



Temporal Assessment of Crop Protection Agents in Water Bodies of Haryana Districts

S. Mishra¹, M.K. Singh¹, M.K. Saini¹, S. Alam¹, L.K. Thakur¹, I. Mukherjee¹, J. Kumar¹

10.18805/BKAP607

ABSTRACT

Background: The study was conducted to quantify the presence of crop protection agents in 233 water samples collected from water bodies situated in cities of Panipat, Karnal, Rohtak, Sonipat and Hisar districts of Haryana, India. Water samples were collected during different seasons the year for the period from 2014-2018.

Methods: The samples were processed by liquid- liquid partitioning method and quantified by Gas Chromatography and Mass Spectrometry. The water samples were screened for 55 pesticides.

Result: Estimation of the residues revealed that 23.5 and 6.6% of pesticides were detected in 68 and 165 monsoon and winter samples, respectively. Chlorpyrifos, pretilachlor, butachlor and lambda cyhalothrin were predominantly present in all the water samples analyzed. Chlorpyrifos detected in water samples from Karnal were above standard limit prescribed by EPA 8081 and 8141 but some samples were below UAS Health advisory life time value.

Key words: Crop protection agents, GC-MS, Pesticide Residue, Temporal, Water bodies.

INTRODUCTION

Water is one of the most precious natural resources, which is essential for life. The presence of xenobiotics, namely pesticides in water is a matter of global concern. Several pesticides, belonging to different chemical class are being used in agriculture throughout the world Sneh *et al.* (2012). Pesticides move into water bodies due to wet precipitation Kumar *et al.* (2007), leaching, field runoff, municipal, agricultural and industrial disposal. In many developing countries water from rivers, canals, wells, tube wells are used both for drinking and irrigation purpose.

The contamination of the ground water with several of the organochlorine pesticides (OCPs) has been reported (Singh *et al.*, 2005). Surface water contamination may impact eco-toxicological effect on aquatic flora and fauna and also on human health through food chain Miyamoto *et al.* (1990). Contamination of ground water resources by pesticides is a matter of grave concern Papadopoulou-Mourkidou *et al.* (2004). DDT, is under restricted use for disease vector control (UNEP 2003). The major issue arises in the countries where ground water is the source of drinking water for rural and adjacent urban areas (Tuxen *et al.*, 2000).

The water supply in north of India is from the rivers, tributaries in the region. Haryana in northern part is mainly responsible for supply of water to the National Capital, Delhi. Haryana is predominantly an agricultural state in India extends between 27°39'N to 30°55'N latitude and 74°27' to 77°36'E longitude and covers a total geographical area of 442100 ha. The state's economy is mainly based on agriculture and industry. The major sources of irrigation and drinking water of the region are Anangpur dam, Hathni Kund Barrage, Sutlej Yamuna link canal, Munak Canal, Agra Canal etc. The study highlights the contamination of pesticides in irrigation water bodies like wells, tube wells,

¹Institute of Pesticide Formulation Technology, Udyog Vihar, Gurugram-122 016, Haryana, India.

Corresponding Author: S. Alam, Institute of Pesticide Formulation Technology, Udyog Vihar, Gurugram-122 016, Haryana, India.

Email: alam_samsul@rediffmail.com

How to cite this article: Mishra, S., Singh, M.K., Saini, M.K., Alam, S., Thakur, L.K., Mukherjee, I. and Kumar, J. (2023). Temporal Assessment of Crop Protection Agents in Water Bodies of Haryana Districts. Bhartiya Krishi Anusandhan Patrika. doi: 10.18805/BKAP607.

Submitted: 14-11-2022 **Accepted:** 28-08-2023 **Online:** 04-10-2023

canals, ponds and rivers of region from Panipat, Karnal, Rohtak, Sonipat and Hissar districts of Haryana, India.

MATERIALS AND METHODS

Geographical location

Total 233 water samples collected from the water bodies from cities of Panipat, Karnal, Rohtak, Sonipat and Hissar districts of Haryana, India. The water samples from irrigation system i.e. wells, tube wells, canal and river system were collected throughout the different seasons of the year for the period from 2014-2018. Fig 1 shows districts map of Haryana. Water samples were collected in one-Litre capacity pre-cleaned and rinsed amber-colored bottles. Samples were stored in refrigerator at a temperature of 4°C till analysis to prevent degradation of pesticide residues before processing.

Na₂SO₄, (AR-grade), sodium chloride (AR grade) dichloromethane, acetone, methanol and n-hexane solvents of pesticide residue grade purchased from Merck (Darmstadt, Germany). 1L separating funnel, 250 ml round bottom flask, volumetric flask of 100, 50, 10 ml was used

for standard stock solution and its mixture preparation. 1.5 ml sample vials were used for final sample extract injection to instrument. Turbo-Vap LV evaporator (Caliper Life Sciences, USA), Liquid dispensers (Coleparmer USA), adjustable pipette 1 to 5 ml (Eppendroff, USA) was used. An electronic weighing balance (Mettler Germany) with digital display was used to weigh the certified reference materials (CRM) and other reagents purchased from Sigma Aldrich, USA whose purity were above 99%.

The samples were extracted using conventional liquid-liquid partitioning method for the determination of organic pollutants in water [AOAC official methods (2019) and Veeraiah and Prasad (1996)]. The method was validated for its effectiveness. The LOD, LOQ recovery, repeatability was calculated. The samples were processed for residue estimation of different groups of pesticides viz. organochlorines (OC), synthetic pyrethroids (SP) and organophosphates (OP). The samples were extracted as per above method and were injected in gas chromatography–mass spectroscopy (GC-MS) at Institute of Pesticide Formulation Technology.

The water samples were screened for 55 pesticides (Table 1). The Certified Reference Material (CRM) were purchased from Sigma Aldrich (USA). Individual pesticide solution of 100 mg/L concentration was prepared in n-hexane. 55 individual pesticide standard stock solutions were prepared for the preparation of pesticides mixture of 10 mg/L. Working standards and were prepared by serially diluting 10 mg/L pesticides mixture stock as per the sensitivity of the instrument. The standard stock and working solutions were stored at 4°C.

Gas chromatography system (Agilent Technology 7890A) with DB-5MS fused silica capillary column (Agilent JandW, GC Column, 30 m × 0.25 mm × 0.25 µm) was used for quantitative analysis. Agilent Chem Station System software was used for instrument control and data analysis. Gases

were passed through purification filters which can trap oxygen and moisture, before supply to the column. Agilent mass spectrometer (5975C inert XL EI/CI MSD) was used for identification and quantification and confirmation of 55 pesticides. The mass spectrometer was operated in the positive ion electron impact energy of 70 eV and an emission current 60 µA. Full scan data were obtained with a mass range of m/z 45–500. Scanning interval and SIM sampling rate were kept at 0.5 and 0.2 s, respectively. The full scan TIC chromatogram of Standard Mixture (0.5 ppm) and Control water samples are given in Fig 2 and 3 respectively. The presence of pesticides residues were quantified and confirmed by comparing the retention time, peak area, m/z of the sample with those of the standards. The fragmentation patterns of detected pesticides are given in Table 2.

Liquid-liquid partitioning extraction followed by gas chromatographic detection (USEPA 1980; AOAC official methods (2019) and Veeraiah and Prasad (1996) was used for the determination of pesticide residues. The percent recovery was performed to evaluate the procedure, by spiking 55 pesticides mixture with known concentrations. For water samples, the mean recovery ranged from 75 to 90%, with a relative standard deviation between 5-20%, at 0.050 µg/L level. The detection limit was 0.010 µg/L. The efficacy of the methodology was within the 95% confidence level. The instrument is repeatable with the precision (RSDr), precision (RSDwr) is below 5% and LOQ for the pesticides is 0.050 ppm (As per SANTE guideline).

RESULTS AND DISCUSSION

Total 233 water samples were analysed for the presence of 55 pesticides, which were collected from cities of Panipat, Karnal, Rohtak, Sonipat, Hissar and Narnaul districts of Haryana, India (Table 3). Samples were collected during

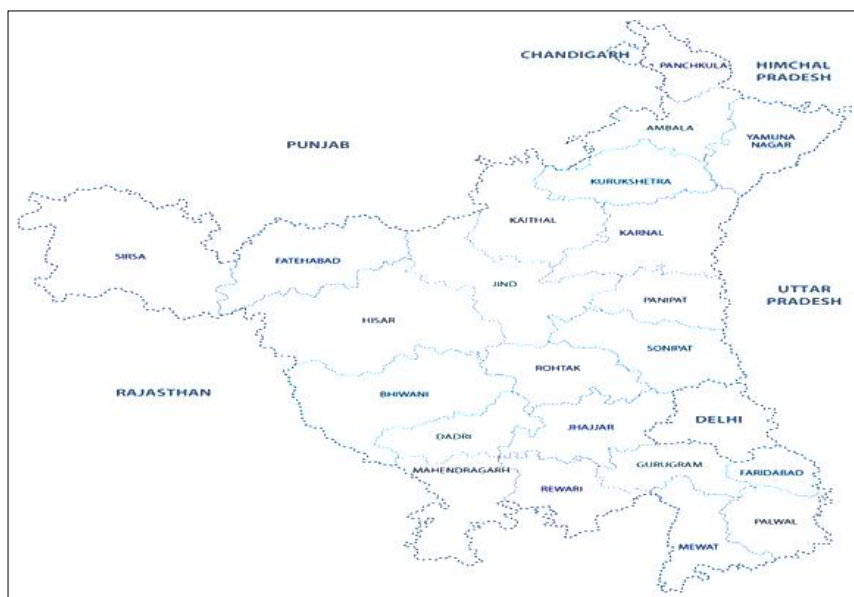


Fig 1: Geographical map of the state Haryana showing districts of water sampling.

Table 1: Pesticides detected, concentration range and with regulatory limits in drinking water.

Pesticides detected	Pesticide detection range (µg/L)						EPA 8081 and 8141	WHO (GV) µg/L	USA (MCL) µg/L	USA (MCLG) µg/L	USA Health advisory time µg/L	USA10 ⁻⁴ cancer risk µg/L
	Panipat	Karnal	Rohtak	Sonipat	Hissar	Narnaul						
Dichlorvos	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Monocrotophos	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Phorate	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Dimethoate	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Diazinon	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	0.6	-
Paraxon-methyl	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Phosphomidon	BQL	BQL	BQL	BQL	BQL	BQL	1.0	-	-	-	-	-
Chlorpyrifos-methyl	BQL	BQL	BQL	BQL	BQL	BQL	0.3	-	-	-	-	-
Parathion methyl	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Fenitrothion	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Malathion	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	100	-
Chlorpyrifos	BQL	2-1515	BQL	30	BQL	1	0.3	-	-	-	20	-
Fenthion	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Parathion	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Chlorfenvinfos	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Quinolpos	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Fenamiphos	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Profenofos	BQL	BQL	BQL	BQL	BQL	BQL	1.0	-	-	-	-	-
Ethion	BQL	BQL	BQL	BQL	BQL	BQL	0.5	-	-	-	-	-
Trizophos	BQL	122-439	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Edfinphos	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Fipronil	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Anilophos	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Buprofezin	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Phosalone	BQL	BQL	BQL	BQL	BQL	BQL	1.5	-	-	-	-	-
Alpha-HCH	BQL	BQL	BQL	BQL	BQL	BQL	0.05	-	-	-	-	-
Dicofol	BQL	BQL	BQL	BQL	BQL	BQL	0.10	-	-	-	-	-
Beta-HCH	BQL	BQL	BQL	BQL	BQL	BQL	0.05	-	-	-	-	-
Gamma HCH (Lindane)	BQL	BQL	BQL	BQL	BQL	BQL	0.05	2	0.2	0.2	0.2	-
Delta HCH	BQL	BQL	BQL	BQL	BQL	BQL	0.05	-	-	-	-	-
Heptachlor	BQL	BQL	BQL	BQL	BQL	BQL	0.03	0.03	0.4	0	-	0.8
Alachlor	BQL	BQL	BQL	BQL	BQL	BQL	0.50	20	2	0	-	40
Atrazine	BQL	BQL	BQL	BQL	BQL	BQL	0.5	2	3	3	200	-
Aldrin	BQL	BQL	BQL	BQL	BQL	BQL	0.04	0.03	-	-	-	0.2

Table 1: Continue...

Table 1: Continue..

Pretilachlor	BQL	87-906	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Pendimethalin	BQL	14	BQL	BQL	BQL	BQL	0.02	20	-	-	-	-
O,P DDE	BQL	BQL	BQL	BQL	BQL	BQL	0.04	-	-	-	-	-
Alpha-Endosulphan	BQL	BQL	BQL	BQL	BQL	BQL	0.04	-	-	-	-	-
Butachlor	BQL	16-51	2-279	BQL	BQL	BQL	-	-	-	-	-	0.2
Dialdrin	BQL	BQL	BQL	BQL	BQL	BQL	0.02	0.03	-	-	-	-
P,P DDE	BQL	BQL	BQL	BQL	BQL	BQL	0.04	-	-	-	-	-
O,P DDD	BQL	BQL	BQL	BQL	BQL	BQL	0.04	-	-	-	-	-
P,P DDT	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Beta- Endosulphan	BQL	BQL	BQL	BQL	BQL	BQL	0.04	-	-	-	-	-
P,P DDD	BQL	BQL	BQL	BQL	BQL	BQL	0.10	-	-	-	-	-
O,P DDT	BQL	BQL	BQL	BQL	BQL	BQL	0.10	-	-	-	-	-
Endosulphan Sulphate	BQL	BQL	BQL	BQL	BQL	BQL	0.04	-	-	-	-	-
Bifenthrin	BQL	BQL	BQL	BQL	BQL	BQL	-	-	-	-	-	-
Fenpropathrin	BQL	BQL	BQL	BQL	BQL	BQL	0.05	-	-	-	-	-
Lambda Cyhalothrin	BQL	BQL	BQL	BQL	BQL	BQL	0.05	-	-	-	-	-
Beta Cyfluthrin	BQL	5-520	BQL	BQL	BQL	BQL	0.25	-	-	-	-	-
Cypermethrin	BQL	728-935	60	BQL	BQL	BQL	0.25	-	-	-	-	-
Fenvalarate	BQL	BQL	BQL	BQL	BQL	BQL	0.10	-	-	-	-	-
Fluvalinate	BQL	BQL	BQL	BQL	BQL	BQL	0.25	-	-	-	-	-
Deltamethrin	BQL	292	BQL	BQL	BQL	BQL	0.25	-	-	-	-	-

BQL- Below quantification limit- (<0.050 µg/L); GV- Guideline value; MCL- Maximum contaminant level; MCLG- Maximum contaminant level goal.

Table 2: Mass fragmentation of Pesticides detected in drinking water.

Pesticide detected	Molecular mass	Qualifier Ions		
		Q1	Q2	Q3
Chlorpyrifos	350	97	197	199
Pendimethlin	281	252	162	281
Trizophos	313	172	161	97
Fipronil	437	369	367	351
Bifenthrin	181	166	141	-
Butachlor	312	160	176	57
Cypermethrin	209	163	181	91
Pretilachlor	312	162	238	176
Lambda cyhalothrin	450	181	197	208
Deltamethrin	253	181	77	93
Buprofezin	105	41	57	43

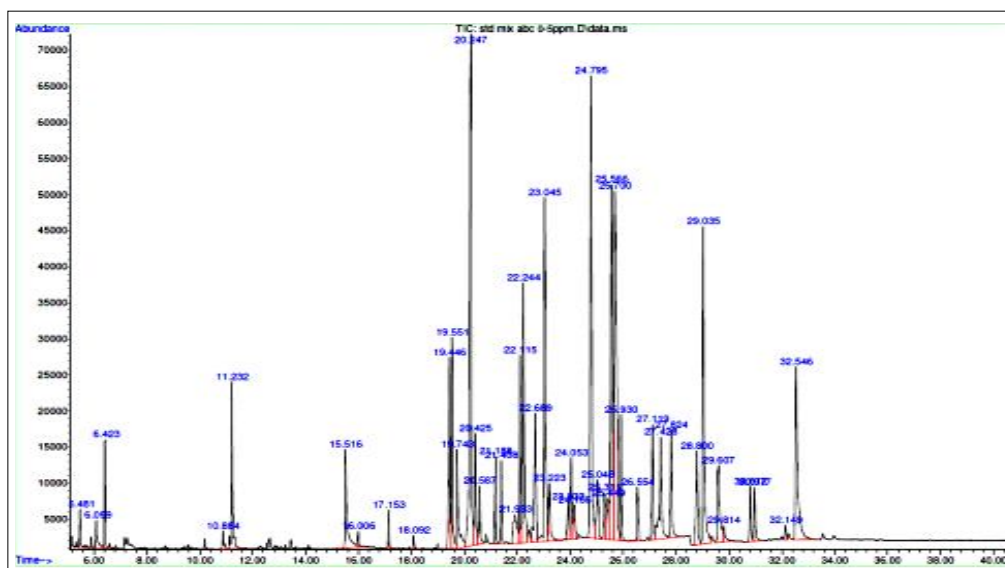
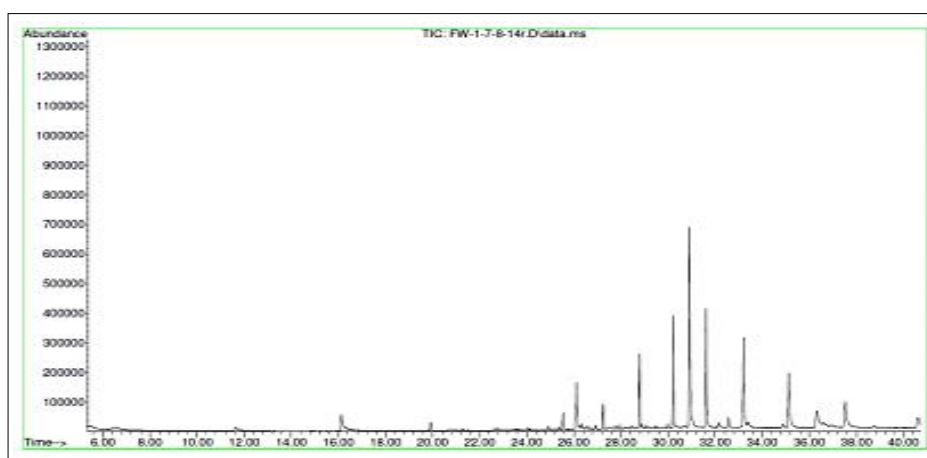

Fig 2: Standard mixture TIC chromatogram.

Fig 3: Control water sample TIC chromatogram.

Table 3: Summarized pesticide residues in water samples of northern India.

Districts	Month and year	Season	No. of samples collected	Total no. of samples	Pesticides detected in no. of samples	Contaminated samples	% of samples detected with pesticides	No. of samples with multi pesticide residues	Total multi pesticide residues samples	Multi pesticides (%)
Panipat	April 2014	Post winter	9	70	-	-	-	-	-	-
	July 2014	Monsoon	10	-	-	-	-	-	-	-
	Jan 2016	Winter	19	-	-	-	-	-	-	-
	Feb-2016	Winter	19	-	-	-	-	-	-	-
	Sep- 2017	Post monsoon	5	-	-	-	-	-	-	-
	Dec-2017	Winter	8	-	-	-	-	-	-	-
	Jan-2016	Winter	10	43	7	19	40.4	2	11	23.4
	Jan-2016	Winter	5	-	-	-	-	-	-	-
Karnal	Nov-2017	Pre-winter	10	-	-	-	-	-	-	-
	Mar-2018	Post winter	4	-	-	-	-	-	-	-
	Oct-2018	Post monsoon	14	-	12	-	-	9	-	-
	Dec-2015	Winter	10	45	-	7	15.5	-	2	0.04
	Sep-2017	Post monsoon	11	-	5	-	-	1	-	-
	Dec-2017	Winter	10	-	2	-	-	1	-	-
	July-2018	Monsoon	8	-	-	-	-	-	-	-
	Oct-2018	Post monsoon	6	-	-	-	-	-	-	-
Sonipat	Aug-2014	Monsoon	4	30	1	1	0.03	-	-	-
	Dec-2014	Winter	14	-	-	-	-	-	-	-
	Feb-2016	Winter	12	-	1	-	-	-	-	-
	Jan-2016	Winter	10	26	-	-	-	-	-	-
Hissar	Oct-2017	Post monsoon	6	-	-	-	-	-	-	-
	Nov-2017	Winter	10	-	-	-	-	-	-	-
Narnaul	Jan-2016	Winter	5	15	1	1	0.07	-	-	-
	Jan-2016	Winter	10	-	-	-	-	-	-	-
	Jan-2016	Winter	10	-	-	-	-	-	-	-

pre and post monsoon and pre and post winter season. Most of the crops are grown during these seasons due to conducive weather conditions. Intensive agriculture during this period leads to high irrigation and frequent use of fertilizers and pesticides. This may lead to runoff from fields into water bodies and aquifers. Temporal assessment of pesticides in water bodies during these months may give an insight into the levels of crop protection agents in water and their safety towards consumption for drinking purpose. The pesticides selected for analysis are based on the consumption pattern of pesticides in the area and the crops grown.

Analysis of results of Karnal districts indicate that 19 water samples showed the presence of pesticides, out of which multiple pesticide residues were detected in 11 samples. The pesticides detected in the samples were chlorpyrifos, triazofos, fipronil, bifenthrin, pendimethalin, butachlor, cypermethrin, pretilachlor, lambda-cyhalothrin, deltamethrin and buprofezin (Table 4). Chlorpyrifos was detected in 12, butachlor in 5, pretilachlor in 7 and lambda cyhalothrin in 7 samples. Water samples along the 230km stretch of the river in Haryana were analyzed for the presence of organochlorine insecticide residues (Kaushik *et al.*, 2010). Among 100 farmers, a survey was conducted in cauliflower and tomato cultivating areas of district Faridabad, Haryana, India from December 2012 to February 2013. Cypermethrin (62%) and profenofos (58%) were found as the most popular insecticides (Tyagi *et al.* 2015).

The range of contamination of pesticides in water samples was 2-1500 µg/L. Total 45 samples were collected from Rohtak in which 7 samples showed the presence of pesticides. Butachlor was detected in 7 samples (Table 4). From 30 and 15, samples from Sonipat and Narnaul, one sample each showed the presence of pesticides, (Table 3). A total 233 water samples were analyzed; out of which 70 samples were from Panipat, 43 samples from Karnal, 45 samples from Rohtak, 30 water samples from Sonipat, 26 samples from Hissar and 15 samples from Narnaul. Amongst the samples analyzed, 25 water samples showed the presence of at least one pesticide and in 11 samples multiple pesticide residues were recorded. Chlorpyrifos, butachlor, pretilachlor and cypermethrin were detected in 14, 12, 8 and 7 samples, respectively, whereas 2 samples showed the presence of triazofos and cypermethrin and 1 sample recorded the presence of five pesticides namely, fipronil, bifenthrin, pendimethalin, deltamethrin and buprofezin respectively (Table 3 and 5).

Temporal distribution of pesticides in water samples during different seasons is presented in Table 5. The pesticides detected during seasonal variation in 68 water samples of monsoon (pre and post) and 165 samples of winter (pre and post). It is observed that about 70% of crops are cultivated during winter season from mid-October to mid-April whereas only 30% of crops are grown during rainy season and localized farming is done during the months June to October. Thus, leading to increased inputs during winter season and subsequently prompting collection of

Table 4: Summary of pesticides detected and concentration range in water samples.

Districts	Pesticides detected in no. of samples	% of samples detected with pesticides	Samples with multi pesticide residues	Conc range µg/L	Number of samples detected with pesticides									
					Chlorpyrifos	Pendimethlin	Triazophos	Fipronil	Bifenthrin	Butachlor	Cypermethrin	Pretilachlor	L- Cyhalothrin	Bprofenzin
Panipat	70	0	-	-	-	-	-	-	-	-	-	-	-	-
Karnal	47	16	11	1-1500	13	2	1	1	1	5	1	7	7	1
Rohtak	45	7	2	0.20-132	-	-	-	-	-	7	1	1	-	-
Sonipat	30	1	-	BQL-30	1	-	-	-	-	-	-	-	-	-
Hissar	26	0	-	-	-	-	-	-	-	-	-	-	-	-
Narnaul	15	1	-	BQL-1	1	-	-	-	-	-	-	-	-	-
Total districts	233	25	13		14	2	1	1	1	12	2	8	7	1

BQL- (<0.050 µg/L).

Table 5: Details of samples detected with pesticides residues in water during monsoon and winter season.

Season	Districts	No. of samples region wise	Total no. of samples	No. of samples detected with pesticides	Pesticides detected in total no. of samples	% of samples detected with pesticides	No. of samples with multi pesticide residues	Total no. samples with multi pesticide residues	% of samples with multi pesticide residues
Monsoon (Pre and post)	Panipat	15	68	-	16	23.50	-	10	0.15
	Karnal	18		11			9		
	Rohtak	25		5			1		
	Sonipat	4		-			-		
	Hissar	6		-			-		
Winter (Pre and post)	Panipat	55	165	-	11	6.60	-	3	0.02
	Karnal	29		7			2		
	Rohtak	20		2			1		
	Sonipat	26		1			-		
	Hissar	20		-			-		
	Narnaul	15		1			-		

larger number of water samples in winter season than during the monsoon. A total of 68 samples were collected from Panipat, Rohtak, Karnal, Hissar and Sonipat during monsoon seasons (pre and post), among which 16 samples showed the presence of pesticides residues and 10 samples recorded the presence of more than one pesticide. Among the 165 samples of winter season, only 11 samples recorded pesticides and multiple pesticide residues were detected in 3 samples. The low pest incidence during the winter season leads to lesser use of pesticides and resulting in lower detection of pesticides in water samples during the winter months. In contrast, the pest and disease attack during the monsoon season is high due to the conducive climatic conditions, thus prompting high use of crop protection agents and leading to higher detection of pesticides. Regulatory limits by various regulatory bodies (Hamilton *et al.*, 2003) has been compared with the contamination of the detected pesticides. The water samples of Panipat and Hissar region detected pesticide levels below the quantification level (Table 4 and 1). Chlorpyrifos was detected in the range of 1-1515 µg/L, BQL (<0.050 µg/L) -30 µg/L and BQL (<0.050 µg/L) -1 µg/L in Karnal, Sonipat and Narnaul samples, respectively. The level of concentration in 13 water samples of Karnal districts were above EPA 8081 and 8141 value of 0.3 µg/L but 4 samples were below UAS health advisory life time value of 20 µg/L. Chlorpyrifos detected in one samples from Sonipat was above EPA and USA health advisory life time, however one sample of Narnaul was above EPA but below USA Health advisory life time. Triazofos, pretilachlor, bifenthrin, fipronil and buprofezin were detected in the range of 122-439 µg/L; 87-906 µg/L, BQL (<0.050 µg/L-33µg/L; BQL (<0.050 µg/L-18 µg/L and BQL (<0.050 µg/L-2 µg/L, respectively in Karnal water samples, no limit has been ascertained by any of the regulatory authorities. Butachlor pesticide detected in Karnal and Rohtak water samples ranged from 16-51 µg/L and 0.2-28 µg/L, respectively. Seven water samples from Karnal recorded the presence of lambda cyhalothrin in the range of 5-520 µg/L and were above the EPA value of 0.05 µg/L. Similarly, cypermethrin residues in 2 water samples of Karnal and 1 sample of Rohtak was in the range of 728-935 µg/L and 60 µg/L, respectively were above EPA value of 0.25 µg/L. In one sample from Karnal, deltamethrin was detected at 292 µg/L concentration which was above EPA value of 0.25 µg/L. A similar study conducted on groundwater samples from tubewells during the year 2002-2003 in Hissar revealed that synthetic pyrethroids like deltamethrin was detected in water samples varying from 0.017-0.06 µg/L and cypermethrin from 0.022-0.090 µg/L. The most predominantly detected pesticide was chlorpyrifos, in the range 0.607-1.121 µg/L, (Kumari *et al.*, 2008). Chlorpyrifos was detected from groundwater samples of the agricultural area of Amravati, Bhandara and Yavatmal region of Maharashtra in the concentration of 0.25, 0.11 and 0.18 µg/L, respectively (Lari *et al.*, 2014). The studies conducted by Kumar *et al.* (2007), in Hissar district of Haryana revealed that the rain water were detected with

cypermethrin (0.2-1.0 µg/L), deltamethrin (0.1-0.8 µg/L) and triazofos (0.05-0.009 µg/L) pesticides.

CONCLUSION

Panipat, Karnal, Rohtak, Sonipat, Hissar and Narnaul are the prominent agricultural districts of Haryana, India. Sufficient numbers of samples were collected for analysis of pesticides from these districts of Haryana. Temporal and seasonal pesticide residue variation was focused in the study. Pesticide residues in the water samples from Panipat and Hissar regions were below the quantification levels. 40.4; 15.5; 0.03; and 0.07% of pesticides were present in Karnal, Rohtak, Sonipat and Narnaul samples, respectively. In 23.4 and 0.04% of water samples of Karnal and Rohtak multi pesticide residues were detected Temporal variation reveals that 23.5% and 6.6% of pesticides were recorded in 68 and 165 samples of monsoon and winter samples. 0.15 and 0.02% of water samples from Karnal and Rohtak area showed the presence of multiple pesticide residues Chlorpyrifos, pretilachlor, butachlor and lambda chalthrin were predominantly present in all water samples analyzed. Water samples from Karnal detected with chlorpyrifos were above EPA method 8081 B and 8141 but few samples were below UAS Health advisory life time. Some water samples from Karnal region, detected with chlorpyrifos, deltamethrin, lambda cyhalothrin were above EPA method 8081 B and 8141. One sample each from Sonipat and Narnaul showed the presence of chlorpyrifos above EPA method 8081B and 8141. Cypermethrin residues in water sample from Karnal and Rohtak were above EPA method 8081B and 8141 value.

ACKNOWLEDGEMENT

The authors are highly thankful to Directorate of Horticulture, Haryana and Director IPFT for their help and support.

Funding

This work was supported by Institute of Pesticide Formulation Technology.

Disclosure statement

No potential conflict of interest was reported by the author.

REFERENCES

- AOAC. (2019). Official Methods of Analysis of the Association of Official Analytical Chemists: Official Methods of Analysis of AOAC International. 21st Edition, AOAC, Washington DC.
- Hamilton, D.J., Ambrus, A., Dieterle, R.M., Felsot, A.S., Harris, U.A., Holland, P.T., Katayama, A., Kurihara, A., Linders, J., Unsworth, J. and Wong, S.S. (2003). Regulatory Limits for pesticide residues in water. *Pure Applied Chemistry*. 75(8): 1123-1155.
- Kaushik, A., Sharma H.R., Jain S., Dawra J., Kaushik C.P. (2010). Pesticide pollution of River Ghaggar in Haryana, India. *Environment Monitoring Assessment*. 160: 61-69.
- Kumar, B., Madan, V.K. and Kathpal, T.S. (2007). Pesticide residues in rain water from Hissar, India. *Environmental Monitoring and Assessment*. 133(1-3): 467-71.
- Kumari, B., Madan, V.K. and Kathpal, T.S. (2008). Status of insecticide contamination of soil and water in Haryana, India. *Environmental Monitoring and Assessment*. 136: 239-244.
- Lari, Z.S., Khan, N.A., Gandhi, K.N., Meshram, T.S. and Thacker, N.P. (2014). Comparison of pesticide residues in surface water and ground water of agriculture intensive areas. *Journal of Environmental Health Science and Engineering*. 12: 11. doi: 10.1186/2052-336X-12-11.
- Miyamoto, J., Mikami, N. and Takimoto, Y. (1990). The Fate of Pesticides in Aquatic Ecosystems. In: *Environmental Fate of Pesticides*. [Hutson, D.H., Roberts, T.R. (eds.)]. Chichester, England: Wiley. 123-147.
- Papadopoulou-Mourkidou, E., Karpouzas, D.G., Patsias, J., Kotopoulou, A., Milothridou, A., Kintzikoglou, K. *et al.* (2004). The potential of pesticides to contaminate the ground water resources of the Axios river basin in Macedonia, North Greece: Part 1. Monitoring study in the north part of the basin. *Science of Total Environment*. 321: 127-46.
- Singh, K.P., Malik, A., Mohan, D. and Takroo, R. (2005). Distribution of persistent organochlorine pesticide residues in Gomti River, India. *Bulletin of Environmental Contamination and Toxicology*. 74: 146-154.
- Sneha, D. and Bhimte, P.U. (2012). Meshram persistent organochlorine pesticide residues in ground and surface water of Nagpur and Bhandara district. *Bionano Frontier*. 5: 244-249.
- Tuxen, N., Tuxsen, P.L., Rugge, K., Albrecht, H.J. and Bjerg, P.L. (2000). Fate of seven pesticides in an aerobic aquifer studied in column experiments. *Chemosphere*. 45: 1485-94. doi: 10.1016/S0045-6535(99)00533-0.
- Tyagi, H., Gautam, T., Prashar, P. (2015). Survey of pesticide use patterns and farmers' perceptions: A case study from cauliflower and tomato cultivating areas of district Faridabad, Haryana, India. *International Journal Medipham Research*. 1(3): 139-146.
- USEPA (United States Environment Protection Agency). In: *Analysis of Pesticide Residues in Human and Environmental Samples-A Compilation of Methods Selected for use in Pesticide Monitoring Programs*; 1980. [Watts, R.R. (editor)]. EPA-600/80-038.
- UNEP, (2003). Global reports on regionally based assessment of persistent toxic substances, UNEP Chemicals, Geneva, Switzerland.
- Veeraiah, K. and Prasad, M.K.D. (1996). A study on the organochlorine pesticides residue input into Kolleru through Tammieleru river. *Ecology Environmental and Conservation*. 2: 83-86.