



Distribution of Organochlorine pesticides in surface water from Hyderabad city, India

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ABSTRACT

Organochlorine Pesticides (OCPs) have stable chemical properties and less biodegradability. OCPs are regarded as persistent organic pollutants; they have high risk to the environment and human health. OCPs have been prohibited in India since 1996, although they are still found in water now days. Water resource is very important in natural environment and essential for agriculture. The samples are extracted by solid phase extraction (SPE) procedure, and are investigated by gas chromatography coupled with quadruple mass spectrometer (GC-q MS). The existence of OCPs in surface water from the study area has been detected with different levels of concentration. The results showed that the contents of Σ HCHs, Σ DDTs and cyclodienes are 2.26 –12.79, 0.72–4.25 and 1.33–6.45 $\mu\text{g L}^{-1}$, respectively. According to the indicators of the ratio values of (DDD+DDE)/DDT and α -HCH/ γ -HCH, the source of pollution and its potential risk are also discussed. In addition, spatial distribution of organochlorine pesticides in this area is also discussed in this article.

Keywords: Distribution; Organochlorine pesticides; Statistical indicators; Solid phase extraction.

INTRODUCTION

Organochlorine pesticides (OCPs) are one of the most important persistent organic pollutants (POPs) and have been of great concern around the world owing to their chronic toxicity, persistence and bioaccumulation [1]. These compounds pose great threats to ecosystems and human health. Although the application of these chemicals has been banned or restricted in many countries especially the developed ones, some developing countries are still using these compounds because of their low cost and versatility in industry, agriculture and public health [2,3]. The input pathways of OCPs into the river environments include runoff from non-point sources, discharge of industrial wastewater, wet or dry deposition and other means. Therefore, the residues of OCPs might ultimately pass onto people through consumption of drinking water, fish and agriculture food [4–6].

Residue levels of chlorinated pesticides have declined significantly in the world from last two decades [7], but some OCPs such as DDTs, HCHs, cyclodiene, etc are still used in developing countries, including India. Annual consumption of pesticides in India is approximately 85, 000 t, of which dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane isomers (HCHs), and

Malathion accounted for 70% [8]. India is permitted to use organochlorine pesticides (OCPs) like DDT 10,000 t/year. Use of technical HCH in India increased before 1970 and from 1980 to 1990, peaking at 36 000 t/year in 1990, and has remained at ~17 000 t/year since 1991 [9], until it was banned in 1997. Use of γ -HCH (as Lindane) in India reached 7700 t/year in 1990, has remained at approximately 600 t/year since 1991. India is the world's largest ship-breaking nation in terms of volume, conducting 38% of the world ship-breaking activities. The ship-breaking industry is mostly confined in the west coast of the country at Gujrat and Mumbai. India is growing at an exponential rate in terms of electronic waste, generating approximately 150000 t/year, much of which is stockpiled or poorly managed [10].

The present study focused on the (i) characterize the OCP residues in surface water from fresh water lakes; (ii) establish the OCPs contamination profiles and identifying possible sources via composition analysis in surface water from Bonthapally watershed.

MATERIALS AND METHODS

Sampling: The locations of the sampling sites from Bonthapally watershed are shown in fig. 1. The sites were chosen based on hotspots of pollution around the area such as industrial region, domestic wastewater discharge areas and agricultural zone. Throughout the survey a global positioning system (GPS) was used to locate the sampling locations. Surface water samples were collected throughout the area. Samples were taken using pre-cleaned glass bottles held in a weighted stainless-steel frame fitted with a spring loaded PTFE (polytetrafluoroethylene) stopper with a subsurface trigger to avoid sampling the surface micro layer, and then filtered under vacuum to remove suspended particulate matter (SPM) after returning to the laboratory within one or two days.

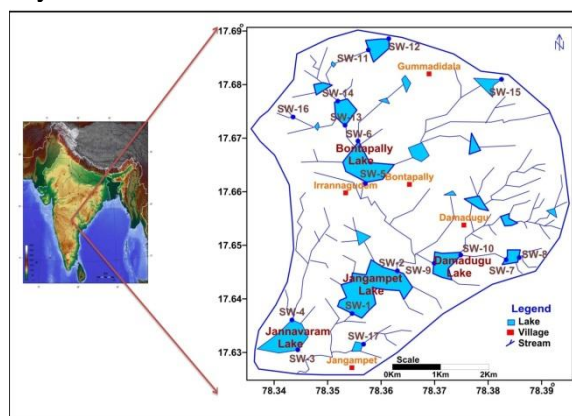


Fig 1 .Geographical location map and sampling sites in the study area

Chemicals and materials: All analytical standards (α , β , γ , δ -HCH, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, endrin aldehyde, endrin ketone, endosulfan-I, endosulfan-II, endosulfan sulfate, *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD) each at a concentration of 10 mg mL⁻¹ are purchased from Supelco, Bellefonte, PA, USA. Column packing material florisil is purchased from Spectrachim pvt. Ltd, India. All solvents used are HPLC grade. Anhydrous granular sodium sulfate is obtained from Merck, India and baked at 400°C overnight before use. All the reagents are used throughout analysis analytical grade only. Deionized water is produced by Milli-Q system (Millipore Co., India). Rotary evaporator is used for Pre concentrated of sample extracts.

Sample preparation: Solid phase extraction (SPE) is used for enrichment of organochlorine pesticides from surface water. Water samples are extracted using SPE system with the following of the method reported elsewhere [11]. Briefly, the Bond Elut LRC-C18 Solid phase extraction cartridges (Varian, USA) are first activated with 5 mL of dichloromethane, and then consecutively washed with 5 mL of methanol

and 10 ml of deionized water. Water samples are passed through the cartridges at a rate of 5 mL/min under vacuum. After extraction, the cartridges are eluted with 10 ml of dichloromethane. Then, the extracts are dehydrated with anhydrous Na₂SO₄, concentrated to 0.2 mL by rotary evaporator using a gentle stream of high purity nitrogen and is analyzed using GC-q MS.

Analytical method: The OCPs residues are analyzed with a GC-q MS (Thermo Scientific Trace GC Ultra with DSQ II model) coupled with mass spectrometer detector using TR-5MS fused silica capillary column, 30m x 0.25mm i.d. 0.25µm film thickness (J&W Scientific, CA, USA). The GC system is operated in split less mode, and 1µL aliquots of extracts are injected via an auto sampler. The oven temperature is programmed from 80°C (initial time, 2 min) to 205°C at a rate of 30°C per minute and held for 5 min. Then programmed set to 290°C at a rate of 10°C per min with a final held of 3 min. Helium is the carrier gas at a constant flow rate of 1.0 mL min⁻¹. The electron ionization energy was 70eV. Chromatographic data are collected in full scan mode as well as selected ion monitoring mode and processed using Turbo Mass software. Quantification for individual OCPs is performed using the external standard and a four-point calibration curve.

Quality control: All data are subject to strict quality control procedure. For every set of samples, a procedural blanks and spiked samples with standards are used to check interference, cross contamination and instrument performance. Surrogate standards in sediment samples are determined good precision. The mean recovery of surrogate standards is 89.6 ± 15.2 got in this extraction method. The detection limit of the method ranged from 0.01 to 0.11µg L⁻¹. Each sample extracts were analyzed in triplicate and relative standard deviations were less than 10%.

RESULTS AND DISCUSSION

Characterization OCP residues : Characterization of surface water samples for OCP residues such as HCHs, DDTs and cyclodienes is carried out in order to demonstrate their compositions and sources. The concentration of HCHs including α-HCH, β-HCH, γ-HCH and δ-HCH and DDTs include *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT detected in all the surface water samples are illustrated in Table.1.

Table 1. Statistical parameters of OCPs concentrations in surface water from the study area

	Compound	Units	Min	Max	Avarage	SD
HCHs	α-HCH	µg L ⁻¹	0.14	4.25	1.34	1.13
	β-HCH	µg L ⁻¹	BDL	6.54	1.73	1.94
	γ-HCH	µg L ⁻¹	0.11	4.52	1.13	1.35
	δ-HCH	µg L ⁻¹	0.12	1.97	0.90	0.59
DDTs	<i>p,p'</i> -DDD	µg L ⁻¹	BDL	1.32	0.45	0.39
	<i>p,p'</i> -DDE	µg L ⁻¹	BDL	1.59	0.50	0.46
	<i>p,p'</i> -DDT	µg L ⁻¹	0.1	3.21	1.14	0.96
Cyclodienes	Heptachlor	µg L ⁻¹	BDL	1.2	0.19	0.36
	Heptachlor epoxide	µg L ⁻¹	0.11	3.97	1.00	1.18
	Aldrin	µg L ⁻¹	BDL	1.26	0.27	0.41
	Dieldrin	µg L ⁻¹	0.01	2.48	0.85	0.70
	Endosulfan-I	µg L ⁻¹	BDL	0.74	0.17	0.23
	Endosulfan-II	µg L ⁻¹	BDL	1.01	0.22	0.31
	Endosulfan sulfate	µg L ⁻¹	BDL	1.1	0.38	0.42
	Endrin	µg L ⁻¹	BDL	3.8	0.61	1.12
	Endrin aldehyde	µg L ⁻¹	BDL	1.428	0.36	0.46
	Endrin ketone	µg L ⁻¹	BDL	4.8	0.57	1.45

BDL=Bellow Detection Limit

HCHs : The contents of α -HCH, β -HCH, γ -HCH and δ -HCH are $0.14\text{--}4.25\ \mu\text{g L}^{-1}$, $\text{BDL}\text{--}6.54\ \mu\text{g L}^{-1}$, $0.11\text{--}4.52\ \mu\text{g L}^{-1}$, and $0.12\text{--}1.97\ \mu\text{g L}^{-1}$, respectively. From the results, the highest level is $\Sigma\beta$ -HCH ($26.39\ \mu\text{g L}^{-1}$), $\Sigma\alpha$ -HCH ($21.05\ \mu\text{g L}^{-1}$), $\Sigma\gamma$ -HCH (16.85), and the lowest is $\Sigma\delta$ -HCH ($14.96\ \mu\text{g L}^{-1}$) shown in fig.2. It can be observed that the concentration of HCHs is lower in the Bonthapally Lake and Jannavaram Lake whereas the pollution is relatively serious in the Jangampet Lake (Fig. 3a). Generally, commercial HCH contains 55–80% of α -HCH, 5–14% of β -HCH, 12–14% of γ -HCH, 2–10% of δ -HCH, and 3–5% of other compounds [12, 13]. The effective compound is γ -HCH isomer also known as lindane. But α -HCH, β -HCH, γ -HCH and δ -HCH had 26.56%, 33.29%, 21.26% and 18.87%, respectively (Fig. 2).

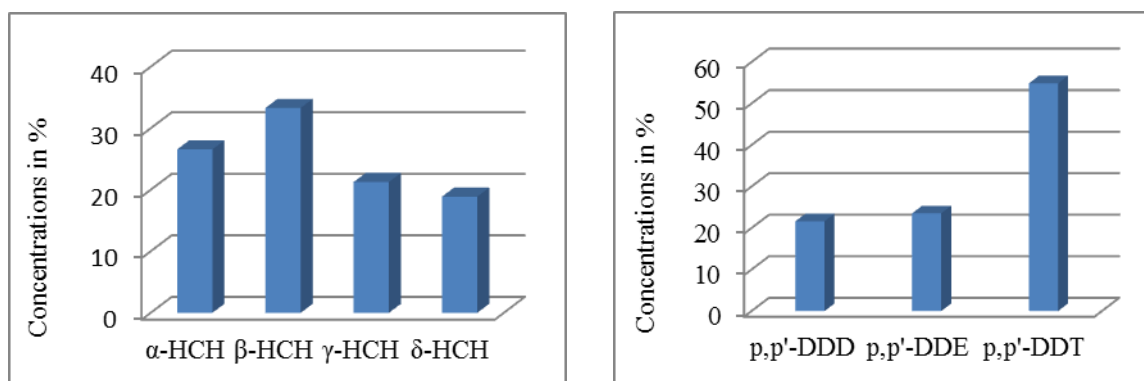


Fig. 2. Composition of HCHs and DDTs in the study area

In this study, the α -HCH/ γ -HCH ratio in surface water ranged between 0.12 and 6.88 in Jangampet Lake, and 0.67 and 3.06 in Damadugu Lake. The results showed that in 34% of all samples has the α -HCH/ γ -HCH ratio are below 1, suggesting lindane as the source of contamination in some sampling sites. Higher ratios may be explained by the use of technical HCH mixtures in the past, due to photochemical transformation of γ -HCH into α -HCH in the atmosphere, with subsequent deposition in the surface water (Fig.3). The key environmental sources of the surface water could be the regional use of HCH isomer pesticides in adjacent in processing chemical industries and agricultural activities in both regions. But DDTs and cyclodienes are found maximum concentrations Bonthapally and its surroundings.

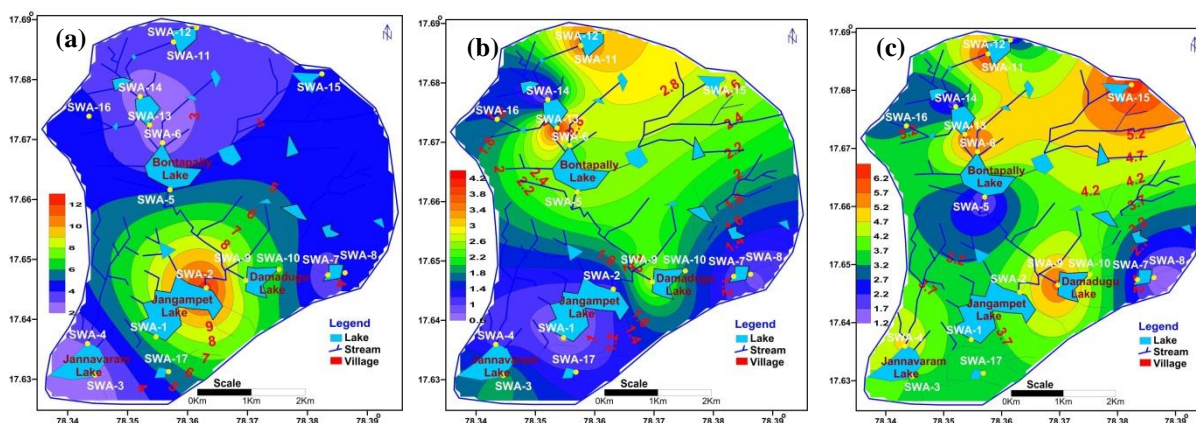


Fig.3 .Spatial distribution and contour maps of (a) HCHs (b) DDTs and (c) Cyclodienes individual OCPs in surface water

The result shows that β -HCH has predominant in HCHs. Lindane is not used recently in some areas from the above statistical explanation (Fig. 4). Further, the α -HCH/ γ -HCH ratio can be used to identify the source of HCHs in water [14, 15]. The ratio of α -HCH/ γ -HCH identified in the study area, where typically ranged from 0.28 to 1 indicates lindane is used recently. This is due to the photochemical transformation of γ -HCH into α -HCH, compared to a range of 4–15 for technical mixtures of HCH [16].

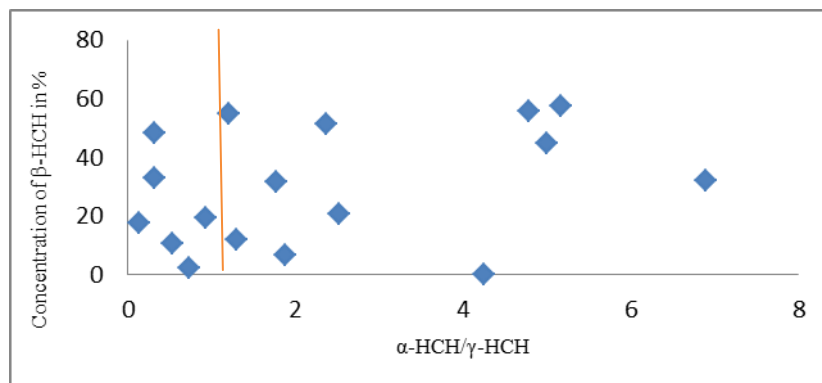


Fig.4. Statistical indicator α/γ -HCH and % of β -HCH

DDTs: The isomers of DDT are found in almost all the samples in this investigation except the Jangampet Lake. The sample detection ratio is 82%, and the contents of p,p' -DDE, p,p' -DDD and p,p' -DDT were $\text{BDL}-1.59 \mu\text{g L}^{-1}$, $\text{BDL}-1.32 \mu\text{g L}^{-1}$ and $0.1-3.21 \mu\text{g L}^{-1}$ respectively (Table 1). The content of p,p' -DDD is relatively low and p,p' -DDT still can be found higher in surface water from the study area. DDE and DDD are the degradation products of DDT. DDT could transform to DDD or DDE under anaerobic or aerobic condition [17]. The ratios of DDE/ Σ DDTs and DDD/ Σ DDTs can be used to assess how recent DDT contaminations occurred in the environment. In this study, the DDE/ Σ DDTs and DDD/ Σ DDTs ratios in surface water ranged between 0.0–2.1 and 0.0–6.7, respectively (Fig.5).

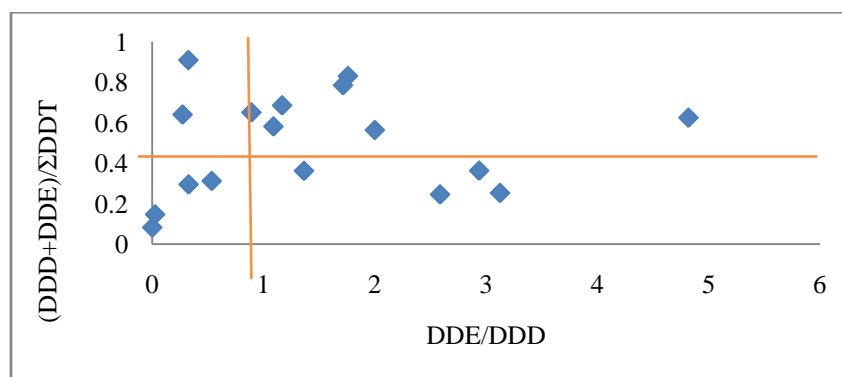


Fig. 5. Relationship between $(\text{DDD}+\text{DDE})/\text{DDT}$ and DDE/DDD in surface water

It is notable that 82% of the water samples presented the $\text{DDE}/\Sigma\text{DDTs}$ and $\text{DDD}/\Sigma\text{DDTs}$ ratios below unity. It seems that DDT contaminations are still exist in this area, or may be derived from atmospheric transport from other parts of area. The ratio of $(\text{DDD} + \text{DDE})/\text{DDT}$ can be the indication of either the extent of degradation or the inputs [18]. In the present investigations, the value of $(\text{DDD} + \text{DDE})/\text{DDT} > 1$ in Jannavaram Lake and Jangampet Lake surface water samples indicates that the pollution is due to DDT degradation from the former residues. This could be evident as no p, p' -DDT was detected in the study area. The ratio of $(\text{DDD} + \text{DDE})/\text{DDT} < 1$ in the Bonthapally Lake and Damadugu Lake surface water

samples showed that there may be new source of pollution near these water systems, which can also be proved by the *p,p'*-DDT found in these samples (Fig. 3).

Spatial distribution of OCPs: The average concentration profiles of OCPs residues in surface water is shown in Fig.6. The highest concentrations are identified in some sampling sites (SWA-04; SWA-09 and SWA-17) of surface water samples collected from Jannavaram and Jangampet surrounding areas. Similarly the high concentration of OCPs was also observed Jangampet and Jannavaram lakes which were down stream of industrial zone and intensive agricultural activity areas. The concentrations range and mean values of organochlorine pesticides in surface water are shown in Table.1. The concentrations of HCHs in surface water (including α -HCH, β -HCH, γ -HCH, δ -HCH), DDTs (including *p, p'*-DDE, *p, p'*-DDD, *p, p'*-DDT) and Cyclodienes are 2.26 –12.79, 0.72–4.25 and 1.33–6.45 $\mu\text{g L}^{-1}$, respectively. The results indicate that the cyclodienes are the predominant contaminant pesticides in surface water, and dieldrin is the most often found in all sampling sites, followed by aldrin, endrin, endosufane. The mean concentrations of heptachlor, aldrin, endrin and endosulfan are 0.19, 0.27, 0.61 and 0.17 $\mu\text{g L}^{-1}$, respectively. The mean concentrations of *p,p*-DDE, *p,p*-DDD and *p,p*-DDT were found in surface water 0.5, 0.45 and 1.14 $\mu\text{g L}^{-1}$ respectively. On the other hand, spatial distribution of Σ DDTs in surface water is shown in Fig. 6. These distribution indicating that the highest concentration levels of DDTs are found in Bonthapally and its surroundings that are probably using DDT for vector control purpose with different commercial formulations.

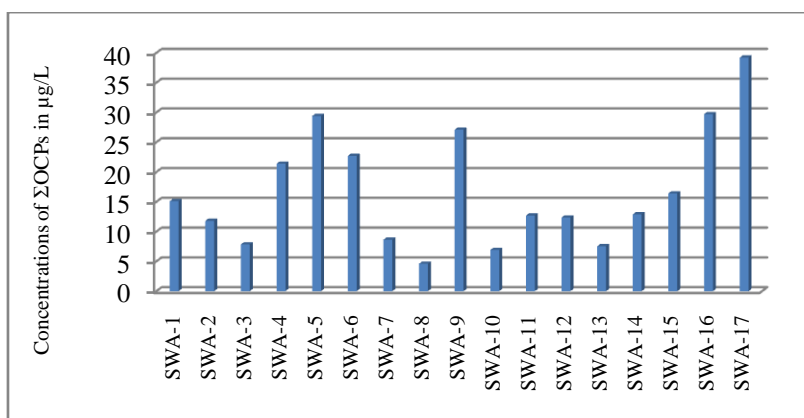


Fig. 6. Distribution of OCPs concentration in surface water

APPLICATIONS

Persistent Organic Pollutants (POPs) are toxic and bio accumulative compounds that have been introduced to the environment through anthropogenic activities since the mid – 1900's. Their extreme persistence and effective environmental dispersal mechanism have resulted in global contamination of all environmental matrices. This study illuminates spatial distribution and source identification of OCPs. All these results will be necessary for health risk assessment, control and management of this kind of pesticides.

CONCLUSIONS

The work investigated the contamination status of OCPs like, Cyclodiene, HCH and DDT in surface water of Bonthapally industrial area and its surroundings. Results show that although concentrations of the OCP residues in Jangampet and its surroundings had highest concentrations. The distribution of Cyclodienes, HCHs and DDTs was different, indicating their different contamination sources. Composition analysis and high residue levels of HCH and DDT indicated that a recent input of these two OCPs in the study area.

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