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ORGANOCHLORINE PESTICIDES IN THE DRINKING WATER SAMPLES FROM DIFFERENT ZONES OF THE ALWAR, NCR OF DELHI

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Abstract: *The large-scale use of persistent organochlorine pesticides (OCPs) in agriculture and public health is a major source of contamination in the environment. In agriculture, pesticides are used to protect crops from pests, while in public health, they are used to control disease vectors such as mosquitoes. Higher toxicity, slow degradation, and bioaccumulation are the significant challenges associated with OCPs. These Organohalogens, leach into the soil and contaminate groundwater and they are carried by runoff into surface water sources. Due to their high chemical stability and non-biodegradable nature, contamination of drinking water and water table is increasing day by day. Due to the high persistence and bioaccumulation potential, the Stockholm Convention has classified most of the OCP compounds as environmental hazards and banned the use of many of them. However, in many developing countries they are still in use making the ban ineffective. Contaminated drinking water with OCPs pose a variety of health risks, depending on the specific pesticides present and the level of exposure. Contaminated drinking water has become a significant issue and alarming signal for public health globally. The purpose of this study is to assess the recent trend of OCPs level in drinking water collected from four zones of Alwar city and its surrounding area-East, West, North and South. The results revealed the presence of isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin in water samples. The OCPs residues present in the drinking water indicate the contamination of water bodies, which in turn is a risk to human health and safety of the environment. Secondly, now it has become challenging to arrange for a clean and safe drinking water for consumption which may pose various problems of management of human health and biodiversity conservation.*

Key words: Organochlorine Pesticides, Water Pollution, Gas Chromatograph, Alwar, NCR of Delhi

Introduction

Organochlorine Pesticides (OCPs) fall in the category of Persistent organic pollutants (POPs) are chemical substances that resist to environmental, chemical, physical and biological degradation; because of their characteristic persistence, they are transported through air, water and migratory species across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems [1]. The contamination of drinking water by pesticides is a global issue, affecting both developed and developing countries. In developing countries, the problem may be exacerbated by the lack of adequate water treatment facilities and regulations on pesticide use. According to the UN study on global population shows that India has become the most populous country in the world with a present size of 1.42 billion. India currently shows approximately 17.76 percent of the world population, with 2.4 percent land resources and 4 percent of water resources [2]. The growing population has led to the increasing food demand all over the world. Agricultural sector of India, is a vast and multifaceted system and is the cornerstone of its economy. It has a story of remarkable success since, the independence which is a result of the Green Revolution technologies invented and implemented with time. This revolution transformed the nation's agricultural landscape, achieving food self-sufficiency and uplifting rural livelihoods. Rajasthan's agriculture sector has faced, significant steeplechases in time lapse, primarily due to its harsh arid and semi-arid climate. Water scarcity reigns supreme, with the state's limited surface water resources forcing heavy dependence on groundwater for irrigation [3]. Irrigation is a crucial component of modern agriculture, enabling farmers to overcome water limitations and maximize the use of other inputs. This leads to increased crop yields, higher cropping intensity, and overall improvement in crop productivity, contributing significantly to food security and economic development [4]. The main source of irrigation in Alwar are wells, tube wells, pumps, canals and lakes.

In India, OCPs are registered for agriculture, public health and for the use in households. According to the report by Kumar & Reddy in 2017 as30th October 2016, 275 pesticides were registered for use India, of which about 255 are chemical poisons. An analysis by PAN India reveled that115 pesticides out of the 275 are highly on hazardous that means they have the potential to cause severe health implications such as high acute toxicity, long-term toxic effects like cancers, hormone disorders, reproductive and developmental disorders. [5]. The environment and human health are closely interconnected and this reflects on the general population as a whole. It has been well established that OCPs, being lipophilic in nature are found in human samples and transmitted to developing baby through placenta and cord blood, breaking the concept that placenta act as barrier or sieve and stop xenobiotic to reach to the Prenates. Even more frightening studies indicate that right from the day our babies begin to suckle, the are taking the pesticides deposited in the breast milk and some ready made babyfoods too are similarly contaminated.This has been confirmed in all the mammlian species that have been examined including humans.[6-10].

The organochlorine pesticides (OCPs) are very enduring when it comes to degradation. Due to their lipophilicity, they bioconcentrate and bioaccumulate in adipose tissue and blood stream of animal leading to environmental persistence and then they tend to biomagnified through the food chain. Health Hazards are dependent on the exposure and toxicity of the pesticide and can be calculated by the following formula -Hazard= Toxicity X Exposure [11].
Recognizing the environmental and health risks, many countries have implemented regulations and restrictions on the use of OCPs. Some of these pesticides have been banned, and others are subject to strict controls. Taking above points into consideration, a continued surveillance on the levels of pesticide pollutants in the drinking water is an important task to

ensure the wellbeing of the human health and safety of the environment. There are many reports from India and all over the world giving an idea about the concentration of detectable OCPs in the potable or drinking water but no such report is available from Alwar, NCR of Delhi of India. A monitoring study was, therefore, planned and conducted in Alwar, Rajasthan, India to assess the OCPs residues in the drinking water samples using Gas Liquid Chromatography (GLC). The drinking water samples were collected from four zones of Alwar city and its surrounding area-East, West, North and South. The results revealed the presence of isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin in all the water samples analyzed. This is the very first report from Alwar, India on the water contamination of the OCPs residues indicating the pesticide pollution by OCP. The above study is of special significance for the Indian population, since, Indians have been reported to possess the highest body burden of pesticides [12].

Materials & Methods

Study Area: Alwar District in Rajasthan which is located in the northeast of the state, is chosen as the site for the monitoring study. The district encompasses an area of 8,720 square kilometers, representing approximately 2.45 percent of Rajasthan's total landmass. The Aravalli Hills, a range running north-south with peaks between 450 and 700 meters, dominate the central portion of the district. Nestled between them lie fertile valleys, one of which houses the world-renowned tiger sanctuary in Sariska forest. Seasonal rivers like Landoha, Ruparail (Barah), Chuhar Sidh, and Sabi (Sahibi) carry rainwater runoff from the hills. Alwar's most important water body is the majestic Siliserh Lake.

Sampling: Collection of water sample was done during the study period, from June 2023-June 2024 from Alwar city and surrounding areas which was divided into four zones- East, West, North, and South. Total 80 water sample were collected which comprises of 20 sample from each zone. Samples were collected from Sariska, Siliserh lake and from different sites in and around Alwar (Pic.3 & 4). All the water samples were stored at room temperature and were extracted within 48 hrs. of collection. All the glassware were properly washed with soap water followed by distilled water and finally rinsed with acetone and heated at 220 degrees Celsius in an oven to eliminate any potential pesticide contamination

Pic. 1: Siliserh lake, Alwar

Pic. 2: Ram Nagar, Alwar

Extraction and Cleanup: Extraction of organochlorine pesticide residues of isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin from the water samples as per the Method prescribed by APHA (1995) [13] with some modification according to prevailing laboratory condition. 500 ml of water samples were treated with 28 ml hexane and 15 ml saturated sodium chloride. Pesticides were re-extracted using 25 ml hexane. Extracts were pooled and were washed twice with 10 ml hexane. Clean up of the extract was done using glass column packed with 5 gm neutral alumina and 5

gm anhydrous sodium sulphate and eluted with 15 ml hexane. The final extracts, after cleanup, were evaporated to dryness using rotatory vacuum evaporator. The dried extract was dissolved in 2 ml hexane for Gas Chromatograph analysis.

Quantitative Estimation: Quantitative estimation of pesticide residues in all the extracts was done by GC model Agilent 8890, equipped with Electron Capture Detector (ECD) Ni63 device regulatory model no-G2397A. Capillary Column used was Agilent J & W GC Column (DB-CLP1). The Purified nitrogen (IOLAR-1) was used as a carrier gas at the flow rate of 65 ml per min. Temperature in the GC maintained as follows: Injector temperature: 250 ◦C, Column temperature: 275 ◦C and Detector temperature: 340 ◦C. A known volume of sample was injected in the column with the help of the 10 µl Hamilton syringe. Different peaks of the samples were identified by comparing their retention times with those of standards. Quantitation of the samples were done by the data obtained from the chromatogram on the computer system attached with GC and were based on peak areas. Standards were obtained from Environmental Protection agency (EPA) U.S.A.

Recovery Analysis and Confirmation of Pesticide Residues

Recovery analysis was done by fortification experiments and the percentage recovery was 95–98 percent. The pesticides for which the GC was standardized and were estimated are isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin. Thin Layer Chromatography (TLC) was used for confirming the identity of the OCPs already detected by the GC according to the modified method of Thompson et al. (1970)
[14].

Statistical Analysis: The data obtained from the above experiments were subjected to statistical analysis. The calculations are based on biological statistics and values are expressed as mean± standard error (S.E.).

Observations and Results

High concentrations of OCPs were found in all the water samples analyzed for isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin.

Discussion

Environmental contamination by organochlorine pesticides (OCPs) in the drinking water have been a global issue, since most of these compounds are very persistent, bio accumulative and highly toxic. This work is the first effort to assess the contamination levels of OCPs in the drinking water of Alwar and surrounding areas. In the present study, we report the recent trend of OCPs level in drinking water collected from four zones of Alwar city and its surrounding area-East, West, North and South. The results revealed the presence of isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin in water samples. It has been observed that there is no statistically significant difference in the values of the OCP's detected in the different drinking water samples collected from the four zones of Alwar and its surroundings. This indicates that OCPs have entered and contaminated every water body in and around Alwar including ground water (Table.1.). However, comparing the mean values of the total OCPs from four parts of the Alwar, a slightly higher values were observed in the western part of Alwar. Alwar district is quadrilateral in shape and is situated in the north-east of Rajasthan. It is bounded on the north and north-east by Gurgaon (of Haryana) and Bharatpur district and on the north-west by Mahendragarh district of Haryana, on the south-west by Jaipur and on the south by Sawai- Madhopur and Jaipur

districts. The Aravalli ranges from ridges of rocky hills in most parts and are generally parallel but western part of Alwar has less hills and more of agricultural fields. Therefore, the presence of higher levels of OCPs in water samples from the western part of Alwar likely reflects the historical and/or current use of these pesticides in the agricultural fields in that area.

The most copious class of pesticide found in all the water samples analyzed is Benzene Hexachloride (BHC) with concentration range from 0.008 to 4.736 ppb. BHC is a combination of isomers of α BHC (30-35 percent), γ BHC (50-55 percent), β BHC (80-85 percent) and δ BHC is 60-65 percent. γ-BHC isomer is about 1,000 times more toxic than other diastereomers of BHC and was found in almost all the water samples analyzed. Among the BHC isomers, the mean concentration of β isomer is dominant over α, δ, γ as it is more stable than other isomers of hexachlorocyclohexane (HCH). Endrin, Chlordane, endosulfan, endrin, heptachlor was detected in more than 90 percent of the analyzed water samples. The mean concentration of total BHC was found to be 0.340 ppb in East, 0.336 in North, 0.461 in South and 0.466 in West region of Alwar. The total Heptachlor was found to be 0.202 ppb in East, 0.189 ppb in North, 0.252 ppb in South and 0.257 ppb in West region of Alwar. The mean concentration of total Chlordane detected was 0.215 ppb in East, 0.207 ppb in North, 0.166 ppb in South and 0.199 ppb in western part of Alwar. Overall Endosulfan observed in the samples was 0.254 ppb in the East, 0.260 ppb in the North, 0.260 ppb in the South and 0.084 ppb West. Total DDT detected was 0.187 ppb in the East, 0.102 ppb in the North, 0.050 South and 0.304 ppb in Western part of Alwar. Total Endrin detected was 0.392 ppb in East, 0.343 ppb in North, 0.342 ppb in South and 0.414 ppb in the western part. Total OCPs detected in four different parts of Alwar was 1.756 ppb in East, 1.566 ppb in North, 1.671 ppb in South and 1.909 ppb in west. More petrifying studies have indicated that we have largely over looked the murkier side of these chemicals as OCPs are reported to be carcinogenic [15], mutagenic [16-18], teratogenic [19,20], immunosuppressive [21,22], deplete the Vitamin D levels [23] , create endocrine dysfunction such as hypothyroidism or high estrogenic activity [24, 25], diabetes [26], disturb reproductive processes [27,28], growth depressants [29, 30], associated with gallstone disease [31], induces several psychogenic and neurogenic abnormalities in adult stages [32,33] and are associated with abortions, premature deliveries, still births and infants with low birth weights [34,35,6]. OCPs have been in use in India nearly for a half century now. Even after having clear cut evidence suggesting that these chemicals have the ability to eliminate entire species from the planet, the annual consumption of pesticides in India is about 85,000 tons of which OCPs comprise the bulk [36]. The widely held of population is affected indirectly through the food, water and environment. It has been well established that 85 to 90 percent of pesticide residues in human bodies are received through food and water. [37,38].

Conclusion

Consumption of clean and safe drinking water is one of the significant challenges these days. In India, surface and groundwater are the major sources of drinking water. Degraded quality due to contamination of surface and groundwater with OCPs is a significant issue worldwide. We discovered the negative impact of OCPs on the environment and have successively banned few of them in India. However, due to their persistence in the environment and their use in public health and in agriculture, OCPs have still been detected in environmental media such as water bodies, sediments, and organisms in recent years. In the present study, we reported the recent OCPs level in drinking water collected from four zones of Alwar city and its surrounding. The results indicated the presence of isomers of HCH, heptachlor, DDT, Endrin, Endosulphan, Chlordane and its metabolites and Methoxychlor, Dieldrin, Aldrin in water samples. From the present study, it must be accentuated that there is a rising protest that pesticides are destroying environment equilibrium and endangering the health of man himself.

Integrated pest management (IPM) strategies should be implemented which emphasizes on the use of non-chemical methods of pest control, such as biological control, cultural practices, and habitat modification. The battle against the harmful insects would be much less costly and more efficient, and the problem of contamination of the environment by toxic materials would be vastly reduced, if insect activities are controlled by natural means. The use of pest-specific predators; parasites or pathogens; sterilization of insects with the help of radiations; trapping insects using insect attractants like pheromones; use of juvenile hormones or hormone inhibitors may therefore be suggested as alternate ways of pest control. chemical pesticides will continue to perform a vital role in pest management. We need to phasing out the chemical pesticide and replace with bio-pesticide and more sustainable agricultural practices. Public awareness campaigns can help to reduce exposure to OCPs and promote the use of safer alternatives. It is crucial to continue research, monitoring, and education efforts to fully understand the impacts of pesticides and to promote safer and more sustainable solutions.

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Table Abbreviations:

ΣBHC= α- BHC + γ- BHC + β- BHC + δ- BHC
ΣHeptachlor= heptachlor+ Heptachlor Epoxide
ΣClordane= γ- Clordane+ α- Clordane
ΣEndosulfan= Endosulfan Sulphate+ Endosulfan I + Endosulfan II
ΣDDT=4,4-DDE+4,4-DDD +4,4-DDT
ΣEndrin= Endrin+ Endrin Ketone + Endrin Aldehyde
ΣOCPs= α- BHC + γ- BHC + β- BHC + δ- BHC+ γ- Clordane+ α- Clordane+ Endrin+ Endrin Ketone + Endrin Aldehyde+ Aldrin + Dieldrin+ heptachlor+ Heptachlor Epoxide+ Endosulfan Sulphate+ Endosulfan I + Endosulfan II+ Methoxychlor+4,4-DDE+4,4-DDD +4,4-DDT
N-No of sample
n-no of positive samples
ND- Not Deleted. .

Table 01: Amount of OCPs detected in the Drinking Water Samples from East, West, North and South Zone of Alwar

#	OCPs detected	East Zone		West Zone		North Zone		South Zone	
	(N=20)	Range	Mean ± S. E	Range	Mean ± S. E	Range	Mean ± S. E	Range	Mean ± S. E
1.	α BHC	0.007-0.132	0.022±0.009 (n=07)	0.002-0.184	0.023±0.011 (n=07)	0.015-0.132	0.021±0.009 (n=07)	0.002-0.171	0.018±0.011 (n=07)
2.	β BHC	0.031-0.425	0.131±0.026 (n=19)	0.007-4.599	0.340±0.226 (n=15)	0.035-4.599	0.351±0.224 (n=18)	0.035-4.599	0.351±0.224 (n=18)
3.	γ BHC	0.015-0.825	0.074±0.041 (n=19)	0.003-0.174	0.018±0.009 (n=09)	0.003-0.174	0.070±0.041 (n=14)	0.003-0.174	0.009±0.042 (n=09)
4.	δ BHC	0.023-0.177	0.113±0.015 (n=17)	0.008-0.229	0.085±0.020 (n=12)	0.017-0.281	0.106±0.019 (n=16)	0.022-0.215	0.075±0.019 (n=11)
5.	Heptachlor	0.037-0.351	0.113±0.020 (n=15)	0.015-0.769	0.194±0.045 (n=17)	0.032-0.199	0.105±0.016 (n=16)	0.042-0.687	0.181±0.032 (n=18)
6.	Heptachlor Epoxide	0.044-0.568	0.089±0.030 (n=14)	0.069-1.195	0.063±0.060 (n=02)	0.042-0.568	0.084±0.031 (n=11)	0.066-1.195	0.071±0.059 (n=04)
7.	Aldrin	0.021-0.088	0.019±0.007 (n=13)	0.06-0.068	0.006±0.004 (n=02)	0.013-0.088	0.009±0.005 (n=04)	0.051-0.068	0.006±0.004 (n=02)
8.	Dieldrin	0.048-0.195	0.059±0.012 (n=14)	0.084--0.113	0.014±0.008 (n=03)	0.033-0.195	0.050±0.013 (n=12)	0.023-0.089	0.029±0.009 (n=03)
9.	α Clordane	0.036-0.262	0.137±0.019 (n=19)	0.005-0.448	0.124±0.034 (n=14)	0.018-0.287	0.118±0.019 (n=19)	0.005-0.368	0.105±0.026 (n=17)
10.	γ Clordane	0.023-0.375	0.078±0.024 (n=15)	0.035-0.461	0.075±0.030 (n=08)	0.012-0.375	0.089±0.024 (n=17)	0.033-0.337	0.061±0.020 (n=12)
11.	Endosulfan I	0.038-0.204	0.060±0.014 (n=12)	0.051-0.513	0.098±0.027 (n=13)	0.036-0.204	0.077±0.012 (n=17)	0.044-0.241	0.080±0.013 (n=16)
12.	Endosulfan II	0.048-0.232	0.080±0.011 (n=20)	0.037-0.428	0.102±0.020 (n=20)	0.033-0.232	0.079±0.012 (n=20)	0.033-0.428	0.081±0.020 (n=20)
13.	Endosulfan Sulphate	0.056-0.279	0.114±0.015 (n=20)	0.082-0.192	0.104±0.012 (n=17)	0.058-0.279	0.103±0.014 (n=20)	0.068-0.179	0.099±0.008 (n=19)
14.	4,4-DDE	0.043-0.526	0.104±0.034 (n=13)	0.094-0.149	0.023±0.011 (n=04)	0.020-0.228	0.038±0.014 (n=09)	0.037-0.097	0.011±0.007 (n=03)
15.	4,4-DDD	0.043-0.240	0.038±0.017 (n=05)	0.0237-0.440	0.062±0.029 (n=04)	0.127-0.177	0.024±0.013 (n=03)	0.255-0.440	0.035±0.025 (n=02)
16.	4,4-DDT	0.006-0.220	0.045±0.011 (n=19)	BDL	0.000±0.000 (n=0)	0.024-0.22	0.040±0.012 (n=15)	0.033-0.035	0.003±0.002 (n=02)
17.	Endrin	0.055-0.765	0.172±0.043 (n=19)	0.073-0.452	0.157±0.024 (n=19)	0.062-0.276	0.115±0.014 (n=19)	0.023-0.204	0.100±0.011 (n=19)
18.	Endrin Aldehyde	0.069-0.370	0.126±0.018 (n=20)	0.104-0.744	0.115±0.036 (n=14)	0.067-0.370	0.129±0.018 (n=20)	0.079-0.744	0.136±0.033 (n=18)
19.	Endrin Ketone	0.045-0.281	0.094±0.014 (n=20)	0.079-0.259	0.141±0.015 (n=19)	0.045-0.281	0.099±0.014 (n=20)	0.057-0.251	0.105±0.012 (n=19)
20.	Methoxychlor	0.035-0.446	0.088±0.024 (n=20)	0.052-0.483	0.163±0.030 (n=20)	0.036-0.267	0.070±0.014 (n=20)	0.039-0.395	0.105±0.023 (n=20)
21.	∑BHC	0.126-1.358	0.340±0.065 (n=20)	0.008-4.736	0.466±0.227 (n=20)	0.036-1.358	0.336±0.069 (n=18)	0.031-4.736	0.461±0.227 (n=20)
22.	∑Heptachlor	0.056-0.759	0.202±0.037 (n=20)	0.015--1.522	0.257±0.080 (n=18)	0.032-0.759	0.189±0.037 (n=16)	0.042--1.522	0.252±0.073 (n=20)
23.	∑Clordane	0.041-0.594	0.215±0.033 (n=20)	0.005-0.675	0.199±0.040 (n=18)	0.030-0.594	0.207±0.035 (n=19)	0.005-0.368	0.166±0.024 (n=20)
24.	∑Endosulfan	0.107-0.690	0.254±0.036 (n=20)	0.094-0.537	0.304±0.027 (n=06)	0.107-0.690	0.260±0.035 (n=20)	0.149-0.506	0.260±0.019 (n=20)
25.	∑DDT	0.025-0.539	0.187±0.045 (n=20)	0.093-0.618	0.084±0.036 (n=06)	0.024-0.539	0.102±0.034 (n=15)	0.035-0.537	0.060±0.029 (n=05)
26.	∑Endrin	0.142-0.980	0.392±0.058 (n=20)	0.251-0.894	0.414±0.037 (n=20)	0.180-0.808	0.343±0.043 (n=20)	0.220-0.894	0.342±0.034 (n=20)
27.	∑OCPs	0.763-5.004	1.756±0.252 (n=20)	0.958-8.324	1.909±0.353 (n=20)	0.759-5.005	1.566±0.251 (n=20)	0.805-8.324	1.671±0.361 (n=20)