectively. In PIγ–HCH contributed about 40 to 70 % ∑HCHs. Dominance of γ–HCHin all the seasons reflect the fresh use of Lindane. An averagecontribution ofα, β and δ-HCH were 33 %, 8 % and 3 % respectively. Such isomeric composition of HCH indicates thelimited usage of technical HCH in PI. But the level of HCHs has drastically decreased by several thousand folds lower than the previous study at Parangipettai (Baburajendran et al., 1999) there by clearly showing the restricted use of technical HCH after it was strictly banned in India.

Although the average atmospheric α and γ-HCH concentration in PI is several folds lower than major Indian cities (Chakraborty et al., 2010), but the level is higher than Asian countries like suburban site of Guangzhou in south China, Hong Kong, Japan, Korea and USA (Table S1)**.**

HCH isomers were high with the maximum levels of γ-HCHin the pre-monsoon season (Fig 2). A significant difference was observed in the occurrence of γ-HCH between pre-monsoonal and monsoonal phases. During the monsoonal phase the median value for α/γ-HCH ratio was greater than 1 (Fig 3a). Current observation indicates the use of technical HCH in addition to Lindane and is consistent with other parts of India (Chakraborty et al., 2010). Highest level of all the HCH isomersduring late September and increasing level of α-HCH in October can be

associated with the application of technical HCH during flowering season of paddy (Baburajendran et al., 1999).

DDTs

Sum of DDT isomers and metabolites (ΣDDTs, sum of *p,p*'-DDT, *o,p*'-DDT and *p,p*'-DDE), ranged from 1314- 1976 pg/m^3 in summer followed by pre-monsoon (351-1024) and monsoon (below detection limit to 651) (Fig.2). India has provision of restricted DDT usage in vector control programs but has banned DDT for agricultural usage. Dominance of *p,p*'-DDT contributing about 60 % of the total DDT concentration indicates a fresh source and is consistent with the observation along the coastal length of India (Zhang et al., 2008). Although average *p,p'*-DDT in PI is comparable or lower than other sites of India but *o,p'*-DDT is lowest compared to other places in India or across the globe (Table S1).About 33% of total DDTs is comprised of *p,p*'-DDE reflecting an aged DDT source. The average *p,p*'-DDE concentrations is lower than other places in India but slightly higher than Kolkata (Chakraborty et al., 2010) and comparable to China and Hong Kong (Table S1).Overall atmospheric DDT level has decreased by nearly five times compared with the previous study(Baburajendran et al., 1999) due to the strict ban on the use of technical DDT for agricultural purpose.

Both *p,p'*-DDT and *p,p'* –DDE were strongly correlated with each other (R^2>0.7) and concentration of these two pesticidal POPs were maximum during summer followed by pre-monsoon and monsoonal phases (Fig 2). Also *p,p'*-DDT and *p,p'* –DDE in summer significantly (p<0.0001) differed from the pre-monsoon and monsoonal phases. Moreover the ratio of *p,p'*-DDE and *p,p'* –DDT were maximum in pre-monsoon and summer (Fig 3b)when the ambient temperature is relatively high compared with the monsoon.Historically applied *p,p*'-DDT gets converted to *p,p*'-DDE in soil and tropical climate favors the emission of *p,p*'-DDE from the soil due to high temperature round the year (Chakraborty et al., 2015). During the pre-monsoon period, the *o,p*'-DDT/*p,p*'-DDT ratio (0.06-0.22) was less than the technical

DDT (technical DDT~0.3), but the ratio increased during the monsoonal phase (0.4-0.8). Since the vapour density of *o,p'*-DDT is 7.5 times greater than *p,p'*-DDT (Cliath and Spencer, 1972), higher *o,p'*-DDT reflects fresh application of DDT in PI during monsoonal phase possibly to combat vector borne diseases.

Endosulfan

Overall range of sum of endosulfan isomers and metabolites in PI(in pg/m^3) were between 188-351, 68-290 and 66-1012 during summer, pre-monsoon and monsoon respectively (Table 1 & Fig 2). In the past, endosulfan has been extensively used around the Vellar estuary (Rajendran and Venugopalan, 1991). More than 81 % of the total concentration of endosulfanwas comprised of endosulfan sulfate most likely resulted from historical usage of technical endosulfan. Range of endosulfan isomers in PI is lower than other parts of India (Chakraborty et al., 2010), China (Li et al., 2007) and Mexico (Alegria et al., 2008).

Endosulfan sulfate was maximum during summer followed by pre-monsoon and monsoonal phases excluding one outlier in monsoon showing highest level of endosulfan (Fig 2). Moreover a significant difference (p<0.001) in the level of endosulfan was observed between pre-monsoon and monsoon. High summer concentrations of this persistent metabolite suggests the possibility of outgassing of endosulfan sulfate in the air from soil, consistent with other parts of India (Chakraborty et al., 2015).

Technical grade endosulfan comprises of two stereo isomers, α and β-endosulfan in a ratio of 7:3 (Sunderam et al., 1992). In PIthis ratio varies between 1-6 (average 0.7) with α-endosulfan contributing 15 % and β-endosulfan 4 % of the total endosulfans. Higher α-endosulfan on 19th and 27th Septemberand14th November indicateson spot application of technical endosulfan on those dates. It is interesting to note that the air parcel (Cluster 3) reaching PI on 5thOctober represented over 60 % trajectories originating from Kerala before endingatPI (Fig 1). This date was recorded with maximum concentration of endosulfan sulfate which was 3 to 5 orders

higher than other samples. Apart from local usage, endosulfan has been extensively used in the neighbouringstate, Kerala for cashew plantations(Mahapatro and Panigrahi, 2014).Atmospheric endosulfan sulfate was found to be high in a coastal site of Kerala (Zhang et al., 2008). Re-emission of OCP residues from surface soil has been reported from different parts of India (Chakraborty et al., 2010). Therefore it is suggested that endosulfan sulfate emitted from Kerala and southern part of Tamil Nadu might have been transported with the monsoonal air parcel toPI on 5thOctober, resulting in an unusually high concentration of endosulfan sulfate on that particular date.

Chlordane

The three isomers of chlordane viz., trans-, cis-, and trans-nonachlor in pg/m^3 were in the range of 256-606; 189-434 and 36-840 for summer, pre-monsoon and monsoon respectively. The overall range of chlordanes is much lower than other parts of India (Chakraborty et al., 2010) and Guangzhou, China but comparable to Hongkong (Li et al., 2007). In PIthe total chlordanes concentration was dominated by the *cis* isomer (61 %) over the *trans* isomer (25 %).

It is interesting to note that in summer,low TC/CC ratio (avg<0.5)(Fig 3c) suggests a weathered chlordane source. High temperature in this tropical site might have triggered the degradation of trans-chlordane (Halsall et al., 1998). TC concentrations significantly differed between pre-monsoon and monsoon (p<0.001).During monsoon the TC/CC ratio was close to unity for few samples thereby indicating the possibility of a fresh chlordane input. In places where continuous usage of chlordane was prevalent, the *trans*-nonachlor/*trans*chlordane ratio varies between 0.15-0.45. and the average TN/TC ratio in PIis0.6.

HCB

HCB is not only used as fungicide but also generated as a byproduct during the production and usage of several agrochemical and industrial chemicals and has long half-lives in the air. Furthermore, HCB has been released into the environment by waste incineration (van-Birgelen, 1998), industrial waste (Chakraborty et al., 2015) and in a variety of reactions where it persists because of its thermodynamic stability (Breivik K, 2004). Range of HCB concentrations (in pg/m^3) derived from this study showed an increasing order starting from summer 82-92 followed by 52-101 in pre-monsoon and 78-135 during monsoon (Fig 2). In the developed countries far lower concentration has been recorded typically 50 pg/m^3 (Bailey, 2001). HCB was never registered as a pesticide in India. But during 1995-97,42612 t of technical grade HCB was produced (IMCF, 2000).

HCB has been found to be ubiquitously distributed during the entire sampling campaign but there was a slight elevation in the concentration during monsoon. Even though PI is a village but it is located in an industrial district, Cuddalore. In India in the past, chemical industries were suggested to be the possible source of HCB (Nair and Pillai, 1989).In the recent years industries were found to impact the atmospheric HCB concentration in the Indian metropolitan cities (Chakraborty et al., 2010).

3.1.1.2. PBDEs

Overall atmospheric concentrationof Σ_6PBDEs ranges between 25-155 pg/m^3 (Avg±Stdev; 56±29) in PI(Table 1 and Fig.4). Average PBDE concentration in PI is comparable with the urban sites of USA, while the low emission areas like rural, agricultural region, sites close to water bodies were atleast two folds lower than PI (Hoh and Hites, 2005, Stanberg et al., 2001). Range of PBDEs in PI is within the range of PBDEs observed during PUF based passive air sampling (PAS) in Europe (Jaward et al., 2004) and China (Jaward et al., 2005). Along the coastal length of India although maximum PBDEs was observed in Chennai the PAS site in

Parengipettai was found with least PBDE concentration (Zhang et al., 2008). Several folds higher PBDE levels have been reported along urban-suburban-rural transects from the metropolitan cities of India (Chakraborty et al., 2017).

Seasonal range of Σ_6PBDEs in pg/m^3 followed a strict trend: summer (83-155)>pre-monsoon (32-71)> monsoon (24-47) (Fig 4). Two to three times higher concentrations of terta, penta and hexa homologues during summer compared with pre-monsoon and monsoon can be reasoned with higher summer time temperature.Interestingly, summer PBDE concentrations were significantly differentfrom pre-monsoon and monsoon(p<0.01). Irrespective of the season, BDE-99 was dominant followed by BDE-47.Such a compositional profile of PBDE was interpreted as an indication of far greater use of the penta commercial formulations, Bromkal -70DE and DE-71 in the commercial and electrical products in India (Chakraborty et al., 2017). BDE-47 and –99 altogether contributed three fourth of the total PBDE concentration in PI similar to Chennai particularly the urban centers due to informal electronic waste recycling and industrial emissionsfrom plastic industries and automobile sector (Chakraborty et al., 2017; Zhang et al., 2008). Since no potential source of PBDEs exist in this coastal village, higher tetra, penta and hexa homologues in PI suggests atmospheric transport from the hotspots in Chennai and SIPCOT industrial belt in Cuddalore district. Higher abundance of lighter congeners like BDE-28 and -35 particularly during monsoon altogether contributing 13 to 31% of total atmospheric PBDE concentration, might be associated with open burning of dumped solid waste (Chakraborty et al., 2017).

3.2.PCA and Back trajectory analysis

Compounds showing over 85 % detection frequency were subjected to principal component analysis. Variance for PC-1, 2 and 3 were 30 %, 19 % and 16 % respectively with best fit ≥0.5 (fig. S1). The first component was loaded with *p,p'*-DDT and *p,p'* –DDE contributing about

one third of total OCPs and BDE-47 and BDE-99 contributing nearly three fourth of total PBDEs. All the episodes of high concentrations of these four compoundsduring summer and pre-monsoonwere impacted by the air parcel (Cluster 1 and Cluster 2) traversing through land mass through major metropolitan cities like Bangalore in Karanataka and Chennai in Tamil Nadu before ending at Parangipettai (Fig 1 and Fig S2). Furthermore Cluster 1 and 2 impacted over 85 % concentration of these four compounds (Fig S3). Highest atmospheric *p,p'*-DDT, *p,p'*–DDE and BDE-47 and 99 concentrations in PI was witnessed on a hot summer day (22nd June) impacted by both Cluster 1 and 2. On this day the concentrations of *p,p'*-DDT, and BDE-47 and -99 were two to ten times higher than average concentration observed during pre-monsoon and post monsoon seasons. Major metropolitan cities like Bangalore and Chennai in south India can use DDT for vector control (Zhang et al., 2008).Among major metropolitan Indian cities, highest level of *p,p'*–DDE was observed in Chennai and higher concentration of this metabolite was associated with breakdown of *p,p'*-DDT under tropical climate condition (Chakraborty et al., 2010). Similarly in PI, more than 50% of the total PBDE concentration has been contributed by BDE-99. Chakraborty et al.,2017 reported substantially elevated concentration of BDE-99 from the urban centers and a rural site of Chennai city. Cluster-1 and 2 contributing about three fourth of the total air mass most likely transported the emitted BDE-99 from the source regions in Chennai city (Chakraborty et al., 2017) before ending in this coastal village. Long range atmospheric transport of BDEs in the remote marine atmosphere has been reported in both the European Arctic (Möller et al., 2011)), between Southeast Asia and Antarctica (Möller et al., 2012)and between the North and South Atlantic (Xie et al., 2011). Hence this component has been attributed to atmospheric transport as a potential source for these compounds.

PC-2 was loaded with compounds having relatively higher volatility viz., TC, TN, HCB and

o,p' –DDT among pesticidal POPs and lighter PBDE congeners, BDE-28 and -35. It is to be noted that the maximum concentrations of these compounds were observed in the monsoonal phase and impacted by Cluster 3 and 4(Fig 1& Fig S3). Chlordanes concentrations on 29th Oct and 14th November were unusually high particularly TC and TN levels were comparatively higher than other dates. Back trajectory analysis showed that cluster 3 majorly influenced these dates. Cluster 3 represents air masses traversing through surrounding states like Karanataka and Kerala. Chlordane has been mentioned as an effective control for managing root grubs in Karnataka (Veeresh, 1977). It is possible that ongoing usage of chlordane in these neighbouring states might have impacted the elevated concentration in the sampling site on those particular dates in addition to the local usage in Parangipettai.

Ratio of low molecular PBDEs (BDE-28 and -35) against high molecular weight PBDEs (BDE-99,-100,-154) in monsoon (0.35) was two folds higher than summer and pre-monsoon (0.15). BDE-28 being a highly volatile congener (Tian et al.,2011), we suspect biomass burning might have impacted the atmospheric concentrations of these tri-BDEs (Chakraborty et al.,2017). Localised emission sources due to past usage and limited ongoing usage might equally contribute to the atmospheric concentration of the the pesticides loaded in PC-2. Hence PC-2 represents a mixed source of atmospheric transport from places away from PI as well as fresh emission.

PC-3 was strongly weighted with α, β, γ, δ HCH and CC (Table S2). Historical use of HCH for paddy cultivation have been well documented in south India (Baburajendran et al., 1999). With maximum concentration of HCHs coinciding with the flowering season of paddy crop it is evident that HCHs had a clear fresh source. In open dumping sites, increased levels of HCHs in soil may likely caused is equilibrium in the air–soil interface, thus favoring their emission from the soil (Chakraborty et al 2015). Hence this component represents fresh emission as well as re-emission from surface soil as a potential HCH source in PI.

Conclusion

A drastic decline in atmospheric pesticidal POPs has been observed in Parangipettai from previouslyreported concentrations (Baburajendran et al., 1999) after the strict ban on the technical mixture of these compounds for agricultural purpose. The tropical climate in south India facilitates re-emission of the metabolites of the historically used pesticides. In PI PBDEs showed a distrinct seasonal pattern with higher summer concentrations followed by pre-monsoon and monsoon. Diagnostic ratios showed that DDT, HCH, chlordanes and endosulfansis used in very limited quantity. Weathered compounds, metabolies andBDE-99 and -47 were majorly impacted by atmospheric transport from other areas where past and ongoing sources exist. It is therefore evident that strong source regions in the tropical environment of India, not only cause local contamination problems but also contribute to pollution in areas far away from the point sources via atmospheric transport.

Acknowledgement

This work was supported by the Chinese Academy of Sciences (No. KZCX2-YW-

GJ02), Natural Scientific Foundation of China (NSFC) (Project No. 41025020), and Fast Track Grant under Young Scientist Scheme by the Department of Science and Technology, Government of India (SR/FTP/EE-44/2012).

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Fig 1. Map showing the sampling site at Parangipettai and four clusters of air mass backward trajectories

Fig.2. Distribution of atmospheric each organochlorine pesticide in Parangipettai during summer, pre-monsoon and monsoonal season

Fig.3. Box-whisker plots showing the diagnostic ratios of (a) major isomers of HCHs (b) metabolite and parent isomer of DDT (c) isomers of chlordane

Fig.4. Atmospheric concentration of polybrominated diphenyl ethercongeners during summer, pre-monsoon and monsoonal season in Parangipettai

Seasonal variation of atmospheric organochlorine pesticides and polybrominated diphenyl ethers in Parangipettai, Tamil Nadu, India: Implication for atmospheric transport

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List of Tables

Table1. Derived atmospheric concentrations of OCPs and PBDEs (pg/m^3) inPorto Novo

Concentration in pg/m^3	Summer		Pre-monsoon		Monsoon	
	Range	**Avg ± SD**	**Range**	**Avg ± SD**	**Range**	**Avg ± SD**
α-HCH	112 - 154	133 ± 21	61 - 420	169 ± 102	114 - 235	184 ± 47
β-HCH	21 - 108	64 ± 43	ND - 280	63 ± 67	ND - 57	18 ± 25
γ-HCH	317 - 347	332 ± 15	174 - 668	337 ± 163	118 - 331	204 ± 72
δ-HCH	ND - 25	12 ± 12	ND - 84	18 ± 22	ND - 65	22 ± 24
ΣHCHs	**480 - 603**	**542 ± 62**	**260 - 1135**	**587 ± 282**	**279 - 636**	**428 ± 147**
p,p'-DDE	369 - 421	395 ± 26	136 - 368	243 ± 71	ND - 343	106 ± 112
o,p'-DDT	40 - 106	73 ± 33	ND - 88	38 ± 26	ND - 88	61 ± 29
p,p'-DDT	904 - 1449	1177 ± 272	197 - 661	390 ± 130	ND - 246	141 ± 77
ΣDDTs	**1313 - 1976**	**1645 ± 332**	**352 - 1024**	**671 ± 196**	**ND - 651**	**309 ± 194**
TC	38 - 177	108 ± 69	ND - 119	58 ± 35	16 - 338	155 ± 126
CC	158 - 273	215 ± 58	88 - 374	222 ± 90	20 - 381	235 ± 116
TN	60 - 156	108 ± 48	12 - 63	37 ± 14	ND - 148	59 ± 55
ΣCHLs	**256 - 606**	**431 ± 175**	**189 - 434**	**317 ± 78**	**36 - 840**	**449 ± 281**
α-ENDO	ND - 57	28 ± 28	ND - 146	32 ± 54	ND - 185	35 ± 68
Endosulfan sulfate	188 - 229	209 ± 20	68 - 238	127 ± 43	66 - 1013	258 ± 339
β-ENDO	ND - 66	33 ± 33	ND - 39	6 ± 14	ND - 29	5 ± 11
ΣENDOs	**188 - 351**	**270 ± 81**	**68 - 290**	**166 ± 69**	**66 - 1013**	**298 ± 336**
HCB	82 - 92	87 ± 5	52 - 101	68 ± 16	79 - 135	104 ± 20
BDE-28	4 - 10	7 ± 3	2 - 7	5 ± 1	3 - 10	5 ± 3
BDE-35	2 - 2	2 ± 0	1 - 4	2 ± 1	1 - 5	2 ± 1
BDE-47	18 - 40	29 ± 11	6 - 16	10 ± 3	6 - 14	10 ± 3
BDE-100	15 - 24	20 ± 5	ND - 14	8 ± 4	ND	0 ± 0
BDE-99	43 - 76	59 ± 17	17 - 46	29 ± 8	11 - 23	18 ± 4
BDE-154	1 - 2	2 ± 0	ND - 1	0 ± 0	ND - 2	1 ± 1
Σ_6PBDE	**83- 155**	**119 ± 50**	**32- 71**	**55 ± 17**	**24- 47**	**48 ± 9**

Highlights

- Atmospheric HCHs were high during rice sowing season
- DDTs were high during monsoon suggesting the usage for vector control
- Atmospheric transport from metropolitan cities like Chennai and Bangalore is the major contributor for atmospheric PBDEs in Porto Novo


PAKISTAN
CHINA
NEPAL
INDIA
45
60
75
90
105
30
15
0
-15
Arabian
Sea
Bay of Bengal
Indian Ocean
Parangipettai (PI)
1 (25%)
2 (49%)
3 (10%)
4 (16%)

Figure 1

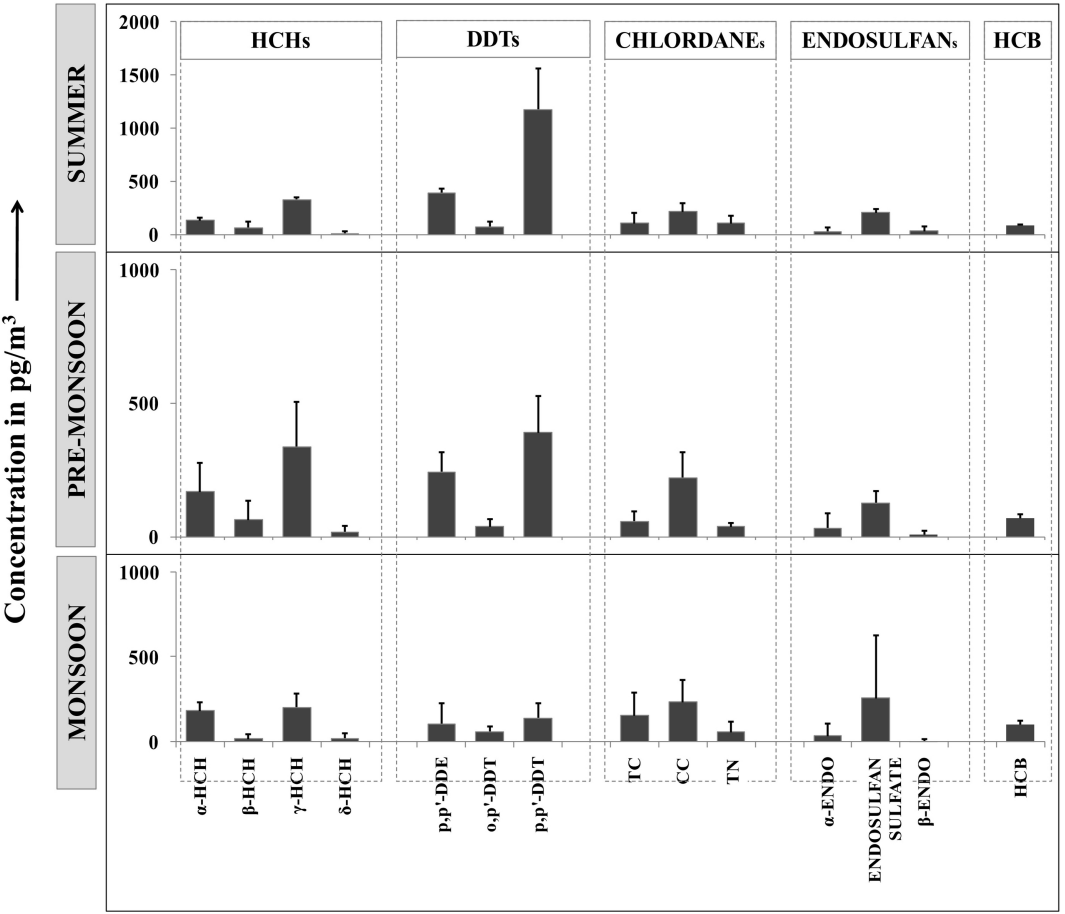
Concentration in pg/m3
SUMMER
PRE-MONSOON
MONSOON
HCHs
DDTs
CHLORDANEs
ENDOSULFANs
HCB
2000
1500
1000
500
0
1000
500
0
1000
500
0
α-HCH
β-HCH
γ-HCH
δ-HCH
p,p'-DDE
o,p'-DDT
p,p'-DDT
TC
CC
TN
α-ENDO
ENDOSULFAN SULFATE
β-ENDO
HCB

Figure 2

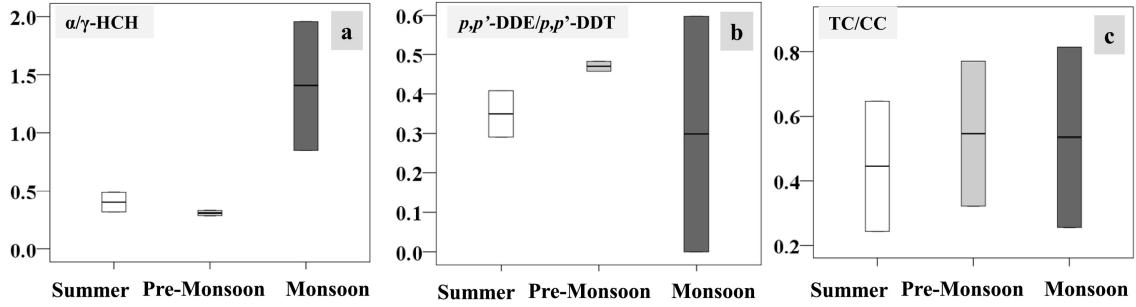
α/γ-HCH
a
2.0
1.5
1.0
0.5
0.0
Summer
Pre-Monsoon
Monsoon
p,p'-DDE/p,p'-DDT
b
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Summer
Pre-Monsoon
Monsoon
TC/CC
c
0.8
0.6
0.4
0.2
Summer
Pre-Monsoon
Monsoon

Figure 3

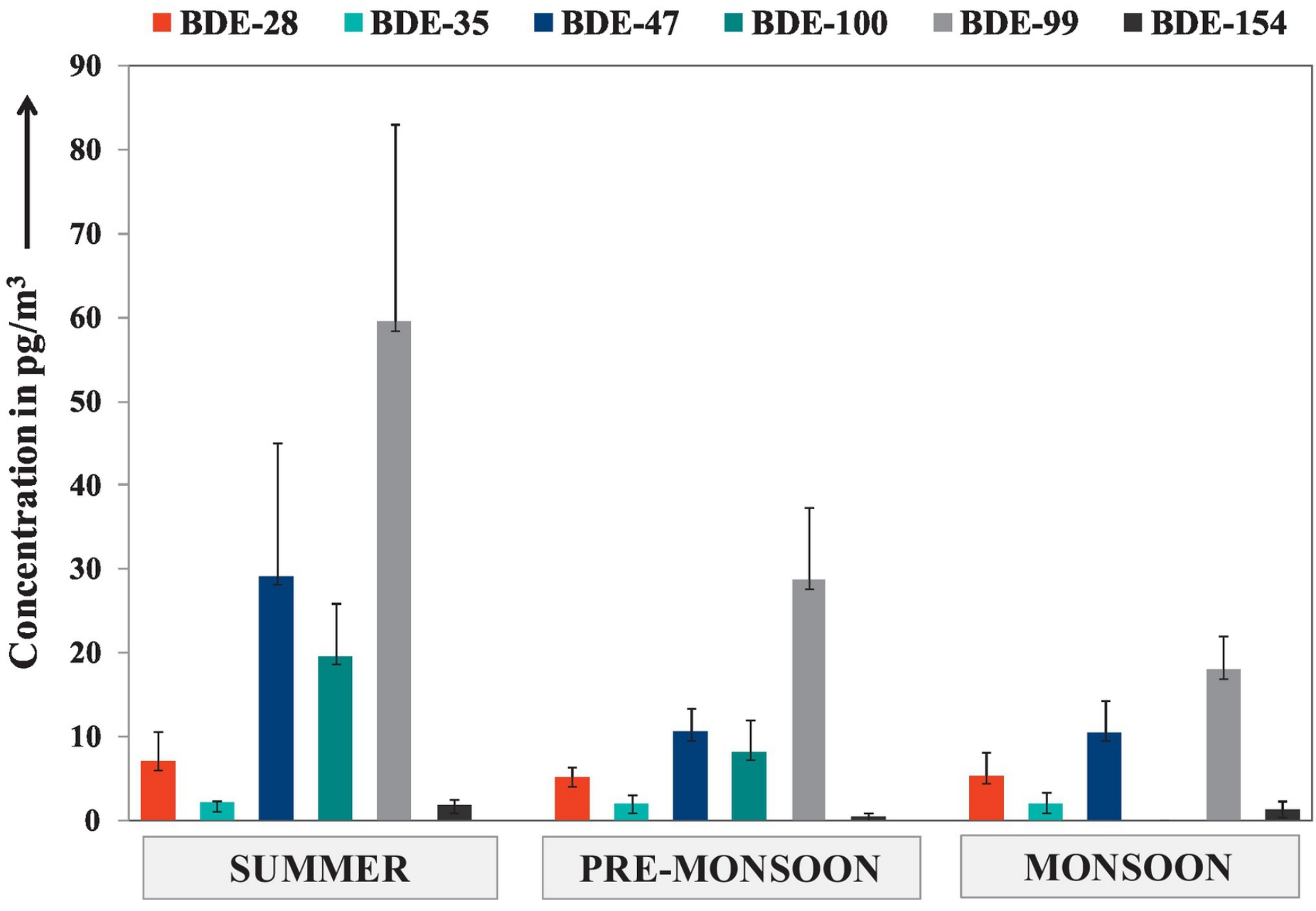
BDE-28
BDE-35
BDE-47
BDE-100
BDE-99
BDE-154
Concentration in pg/m3
90
80
70
60
50
40
30
20
10
0
SUMMER
PRE-MONSOON
MONSOON

Figure 4