IDENTIFICATION AND QUANTIFICATION OF ORGANOCHLORINE PESTICIDE RESIDUES IN GROUND AND SURFACE WATER FROM AGRICULTURAL AREA FROM CHHINDWARA DISTRICT

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ABSTRACT

A study undertaken in Chhindwara district in Madhya Pradesh state of India has shown the presence of high concentrations of Organochlorine pesticides in the surface and ground water samples located in agricultural area. Total number of 11 water samples was collected from ground and surface water source covering an agricultural area. Liguid-liquid extraction followed by GC-ECD was used for the determination of these compounds. In the ground water samples collected from the various hand pumps, open wells, tube wells located in agricultural area, apart from HCH isomers(α-HCH, β-HCH, and δ-HCH), Endosulfan isomers (α-Endosulfan and β-Endosulfan), was also detected. The maximum concentration value of α-Endosulfan (0.292ppb), β- Endosulfan (0.16 ppb), α-HCH (0.16ppb), β-HCH (0.15ppb) respectively.

Key Words: Organochlorine pesticides residues, Ground and Surface water, Gas chromatography, Contamination, Integrated Management Programme (IMP).

Introduction

Pesticide contamination of fresh water, which has emerged as an important environmental problem in the last few decades. It is causing concern with respect to the long-term and low dose effects of pesticides on public health as well as non-target species (Sudo, M., *et al* 2002). Some insects and fungi gradually become resistant to chemical compounds many farmers feel they must apply higher concentrations after a period of time to achieve the same result for agricultural use (Noori,J.,*et al*1994).The use of pesticides in agriculture may lead to

contamination of surface and ground water by drift, runoff, drainage and leaching. Surface water contamination may have ecotoxicological effects for aquatic flora and fauna and also for human health if used for public consumption (Forney,D.,*et al* 1981,Mulla,M.,*et al* 1981). Surface water contamination usually depends on the agricultural season and does not last long, while ground water contamination has a strong inertia, which may cause a continuous human exposure (Funari, E., *et al* 1995). Growing demand for food as a result of increasing population has lead to substantial rise in the production and utilization of wide of pesticides in agriculture. The water supplies of several Indian cities as well as the ground water in rural areas have been contaminated with high levels of pesticides, mainly the Organochlorines (Dikshith *et al* 1990, Jani *et al* 1991 and Mohapatra *et al* 1995)[3, 8, 10.] Many authors have reported, exceed the WHO guideline value for pesticides in drinking water (WHO 1992)[19]. Organochlorine usages are more (67%) among the total pesticides used in India, which includes Hexachlorocyclohexane (HCH), Endosulfan, Dicofol, Hexaconazol. Pesticides are currenly used in about 25% of the total cultivated land. About 25-35% of the total pesticides consumption in India is in public health applications. HCH is used to control disease transmitting vectors, termite control. HCH and Endosulfan are used to control other phytophagous pests. (Mohapatra). However, Organochlorine pesticides are still used extencively in India due to their effectiveness and low cost (Postel 1988 and Goldberg 1991)[14, 5].

Study Area

Chhindwara districts these are located in Madhya Pradesh state of India. (Fig.1and2). The Chhindwara district located in 21.28 to 22.49^0 North (longitude) and 78.40 to 79.24^0 East (latitude). Chhindwara district occupies an area of 11,815 km^2 and total number of population is 2,0905,306 (2011 census).The climate Chhindwara of district is subtropical. The mean monthly temperature ranges between 32^{0}C to

45^{0}C. It receives an annual rainfall is 1,183mm. The study area is basically an agriculture area and land use for crop production is 66%. Wheat and paddy being the major crops cultivated in Chhindwara district respectively, the following pesticides are used extensively to control pest. Among the insecticides Hexachlorocyclohexane (HCH), Dicofol, Hexaconazol, malathion, monocrotophos, carbaryl, carbofuron are used but mosly being used Endosulfan.

Fig.1: Location of Chhindwara District

Objective

A large number of pesticides are now used in agriculture protection against diverse pest. Pesticides being poisonous in nature not only to the target pests, but also to warm blooded animals including men, their residues left over the spray surface of the crops, or in the soil and water have become a matter of concern in respect of health hazards to men and animals and environmental population. The main objective of this project is Organochlorine pesticide residues in the ground and surface water near agricultural area from Chhindwara districts.

Instrumental components of Gas Chromatography

Gas chromatography (GC) is a separation technique where analyses are done for volatile compounds of a mixture. It consists of stationary phase and mobile phase. In it the sample is vaporized and injected onto the head of a chromatographic column. A carrier gas such as helium or nitrogen, flows through the injector and pushes the gaseous components of the sample onto the GC column. It is within the column that separation of the component takes place. Molecules partition between the carrier gas (the mobile phase) and the high boiling liquid (the stationary phase) within the GC column and finally reach the detector. The detector sends a signal to the chart recorder which results in a peak on the chart paper. The area of the peak is proportional to the number of molecules generating the signal. The compounds are eluted at different retention time. The comparison of retention times is what gives GC its analytical usefulness.

a) Carrier gas

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependent upon the type of detector used. The carrier gas system also contains a molecular sieve to remove water and other impurities.

b) Sample injection port

For optimum column efficiency, they should not be too large, and should be introduced onto the column as a "plug" of Vapour- slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a micro syringe is used to inject samples through a rubber septum into a flash vaporizer port at the head of the column. The injector can be used in one of two modes; split or split less.

c) Columns

There are two general types of column, packed and capillary (also known as open tubular). Packed columns contain a finally divided, inert, solid support materials (commonly based on diatomaceous earth) coated with liquid stationary phase. Most packed columns are 1.5-10m in length and have an internal diameter of 2-4mm. Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; wall- coated open tubular (WCOT) or support-coated open tubular (SCOT). Both types of capillary column are more efficient than packed columns.

d) Column temperature

For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependent upon the boiling point of the sample.

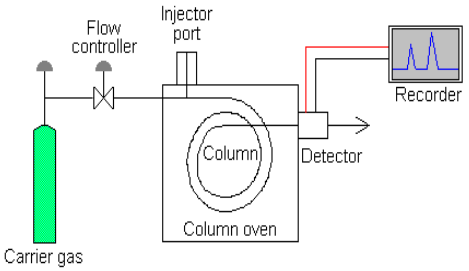
e) Detectors

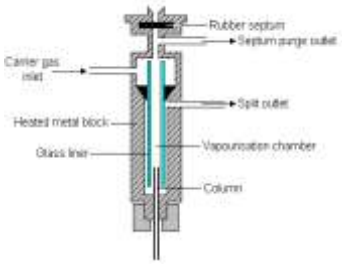
There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity.

Electon Capture Detector (ECD)

The Electron Capture Detector (ECD) has become one of the most widely used detectors for environmental samples because this detector selectivity detects halogen containing compounds, such as pesticides and polychlorinated biphenyls. The effluent from the column is passed over a β emitter, usually nickel-63. An electron emitter causes ionization of the carrier gas (often nitrogen) and the production of a burst of electrons. In the absence of organic species, a constant standing current between a pair of electrodes result from this ionization process. The current decreases markedly, however, in the presence of those organic molecules that tend to capture electrons. The response is nonlinear unless the potential across the detector is pulsed. The electron-capture is selective in its response, being highly sensitive to molecules containing

electronegative functional groups such as halogens, peroxides, quinines, and nitro groups. An important application of the detection and determination has been for the determination of chlorinated insecticides.





Scheme for Gas Chromatography

Sample Injector

Result and Discussions

Recovery of spiked samples

The recovery experiment is carried out to check the accuracy and standardized suitable method. Detailed investigations were carried out to study and check the efficiency of liquid –liquid extraction techniques. In the experiment distilled water were spiked with known amount of standards with varying concentrations. The spikes samples were extracted, concentrated and further analyzed using Gas chromatography. The recovery is calculated by comparing sample chromatogram with those of standards chromatogram. The recovery factor has been calculated and percent recovery was obtained. Spiking level was 1 ppb (µg/L)

Percent recovery of samples (µg/L) (Organochlorine pesticides)

S.No.	Pesticides	% Recovery	
		Sample 1	Sample 2
1	α –HCH	71	68
2	β-HCH	74	71
3	γ-HCH	79	63
4	δ-HCH	86	61
5	α- Endosulfan (Endo I)	85	60
6	β- Endosulfan (EndoII)	85	70
7	Endosulfan sulphate (Endo-SO_4)	64	63
8	Dicofol	56	62

Water sampling sites for the analysis

Groundwater- tubewells and handpumps from Chhindwara districts.

Surface water- lakes and river water from Chhindwara districts.

Results for the Ground water

Samples were analyzed the analytical method by using simulated samples. Results for the ground water study are given

Organochlorine pesticide residues (ppb) in ground water samples near in agricultural area (January 2011)

Sites	Pesticide residues (ppb)								
District	α - HCH	β-HCH	γ-HCH	δ-HCH	Endo I	Endo II	Endo -SO_4	Dicofol	Hexaconazol
Chhindwara									
Sample 1	ND	ND	ND	ND	0.292	ND	ND	ND	ND
Sample 2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 4	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample 5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 6	ND	ND	ND	0.086	ND	ND	ND	ND	ND
Sample 7	0.161	0.150	ND	ND	0.031	0.017	ND	ND	ND
Sample 8	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 9	0.019	ND	ND	ND	ND	ND	ND	ND	ND
Sample 10	ND	ND	ND	ND	ND	ND	ND	ND	ND

Organochlorine pesticide residues (ppb) in ground water samples near agricultural area (February 2011)

Sites	Pesticide residues (ppb)								
District	α - HCH	β-HCH	γ-HCH	δ-HCH	Endo I	Endo II	Endo-SO_4	Dicofol	Hexaconazol
Chhindwara									
Sample 1	ND	ND	ND	ND	0.056	ND	ND	ND	ND
Sample 2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 8	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 9	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 10	ND	ND	ND	ND	ND	ND	ND	ND	ND

Organochlorine pesticide residues (ppb) in ground water samples near agricultural area (March 2011)

Sites	Pesticide residues (ppb)								
District	α -	β-	γ-	δ-	Endo	Endo	Endo-	Dicofol	Hexaconazol

	HCH	HCH	HCH	HCH	I	II	SO_4		
Chhindwara									
Sample 1	ND	ND	ND	ND	ND	0.16	ND	ND	ND
Sample 2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 4	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 5	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 6	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 7	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 8	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 9	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sample 10	ND	ND	ND	ND	ND	ND	ND	ND	ND

Organochlorine pesticide residues (ppb) in Surface water samples near agricultural area (January 2011)

Sites	Pesticide residues (ppb)								
District	α – HCH	β-HCH	γ-HCH	δ-HCH	Endo I	Endo II	Endo-SO_4	Dicofol	Hexaconazol
Chhindwara									
Jam	ND	ND	ND	ND	ND	ND	ND	ND	ND

Organochlorine pesticide residues (ppb) in Surface water samples near agricultural area (February 2011)

Sites	Pesticide residues (ppb)								
District	α - HCH	β-HCH	γ-HCH	δ-HCH	Endo I	Endo II	Endo-SO_4	Dicofol	Hexaconazol
Chhindwara									
Jam	ND	ND	ND	ND	ND	ND	ND	ND	ND

Organochlorine pesticide residues (ppb) in Surface water samples near agricultural area (March 2011)

Sites	Pesticide residues (ppb)								
District	α - HCH	β- HCH	γ- HCH	δ- HCH	Endo I	Endo II	Endo-SO_4	Dicofol	Hexaconazol
Chhindwara									
Jam	ND	ND	ND	ND	ND	ND	ND	ND	ND

Discussion

Pesticide residues in groundwater

Organochlorine pesticide residues were monitored in ground water samples collected from various tube wells, open wells and hand pumps located near the agricultural fields and non agricultural fields. Samples were collected from Chhinwara district during January 2011 to March 2011. In the Chhindwara district the concentration range of the pesticides was detected for α-HCH (ND to 0.16 ppb), β-HCH (ND to 0.15 ppb), γ-HCH (ND), δ-HCH (ND to 0.086 ppb), Endo I (ND to 0.29 ppb), Endo II (ND to 0.16 ppb), Endo-SO_4 (ND), Dicofol (ND), Hexaconazol (ND).

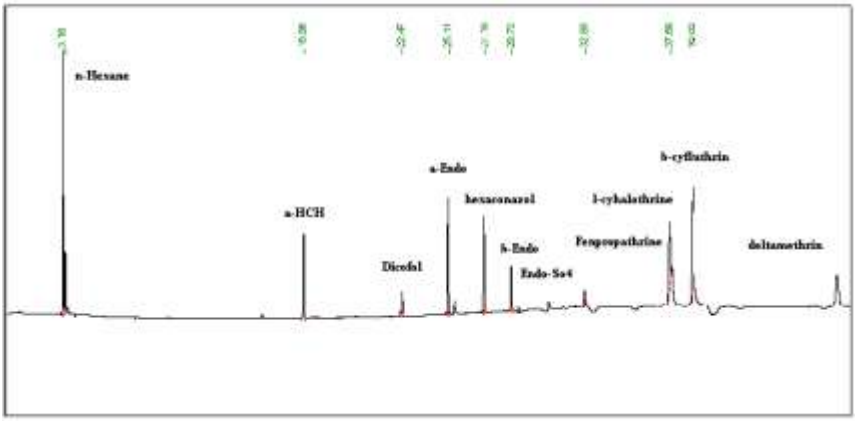
Among the various Organochlorine pesticides detected α-HCH was found to be highest (0.42 ppb) in Bhandara district (Sample no-12) in March. Presence of HCH isomers is possibly due to their extensive use in the past. Residues of Endosulfan are still detected in the water as Endosulfan is the most commonly used pesticide in the studied area.

The Organochlorine pesticide, which have been detected were found well below the WHO Guidelines.

Pesticide residues in Surface water

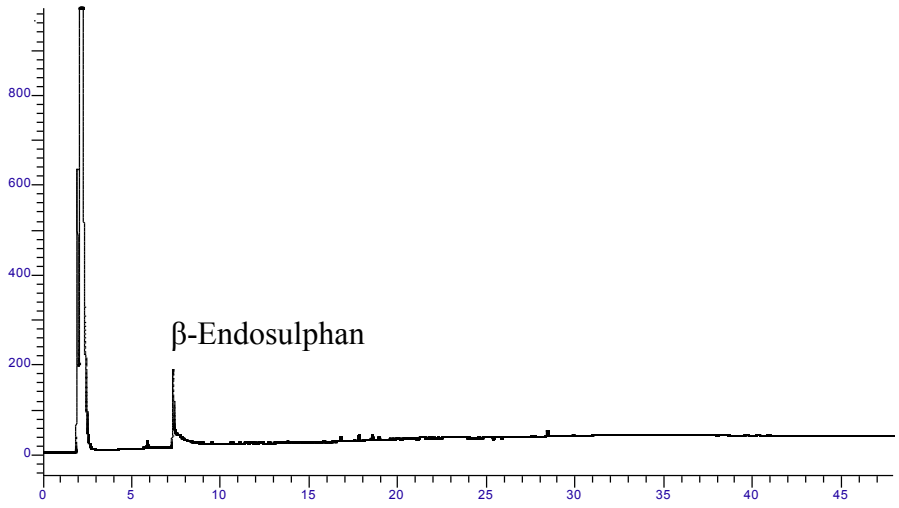
Among the three districts studied in the Chindwada district, Jam River was not detected pesticide any month. The surface water polluted due to HCH and their isomers.

Standard Chromatogram for Organochlorine Pesticide



Standard Chromatogram for Organochlorine Pesticide in Chhinwara district

Operator	Tcinstall
Sample no	CH-11
Instrument name	PERKINELMER CLARUS-500
Sample Volume	1(µL)
Study	Pesticides
Channel	A
End time	48:00 min



Ch 11 ground

Peak	Retention time (min)	Area()	Height (µV)	Pesticide used
1	2.077	17217272.44	987543.85	Endosulphan
2	5.853	59305.78	14984.78	
3	7.576	95017.82	15518.93	
4	15.773	525509.93	11099.28	
5	18.383	10212.80	1784.83	

Conclusion

Pesticides are often considered as quick, easy, and inexpensive solution for controlling weeds and insect pests in urban landscapes. However pesticides use comes at a significant environmental cost. Pesticides have contaminated almost every part of our environment. Pesticide residues are found in soil, air, and in surface and ground water across the nation. The important pesticides that are found as contaminants are Organochlorine pesticides and their derivatives as they persist long in the environment. The present study reports the contamination status of Organochlorine pesticides in ground and surface water of agricultural and non-agricultural areas. Among the various pesticides detected HCH isomers especially α-HCH accounts major percentage in ground and surface water of both agriculture and non agriculture areas. In general, HCH has limited use as pesticide for agriculture purposes. From the

result of its concentration, the conclusion could be drawn that HCH use was extensive previously. Presence of Organochlorine pesticides in surface water is due to possible transfer from agricultural fields and health protection activities carried out near the city. Although, this study was conducted for short period of time (January to March 2011), the results obtained indicated moderately pollution of ground and surface water bodies. These results obtained can be used to design an integrated management program to control the further contamination in the water bodies.

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