

RESEARCH PAPER

## Prevalence of Pesticide Residues in Pond Water Samples at some Districts of Haryana

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### ABSTRACT

The study is assessment of pesticide residues in water bodies/ponds of agriculture intensive areas, as the principal source of pesticides in crops and animal/poultry feed are soil and water. The farmers dump the remaining pesticide solutions and wash the containers with pond water near to their fields after spraying the pesticide on their crops. These measurements can be used as baseline levels to monitor and to predict their impact on the population of the area. The determination of organochlorine (OC), pyrethroids and organophosphorous (OP) insecticide residues was carried out in the samples collected from different village ponds of six districts of Haryana and analyzed at Department of Veterinary Public Health and Epidemiology, COVS, LUVAS, Hisar. A gas chromatograph equipped with an electron capture detector (GC-ECD) for OC and pyrethroids and nitrogen phosphorous detector (GC-NPD) for OP's was employed for analysis. The testing protocol was standardized w.r.t. system precision, specificity and accuracy. The system precision values indicated a good consistency in response by the GC instrument used during present study. A good linearity was noted for standards and spiked tissue samples. Absence of interfering peaks in blank samples indicates good specificity of extraction and clean up method. Accuracy and precision of the method were in accepted range in comparison with international guidelines. Out of 50 samples, none of the sample was found to be positive for OC and Pyrethroid pesticide residues; but 16 pond water samples were detected with OP pesticide residues with prevalence rate of 32%. Monocrotophos and chlorpyriphos were detected in a maximum of eight samples each. Four samples out of 5 from Rohtak, 3 out of 5 from Jind, 3 out of 12 from Mahendergarh and 2 out of 8 from Hisar were found positive for different OP pesticide residues. All the 10 pond water samples from Ambala were found to be below detectable limit for all of the OP pesticides in study. The concentration of 16 positive samples was compared with the MRL's of drinking water, and it was observed that 4 samples, 2 each from Rohtak and Jind for monocrotophos (3.99 & 1.99 ng/ml from Rohtak and 1.82 & 6.88 ng/ml from Jind) violated the normal MRL values (0.5 ng/ml). The investigation revealed that the pond water samples of Rohtak and Sirsa were found to be most contaminated with OP pesticides, mainly with Monocrotophos followed by Chlorpyriphos which indicates the excessive and irresponsible use of these pesticides in these two districts.

**Keywords:** Pesticides residues, pond water, Gas chromatograph, Haryana

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In general the pattern of pesticide usage in India is different from that of the rest of the world. In India 76% of the pesticides used is insecticide, as against 44% globally (Mathur, 1999). Accordingly, the use of herbicides and fungicides is less. India has agrarian economy, where till today agriculture and animal husbandry constitutes important source

of livelihood to more than 70% of the population. Indian farmers have adopted modern techniques of pest management which are required to protect their crops from deadly pests. In India, pesticides are used mainly for disinfestations of crops such as cotton, paddy, fruits, vegetables, cereals, pulses and oilseeds

while a few are also used for domestic pest control and public health.

Several hundred pesticides of different chemical nature are currently used for agricultural purposes all over the world. Because of their widespread use, they are detected in various environmental matrices such as soil, water and air. Pesticides are divided in many classes of which the most important are Organochlorines (OC) and Organophosphorous (OP) compounds. OC pesticides are known to resist biodegradation and therefore, they can be concentrated through food chains and produce a significant magnification of the original concentration at the end of the chain whereas OP pesticides are known to degrade rapidly depending upon their formulation, method of application, climate and the growing stage of the plant (Sankararamkrishnan *et al.* 2004), whereas Pyrethroids (synthetic insecticides) are very commonly applied to many crops because of their efficacy at low doses, their high degradation rate in the environment and their relatively low toxicity with regard to non-target organisms. Pyrethroids are used all over the world to control a wide range of insects in agricultural fields, in greenhouses and in post-harvest storage. Some of them are used in veterinary medicine against some common domestic and farm animal parasites. The positive side of the use of pesticides include enhancement of economic potential in terms of increased production of food and fibre as well as prevention of vector-borne diseases, whereas, on the negative front this resulted in serious health implications to man and the environment.

Pesticide residues reach the aquatic environment through direct runoff, leaching, careless disposal of empty containers, equipment washing, etc. (Miliadis, 1994). The principal sources of pesticides in crops, animal/poultry food products, soil, water and almost all food commodities are (i) carry-over from insecticide application to soil or to growing crops, (ii) leaching of pesticides into ground water, (iii) drift of the pesticides from adjacent field, (iv) translocation from soil applied pesticide into growing crops, (v) disposal of pesticides in streams, rivers and lakes and (vi) washing of empty spray containers in pond

water and drainage along with water from insecticide sprayed fields (vii) effluents of pesticide industry in rivers and streams, and into soil which may be translocated in crops (Mukherjee and Gopal, 1996). There is now overwhelming evidence that some of these chemicals do pose potential risk to humans and other life forms and unwanted side effects to the environment (Igbedioh, 1991).

OP compounds have been widely used for a few decades in agriculture for crop protection and pest control, thousands of these compounds have been screened and over one hundred of them have been marketed for these purposes (Mogda *et al.* 2009). OPs constitute a heterogeneous category of chemicals specifically designed for the control of pests, weeds or plant diseases. Their application is still the most effective and accepted means for the protection of plants from pests, and has contributed significantly to enhanced agricultural productivity and crop yields (Bolognesi 2003).

These pesticides are known to cause endocrine disruption by mimicking or antagonizing natural hormones in the body and it has been postulated that their long term, low dose exposure is linked to animal and human health effects such as immunosuppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer (Crisp *et al.* 1998; Hurley *et al.* 1998; Khurana and Chauhan, 2005).

Perusal of the residue data on pesticides in samples of fruits, vegetables, cereals, pulses, grains, wheat flour, oils, eggs, meat, fish, poultry, bovine milk, butter and cheese in India indicates their presence in sizable amounts (Bhusan, 2006). Food of animal origin has maximum contamination followed by leafy vegetables and garden fruits (Rathore *et al.* 1996). Most of commonly encountered residues of pesticides in food are organochlorines followed by organophosphates and carbamates (Kulkarani and Mitra, 1990). In spite of the fact that organophosphorous pesticides are biodegradable, presence of a few of them has been validated in oil seeds (Singh *et al.* 1998), rice and rice bran (Chinniah *et al.* 1998).

It has been observed especially in the rural agrarian areas that the farmers, after spraying/applying the pesticide solutions to their fields, they dump the left over solutions nearby their fields and wash the containers in the pond water. The dumped solutions and the over sprayed solutions leach out and through rain water reaches the pond and in turn contaminate the pond water. This pond water is used for drinking as well as bathing purposes by the cattle's and poultry; also it is used in the washing of vegetables after harvesting which enables the pesticides to contaminate the foods. Therefore, this study was conducted to know the overall contamination rate of pesticides and their comparative prevalence rate in agriculture oriented and industrialised districts of Haryana. The objective of the present investigation was to standardize the gas liquid chromatography (GLC) technique for detection and quantification of pesticides residues of *Organochlorines* (endosulfan, HCH), *Pyrethroids* (cyhalothrin, cypermethrin and deltamethrin) and *Organophosphates* (dichloroovas, monocrotophos, pirimiphos methyl, fenitrothion, malathiopn, chlorpyriphos, quinalphos and edifenphos) from the pond water samples collected from six different districts of Haryana.

## MATERIALS AND METHODS

**Collection of samples:** The present work was carried out in the Department of Veterinary Public Health and Epidemiology, LUVAS, Hisar. For this study a total of 50 pond water samples were collected from six districts of Haryana viz. Hisar (8 samples), Rohtak (5 samples), Jind (5 samples), Mahendergarh (12 samples), Ambala (10 samples) and Sirsa (10 samples). One litre of pond water samples collected in sterilized glass bottles and stored in a deep freezer at -20 °C until the time of analysis.

**Chemicals and Reagents:** All the individual pesticide reference standards ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, endosulfan sulphate,  $\lambda$ -cyhalothrin, cypermethrin, deltamethrin, dichloroovas, monocrotophos, pirimiphos methyl, fenitrothion, malathion, chlorpyriphos, quinalphos and edifenphos) of purity >98.0% were obtained

from Sigma Aldrich, U.S.A. Ethyl acetate, methanol, dichloromethane, supelclean LC- 18 500 mg per 6 ml SPE cartridges, n-hexane and ultrapure HPLC grade water was also procured from, Sigma Aldrich, U.S.A.

**Preparation of reagents:** Reagents were prepared and calibrated as per the instructions given in Pesticides Residues Manual (AMPRE, 1996). Stock solution of each pesticide (primary standard solution) was prepared in n-hexane. For preparation of working standard solutions, the maximum residue limits (MRLs) prescribed by European Union (EU, 2006) in drinking water and which has been currently enforced in India (Anonymous, 2003) were considered depending upon their existence. Based on the MRLs, a linearity range (10, 20, 30, 40 and 50 ng/ml) was selected to cover the lowest MRL prescribed. Then appropriate dilutions of secondary standard solution in n-hexane were made to produce a required dilution of working solution.

## Analytical Procedures

**Sample extraction and cleanup:** Laboratory method for detection of pesticide residues in pond water was standardized and processed as per the method of Kouzayha *et al.* (2012).

500 ml sample of pond water was passed through the Supelclean<sup>TM</sup>ENVI-18 cartridges conditioned with 3 ml of methanol followed by 3 ml of ultrapure HPLC grade water in a vacuum manifold at the rate of 5-10 ml per minute. The cartridges were then dried on the vacuum manifold for 10 min and centrifuged at 2500 rpm for 2 minutes, then eluted with 3 ml of dichloromethane twice followed by 3 ml of methanol. The elute was then dried in rotary vacuum evaporator at a bath temperature of 60-65°C and reconstituted in 10 ml of ethyl acetate for chromatographic analysis.

## Chromatographic Analysis

**Organochlorines, Pyrethroids and Organophosphate pesticides:** A Shimadzu gas chromatograph model GC 2010 plus equipped with autosampler AOC-20i mounted on a split /splitless injector port connected to <sup>63</sup>Ni electron capture detector through Equity®

5 capillary column (30 m × 0.25 mm I.D.) was used in the study for analysis of both OC and pyrethroid pesticides, with following instrumental conditions:

Initial temperature of column was adjusted to 60°C and held for 0.5 min., then temp was raised at the rate of 20°C/min to 204°C, 2°C/min to 208°C, 0.5°C/min to 210°C then 20°C/min to 300°C held for 5 min. The total run time was 23.20 min. Split ratio used was 1:47 with column flow at the rate of 4.0 ml/min. Injector and detector temperature was set to 200°C & 320°C respectively. Whereas, a programmed temperature vaporizer (PTV) injection port (manual injection) connected to nitrogen-phosphorous detector through Equity 1 capillary column (30 m × 0.25 mm I.D.) was used for analysis of OP pesticides with instrumental conditions as - initial temperature of column was 100°C with hold for 1 min., and then, raised 10°C/min to 200°C without hold, 20°C/min to 260°C with hold for 2 min. The total run time was 16 min, pressure 107.9 kPa, split ratio 1:14, total flow 25 ml/min, column flow 1.47 ml/min, detector temperature was 300°C and injector temperature was 280°C.

## RESULTS AND DISCUSSION

**Standardization and validation studies of Gas Chromatography technique:** In the present study, GC-ECD and GC-NPD techniques were standardized for the extraction of residues of OC/pyrethroid and OP pesticides respectively from pond water as per the method described by Kouzayha *et al.* (2012) with slight modifications. Standard mixtures of selected OC, Pyrethroid and OP pesticides were prepared separately and validated using following parameters:

**(i) System Precision:** The system precision was evaluated by studying the reproducibility of the instrumental response with respect to retention time and area of an analyte. The percent Relative Standard Deviation (%RSD) for all OC, pyrethroids and OP's was found to be less than 0.02 percent for area whereas it was 0.009 percent and 0.34 percent for retention time for OC/pyrethroid and OP's respectively.

**(ii) Specificity:** It was evaluated by visual observation of chromatograms of blank sample matrix and

sample matrix spiked with standard mixture. It was found that the chromatographic signals at the retention times of pesticides were absent in blank sample matrix.

**(iii) Linearity:** The standard calibration curves of the analyzed OC, Pyrethroid and pesticides presented a good regression line ( $r^2 > 0.987$  for OC & pyrethroids and  $r^2 > 0.985$  for OP) in the range of explored concentrations i.e. from 10 to 50 ng/ml. The graphs showing calibration curve of these pesticides, revealed that all concentrations of the OC, Pyrethroid and OP pesticides under study were collinear and thus, calibration curves were further employed for the detection of analytes under study.

**(iv) Limit of detection and Limit of quantitation:** Table 1 and 2 summaries the LOD and LOQ obtained for each analytes in OC, Pyrethroid and OP pesticide group. Perusal of tables clearly indicates that the LOD and LOQ for individual analytes were well below their respective MRLs indicating that the method was able to detect the given pesticide at sufficiently low level. The limit of detection and quantitation are estimated to check the ability of analytical method to detect the analyte at sufficiently low level. Beside method protocol it largely depends upon the skills of analysts. Therefore even for exactly same protocol, the LOD and LOQ estimated by two different analysts in two different laboratories cannot remain same. It is therefore not customary to compare the values of LOD and LOQ estimated by other researchers because the set of experimental conditions, instrumentations and sample protocol does not remain same. In the present investigation the LOD and LOQ values were found to be sufficiently low to detect the pesticides at nanogram levels to serve the purpose of method.

**(v) Accuracy:** The accuracy in terms of percent recovery of each pesticides in all OC, Pyrethroid and OP pesticide group at five different fortification levels (10, 20, 30, 40 and 50 µg/kg) were evaluated and the results are presented in Tables 1, 2 and 3. Satisfactory results were found in almost all the instances. The analyte - matrix combinations recoveries ranged between 83.89 – 92.13, 70.70 – 84.58 and 77.42 - 92.62

**Table 1:** Method performance parameters for detection of OC pesticide residues in pond water

Sl. No.	Analyte	Limit of Detection (mg/L)	Limit of Quantitation (mg/L)	Accuracy (Average recovery %)	Precision (Average CV %)
1	$\alpha$ - HCH	0.000124	0.000261	92.13	9.63
2	$\beta$ - HCH	0.000034	0.000084	90.79	11.19
3	$\gamma$ - HCH	0.000062	0.000170	88.01	11.04
4	$\delta$ - HCH	0.000117	0.000256	84.43	5.01
5	$\alpha$ - Endosulfan	0.000015	0.000035	87.44	4.69
6	$\beta$ - Endosulfan	0.000073	0.000189	92.71	10.37
7	Endosulfan Sulfate	0.000031	0.000081	83.89	5.55

**Table 2:** Method performance parameters for detection of Pyrethroid pesticide residues in pond water

Sl. No.	Analyte	Limit of Detection (mg/L)	Limit of Quantitation (mg/L)	Accuracy (Average recovery %)	Precision (Average CV %)
1	$\lambda$ -Cyhalothrin	0.000013	0.000034	76.32	6.76
2	Cypermethrin	0.000065	0.000174	70.70	6.08
3	Deltamethrin	0.000004	0.000009	84.58	3.95

**Table 3:** Method performance parameters for detection of OP pesticide residues in pond water

Sl. No.	Analyte	Limit of Detection (mg/L)	Limit of Quantitation (mg/L)	Accuracy (Average recovery %)	Precision (Average CV %)
1	Dichloroavas	0.00023	0.00051	77.42	4.89
2	Monocrotophos	0.00003	0.00007	81.71	3.06
3	Pirimiphos Methyl	0.00003	0.00005	92.06	13.58
4	Fenitrothion	0.00006	0.00013	90.48	7.59
5	Malathion	0.00006	0.00012	87.70	10.57
6	Chlorpyriphos	0.00004	0.00008	84.45	6.19
7	Quinalphos	0.00002	0.00004	89.84	10.30
8	Edifenphos	0.00003	0.00005	92.62	13.16

percent for OC's, pyrethroids and OP's respectively. However, in general, the pesticides gave acceptable recoveries within the mentioned validation interval as per EU legislation (EU, 2002) between 70 and 110 percent. The recovery of an analyte in an assay is the detector response obtained from an amount of the analyte added to and extracted from the matrix, compared to the detector response for the true concentration of the pure authentic standard. In the present investigation recoveries were close to 100 % but not more than 100%. Therotically, the recovery should be 100%. However, practically during the chromatographic analysis especially at

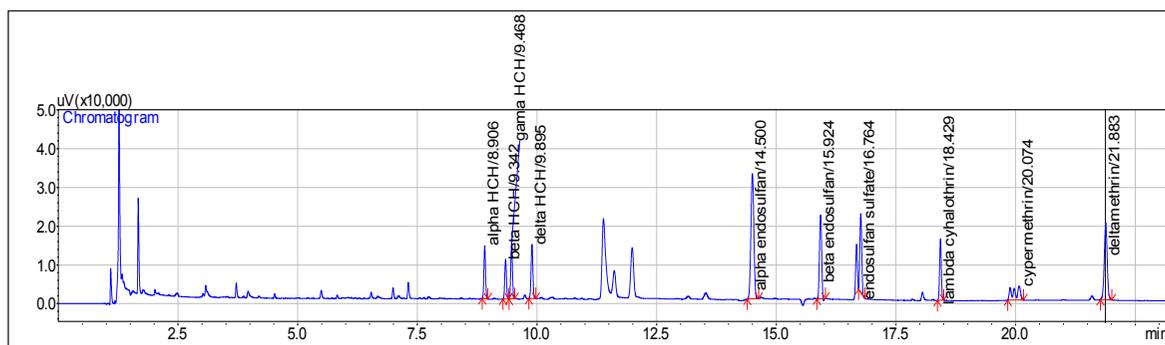
very low concentration of analyte, the recoveries can be found to be less than or more than 100%. Therefore, international standards on method validation has outlined the method requirment in which more than 100% recovery is acceptable to methods in which analytes are detected in certain low range of concentrations. The lower recoveries can be attributed to the loss of analyte during sample preparation. But the reason for higher recoveries is still not clear. Matrix effects are common phenomena in environmental and food analysis when detecting pesticide residues in fat, oil, food and water. Erney *et al.* (1993) studied and reported in detail the matrix-

induced overestimation of organophosphorus pesticides and proposed the mechanism of matrix effects. It was stated that the sample matrix protects the analytes from thermal decomposition or blocks them from adsorption to the active sites of the GC system, primarily inside the injector liner. Thermolabile compounds or polar compounds that are capable of hydrogen bonding tend to have matrix-induced chromatographic enhancement. The chromatographs of standard mixture of OC, Pyrethroid and OP pesticides are shown in Fig.1.

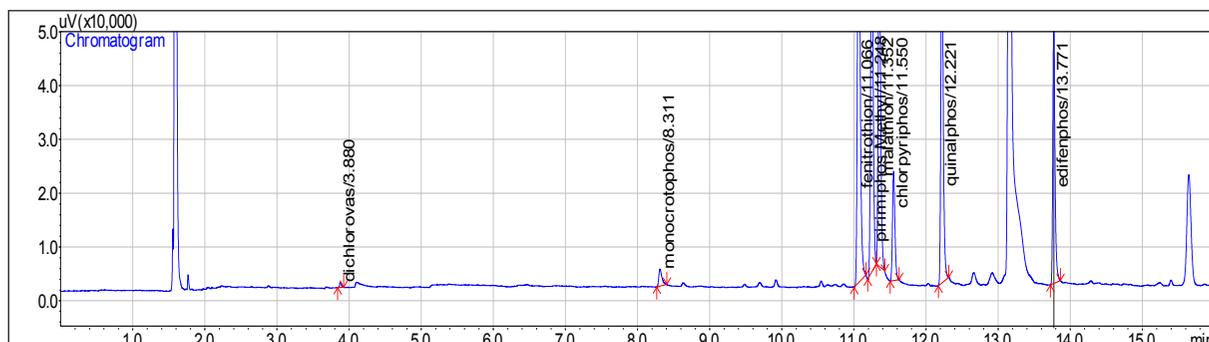
**(vi) Precision:** The precision was assessed, at five concentration levels (10, 20, 30, 40 and 50 ng/ml) of the recovery studies, by extraction and analysis. Repeatability and intermediate precision values, expressed as relative standard deviation (CV percent) were found <11.19 for OC, < 6.76 for pyrethroids and < 13.58 for OP (Tables 1, 2 and 3).

Overall the multiresidue method followed for detection and quantification of OC, Pyrethroid and OP pesticide residues in pond water was subjected to rigorous validation parameters. The system precision values indicated a good consistency in response by the GC instrument used during present study. A good linearity was noted for standards and spiked tissue samples. Absence of interfering peaks in blank samples indicates good specificity of extraction and clean up method. Accuracy and precision of the method were in accepted range in comparison with international guidelines. These results of validation study clearly demonstrated that the present method is suited for routine analysis of OC, Pyrethroid and OP pesticides in water samples.

**Determination of residues of OC, pyrethroids and OP in pond water samples:** After successful standardization and validation of techniques for



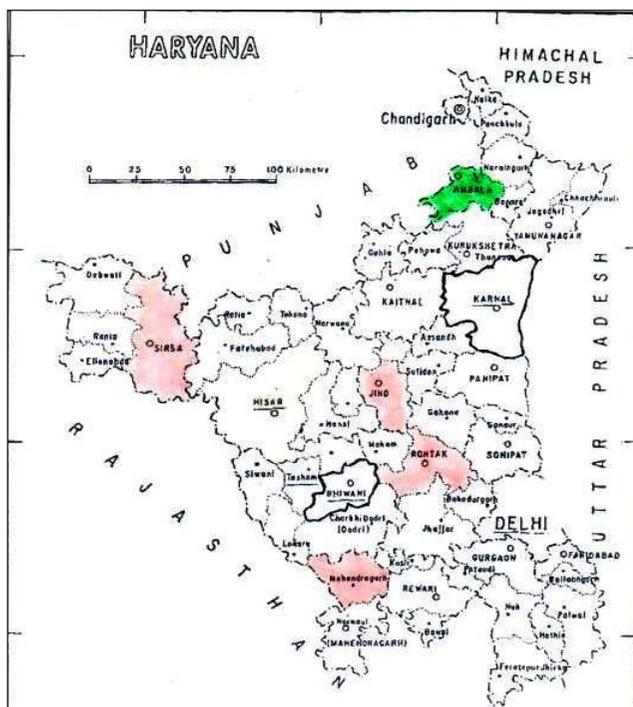
**Fig. 1a:** Standard mixture of OC and Pyrethroid pesticides spiked in the concentration of 10 ng/ml



**Fig. 1b:** Standard mixture of eight OP pesticides spiked in the concentration of 10 ng/ml

**Fig. 1:** Chromatographs of standard mixture of OC, pyrethroid and OP pesticides spiked in water in concentration of 10 ng/ml

detection of OC, Pyrethroid and OP pesticide residues, the extraction, detection and quantification was carried out on 50 samples of pond water collected from six different districts of Haryana. The results obtained are presented in the Table 4. Fig. 2a and 2b show the prevalence of OP pesticides (sample wise as well as district wise) and chromatograms of pond water samples found positive for OP pesticides are shown in Fig. 3.



Map of Haryana indicating the districts under study

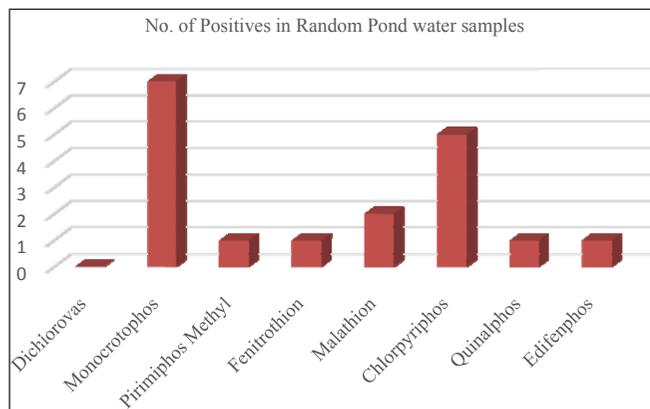


Fig. 2(a): Prevalence of OP pesticide residues in pond water samples

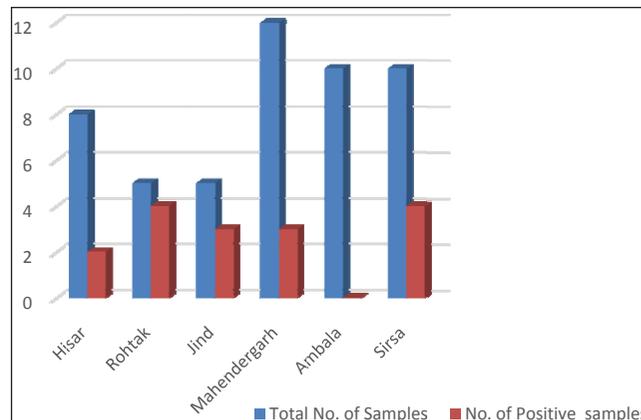


Fig. 2(b): District wise prevalence of OP pesticide residues in pond water samples

Out of 50 samples of pond water collected from six districts of Haryana, none of the samples were found to be positive for OC as well as Pyrethroid pesticide residues. However, in case of OP pesticides 16 samples were found positive with prevalence rate of 32%. In case of Hisar, out of 8 samples, two samples were found to be positive with pond water sample no. 3 (PWS-3), revealing maximum six different types of pesticides viz. pirimiphos methyl (0.121ng/ml), fenitrothion (0.134ng/ml), malathion (0.119ng/ml), chlorpyrifos (0.043ng/ml), quinalphos (0.187ng/ml) and edifenphos (0.285ng/ml) whereas the other sample (PWS-1), revealed only monocrotophos in the concentration of 0.234ng/ml. Out of 5 samples from Rohtak 4 samples (PWS No. 9, 11, 12 and 13) were positive for monocrotophos only in the concentrations of 3.99, 1.99, 0.212 and 0.092 ng/ml respectively. Three samples (PWS No. 15, 16 and 17) from Jind were found positive, out of which PWS-15 was positive for malathion (0.022ng/ml) & chlorpyrifos (0.023ng/ml) whereas PWS-16 and 17 were positive for monocrotophos in the concentrations of 1.82 and 6.38ng/ml respectively. In case of Mahendergarh three samples (PWS No. 26, 29 and 30) were positive for chlorpyrifos in concentrations of 0.093, 0.099 and 0.084. Out of 10 samples of Sirsa, 4 samples were found positive viz. PWS-41 (chlorpyrifos 0.169ng/ml), PWS-45 (pirimiphos methyl 0.015ng/ml and chlorpyrifos 0.013ng/ml), PWS-48 (pirimiphos methyl 0.027ng/ml and chlorpyrifos 0.116 ng/ml)

**Table 4:** Concentration of Organophosphate Pesticide residues in Pond Water Samples collected from six districts of Haryana (in  $\mu\text{g/kg/ppb}$ )

Sl. No.	Samples	Dichlorovas	Monocroto-phos	Pirimiphos Methyl	Fenitrothi-on	Malathion	Chlorpyri-phos	Quinalphos	Edifenphos
<b>District- Hisar</b>									
1	PWS-1	—	0.234	—	—	—	—	—	—
2	PWS-2	—	—	—	—	—	—	—	—
3	PWS-3	—	—	0.121	0.134	0.119	0.043	0.187	0.285
4	PWS-4	—	—	—	—	—	—	—	—
5	PWS-5	—	—	—	—	—	—	—	—
6	PWS-6	—	—	—	—	—	—	—	—
7	PWS-7	—	—	—	—	—	—	—	—
8	PWS-8	—	—	—	—	—	—	—	—
<b>District- Rohtak</b>									
1	PWS-9	—	3.99	—	—	—	—	—	—
2	PWS-10	—	—	—	—	—	—	—	—
3	PWS-11	—	1.99	—	—	—	—	—	—
4	PWS-12	—	0.212	—	—	—	—	—	—
5	PWS-13	—	0.092	—	—	—	—	—	—
<b>District- Jind</b>									
1	PWS-14	—	—	—	—	—	—	—	—
2	PWS-15	—	—	—	—	0.022	0.023	—	—
3	PWS-16	—	1.82	—	—	—	—	—	—
4	PWS-17	—	6.38	—	—	—	—	—	—
5	PWS-18	—	—	—	—	—	—	—	—
<b>District- Mahendergarh-</b>									
1	PWS-19	—	—	—	—	—	—	—	—
2	PWS-20	—	—	—	—	—	—	—	—
3	PWS-21	—	—	—	—	—	—	—	—
4	PWS-22	—	—	—	—	—	—	—	—
5	PWS-23	—	—	—	—	—	—	—	—
6	PWS-24	—	—	—	—	—	—	—	—
7	PWS-25	—	—	—	—	—	—	—	—
8	PWS-26	—	—	—	—	—	0.093	—	—
9	PWS-27	—	—	—	—	—	—	—	—
10	PWS-28	—	—	—	—	—	—	—	—
11	PWS-29	—	—	—	—	—	0.099	—	—
12	PWS-30	—	—	—	—	—	0.084	—	—

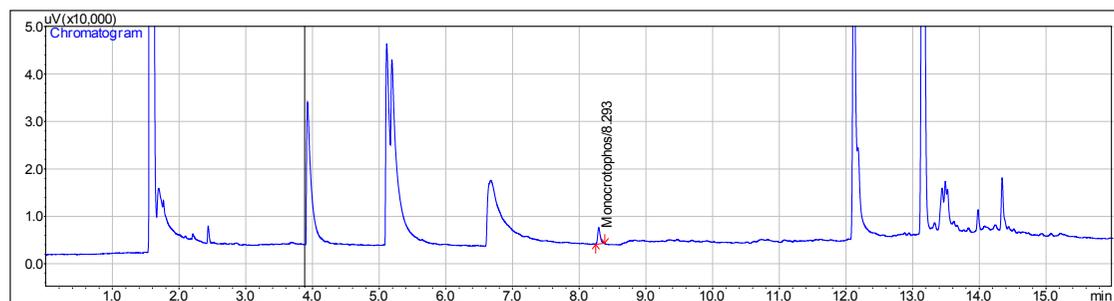
**District- Ambala**

1	PWS-31	—	—	—	—	—	—	—	—
2	PWS-32	—	—	—	—	—	—	—	—
3	PWS-33	—	—	—	—	—	—	—	—
4	PWS-34	—	—	—	—	—	—	—	—
5	PWS-35	—	—	—	—	—	—	—	—
6	PWS-36	—	—	—	—	—	—	—	—
7	PWS-37	—	—	—	—	—	—	—	—
8	PWS-38	—	—	—	—	—	—	—	—
9	PWS-39	—	—	—	—	—	—	—	—
10	PWS-40	—	—	—	—	—	—	—	—

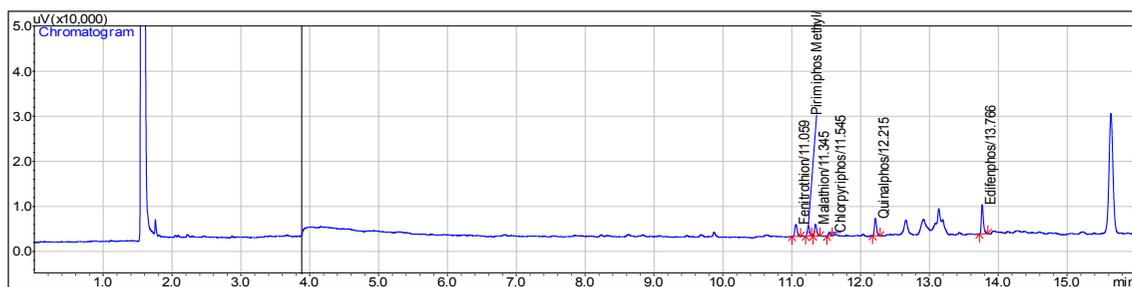
**District- Sirsa**

1	PWS- 41	—	—	—	—	—	<b>0.169</b>	—	—
2	PWS- 42	—	—	—	—	—	—	—	—
3	PWS- 43	—	—	—	—	—	—	—	—
4	PWS- 44	—	—	—	—	—	—	—	—
5	PWS- 45	—	—	<b>0.015</b>	—	—	<b>0.013</b>	—	—
6	PWS- 46	—	—	—	—	—	—	—	—
7	PWS- 47	—	—	—	—	—	—	—	—
8	PWS- 48	—	—	<b>0.027</b>	—	—	<b>0.116</b>	—	—
9	PWS- 49	—	—	—	—	—	—	—	—
10	PWS- 50	—	<b>0.032</b>	—	—	—	—	—	—

*Note: The mark “—” indicates that level of pesticides were below detectable limit.*



**Fig. 3(a):** Sample PWS-1, showing presence of OP pesticides



**Fig. 3(b):** Sample PWS-3, showing presence of OP pesticides

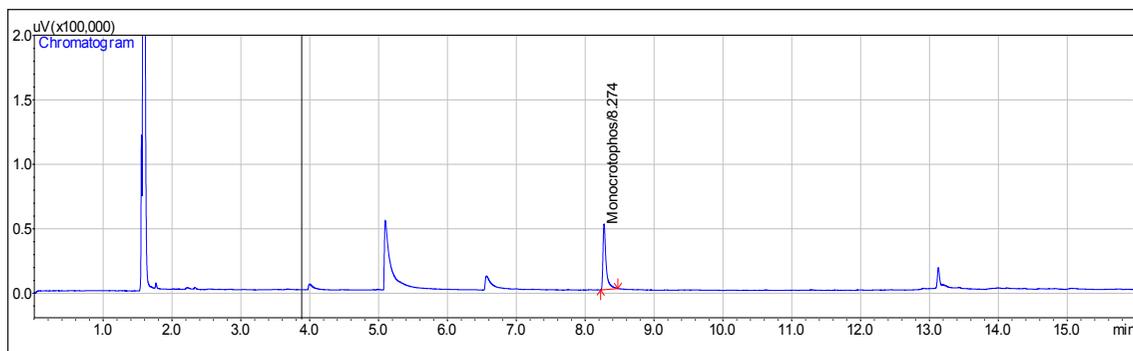


Fig. 3(c): Sample PWS-8, showing presence of OP pesticides

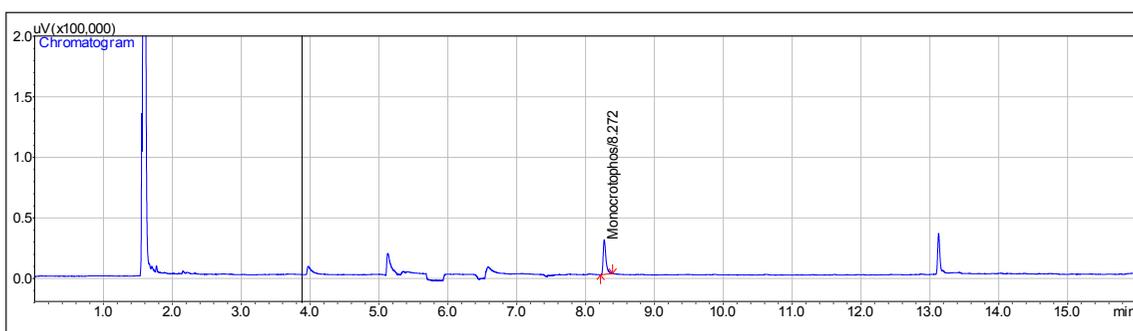


Fig. 3(d): Sample PWS-10, showing presence of OP pesticides

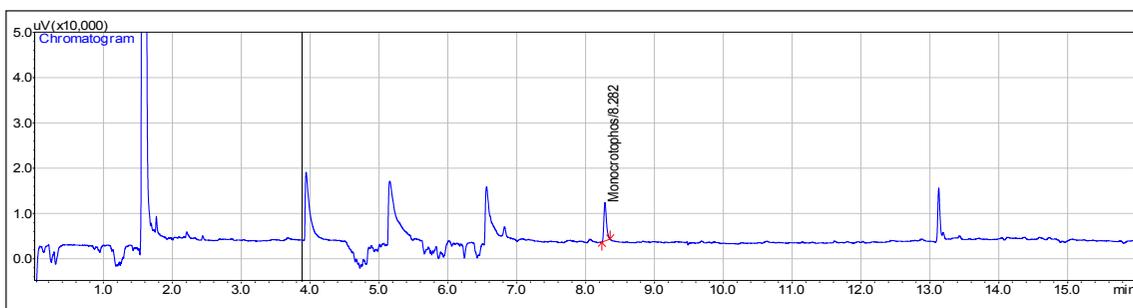


Fig. 3(e): Sample PWS-11, showing presence of OP pesticides

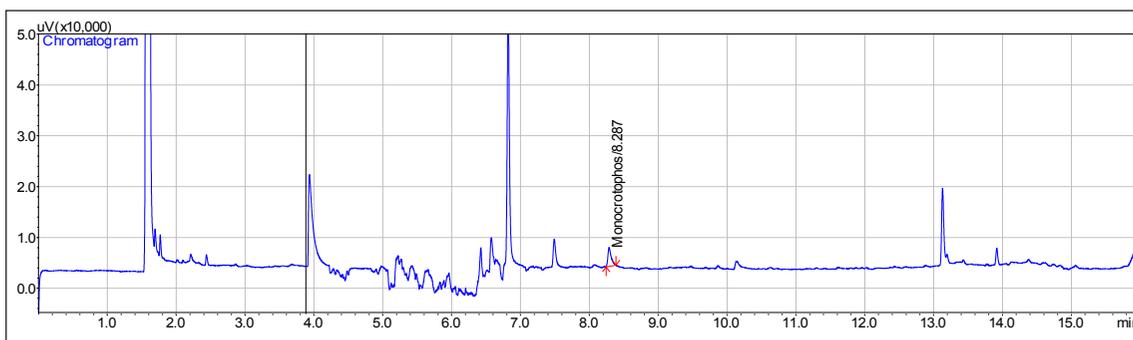


Fig. 3(f): Sample PWS-12, showing presence of OP pesticides

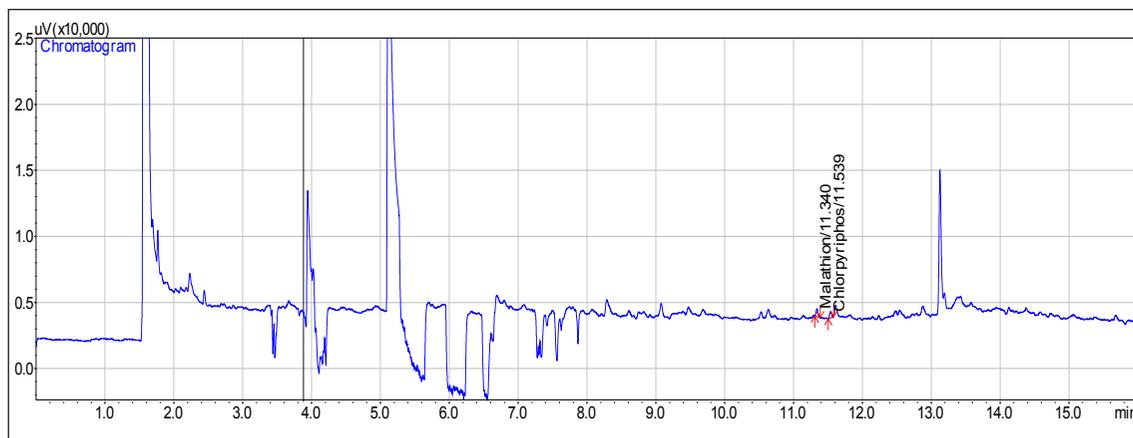


Fig. 3(g): Sample PWS-14, showing presence of OP pesticides

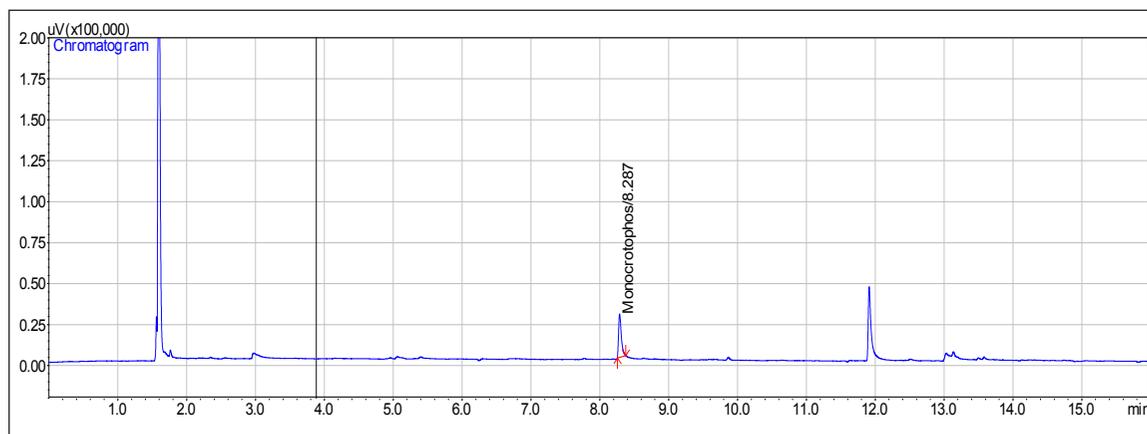


Fig. 3(h): Sample PWS-15, showing presence of OP pesticides

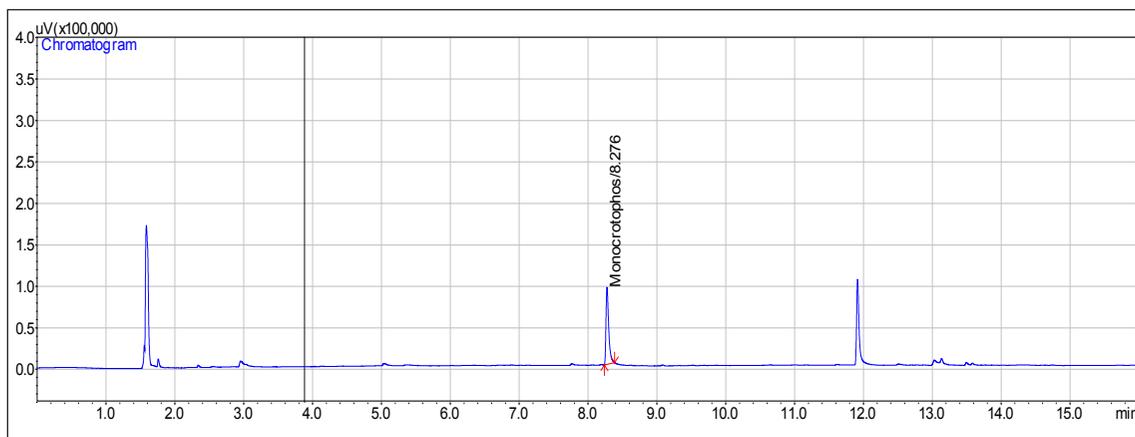


Fig. 3(i): Sample PWS-16, showing presence of OP pesticides

Fig. 3: Chromatograms of pond water samples showing presence of OP pesticides

and PWS-50 (monocrotophos 0.032 $\eta$ g/ml). In case of Ambala out of 10 samples, none of them were found to be positive for OP pesticide residues. Out of all the 50 samples the prevalence of monocrotophos and chlorpyriphos was found to be maximum with 16% percent occurrence of each followed by pirimiphos methyl (6%), malathion (4%), fenitrothion, quinalphos and edifenphos (2% each).

The difference in prevalence of residues in different districts could be attributed to the intensity of agricultural practises as in case of Ambala where most of the areas have been urbanized and many industries have come up due to which the emphasis on Agriculture has reduced as compared to other districts in study. Moreover on analyzing the cropping pattern of the district under study it has been observed that the major crop of Ambala is wheat where as in the rest of the districts cotton is a dominant crop and the use of pesticides in cotton is much more as compared to wheat.

From this study it can be concluded that, monocrotophos and chlorpyriphos were detected in eight samples each, four out of 5 from Rohtak, 3 out of 5 from Jind, 3 out of 12 from Mahendergarh and 2 out of 8 from Hisar. None of the 10 pond water samples from Ambala were found to be positive for any of the OP pesticide residues. The concentration of 16 positive samples was compared with the MRL's of drinking water, and it was observed that 4 samples (2 each from Rohtak and Jind) violated the normal MRL values of 0.5  $\eta$ g/ml (Anonymous, 2003). The pesticide residues through contaminated pond water enter the food chain as the food animals drink and bath in these waters and also through the irrigation of agricultural fields and then to the agricultural produce. This study suggests to establish a baseline residue data bank at the village levels. The data may be utilized in formulating the future programs of pesticide restriction, awareness/training programs of farmers and encouraging organic production. This would help to curtail incidences of diseases caused by prolong exposure to pesticide residues through food. It is suggested that a broader study encompassing more districts of, may be undertaken

to know the prevalence of OP pesticide residues in Haryana. OC's and pyrethroids seems to be not of much public health concern as these pesticides were not detected in any of the samples.

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