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## Source identification and contaminant risks of organochlorine pesticide residues in ground water from Hyderabad city, India

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### ABSTRACT

*This study was conducted the contaminant risks and source identification of organochlorine pesticide residues in ground water from northwestern part of Hyderabad City. Hyderabad is the Capital and largest city of the Indian state of Andhra Pradesh. It occupies 650 sq km on the banks of the Musi River on the Deccan Plateau in South India. Water samples were extracted for pesticide residues by using solid phase extraction (SPE) procedure, and were investigated by gas chromatography coupled with quadruple mass spectrometer (GC-qMS). The total concentrations of DDTs ranged from 4.52 to 37.32 $\mu\text{g L}^{-1}$  with an average of 12.6  $\mu\text{g L}^{-1}$  and HCHs 3.78 to 10.76 $\mu\text{g L}^{-1}$  with an average of 6.13 $\mu\text{g L}^{-1}$ . The ratios of (DDD+DDE)/DDT and  $\alpha/\gamma$ -HCH revealed that residue levels in water were originated from long past to recent mixed source of contamination. About 91% samples for DDT and 84% samples for HCH exceeded the WHO recommended drinking water limits.*

**Keywords:** GC-qMS, Ground water, Organochlorine pesticides- DDT and HCH, Solid Phase Extraction, Total Organic Carbon.

### INTRODUCTION

Organochlorine pesticides (OCPs) such as hexachlorocyclohexanes (HCHs) and dichlodiphenyltrichloethane (DDTs) are of great concern around the world due to their persistence in the environment, impact on organisms, and bioaccumulations in the tissues of animals as well as humans via the food chain [1]. Also these compounds create great threats to ecosystem and human health. Although the application of these chemicals has been restricted or banned in many countries especially the developed ones, some developing countries are still using these compounds because of their low cost and adaptability in industry, agriculture and public health [2]. The input pathways of OCPs into the environments include runoff from non-point sources, discharge of industrial waste water, wet or dry deposition and other means. Therefore, the residues of OCPs might ultimately pass into people through consumption of drinking water, fish, and agricultural food [3, 4].

In India, pesticides are being used in public health for controlling infectious diseases and also for pest control in agricultural operations. On the other hand, production of pesticides (especially includes like

HCH and DDT) also has increased from 5,000 to 85,000 metric tons [5] during 1958-2004. The worldwide consumption of pesticides is about two million tons per year, of which 24% is consumed in the USA alone, 45% in Europe and 25% in the rest of the world. India's share is just 3.75%. The usage of pesticides in India is only 0.5 kg/ha, while in Korea and Japan, it is 6.6 and 12.0 kg/ha, respectively. Currently, the pesticides are being used on 25% of the cultivated area. The three commonly used pesticides, HCH (only gamma-HCH is allowed), DDT and Malathion account for 70% of the total pesticides consumption in India. These pesticides are still preferred by the small farmers because they are low cost, easily available, and display a wide spectrum of bioactivity [6, 7]. In general, Natural Organic Matter (NOM) and Synthetic Organic Compounds are the sources of TOC [8] in water. Also TOC is one of the parameter to explained sources of organic pollutants [9] in water samples.

Hyderabad is the Capital and largest city of the Indian state of Andhra Pradesh. The population of the city is 6.8 million and that of its metropolitan area is 7.8 million, making it India's fourth most populous city. The study area has six water bodies in Kazipally, Gollagudem, Sulthanpura, Krishnareddypet village and surrounding areas are being steadily polluted by effluents from the Industrial Development Area (IDA). This area has long-term pharmaceutical and few pesticide manufacturing industries releasing their effluents through open drainage system as well as part of the area has residential zone depends majorly on their agriculture farms. Ground water samples were collected throughout the study area. The objectives of this research are to establish (i) source identification of OCPs (ii) Concentration profile and distribution of OCP residues and (iii) correlation of pesticide residues with TOC in ground water from the study area.

## MATERIALS AND METHODS

**Sample Collection :** Ground water samples were collected from the catchment area of the following Lakes, Damara Lake, Mallama Lake, Darmi Lake, Kazi Lake, Dayara Lake and Katva Lake from northwestern part of Hyderabad city. These six water resources using for agriculture, industry and living. The locations of the sampling sites in the study area are shown in Fig.1. Total 15 samples were collected for pesticide analysis. Global positioning system (GPS) was used to locate the sampling locations. Samples were taken using pre-cleaned amber glass bottles with Teflon liner screw cap. Ground water samples were extracted for pesticides after returning to the laboratory. All the equipments used for sample collection, transportation, and preparation were free from organochlorine pesticide contamination.

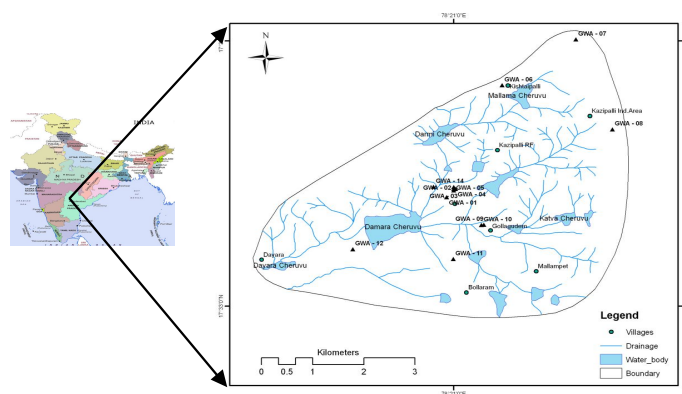


Fig.1 The study area and sampling locations of Northwestern part of Hyderabad, India.

**Chemicals and materials :** All analytical standards ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -HCH,  $p,p'$ -DDT,  $p,p'$ -DDE and  $p,p'$ -DDD) each at a concentration of  $2000\mu\text{g mL}^{-1}$  were purchased from Supelco, Bellefonte, PA, USA. Column packing material Florisil was purchased from Spectrachim pvt.ltd, India. The SPE cartridges, Bond Elute LRC- C18 (Varian, USA) containing 500mg reversed phase octadecyl were obtained from Merck. All solvents used were HPLC grade. Anhydrous granular sodium sulfate was obtained from Merck, India and

baked at 400°C overnight before use. Turbovap LV instrument (Biotage, Sweden) was used for Pre-concentrated of sample extracts.

**Extraction and Cleanup:** Water samples were extracted using an SPE system with the following reported method [10], Briefly the Bond Elut LRC- C18 Solid Phase Extraction cartridges (Varian, USA) were first activated with 5 ml of dichloromethane, and then consecutively washed with 5 ml of methanol and 10 ml of deionized water. Water samples were passed through the cartridges at a rate of 4 ml/min under vacuum. After extraction, the cartridges were eluted with 10 ml of dichloromethane. Then, the extracts were dehydrated with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated to 0.2 ml by TurboVap LV, (Biotage, Sweden) using a gentle stream of high purity nitrogen and was analysed using GC-MS.

**Analytical procedure :** The OCPs residues were analyzed with a GC (Perkin Elmer, *Clarus500*) coupled with mass spectrometer detector (Perkin Elmer, *Clarus 500*) using DB-5MS fused silica capillary column, 30m x 0.25mm i.d.0.25µm film thickness (J&W Scientific, CA, USA). The GC system was operated in split less mode, and 1µl aliquots of extracts were injected via an auto sampler. The oven temperature was programmed from 80°C (initial time, 1 min) to 200°C at a rate of 10°C per minute and held for 5 min. Then programmed set to 270°C at a rate of 5°C per min with a final held of 5 min. Helium was the carrier gas at a constant flow rate of 1.0 ml/min. The electron ionization energy was 70eV. Chromatographic data were collected in full scan mode as well as selected ion monitoring mode and processed using TurboMass software. Quantification for individual OCPs was performed using the external standard and a four-point calibration curve. Total Organic Carbon (TOC) of water samples were analyzed by using TOC Analyzer (Vario TOC cube, Elementar).

## RESULTS AND DISCUSSION

**Concentration profile and distribution of OCPs :** The OCPs concentration statistics in ground water of the study area is illustrated in Table 1. Concentrations of OCPs in ground water were ND–2.6 µg/L (average, 0.82 µg L<sup>-1</sup>) for α-HCH, 0.2–3.8 µg L<sup>-1</sup> (average, 1.98 µg L<sup>-1</sup>) for β-HCH, ND–0.82 µg L<sup>-1</sup> (average, 0.25 µg L<sup>-1</sup>) for γ-HCH, 2.61–3.87 µg L<sup>-1</sup> (average, 3.03 µg L<sup>-1</sup>) for δ-HCH, 2.11–13.09 µg L<sup>-1</sup> (average, 5.4 µg L<sup>-1</sup>) for *p,p'*-DDT, ND–21.8 µg L<sup>-1</sup> (average, 4.2 µg L<sup>-1</sup>) for *p,p'*-DDD and 2.41–3.04 µg L<sup>-1</sup> (average, 2.5 µg L<sup>-1</sup>) for *p,p'*-DDE were found in the study area. Concentration of DDTs is much higher than those of HCHs in ground water samples. About 91% samples for DDT and 84% samples for HCH exceeded the WHO recommended drinking water limits which is a matter of great public health concern. Sampling location number 1 and 4, which are nearer to Kazi Lake had highest concentration.

**Table 1.** Statistical parameters of OCPs concentrations in ground water

Compound	Concentration	Min	Max	Mean	S.D
α-HCH	µg/L	ND	2.6	0.82	0.85
β-HCH	µg/L	0.2	3.8	1.99	1.11
γ-HCH	µg/L	ND	0.82	0.26	0.31
δ-HCH	µg/L	2.61	3.87	3.03	0.47
<i>p,p'</i> -DDE	µg/L	2.41	3.04	2.50	0.20
<i>p,p'</i> -DDD	µg/L	0.2	21.8	4.21	8.25
<i>p,p'</i> -DDT	µg/L	2.11	13.09	5.45	3.84

ND\*= Not Detectable

The spatial distribution of OCPs from northwestern part of Hyderabad city are shown in Fig.2, HCHs were identified in most of the sampling sites. The highest concentration of HCHs found in catchment areas of

kazi Lake, damara Lake and darmi Lake. The concentration levels of HCH isomers were observed in following order,  $\delta$ -HCH >  $\beta$ -HCH >  $\alpha$ -HCH >  $\gamma$ -HCH. Neverthelen  $\delta$ -HCH was the most contaminant isomer and  $\gamma$ -HCH was found low concentration in HCHs. Interestingly, DDTs were identified in all samples, the highest concentration of DDTs were found in some sampling sites that are nearer to the water bodies like damara Lake and kazi Lake. The concentration levels of DDT isomers were following order,  $p,p'$ -DDT >  $p,p'$ -DDD >  $p,p'$ -DDE in study area. Among DDTs  $p,p'$ -DDT was the most contaminant isomer and  $p,p'$ -DDE is found low concentration observed in the investigated ground water samples.

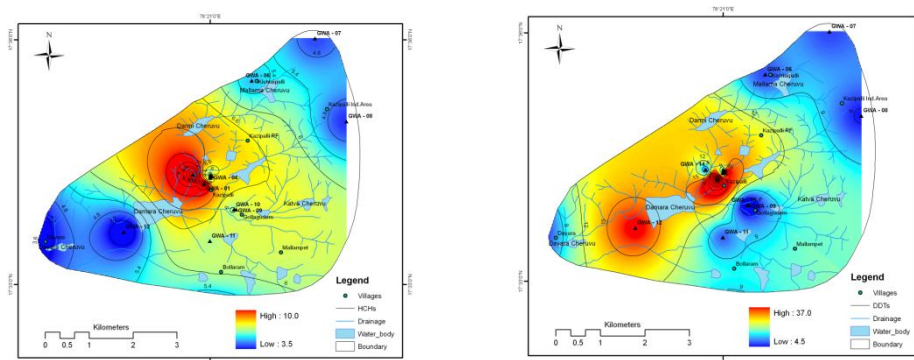


Fig.2 Spatial distribution of OCPs concentration in ground water for the area

The content of Total Organic Carbon (TOC) could make an impact on the residue of organochlorine pesticides in water. The TOC content in ground water found ranged from 6.3 to 19.1 mg L<sup>-1</sup> with an average of 10.5 mg L<sup>-1</sup> in the study area, that shown a good correlation ( $R^2=0.82$ ) with DDTs, this is further demonstrated the effect on DDT residues influenced by TOC, but such relationships were not found with HCHs ( $R^2=0.29$ ) (Fig.3). The analyses of linear regression indicated that TOC is the major ground water properties playing an important role in the residues of DDTs, but not for HCHs in the study area.

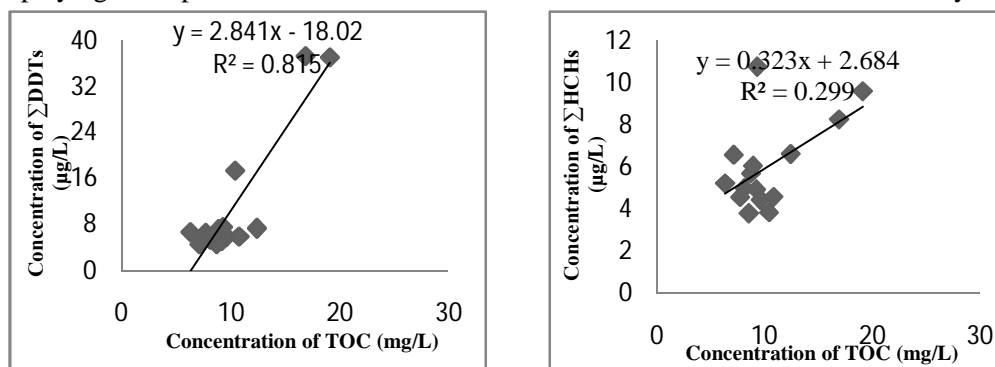


Fig. 3 Correlations between OCPs and TOC in ground water

**Compositions and Sources of OCPs :** The average percentages of HCH isomers are detected as,  $\alpha$ -HCH (12.75%),  $\beta$ -HCH (33.4%),  $\gamma$ -HCH (3.32%) and  $\delta$ -HCH (50.48%) in this area. Generally, technical HCH contains 65–70%  $\alpha$ -HCH, 7–10%  $\beta$ -HCH, and 6–10%  $\gamma$ -HCH and other isomers, respectively. The results shows that  $\delta$ -HCH isomer has highest occurrence, indicates that there are degradation occurs in the study area. Further,  $\alpha$ -HCH can be easily degradable followed by  $\gamma$ -HCH, and then  $\beta$ -HCH, which is the most persistent isomer in environment [11]. Moreover, the isomers of  $\alpha$ -HCH and  $\gamma$ -HCH can be transformed into  $\beta$ -HCH in the environment [12, 13]. The percentage of  $\beta$ -HCH found ranged from 5.2 to 44.8%, with an average of 33.4%. On the other hand the high percentage of  $\beta$ -HCH compared to  $\alpha$ -HCH, implied that HCH residues derived mainly from historical usage of technical HCH in this catchment. If there were no fresh inputs of technical HCH,  $\beta$ -HCH would be predominant in most of ground water samples.

Compositions of HCH isomers in this study are described in Fig.4. The ratio of  $\alpha$ -HCH/ $\gamma$ -HCH varied from 1.1 to 6.0 (mean, 4.1) is observed in the ground water, indicated that most of the HCHs derived not only from technical HCH usage historically in this area [14], but also The lower  $\alpha$ -HCH/ $\gamma$ -HCH ratio in the ground water samples implied the usage of lindane formulation [15]. There is a significant positive correlation between the levels of  $\alpha$ -HCH and  $\gamma$ -HCH ( $R^2=0.6$ ) in the ground water, suggesting that they had a common source. This result further suggesting, that technical HCH was more widely used than lindane in the studied area.

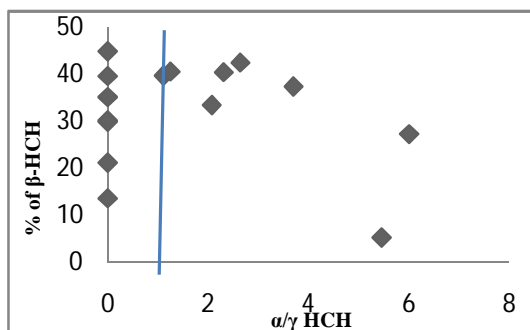


Fig. 4 Relationship between ratios of  $\alpha/\gamma$ - HCH Vs percentage of  $\beta$ -HCH

The ratios of (DDE+DDD)/DDTs found in the range of 0.48–1.85 (Fig.5), with most values being  $>0.5$ , it indicates that there are no recent inputs of DDT were observed nearer to Damara Lake and Katva Lake. But some samples which are nearer to Kazi Lake and Mallama Lake has the ratio of (DDE+DDD)/DDTs  $<0.5$ , which indicates that recent inputs of DDT in this area. On the contrary most of the samples, has the ratios of DDD/DDE  $<1.0$ . DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions [16], while these ratios of DDD/DDE denoted the condition of DDT biodegradation. Furthermore, the ratio of (DDE+DDD)/DDTs can be used as an indicative index to assess possible pollution sources [17]. Generally, technical DDT contains 75%,  $p,p'$ -DDT, 15% of  $o,p$  DDT, 5%,  $p,p'$ -DDE and  $<5\%$  others. From the results the average percentage of DDT isomers are 22.58% for  $p,p'$ -DDE, 30.26% for  $p,p'$ -DDD and 47.15% for  $p,p'$ -DDT, respectively. It is well known that, the ratio of  $p,p'$ -DDT/ $\Sigma$ DDT can be used as an indicator to identify a recent input of technical DDT. A high ratio indicates a recent input of technical DDT, while a low ratio indicates no recent input. In this study, relatively low ratios of  $p,p'$ -DDT/ $\Sigma$ DDT, ranging from 0.54–2.08 (average, 1.29) were found in some sampling sites. High ratios were still detected at some sites. These high ratios of DDT/ $\Sigma$ DDT indicated that there was a recent input of technical DDT in the catchment area of kazi cheruvu and Mallama cheruvu. A significant correlation between  $p,p'$ -DDT and  $p,p'$ -DDD ( $R^2=0.9$ ) indicates that  $p,p'$ -DDD is originated mainly from the degradation of  $p,p'$ -DDT. However, the positive correlation between  $p,p'$ -DDT and  $p,p'$ -DDE was weak ( $R^2=0.03$ ), suggesting that both of them probably derive partly from DDT in this study area.

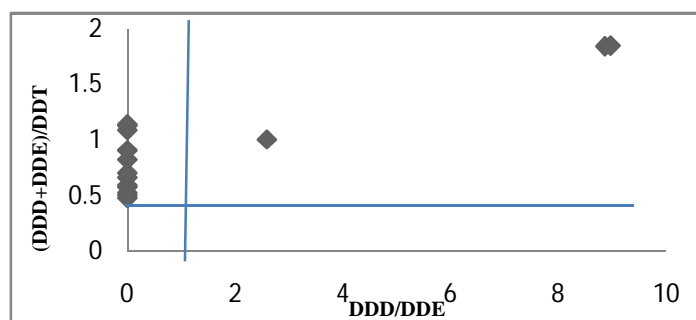


Fig. 5 Relationship between ratios of (DDD+DDE)/DDT and DDD/DDE



## APPLICATIONS

Organochlorine pesticides are a set of chemicals that are toxic, persist in the environment for long periods of time, and bio magnify as they move up through the food chain. This study explains the spatial distribution and identified possible sources of OCP residues. All these results will be necessary for health risk assessment, control and management of this kind of OCPs.

## CONCLUSIONS

The results interpreted, about 91% samples for DDT and 84% samples for HCH exceeded the WHO recommended drinking water limits.  $\delta$ -HCH was the major contaminant of HCHs in the study area. The ratio of  $\alpha/\gamma$ -HCH indicated in all regions indicating there is no recent inputs of lindane. DDTs were also found in all water samples in this study area.  $p,p'$ -DDT was the most predominant contaminant in DDTs. Statistical data representing  $(DDD+DDE)/DDT < 0.5$  in most of the sampling sites, which indicates recent inputs of  $p,p'$ -DDT in this area. A good correlation between  $p,p'$ -DDT and  $p,p'$ -DDD ( $R^2=0.9$ ) indicated that  $p,p'$ -DDD originated mainly from the degradation of  $p,p'$ -DDT. Significant correlation between TOC and DDTs concentrations were observed.

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