

Residual Contamination of Pesticides in Irrigation Water of Some of the Districts of Haryana, India

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Abstract

A survey was conducted to determine the pesticide levels in surface and ground water from thirteen districts of Haryana, India. The samples were collected from various irrigation sources i.e. ponds, river, canal, wells and tube wells. A total of 179 samples of water were analysed for the presence of 53 pesticides. Pesticides were detected in 26% of the samples and in 25 % of the samples, residue levels were above maximum residue limit (MRL). The samplings were conducted during different seasons viz. pre-monsoon, monsoon, post monsoon, summer and winter for a period of five years.

Water samples were processed by Liquid-liquid extraction (LLE) method and samples were analysed by Gas chromatography mass spectroscopy (single quadrapole system). Amongst the total water samples analysed, pesticides were detected 54.5% in monsoon, 70.6% in summer and 0.05% in winter season samples. Pretilachlor was recorded predominantly in the monsoon and summer season samples, while chlorpyrifos was detected in winter season samples.

Keywords: Water, Haryana, Liquid-Liquid Extraction, Regulatory limit, GCMS, DCM, Pre-monsoon, Monsoon, Summer, Winter.

Introduction

Water is one of the essential things on the planet earth without which life is not possible. The quality of drinking water is a problem throughout India, both in rural and urban areas. Consumers depend mainly on rivers, lakes, ponds and deep wells. The consumption of pesticides in India is about 25 % as compared to the rest of the world. India is second largest producer of pesticides in Asia and fourth largest in the world¹³. In 1985, India banned the use of some pesticides listed as Dirty Dozen in the Stockholm Convention, except DDT. DDT is banned in agriculture but however used for malaria control²¹.

In India, the use pattern of insecticide is 80%; herbicide 15% and fungicide 2% whereas globally herbicides are used most: about 47.5% and fungicide 17.5%¹. Pesticides accumulate not only in crops, but also in the soil and move into surface water and other environmental matrices.

River water contamination due to pesticides is a result of agricultural runoff^{15,22}. The pesticides reach the water bodies via soil percolation, or surface runoff, leaching etc. Rivers are main sources of water which are exposed to pollution by pesticides⁶. The maximum limit recently prescribed by the Bureau of Indian Standards (BIS) for drinking water is 0.5 µg/L for total pesticide load and 0.1 µg/L for individual pesticide^{5,17}. The rain water has also been reported to be contaminated¹⁴. Organochlorine pesticides (OCP's) were reported in drinking water from different cities of India namely Hyderabad¹⁹, Jaipur⁶ and Kanpur¹⁸.

The presence of organochlorine pesticides has been reported in Indian rivers system like Hindon¹⁴, Gomti, Ganga²⁰, Ghaggar² and Yamuna¹² and in the Bay of Bengal¹⁶. Organochlorine pesticides have been reported to be present in the Yamuna river and in other major rivers of eastern region of Haryana. Some herbicides like metolachlor and alachlor have been detected in both surface and ground waters⁹. The persistence of pesticides residues in soil and water affects the aquatic life, soil micro-organism and drinking water quality⁴.

Material and Methods

Study Location: The focus of the study was assessment of the irrigation water for the presence of pesticides. The sampling area covered the 13 major districts of Haryana viz. Faridabad, Bhiwani, Sirsa, Mewat, Jind, Fatehabad, Kaithal, Rewari, Ambala, Gurugram, Kurushetra, Yamunanagar and Palwal. The sampling was conducted throughout the year summer, winter, pre-monsoon, monsoon, post monsoon and winter season. The frequency of the sampling was increased to know the real status of the effect of crop protection agents in the water bodies in the State of Haryana.

Chemicals: The Certified Reference Materials (CRM) for the residue analysis were procured from the AccuStandard (USA) and Sigma Aldrich (USA). Certified pesticide reference standards used for screening were alpha-HCH, beta-HCH, gamma HCH, delta HCH, alachlor, aldrin, dicofol, pendimethalin, O,P DDE, α- endosulphan, heptachlor, P,P DDE, endosulphan sulphate, deldrin, O,P DDD, β- Endosulphan, P,P DDD, O,P DDT, P,P DDT, bifenthrin, fenpropathrin, lambda cyhalothrin, beta cyfluthrin, cypermethrin, fenvalarate, fluvalinate, deltamethrin, anilophos, chlorfenvinfos, chlorpyrifos, butachlor, pretilachlor, chlorpyrifos-methyl, dichlorvos, ethion, malathion, parathion methyl, monocrotofos, phorate, profenofos, quinalfos, triazofos, fenitrothion, phosalone, paraxon-methyl, fenamifos, edifenfos, dimetoate, diazinon,

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fenthion, parathion phosphomidon and atrazine. Anhydrous sodium sulfate (AR-grade) and sodium Chloride (AR grade) were purchased from Hi-Media, Mumbai, India. Anhydrous sodium sulfate and sodium Chloride were washed with acetone and air dried and thereafter dried in Muffle furnace for 3 hr at 400 °C, before use. Solvents like dichloromethane, acetone, methanol and n-hexane were of pesticide residue grade obtained from Merck (Darmstadt, Germany).

Glasswares: 1L separating funnel (Borosil, India) was used for extraction of samples. Funnel and 250 ml round bottom flask (Borosil, India) were used for collection of the extract. Volumetric flasks (Borosil, India) of 100, 50, 10 ml were used for preparation of individual standard stock solution and standard mixture solutions, Spatula small, 1.5 ml sample vials with septa (Agilent Technologies, USA) were used for extract injection.

Equipment: Turbovap-LV evaporator (Caliper Life Sciences, USA) was used to concentrate the sample. Liquid dispensers (Coleparmer USA) were used to dispense solvent. An adjustable pipette 1ml to 5ml (Eppendroff, USA) was used to transfer the solvent and sample extract to autosampler vials for residues analysis. An electronic weighing machine (Meteller Germany) with digital display was used to weigh the certified reference materials (CRM) and other reagents.

Standardization of GLC condition: Samples were analysed using Gas chromatography system (Agilent Technology 7890A). The chromatographic separation was performed with DB-5MS fused silica capillary column (Agilent J and W, GC Column, 30 m × 0.25 mm × 0.25 µm) which was used for quantitative analysis. 1 µl of sample was injected with linear flow at 1 ml/min in splitless mode with helium (99.995% purity) as carrier gas. Gases were passed through gas purification filters containing oxy trap and moisture trap before supply to the column.

The operating conditions for column oven were programmed from 50°C (hold for 2 min) and then increased to 280°C @ rate of 8 °C / min (hold for 15 min). The injector was operated in splitless mode at 280 °C temperature. Agilent Chem Station System software was used for instrument control and data analysis. GLC parameters for the analysis of pesticides were standardized to give proper resolution and sensitivity for all the pesticides. Figure 2 shows the GLC profile of the mixture of pesticides at 0.1 µg/mL concentration.

Standardization of MS condition: Agilent mass spectrometer (5975C inert XL EI/CI MSD) was used for identification and quantification of 53 pesticides in water samples. A solvent delay of 4 min was set to protect the filament from oxidation. The mass spectrometer was operated with an interface temperature of 280°C and an ionization source temperature of 250°C and quadruple temperature at 150°C. The mass spectrometer was operated

in the positive ion electron impact energy of 70 eV and an emission current 60 µA. Full scan data was obtained with a mass range of m/z 35–500. Scanning interval and SIM sampling rate were kept at 0.5 and 0.2 s respectively. The presence of pesticides residues in collected water samples was quantified by comparing the retention time, peak area and peak height of the sample with those of the standards.

Standard stock solutions preparation: Steps for preparation are:

1. 10 mg of the individual pesticide was accurately weighed in 10mL volumetric flask and then made upto mark with n-hexane, giving a stock solution of 1000 µg/mL (taking into account the purity of the compound as reported).
2. This standard stock solution was used to make working standard by serial dilution of 100 µg/mL.
3. All the 53 individual pesticide standard stock solution which were prepared were used for the preparation of 53 pesticides mixture of 10 µg/mL using n hexane solvent.
4. Working standards were prepared by serially diluting 10 µg/mL pesticides mixture stock as per the requirement and sensitivity of the instrument.

Water sampling: A total of 179 water samples were collected from 13 districts viz. Faridabad, Bhiwani, Mewat, Jind, Fatehabad, Kaithal, Rewari, Ambala, Gurugram, Kurushetra, Yammunanagar and Palwal. The water samples were collected from irrigation system i.e wells, tubewells, canal and river system. Water samples were collected in 1 L sterilized bottles. Figure 1 shows the study area and sampling locations. The samples were transported in icebox to protect from degradation at higher temperature and later stored at 4°C in the laboratory till processing and further analysis. Before extraction, the samples were filtered through filter paper to remove any suspended and particulate matter.

Extraction and cleanup: The extraction of water samples was carried out by following the method of Environmental Protection Agency (EPA) 508 for extraction of organic pollutants with slight modification. Liquid–liquid extraction (LLE) method was used for extraction of pesticides from water sample. Prior to the extraction, 100 gm sodium chloride was added to all water samples to make the water alkaline so that water and solvent layer can be separated easily.

Dichloromethane (DCM) was used for extraction of pesticides from water manually by shaking in a separatory funnel. 500ml water sample was transferred to a separatory funnel of 1L capacity. The extraction was carried out by adding DCM (100 ml) by vigorous manually shaking for 3 minutes and later kept undisturbed for layer separation. The lower DCM layer was collected in 250 ml round bottom flask by passing through anhydrous sodium sulphate wetted bed with 50 ml DCM. The extraction was repeated two more times with DCM (50 ml). The combined DCM extract in

round bottom flask was evaporated by rotary evaporator (Buchhi Switzerland) leaving about 5 mL of the solvent. This fraction was further evaporated in a gentle steam of nitrogen in turvovap. The concentrate was made up in 1 ml

by n-hexane in 1.8 mL vial. 1 µl of the sample was injected in gas chromatography–mass spectroscopy (GC-MS) for estimation.



Figure 1: District wise map of Haryana

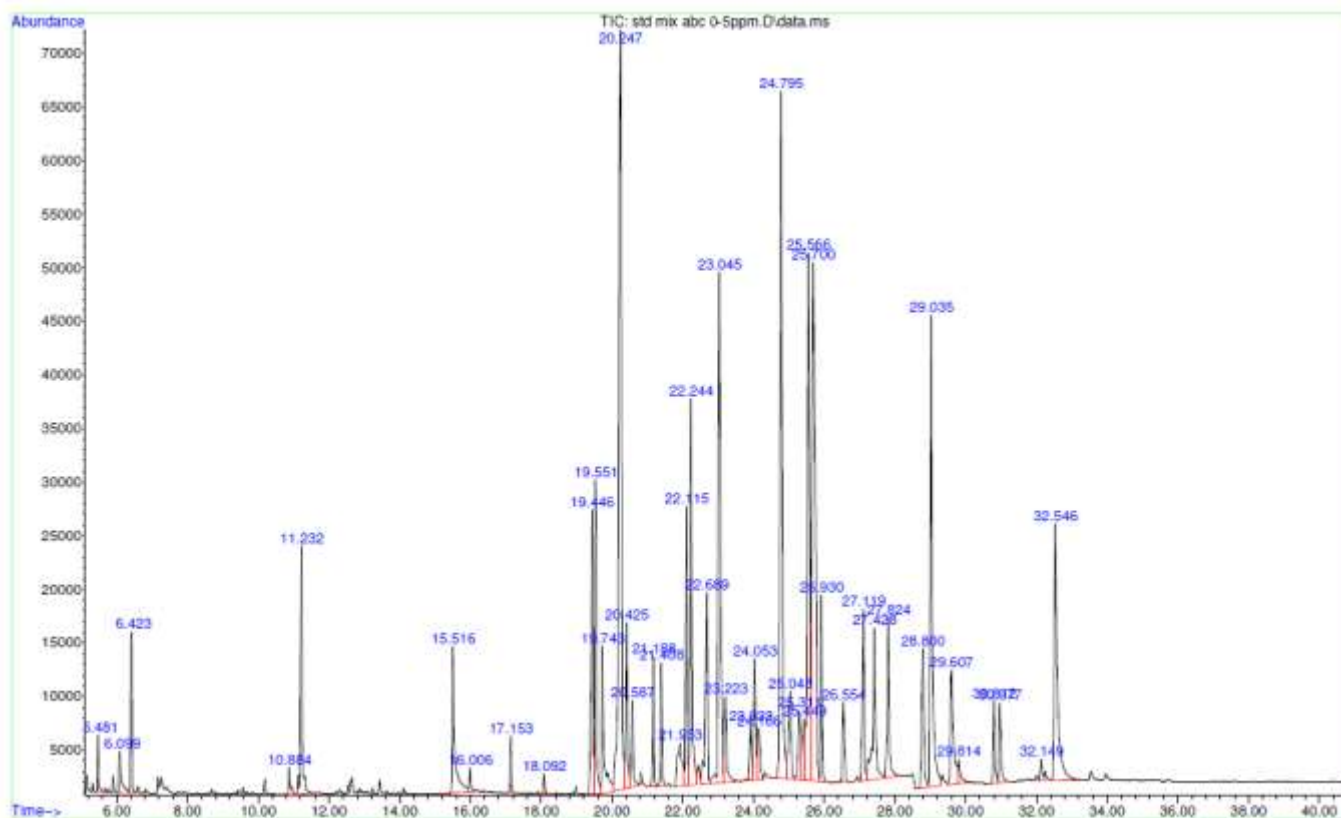


Figure 2: The GC-MS spectra of the mixture of pesticides at 0.5µg/mL

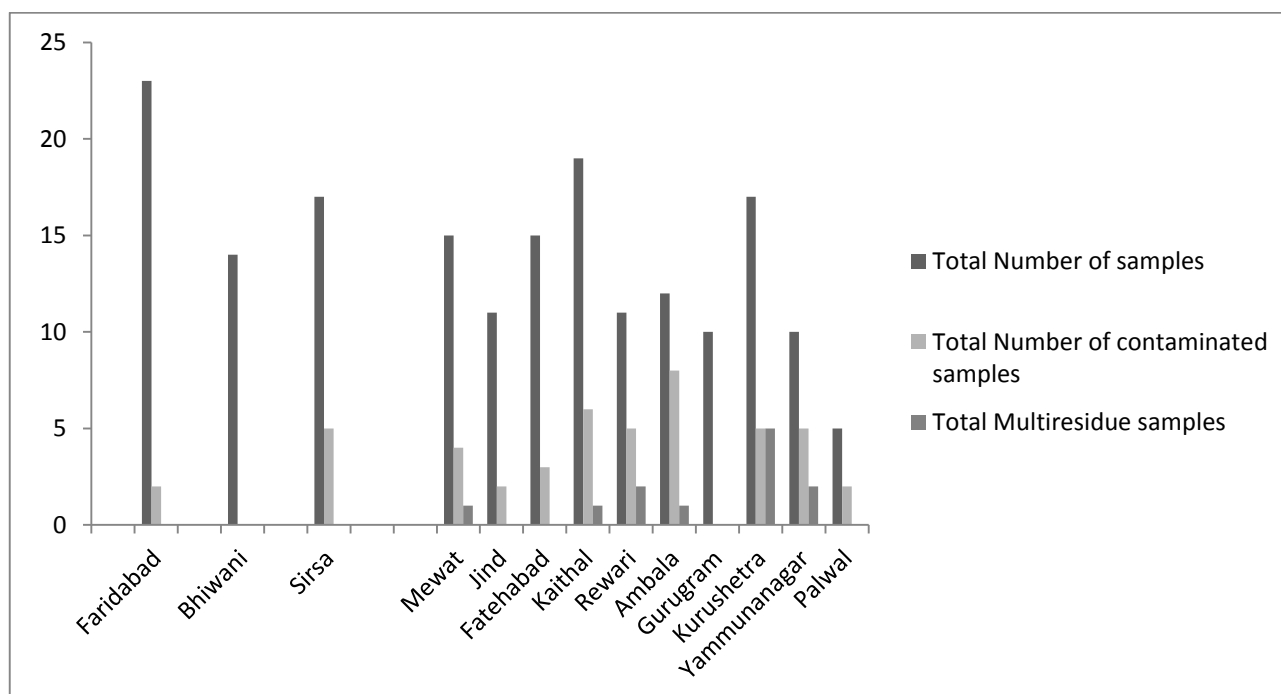


Figure 3: The recorded pesticides in water samples from districts of Haryana.

Qualitative and quantitative determination: The qualitative identification of pesticides present in the water samples was performed by comparing retention times (RT) with respect to the standard for each peak in the real sample chromatogram with those in the standard mixture chromatogram. The pesticides in the sample can be confirmed when mass fragments at particular RT match with

the fragmentation pattern of pesticide library database above 90 per cent. The quantification of pesticides present in the sample can be done by comparing area of standard with that of the sample at the same RT. Figure 2 represents the GC-MS spectra of the mixture of pesticides at 0.5µg/mL.

Evaluation of analytical procedure (Quality Control):

Analytical lab methods and instruments were fully validated as per quality assurance system ISO/IEC 17025(2005). The lab is accredited by National Accreditation Board for Testing and Calibration Technologies (NABL) and Bureau of Indian Standards (BIS) and audited from time to time. The per cent recovery was performed to evaluate the procedure by spiking 53 pesticides mixture with known concentrations in the water samples at concentration levels. For water samples, the mean recovery ranged from 75 - 90% with a relative standard deviation between 5-20% at 0.050 µg/L level. The detection limit was 0.01µg/L. The efficacy of the methodology was within the 95% confidence level.

Results and Discussion

The study was conducted to determine the pesticide residues different sources of irrigation water like ponds, rivers, canals, wells and tube wells during different seasons from different districts of Haryana. The 13 districts were Faridabad, Bhiwani, Sirsa, Mewat, Jind, Fatehabad, Kaithal, Rewari, Ambala, Gurugram, Kurushetra, Yammunanagar and Palwal. The samples were analysed for the presence of pesticide residues in water. A total of 179 water samples were collected. The study focused on those districts of Haryana where use of pesticides is high.

The study was planned to encompass all weather conditions. Keeping this in view, sampling was conducted in pre-monsoon, monsoon, post monsoon, summer and winter seasons. The load of pesticides in the study area is too high as compared to other areas of north India. The districts of Gurugram, Faridabad and Palwal are close to the National Capital Delhi of India.

The supply of drinking water to the capital is mainly done through water distribution system of these areas. Water is also used for drinking purposes; hence the analysis of pesticides residues in water is of utmost importance for the local people of Haryana and adjoining areas. 53 pesticides belonging to different groups of pesticides i.e. insecticides, fungicides and herbicides were commonly used in Indian agriculture system for crop protection were analysed in the 179 water samples. The samplings in these districts were collected during all the months covering all weather conditions. The district wise sampling and pesticides detected and their levels are presented in table 1.

Out of that 179 water samples, the number of samples collected from different district were 23, 14, 17, 15, 11, 15, 19, 11, 12, 10, 17, 10, 5 from Faridabad, Bhiwani, Sirsa, Mewat, Jind, Fatehabad, Kaithal, Rewari, Ambala, Gurugram, Kurushetra, Yammunanagar and Palwal respectively. 26% of the water samples out of the total analysed showed the presence of single pesticides whereas 25% of the samples recorded the presence of multi pesticide residues. Chlorpyrifos, butachlor, pretilachlor, malathion and pendimethalin were detected in the water samples. The two predominant pesticides recorded were chlorpyrifos and pretilachlor. Most of the water samples showed the presence

of herbicides, namely butachlor, pretilachlor, atrazine and pendimethalin, which were applied to crops like wheat and rice for weed control. Some times they are also applied to water bodies for control of aquatic weeds, although these are not recommended. Chlorpyrifos and malathion were the only two organophosphorus pesticides which were detected in the water samples. The pesticides are popular and are used for crop protection in vegetables.

Table 1 also shows the concentration of pesticides present in water samples. The study also focuses on seasonal distribution of pesticides in all the districts of Haryana (Table 2). The water samples were collected during pre-monsoon, monsoon, post monsoon, summer and winter season. A maximum of 112 samples were collected during the winter season, 33 samples in monsoon season (pre and post monsoon included) and 34 samples in summer season, 54.5%, 70.6% and 0.05% of water samples collected during monsoon (pre and post), summer and winter respectively showed the presence of pesticides. The two samples of monsoon season and 10 samples of summer season showed the presence of multi pesticide residues. Chlorpyrifos (3 samples), butachlor (4 samples), pretilachlor (8 samples) and atrazine (5 samples) were detected in the monsoon season samples. Pretilachlor was detected in the monsoon samples in the concentration range of 12-35 µg/L. 24 samples out of 34 samples of summer season showed the presence of pesticides, out of which 10 samples showed the presence of multi pesticides residues.

The concentrations of pesticides detected ranged from 12-9860 µg/L. The water samples of summer season recorded the presence of chlorpyrifos (6 samples), malathion (4 samples), butachlor (7 samples) and pretilachlor (20 samples). A total of 112 water samples were collected during winter season in which pesticides were detected in 5 samples in the concentration level of 18-41 µg/L with pendimethalin in one sample and chlorpyrifos in 4 samples. The seasonal pesticide variation reveals that from total 179 samples, 47 samples showed the presence of single pesticide residues, out of which in 12 samples, multi pesticides residues were detected. Pretilachlor was predominantly present in 28 samples, chlorpyrifos in 13 samples and others with pendimethalin (1 sample), malathion (4 samples) and atrazine (5 samples).

The result is above the WHO acceptable daily intake (ADI) values of 10 µg/l.²³ Water samples detected with chlorpyrifos were above the desirable limit of Indian Standards of 30 µg/L.⁷ Chawdhury et al⁸ reported chlorpyrifos in Rampur districts. Atrazine was found in 5 samples of water in the range of 12-18 µg/L. The pesticides detected were above MRL value of 0.5 µg/l EPA (8081 and 8141), WHO (GV), USA(MCL), USA (MCLG), New Zealand (MAV), Australian (GV) and Canadian MAC value of 2, 3, 3, 2p, 0.5 and 5I^b respectively whereas in some of the samples, concentration was less than Australian Health Value (20 µg/l) and USA health advisory life time (200µg/l).

Table 1
Seasonal analysis of water samples for pesticide residue in all 13 districts of Haryana

Districts	Sampling Season	Number of samples	Total number of samples	Contaminated samples	Total contaminated Samples percent	Sample with multiresidue	Concentration of pesticides (µg/L)
Faridabad	Summer	5	23	2	2		Butachlor (13, 15)
	Winter	2					
	Post monsoon	6					
	Winter	10					
Bhiwani	Summer	4	14				
	winter	10					
Sirsa	Monsoon	7	17	5	5		Atrazine (¹⁹ , 21, 18)
	Winter	10					Butachlor (35) and Pretilachlor (16)
Mewat	Post monsoon	5	15	3	4	1	Butachlor (14, 13, 12), Pretilachlor (17)
	Winter	10		1			Chlorpyrifos (19)
Jind	Summer	5	11	2	2		Pretilachlor (20); Butachlor (15)
	Winter	6					
Fatehabad	Pre monsoon	5	15	3	3		Pretilachlor (16, 159, 29)
	Winter	10					
Kaithal	Pre-monsoon	5	19	5	6	1	Chlorpyrifos (22, 26, 139); Bretilachlor (14, 14, 13)
	Winter	6					
	Winter	8		1			Pendimethalin (18)
Rewari	Summer	5	11	5	5	2	Malathion (69, 63, 70); Pretilachlor (8960, 538, 336, 1300); Butachlor (13, 12)
	Winter	6					
Ambala	Summer	5	12	5	8	1	Chlorpyrifos (13); Pretilachlor (9865, 1260, 794, 3850, 3346)
	Winter	7		3			Chlorpyrifos (47, 41, 80)
Gurugram	Winter	10	10				
Kurushetra	Summer	5	17	5	5	5	Chlorpyrifos (14, 12, 20, 13, 16); Pretilachlor (16, 14, 18, 16, 17)
	Winter	12					
Yammunanagar	Summer	5	10	5	5	2	Butachlor (13, 12); Malathion (49); Pretilachlor (47, 93, 3910, 2600, 180)
	Winter	5					
Palwal	Monsoon	5	5	2	2	-	Atrazine (12, 14)
Total=13 districts			179		47	12	Chlorpyrifos, Pretilachlor, Butachlor, Malathion, Pendimethalin and Atrazine

Table 2
Pesticides Detected in Water Samples in Different Seasons

S. N.	Seasons	Number of samples	Contaminated samples	Percent Contamination	Sample with multi-residue	Conc range $\mu\text{g/L}$	Number of pesticides in water samples					
							Pendimethalin	Chlorpyrifos	Malathion	Butachlor	Pretilachlor	Atrazine
1.	Pre-monsoon samples	10	8	80	1	13-159	-	3	-	-	6	-
2.	Monsoon samples	12	7	58	-	12-35	-	-	-	1	1	5
3.	Post-monsoon samples	11	3	27	1	13-17	-	-	-	3	1	-
4.	Summer samples	34	24	70.6	10	12-9860	-	6	4	7	20	-
5.	Winter samples	112	5	0.05	-	41-18	1	4	-	-	-	-
	Total	179	47	27	12		1	13	4	11	28	5

Table 3 shows the analysis of water samples from Faridabad in which two samples recorded the presence of butachlor in the range of 13-15 $\mu\text{g/L}$. Water samples from Bhiwani were free from any pesticide residues, or below the quantifiable limit (0.01 $\mu\text{g/L}$). Samples obtained from Sirsa detected pesticides in the concentration range of 16-35 $\mu\text{g/L}$ with butachlor and petrialachlor in one sample each and atrazine residues in 3 samples. Concentration ranges of 13-19 $\mu\text{g/L}$ of chlorpyrifos (1sample), butachlor (3 samples) and pretilachlor (1 sample) were detected in water samples from Mewat. Samples of Jind showed the presence of pesticides in the range of 15-20 $\mu\text{g/L}$ with butachlor and pretilachlor in one sample each. Butachlor was detected in three samples of Fatehabad samples in the range of 16-29 $\mu\text{g/L}$.

Pendimethalin, chlorpyrifos and pretilachlor were found in 1, 3 and 3 samples respectively of Kaithal in the concentration range of 13-18 $\mu\text{g/L}$. 5 samples of Rewari recorded the presence of pesticides in the concentration range of 13-8900 $\mu\text{g/L}$ with malathion (3 samples), butachlor (2 samples) and pretilachlor (4 samples). Water of Ambala district showed pesticides in 9 samples in the concentration range of 13-9870 $\mu\text{g/L}$ with chlorpyrifos in 4 and pretilachlor in 5 samples. 5 samples of Kurushetra district showed the presence of chlorpyrifos and pretilachlor in each sample in the range of 14-17 $\mu\text{g/L}$. 5 samples of Yamunanagar detected the pesticides in the range of 12-3910 $\mu\text{g/L}$, with malathion (1 sample), butachlor (2 samples) and pretilachlor in all five samples. 2 water samples of Palwal recorded pesticides in the concentration range of 12-14 $\mu\text{g/L}$ with atrazine in two samples.

Regulatory Limit of Water: Regulatory limits and guideline values issued by EPA, WHO, Australia, United State, Japan, Canada, New Zealand have been mostly developed for drinking water, environmental water, irrigation water and livestock drinking water (Table 4).

Guideline values are used by regulatory authorities for surveillance and enforcement purpose and health values are

used by the health authorities for managing the health risk. Malathion was present in 4 samples of water in the range of 49 -70 $\mu\text{g/L}$. All the 4 samples of water were above MRL as per EPA 8081 and 8141 but less than US health advisory value and Canadian MAC values of 100 and 190 $\mu\text{g/L}$. Some of the samples showed the presence of pesticides above the Australian health values of 50 $\mu\text{g/L}$.

Malathion was also detected by Hossain et al¹⁰ in lakes adjacent to agricultural fields of Savar Bangladesh. 13 samples detected with chlorpyrifos were in the range of 13-139 $\mu\text{g/L}$. All the samples detected pesticides above MRL value as set by EPA value of 0.3 $\mu\text{g/L}$ but less than USA health advisory life time value. New Zealand MAV and Canadian MAV values are 20, 70 and 90 $\mu\text{g/L}$ respectively.

One water samples was found contaminated with pendimethalin which was above maximum residue limit value of EPA (0.02 $\mu\text{g/l}$) and New Zealand MAC value (20 $\mu\text{g/l}$) but less than Australian Health Value (300 $\mu\text{g/l}$). No limit has been prescribed by any regulatory body for pretilachlor and butachlor.

Conclusion

A total of 179 water samples from 13 districts of Haryana were analysed for 53 pesticides in which pesticides were detected in 26%. The pesticides detected were mainly of herbicides i.e. pretilachlor, butachlor, pendimethalin and atrazine whereas organophosphorus pesticides i.e. chlorpyrifos and malathion. 25 % of the samples showed the presence of multiple pesticide residues. Seasonal contamination was also observed throughout the study period in which 54.5% of monsoon (Pre and post included), 70.6% of summer and 0.05% of winter samples showed the presence of pesticides. Pretilachlor was present predominantly in monsoon and summer but chlorpyrifos in winter season. Ambala district had samples with highest pesticides detection followed by Kaithal and thirdly by Mewat. The samples obtained from Bhiwani and Gurugram were free from any pesticide.

Table 3
Status of pesticide contamination of water samples, from districts of Haryana

Districts	Total number of water samples	Total contaminated samples	Percent contamination	Conc range µg/L	Number of Pesticides in water samples					
					Pendimethalin	Chlorpyrifos	Malathion	Butachlor	Pretilachlor	Atrazine
Faridabad	23	2	0.9	13, 15	-	-	-	2	-	-
Bhiwani	14	-	-	-	-	-	-	-	-	-
Sirsa	17	5	29	16-35	-	-	-	1	1	3
Mewat	15	4	26.6	13-19	-	1	-	3	1	-
Jind	11	2	18	15-20	-	-	-	1	1	-
Fatehabad	15	3	20	16-29	-	-	-	-	3	-
Kaithal	19	6	31.6	13-180	1	3	-	-	3	-
Rewari	11	5	45	13-8900	-	-	3	2	4	-
Ambala	12	8	66.6	13-9870	-	4	-	-	5	-
Gurugram	10	-	-	-	-	-	-	-	-	-
Kurushetra	17	5	29	14-17	-	5	-	-	5	-
Yamunanagar	10	5	50	12-3910	-	-	1	2	5	-
Palwal	5	2	40	12, 14	-	-	-	-	-	2
Total districts =13	179	47	26		1	13	4	11	28	5

Table 5
Pesticide contamination and comparison of standard and guideline value for pesticide residue in drinking water

S.N.	Pesticides Detected	Total Contaminated Samples	Range (mg/kg)	EPA 8081 and 8141 µg/L	Samples above Maximum Residue Limit	A	B	C	D	E	F	G	H	I	J
1.	Dichlorvos	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2.	Monocrotophos	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3.	Phorate	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
4.	Dimetoate	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
5.	Diazinon	-	-	0.5	-	-	-	-	0.6	-	10	5 surv	1	3	20
6.	Paraxon-methyl	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7.	Phosphomidon	-	-	1.0	-	-	-	-	-	-	-	-	-	-	-
8.	Chlorpyrifos-methyl	-	-	0.3	-	-	-	-	-	-	-	-	-	-	-
9.	Parathion methyl	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
10.	Fenitrothion	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
11.	Malathion	4	0.049-0.07	0.5	4	-	-	-	100	-	-	-	-	50	190
12.	Chlorpyrifos	13	0.013-0.139	0.3	13	-	-	-	20	-	70	-	-	-	90
13.	Fenthion	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
14.	Parathion	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
15.	Chlorfenvinphos	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
16.	Quinolophos	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17.	Fenamiphos	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
18.	Profenofos	-	-	1.0	-	-	-	-	-	-	-	-	-	-	-
19.	Ethion	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-
20.	Trizophos	-	-	-	-	-	-	-	-	-	-	-	-	-	-
21.	Edfinphos	-	-	-	-	-	-	-	-	-	-	-	-	-	-
22.	Anilophos	-	-	-	-	-	-	-	-	-	-	-	-	-	-
23.	Phosalone	-	-	1.5	-	-	-	-	-	-	-	-	-	-	-

24.	Alpha-HCH	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-
25.	Dicofol	-	-	0.10	-	-	-	-	-	-	-	-	-	-	-
26.	Beta-HCH	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-
27.	Gamma HCH (Lindane)	-	-	0.05	-	2	0.2	0.2	0.2	-	2	-	0.05	20	-
28.	Delta HCH	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-
29.	Heptachlor	-	-	0.03	-	0.03	0.4	0	-	0.8	0.04	-	0.05	0.3	-
30.	Alachlor	-	-	0.50	-	20	2	0	-	40	20 ^a	-	-	-	-
31.	Atrazine	5	0.012-0.018	0.5	5	2	3	3	200	-	2p	-	0.5	20	51 ^b
32.	Aldrin	-	-	0.04	-	0.03	-	-	-	0.2	0.03	-	0.01	0.3	0.7
33.	Pretilachlor	28	0.013-8.96	-	-	-	-	-	-	-	-	-	-	-	-
34.	Pendimethalin	1	0.18	0.02	1	20	-	-	-	-	20	-	-	300	-
35.	O,P DDE	-	-	0.04	-	-	-	-	-	-	2	-	0.06	20	-
36.	Alpha-Endosulphan	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-
37.	Butachlor	-	-	-	-	-	-	-	-	-	-	-	-	-	-
38.	Dialdrin	-	-	0.02	-	0.03	-	-	-	0.2	0.03	-	0.01	0.3	0.7
39.	P,P DDE	-	-	0.04	-	-	-	-	-	-	2	-	0.06	20	-
40.	O,P DDD	-	-	0.04	-	-	-	-	-	-	2	-	0.06	20	-
41.	P,P DDT	-	-	-	-	-	-	-	-	-	2	-	0.06	20	-
42.	Beta-Endosulphan	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-
43.	P,P DDD	-	-	0.10	-	-	-	-	-	-	-	-	-	-	-
44.	O,P DDT	-	-	0.10	-	-	-	-	-	-	2	-	0.06	20	-
45.	Endosulphan Sulphate	-	-	0.04	-	-	-	-	-	-	2	-	0.06	20	-
46.	Bifenthrin	-	-	-	-	-	-	-	-	-	-	-	-	-	-
47.	Fenpropathrin	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-
48.	Lambda Cyhalothrin	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-
49.	Beta Cyfluthrin	-	-	0.25	-	-	-	-	-	-	-	-	-	-	-
50.	Cypermethrin	-	-	0.25	-	-	-	-	-	-	-	-	-	-	-
51.	Fenvalarate	-	-	0.10	-	-	-	-	-	-	-	-	-	-	-
52.	Fluvalinate	-	-	0.25	-	-	-	-	-	-	-	-	-	-	-
53.	Deltamethrin	-	-	0.25	-	-	-	-	-	-	-	-	-	-	-

Abbreviations: p: provisional MAV; std: standard; surv: surveillance; I: interim MAC. ^aExcess lifetime cancer risk of 10⁻⁵ Atrazine+metabolites

A. WHO Guideline Value (GV) µg/L; **B.** USA Maximum Contaminant Level (MCL) µg/L; **C.** USA Maximum Contaminant Level Goal (MCLG) µg/L; **D.** USA Health advisory life time µg/L; **E.** USA 10⁻⁴ Cancer risk; **F.** NZ Maximum Acceptable Value (MAV) µg/L; **G.** Japan Stdsurv µg/L; **H.** Aust

Guideline Value (GV) µg/L; **I.** Aust Health Value (HV) µg/L; **J.** Canada Maximum acceptable Concentration (MAC) µg/L

From the study it was found that pretilachlor, butachlor and chlorpyrifos were predominantly present in many samples and pendimethalin in one sample. Malathion and chlorpyrifos containing samples reported maximum residue level less than EPA 8081, US health advisory value and Canadian MAC values. Atrazine contaminated samples were above MRL as per EPA, WHO (GV), USA (MCL), USA

(MCLG), New Zealand (MAV), Australian (GV) and Canadian MAC values. Pendimethalin containing samples were above MRL as per EPA 8081 and New Zealand MAC values but less than Australian Health Value.

Acknowledgement

The authors are highly thankful to Directorate of

Horticulture, Haryana, Director IPFT, Shri Vinod Deotale and Shri Mangesh A. Pande and other lab staff for their help and support.

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(Received 07th April 2021, accepted 21st June 2021)