GLOBAL JOURNAL OF ENGINEERING, DESIGN & TECHNOLOGY
(Published By: Global Institute for Research & Education)
www.gifre.org

ORGANOCHLORINE PESTICIDES CONCENTRATION IN THE GROUND WATER FROM REGIONS OF EXTENSIVE AGRICULTURE IN LAKHIMPUR KHEERI, UTTAR PRADESH-INDIA

Ashok Kumar Maurya*, Aman Kumar**, Khushbu Sharma*** & P.E. Joseph***

*CSIR-Central Food & Technological Research Institute, Mysore-570020, India (Present Address)
**ICAR-Indian Agricultural Research Institute, Pusa, New Delhi-110012, India
***School of Chemical Sciences, Department of Chemistry, St. John's College, Agra, India

Abstract

Pesticides are found scattered in different environment factors (water, air, soil) wherefrom they are drawn off by vegetal and animal organisms. Water pollution by pesticides results from industry and also massive application of these resources in agriculture and other branches of economy. Pesticides can reach surface water along with dripping waters and by infiltration may reach the groundwater layers, organochlorine pesticides (OCP's) are most often found in the water sources (HCH, DDT, Endosulfan, endrin, dieldrin, aldrin etc) due to their inceased persistence in external environment. Major 21 OCP's were monitored for 27 drinking water samples during three years. Pesticide concentrations were determined using GC-ECD, while GC-MS was used for confirmatory purposes. During the study period, 15% of the samples exceeded the total pesticide level of 0.50 μgL^{-1} indicated in the EECD directive for drinking water. Yearly variations of pesticide residues were also observed during the study period.

Keywords: organochlorine pesticides, drilled well water, Lakhimpur Kheeri region, GC-ECD.

1. Introduction

Water, an essential for life on earth, is one of our most precious natural resources. With the growth of our civilization, the demand for water has increased dramatically and its uses have become much more extensive. Large volume of water is used in industry, agriculture and for personal consumption, highest purity except for some very specific industrial uses. The most common and harmful impurities include bacteria, viruses and different chemical substances including pesticides. Now a days, the contamination of water by pesticides is very important ecological proble, especially in regions with intensive agriculture where leaking of these highly toxic substances into the water supplies may cause strong effects on human and animal health.

Many countries of Asia including India have water quality problems, especially in rural areas where the water networks are small and consumers depend mainly on drilled or deep wells. Water quality standards are difficult to achieve because the treatment of drinking water in these regions is not sufficient. Consequently, drinking water may accumulate high levels of toxic substances including pesticide. Main water intakes in this region are drilled wells or deep wells, which is situated near households or agricultural area.

Organochlorine pesticides (OCPs) are synthetic chemicals and are among the most persistent pollutants in aqueous environments (Baird, 2002). Due to their chronic persistence and bioaccumulation, they have been banned or restricted for some applications, and most of them have been included in the list of priority pollutants in many countries. Several studies have shown that OCPs have deleterious effects on the immune system and increased amounts have been detected. in certain cancerous tissues (Krieger et at., 1994). OCP's have been reported as possibly responsible for stimulating the development of breast cancers in women (Falck et al., 1992) and in male mice normally resistant to breast cancer (Davis et al., 1993). The risk of breast cancer has been related to the possible interaction between organochlorine pesticides and estrogen receptors (Jaga, 2000).

India, having agriculture-based economy, is one of largest insecticide consumers in the world. OCPs present in waters may have an agricultural, domestic, or industrial origin, the most harmful effect being their inclusion in the so-called "nutritionchain". Environmental pollution by pesticides is a major environmental concern (López et al. 2001; Vinas et al. 2002). Organochlorine pesticides are known to resist biodegradation and therefore they can be concentrated through food chains and original concentration at the end of the chain (Sankararamakrishnan et al. 2005). Pesticides are one class of compounds that, despite their benefits, may produce a wide range of toxic side effect that pose a potential hazard to the environment (Golfinopoulos et al. 2003). While pesticides are indispensable in modern agriculture, their use or misuse may

lead to serious water quality problems (Wauchope et al. 1994; El-Kabbany et al. 2000). Pesticide contamination surface and ground waters from agricultural use has been well documented around the world (Wauchope et al.1994; Hairston et al. 1995). Many organochlorine pesticides (OCPs) were used on a global scale from the 1950s to the mid 1980s, most of which are stable and persistent in the environment. Usage of OCPs has been prohibited in most countries including India (Barraet al. 2001; Turgut 2003). Although drinking water contamination from pesticides is rare, it is possible under certain conditions. In India, largest pesticide consumption has been in the state of Uttar Pradesh, according to the data of 1995-1996 and 1999-2000, produced by Central Insecticide Board and Registration Committee, India (Srivastava, S et al.2008; Besbelli 1998). An extremely toxic pesticide can cause the death of fish and other aquatic organisms even at low concentration. They have been reported to alter various reproduction functions in various animals including marine populations. Most surface waters (except deep lakes) have a rapid turn over rate, which means that fresh water dilutes the concentration of the contaminant quickly. In addition, most surface waters contain free oxygen, which enhances the rate at which pesticides are broken down by microorganisms. Pesticides applied immediately before a heavy rain may wash into streams or other surface waters and threaten fish and wildlife. For these reasons, usage of pesticides directly around a drinking water source would be forbidden (Bonner 1993;Pesando et al. 2004).The success of raw water treatment should be examined by pesticide monitoring of the distributed potable water. Certain kinds of older pesticides, such as γ-HCH which may contain persistent α- and β-isomers are still present in the agricultural and could cause the residue problem. Pesticides sorbed to particulates are transported by streams and surface waters (Aydın and Yurdun, 1999).

Monitoring studies in European and Asian countries have shown widespread detection of pesticides in ground and surface water. The levels of pesticides detected in water depend largely on the intensity of agricultural production in a given region. As the council directive 80/778 of the European Union (EU) limits the concentration of individual pesticide and toxic transformation products in drinking water to 0.10 μg $l^{-1}$and the total concentration to 0.50 μg l^{-1}, many methods have been developed for both sample preparation and chromatographic separation and detection. The most common methods of preconcentration of various classes of pesticides from water samples are liquid–liquid extraction and solid-phase extraction (SPE; Quayle et al. 1997; Vassilakis et al. 1998). Solid-phase extraction is a rapidly growing sample preparation method, used most frequently for extracting trace organics in aqueous matrices, prior to injection into a gas chromatography. C-18 SPE has been used in studies of specific materials such as trace metals, individual organic compounds, and pesticides as well as investigations into natural organic matter. Analytical methods for pesticide residues have their main application in the control of food for human consumption, especially in the control of fruit or vegetables and drinking waters since they are generally produced using direct application of pesticides (Nerin et al.1998; Simjouw et al. 2005). Information OCPs in sources of drinking water from Lakhimpur Kheeri (Uttar Pradesh-India) is not available.These studies describe the organochlorine pesticide result in ground waters from Lakhimpur Kheeri region which takes place in the Terai-belt of Uttarpradesh-India, main sources of drinking water are the drilled well waters. Due to high annual rainfall in the region, floods result in transport of contaminants from agricultural areas to ground waters. The objective of the present study was to carry out the levels of various organochlorine pesticide residues in drilled well waters.

2. Material and Methods

Lakhimpur Kheeri (28° 27' 0" North, 80° 35' 0" East) is a largest district in terms of area (Total Area = 7680 sqr km) in Uttar Pradesh, India, on the border with Nepal. Sugarcane, wheat, pulses, oilseeds, rice, and potatoes are grown and processed in this district, forming the backbone of the local economy. Some of India's largest sugar mills are in the district. Bajaj sugar mill in Gola Gokarnathand , Bajaj sugar mill in Palia Kalan and Kishan Sarkari mill in Sampurnanagar are the three largest sugar mills in Asia.

A study was conducted in three areas of Lakhimpur Kheeri namely Palia Kalan (B 1, B 2, B 3), Bhera (B 4, B 5, B 6) and Bhanpur Khajuria (B 7, B 8, B 9). A total of 27 ground water samples were collected from agricultural area. Yearly variations of pesticide detections in drinking water according to the timing of pesticide applications related to sampling intervals have been noticed. Winter months were chosen for sampling because pesticide detections tended to be more frequent and more concentrated during winter seasons. Samples of water were collected from water intakes located within sugarcane growing areas during a three-year period, 2008-2010, in December each year. The examined water supplies were drilled wells whose depth ranged from 15 to 40 meters. The samples were collected from different locations 9 cause changes in the water composition and quality due to defective techniques or improper conditions of material preparation. Before sampling, polyethylene recipients are prepared to clean, rinsed with distilled water, dried, rinsed with petroleum ether, and then dried again. Stored all sample at 4-8 ^{o}C to protect them against changes of their chemical properties.

2.1 Extraction of the Sample

The water samples were extracted following procedure of Environmental Protection Agency (EPA) 508 with slight modification. Liquid –liquid extraction (LLE) is the most commonly used method for water sample preparation. Dichloromethane (DCM) is used as an extraction solvent. Extraction was carried out manually by shaking the water sample and DCM in a separation funnel. A water sample aliquot (1L) was transferred to a separation funnel (2L capacity). Prior to the extraction, 3% (w v^{-1}) sodium chloride was added to all water samples. The extraction was carried out after adding an

aliquot of DCM (150 ml) by vigorous manually shaking till 3 minutes. The phases were then allowed to separate and DCM layer was collected. The extraction was repeated two another times with DCM (100 ml). All DCM layers were collected & evaporated by rotary evaporator. When DCM layer reaches till 5 or 10 mL, fraction was evaporated in a gentle steam of Nitrogen. Final volume was made up into 1 ml by n-hexane and injected 1 µl in gas liquid chromatograph equipped with an electron capture detector (Ni^{63}). The residues were further confirmed on Gas Chromatograph-Mass Spectrometer-Quadrupole on electron ionization (EI) mode.

2.2 Analyte Recovery and Quality Control

The recovery experiment was performed at the three spiking levels (0.002, 0.003 and 0.005 µg L^{-1}) and each concentration was analyzed in triplicate. Recoveries were obtained from 91±3.91 to 108±2.55 % across the three concentrations. The limit of detection (LOD) and Limit of quantification (LOQ) for OCP's was 0.001 µg L^{-1} and 0.002 µg L^{-1}, respectively.

3. Experimental

3.1 ***GC instrument*****:** The residues were quantitatively analyzed on Gas Chromatograph-Shimadzu 2010 (Shimadzu, Kyoto, Japan) equipped with split/splitless auto-injector model AOC-20i. The non-polar stationary phase used was a fused silica capillary column DB-5 (5 % phenyl polysiloxane) of 30 m, 0.25 mm i.d., and 0.25 µm film thickness (J&W Agilent Palo Alto, CA, USA). GC Solution software was used for instrument control and data analysis.

3.2 ***GC/MS instrument*****:** The residues were further confirmed on Gas Chromatograph-Mass Spectrometer-Quadrupole on electron ionization (EI) mode (Shimadzu 2010, Kyoto, Japan) equipped with with split/splitless auto-injector model AOC-20i. The non-polar stationary phase used was a fused silica capillary column DB-1 (1 % phenyl polysiloxane) of 30 m, 0.25 mm i.d., and 0.25 µm film thickness purchased from J&W Agilent Palo Alto, CA, USA. GCMS Solution software was used for instrument control and data analysis.

3.3 ***Turbo-Vap***—Zymark Turbo Vap$^{(R)}$, LV evaporator (Caliper Life Sciences, USA) was used to concentrate the sample.

3.4 ***Liquid dispensers***—Liquid dispensers (Labmax, Witeg Germany, 100 mL) to dispense solvent from the bottle to the samples was used. An adjustable pipette (1mL to 5mL, Finnpipette, Thermo Scientific) was used to transfer the solvent and sample extract to autosampler vials for residues analysis.

3.5 ***Analytical balance***—An electronic weighing balance (Globuz) with digital display was used to weigh the certified reference materials (CRM) and other reagents.

3.6 ***Vials and vessel***— GC autosampler (1.5 mL) vials with septa were used for the final extracts.

4. Reagents

4.1 Dichloromethane, Toluene & n-hexane-Organic solvents were of good quality for pesticide residue analysis and were obtained from Merck (Darmstadt, Germany).

4.2 Pesticide standards- The certified reference material (CRM) for the residue analysis was obtained from Sigma-Aldrich/ Riedel-de-Haen (Zwijndrecht, The Netherlands).

4.3 Preparation of standard solutions- Individual stock solutions (1000 µg mL^{-1}) of pesticide standards were prepared by dissolving 25 mg in 25 mL toluene and n-hexane in the ratio (1:1) in volumetric flask. Each pesticide was successively diluted up to 200, 20, 2 and 1µg mL^{-1}. Standard solution of pesticide mixture of 5 µg mL^{-1} was prepared in n-hexane by mixing each of pesticide in appropriate proportion and the solution (pesticide mixture) was serially diluted to 1, 0.5, 0.1, 0.05, 0.01 and 0.005 µg mL^{-1} n-hexane for the calibration.

Table 1. Concentrations of organochlorine pesticides detected from water samples in 2008

Organochlorine pesticide	Concentration (μg L^{-1})								
	Palia Kalan			Bhera			Bhanpur Khajuria		
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
α−HCH	0.1350	0.0230	ND	ND	ND	ND	ND	ND	ND
β−HCH	0.0563	ND	ND	ND	ND	ND	ND	ND	ND
γ−HCH	0.3562	0.0352	0.2563	0.0526	0.3654	0.3560	0.0523	0.0235	0.2365
δ−HCH	0.0213	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	0.0923	ND	ND	ND	ND	ND	ND	ND	ND
Heptachloreoxide	ND	ND	0.0125	ND	ND	ND	ND	ND	ND
α-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
α-Endosulfane	0.3052	0.1235	ND	ND	ND	ND	0.1252	ND	0.1682
β-Endosulfan	0.3612	0.1025	ND	ND	ND	ND	ND	ND	ND
p,p-DDE	0.2150	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDD	ND	ND	ND	ND	ND	ND	0.0056	ND	ND
p,p-DDT	0.4250	0.0235	ND	0.0135	ND	0.0236	ND	0.3564	0.0235
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin	ND	ND	0.0052	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	0.004	ND	ND	ND
Endosulfan sulfate	0.0235	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	0.0163	ND	ND	0.0142	ND	0.0092
Endrin Ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	0.0125	ND	ND	ND	ND	0.0114	ND	ND

European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water: the total pesticide level should not exceed 0.50 μg L^{-1} and individual pesticide should not be greater than 0.10 μg L^{-1}.
ND not detected

Table 2. Concentrations of organochlorine pesticides detected from water samples in 2009

Organochlorine pesticide	Concentration (μg L^{-1})								
	Palia Kalan			Bhera			Bhanpur Khajuria		
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
α−HCH	0.1021	ND	ND	ND	ND	0.0056	ND	ND	ND
β−HCH	0.0235	0.0201	ND	ND	ND	ND	ND	ND	ND
γ−HCH	0.3012	ND	ND	0.2135	ND	ND	ND	0.0025	ND
δ−HCH	0.0156	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachloreoxide	0.0035	ND	ND	ND	ND	ND	ND	ND	ND
α-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
α-Endosulfane	0.2365	ND	ND	ND	ND	0.1250	ND	ND	ND
β-Endosulfan	0.2754	ND	ND	ND	ND	0.2360	ND	ND	ND
p,p-DDE	0.0068	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDD	ND	ND	ND	ND	ND	0.0045	ND	ND	ND
p,p-DDT	0.2151	ND	ND	0.1578	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin	ND	ND	ND	0.0026	ND	ND	ND	0.0036	0.0029
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	0.0030	ND	ND	0.0314	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	0.0025
Endrin Ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	0.0023	ND	0.0021	ND	ND	0.0025

European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water : the total pesticide level should not exceed 0.50 μg L^{-1} and individual pesticide should not be greater than 0.10 μg L^{-1} .
ND not detected.

5. Results

The concentrations of organochlorine pesticides , including α-, β-, γ-, and δ- hexachlorocyclohexane (HCH), heptachlor, heptachlor epoxide, dieldrin, aldrin, endrin, endrin aldehyde, α-endosulfan, β-endosulfan, endosulfan sulfate, p,p′-DDE, p,p′-DDD, p,p′-DDT, methoxychlor, Heptachlordane, Transchlordane, Endrinketone & hexachlorobenzene were determined to evaluate the level of contamination during 2008-2010 (Table 1, 2, 3). Out of 27 samples, 18 were found to be contaminated viz. DDT, HCH, aldrin, heptachlorepoxide, endosulfan, dieldrin endrin aldehyde, endosulfan sulfate residues methoxychlor and ,hexachlorobenzene. The highest OCP's residues were recorded in 2008 followed by 2009 & 2010. The highest incidence of contamination (>0.10 μg L^{-1}) can be seen in the case of α-HCH, γ- HCH, α-endosulfan, β-endosulfan, p,p′-DDT, and p,p′-DDE (7%, 48%, 26%, 26%, 19% and 4%). Lindane was found most dominant pesticide in maximum contaminated samples. During the three years study, concentration of lindane ranged from 0.0235 to 0.3654 μg L^{-1}.Total 8 samples were exceeded the limit for lindane prescribed by World Health Organization (WHO) and European Union (EU) limit for individual pesticide (0.1 μg L^{-1}) followed by α-endosulfan (7), β-endosulfan (7), p,p′-DDT (5), α-HCH (2), and p,p′-DDE (1) . Throughout the studied period, the γ- HCH was exceeded in five samples of 2008 (B-1; 0.3562, B-3; 0.2563, B-5; 0.3654, B6; 0.3560, B-9; 0.2365) followed by two samples of 2009 (B-1; 0.3012, B-4; 0.2135) and one sample of 2010 (B-2; 0.2365). The total residue of HCH, DDT and Endosulfan were found 0.5688, 0.67 and 0.64 μg L^{-1} in 2008 for Palia Kalan area. However, one sample of endosulfan was found 0.52 μg L^{-1} in 2009 for same location. These values were exceeded the limit prescribed by World Health Organization (WHO) and European Union (EU) limit for pesticides (0.5 μg L^{-1}). Moreover, a large number of water samples contaminated with DDT, endosulfan, HCH and other OCP's was observed during the study.

Table 3. Concentrations of organochlorine pesticides detected from water samples in 2010

Organochlorine pesticide	Concentration (μg L^{-1})								
	Palia Kalan			Bhera			Bhanpur Khajuria		
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
α−HCH	ND	0.0023	ND	ND	ND	ND	ND	ND	ND
β−HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND
γ−HCH	ND	0.2365	ND	ND	ND	ND	ND	ND	ND
δ−HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachloreoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND
α-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
α-Endosulfane	ND	0.1235	ND	ND	ND	0.1654	ND	ND	0.1354
β-Endosulfan	ND	0.1568	ND	ND	ND	0.1365	ND	ND	0.1052
p,p-DDE	ND	0.0034	ND	ND	ND	ND	ND	ND	0.0047
p,p-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDT	ND	ND	ND	ND	ND	0.1269	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin	ND	0.0030	ND	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin Ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	0.0026	ND	ND	0.0236

European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water : the total pesticide level should not exceed 0.50 μg L^{-1} and individual pesticide should not be greater than 0.10 μg L^{-1} .

6. Discussion

Ground water is the principle source of fresh water for rural and industrial region. In Lakhimpur Kheeri rural region the sources of drinking water are drilled wells located mainly within the household or agricultural area. Considerable amount of organochlorine pesticides were detected in this area. Moreover, a high incidence of pollution of water intake by these pesticides (particularly DDT, endosulfan and HCH) was observed.

The median level of pesticides did not change considerably during the three-years observation period. Uttar Pradesh, in several cases high levels of these compounds were detected. This, apparently, could be associated with improper dilution or disposal of pesticide concentrates. Morever, washing spraying equipment near water intakes was a common practice in this area. Finally, the leakage of waste pesticides stored in tomb-like containers can not be excluded.

The high percentage of contaminated samples observed in this study may be related to extensive application of organochlorine in Lakhimpur Kheeri region. High occurrence of DDT, endosufan and HCH in water samples reaching 19 – 48% confirms that these three pesticides are still in use or persistent in the environment.It is clear that agricultural activity can lead to contamination of ground water found in spaces between soil particles and rocks. These are several factors that determine pesticide movement to ground water. These include properties of the pesticide, properties of the soil, rainfall and depth of ground water, method and rate of application of pesticide (Buttler T et al. 1993). Organochlorine pesticides examined in this study persist for many years in soil and refractory to degradation by microorganisms, chemical reaction and sunlight (Martijin A et al. 1993). The health effects of occupational and general population exposures to organochlorine compounds include neurologic deficits, cancer-especially non-Hodgkin's lymphoma and leukaemia, developmental and reproductive impairment (Longnecher MP et al. 1997).

7. Conclusion

It may be concluded that the presence of organochlorine pesticides in high concentrations may cause important sanitary and ecological problems in Lakhimpur Kheeri region, Moreover, since these toxic substances strongly influence human health and are persistant in the environment, improved educational and control activity is needed in this region.

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