Method Development, Validation, Monitoring, Seasonal Effect and Risk Assessment of Multiclass Multi Pesticide Residues in Surface and Ground Water of New Alluvial Zone in Eastern India

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Abstract

A liquid-liquid extraction (LLE) method consisting gas chromatography-mass spectrometric (GC-MS) determination of thirty six pesticides in environmental waters was standardized. The method was validated as per SANTE/11813/2017 guidelines. Effect of three seasons namely summer, monsoon and winter on monitoring of pesticide residues in environmental waters (river, pond and tube well) of rural area was studied and subsequently risk assessment was evaluated. Within two districts (Nadia and North 24paraganas) of new alluvial zone in eastern India, six different places were chosen for sampling of river water. On the contrary, six different ponds and tubewells as well were considered for sampling. 144 samples of 2 liter each (48 each of river, pond and tubewell water) of each district irrespective of seasons were analyzed during the study period. Each water sample (750 ml) was extracted with ethylacetate:dichloromethane (8:2). The total residue was reconstituted in acetone (1 ml) and analysed in GC-MS after proper filtration with 0.22 μm nylon syringe filter. Average percent recovery ranged from 77.84 to 118.15. Irrespective of seasons, maximum total organochlorine (OC) and organophosphorous (OP) pesticide residues were dominated respectively in river and pond water. Irrespective of types of environmental waters, monsoon (July to October) showed presence of total maximum pesticide residues. Risk Quotient (RQ) [acute and chronic] was calculated respectively in pond and river water. Only Seven water samples of tubewell were contaminated with butachlor and chlorpyrifos, although in non-significant average amount ($< 0.1\text{ngml}^{-1}$), irrespective of seasons and thus safe for consumption.

Introduction:

West Bengal is the fourth largest populated state in India. The population density is $1100/\text{km}^2$ in 2020. Barrackpore and Kalyani are two important sub-division towns of west Bengal having population densities $11,500/\text{km}^2$ and $7,500/\text{km}^2$ respectively. The present study was aimed to carry out at Barrackpore and Kalyani because these two locations are situated in new alluvial zone of the river *Hooghly (Ganga)* and are developed agriculturally as well as industrially. Three important sources of environmental waters (river, pond and tubewell) serve as domestic, agricultural and industrial consumption. The water of *Hooghly River* specially is used by the respective municipalities as drinking water after treatment in various plants. Besides, the same water is used in agriculture through irrigation and consumed by various industries directly (KMDA 2017). Water is very crucial for sustaining life. About 50% of urban people and 80% of water for rural people in India are affected by water pollution and therefore scarcity of pure drinking water is being created (Hegde 2012). Environmental waters are usually contaminated with point and non-point source of contamination. However, a major source of water contamination comes from nonpoint sources (Calhoun 2005). Enormous researchers (Ongley et al. 1992; Rickert, 1993; Kaushik et al. 2008, 2012; Maurya and Kumar 2013; Toccalino et al. 2014; Székács et al. 2015; Mohamed and Ahmed 2020) reported contamination of environmental waters. But literature of research in these two areas under present study is scarce. Due to dense population, sources of environmental waters including river, pond and tubewell are limiting for use and consumption. Therefore, the chances of contamination are more. In India, during 2014-15 to 2019-20 consumption of chemical pesticides in agriculture has been increased by 7% in comparison to bio-pesticides by 34%. Awareness is therefore growing towards quality assurance and bio-safety in agriculture. At this point, only persistent pesticides may cause contamination and/or pollution of environmental waters. Considering the fact, thirty six pesticides (12 organochlorines, 7 organophosphates, 7 synthetic pyrethroids and 10 others) were chosen based on the screening of literature and farmers' use in these localities.

Movement of pesticides creates three problems when these reach from the application sites to non-target regions. The possible effects are environmental contamination, economic loss and inefficient pest control (Duttweiler and Malakhov 1977; Waite et al. 2002). The transportation of pesticides and its degradation products to surface waters from soil depends on several factors, including environmental weather condition, soil characteristics, topography, agricultural practices and chemical properties of individual pesticides (Leonard et al. 1988; Arias-Estévez, et al. 2008). As there are huge variations in temperature, rainfall and humidity in seasons like summer, monsoon and winter in these locations (Fig. 1) seasonal effects are also considered for investigation under the present study. Though previous study of overall environmental effect on surface water is available (Mondal et al., 2018) but the data of rainy season correlated with non-point source contamination is pending. So, there is a requirement of the correlation between seasonal residue data and non-point source of contamination. Various methods like solid phase extraction (SPE) (Tsochatzis et al. 2012; Sangchan et al. 2012; Kouzayha et al. 2012; Maurya and Kumar 2013) and liquid-liquid extraction (LLE) (Singh and Mishra 2009; Kaushik et al. 2012; Erkmén et al. 2013) are available to analyse pesticide residues in water. To analyse pesticide residues in water samples Solid Phase Extraction (SPE) is usually applied as it is an easy and fast process (Hatrik and Tekel 1996). The Liquid Liquid Extraction (LLE) method is more reliable than SPE method (Tan 1992). Commercial SPE cartridges or disks have been shown to give extraneous peaks attributed to phthalate esters contained in the housing materials of the cartridges, especially when GC-ECD is used for analysis (Awofolu and Fatoki 2003). In this present method involving LLE three different solvent mixtures namely S_1 (EA:DCM 8:2), S_2 (Hexane:DCM 8:2) and S_3 (100% DCM) were considered to check efficiency of extraction of pesticide residues from water samples. Monitoring of 36 pesticide residues was done collecting samples

from *Hooghly River*, ponds and tubewells maintaining the sampling protocol. Focusing on the ecological risk of pesticides of non-point source, close proximities and huge connectivities with surrounding areas and limited dilution potentials were observed (Karaouzas et al. 2011; Schulz 2004). Therefore, ecological risk assessment is very important evaluating process of toxic effects of pesticide on non-target organism in aquatic system. Based on the result found in the monitoring study, risk assessment was investigated.

Materials And Methods:

Study area:

Barrackpore (22°76'N and 88°37'E) and Kalyani (22°58'N and 88°26'E), two sub-divisional metropolitan towns of respective districts of North 24 Parganas and Nadia have major industrial and agricultural area. Nadia has 79.48% of agricultural area (Matirkatha 2016) whereas Barrackpore is one of the dense industrial areas of West Bengal. Both are situated at the bank of *Hooghly River (Ganga River)*, the water of which is the source of water treatment plants for drinking, agriculture, industrial use and aquaculture (KMDA 2017). Diversified cropping pattern is found in these two areas throughout the year.

Sampling:

River water (RW), pond water (PW) and tubewell water (TW) samples were collected for consecutive 48 weeks to monitor the pesticide residues in the aquatic systems of study area. A total of 144 samples (48 each of river, pond and tube-well water) from each district were collected throughout the year covering winter (November to February), summer (March to June) and monsoon (July to October) seasons. Six different sampling points in river, six different ponds and six different tube-wells were chosen for sampling purposes (Fig. 2). Ponds and tube-wells chosen for sample collection are located within 2–3 km radius under domestic, agricultural and industrial activities. Amber glass bottles (2 liter) with stopper cap were washed with commercial detergent using hot water and rinsed with deionized water and acetone. Bottles were then dried in an oven at 100°C and stored until use for sampling. Samples were collected from a depth of 1 ft from the surface of river and pond water using Kemmerer water sampler and kept in ice box at 4°C. A 2.0 % solution of Sodium azide (NaN_3) was used for the protection of water samples from microbial growth. Samples were extracted immediately and processed subsequently.

Chemicals and Reagents:

A total of 36 pesticides covering different groups namely insecticides, herbicides, fungicides and acaricides were selected for the present study (Table 1). All certified reference materials (CRMs) were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany with purity mostly of > 97%. LC-MS grade dichloromethane (DCM), hexane, acetone and ethylacetate (EA) were obtained from J.T. Baker, Avantor, USA. Analytical grade anhydrous magnesium sulphate, sodium chloride and sodium sulphate were obtained from Rankem, India. Anhydrous magnesium sulphate was heated at 450°C for 5 hours to remove phthalates and then cooled naturally and stored in a desiccator.

Table 1
Parameters recovery experiments of selected pesticides in GC-MS.

Sl. No.	Pesticides	RT ^a	m/z for confirmation with ion ratio			^b R ²	LOQ ^c (ng/ml)	Recovery			RPD ^e
			Target Ion	Q ₁ (% Q ₁ /T)	Q ₂ (% Q ₂ /T)			LOQ (SD ^d)	2x LOQ	5xLOQ	
1	4-Br 2-Cl-phenol	9.01	208	172 (42.09%)	170 (32.58%)	0.996	0.044	110.52 (5.23)	91.3	92.9	4.16
2	Trifluralin	13.69	306	43 (44.72%)	264 (40.28%)	0.998	0.041	97.44 (6.33)	85.6	101.43	4.92
3	Phorate	14.39	75	121 (50.28%)	260 (43.29%)	0.997	0.02	99.31 (9.37)	101.56	106.23	6.83
4	α-HCH	14.67	181	183 (93.37%)	219 (51.04%)	0.999	0.007	113.82 (2.7)	90.69	82.92	12.14
5	Atrazine	15.38	200	215 (97.23%)	58(76.68%)	0.998	0.048	107.43 (10.20)	100.64	99.54	15.09
6	β-HCH	15.6	181	183 (68.78%)	219 (95.78%)	0.998	0.012	83.57 (8.02)	105.11	99.17	18.15
7	Lindane	15.85	181	183 (96.48%)	219(54.23%)	0.999	0.011	77.84 (9.33)	106.58	107.27	14.14
8	Chlorothalonil	16.47	266	264 (76.28%)	268 (50.23%)	0.983	0.099	110.41 (7.02)	100.01	100.38	14.64
9	δ-HCH	16.98	181	183 (92.49%)	219(57.85%)	0.995	0.005	105.04 (5.2)	113.65	109.16	16.59
10	Dimethachlor	17.83	134	197 (40.23%)	77(52.91%)	0.993	0.056	92.12 (11.02)	102	98.45	1.93
11	Alachlor	18.28	45	160 (42.28%)	188 (26.22%)	0.999	0.05	92.57 (8.91)	105.35	103.43	8.93
12	Parathion-methyl	18.38	263	109 (42.21%)	125 (35.23%)	0.995	0.021	85.92 (7.19)	106.09	97.77	4.25
13	Heptachlor	18.79	100	272 (42.28%)	274 (30.56%)	0.998	0.015	111.7 (8.26)	113.44	101.39	8.73
14	Malathion	19.91	125	127 (65.59%)	93(47.54%)	0.996	0.036	86.17 (6.6)	109.4	104.87	15.47
15	Chlorpyrifos	20.23	97	197 (63.28%)	199 (41.56%)	0.997	0.022	96.35 (1.02)	109.84	105.52	13.55
16	Aldrin	20.46	66	263 (57.63%)	91(22.73%)	0.999	0.017	93.45 (5.81)	117.22	111.11	3.52
17	Pendimethylene	21.87	252	162 (18.93%)	181 (20.43%)	0.998	0.056	107.57 (7.19)	102.92	99.3	13.06
18	Quinalphos	22.77	146	118(65%)	156(61%)	0.999	0.031	87.66 (9.63)	109.33	101.39	10.75
19	Butachlor	23.72	57	176 (68.89%)	160 (76.31%)	0.999	0.014	112.24 (10.25)	107.75	99.62	10.98
20	α- Endosulfan	23.96	241	195 (80.25%)	159 (22.91%)	0.999	0.01	113.99 (7.29)	111.03	106.27	14.09
21	Profenophos	24.28	337	97(68.11%)	139 (66.97%)	0.998	0.016	92.47 (9.28)	98.43	94.16	4.04
22	p,p-DDE	25.85	246	318 (75.76%)	248 (54.81%)	0.962	0.023	98.28 (5.27)	102.56	96.05	14.58

Sl. No.	Pesticides	RT ^a	m/z for confirmation with ion ratio			^b R ²	LOQ ^c (ng/ml)	Recovery			RPD ^e
			Target Ion	Q ₁ (% Q ₁ /T)	Q ₂ (% Q ₂ /T)			LOQ (SD ^d)	2x LOQ	5xLOQ	
23	o,p-DDD	25.85	235	165(76.43%)	237(53.85%)	0.993	0.018	86.67 (7.21)	102.47	98.51	4.33
24	Ethion	27.52	231	97(60.28%)	153 (50.78%)	0.997	0.017	90.2 (9.16)	102.7	98.72	12.62
25	p,p-DDD	27.74	235	165 (56.28%)	237 (32.50%)	0.999	0.021	91.94 (12.09)	92.59	93.63	14.54
26	B-Endosulfan	27.86	241	195 (65.23%)	159 (40.21%)	0.997	0.014	89.809 (14.20)	99.04	95.21	9.65
27	p,p-DDT	27.87	235	165(52.28%)	237(61.12%)	0.996	0.015	118.15 (6.37)	110.78	101.28	1.85
28	Endosulfan sulphate	29.7	272	274(53.37%)	239(50.21%)	0.998	0.017	84.92 (4.28)	100.26	96.56	14.94
29	Spiromesifen	31.85	272	99(52.23%)	273(36.16%)	0.972	0.053	80.38 (2.98)	103.32	98.26	17.04
30	Bifenthrin	32.97	181	166(53.27%)	165(62.74%)	0.986	0.039	97.25 (7.23)	95.94	98.42	3.15
31	Fenpropathrin	33.53	97	181 (96.97%)	265 (35.12%)	0.994	0.05	83.49 (8.29)	102.94	103.04	13.55
32	Lamda-cyhalothrin	36.22	181	197(95.70%)	208(58.77%)	0.996	0.087	82.47 (7.08)	98.43	70.67	4.53
33	β-Cyfluthrin	41.27	163	206 (65.23%)	226 (54.15%)	0.999	0.025	82.4 (4.09)	102.56	112.24	18.65
34	Cypermethrin	42.22	181	163 (75.86%)	127 (47.59%)	0.968	0.035	111.44 (4.45)	102.47	113.99	7.53
35	Fenvalerate	44.76	125	167 (57.88%)	225 (44.54%)	0.994	0.044	97.75 (5.23)	102.7	92.48	1.46
36	Deltamethrin	47.82	181	253 (72.62%)	77(69.84%)	0.996	0.041	111.37 (6.37)	85.36	98.29	13.43
^a RT- Retention Time (min.); ^b R ² : Coefficient of regression equation; ^c LOQ: Limit Of Quantification; ^d SD: Standard Deviation; ^e RPD: Relative Percentage Difference.											

Glassware and Equipments:

Separating Funnel shaker (Yamato Scientific, Japan), vortex mixer (Spinix, Tarson, India), Rotary vacuum evaporator with temperature controlled water bath (HS 2001 NS, Germany), Turbo Vap evaporator (Caliper Life Sciences, Hopkinton, Massachusetts, USA) and 100–1000µL and 1-10mL micropipettes (Eppendorf Research, Germany) were also used for sample preparation. The electronic analytical balance Sartorius GD603 (Sartorius, Germany) with readability = 0.001ct/0.2 mg was used for weighing. All the equipments were calibrated externally with certified agencies. All the glassware viz. conical flask (1000 mL), separating funnel (1000 mL), measuring cylinder (500 ml and 1000 ml) and volumetric flasks (100 mL), graduated tubes (25 mL) were calibrated and purchased from Borosil Glass Works Ltd., Gujarat, India. Membrane filter paper, Ultipor N66, Nylon 6,6 membrane, 13 mm (Pall Life Sciences, USA) and syringe filter (SGE Analytical Science, Australia) were used for filtration process.

Preparation of stock and working standards:

Stock solutions of each CRM were prepared into a 100 ml volumetric flask with hexane:toluene (1:1) solvent mixture. Working standards of different concentration (1,00,000 ngml⁻¹, 10,000 ngml⁻¹, 5,000 ngml⁻¹, 2,500 ngml⁻¹, 1,000 ngml⁻¹, 500 ngml⁻¹, 250 ngml⁻¹, 100 ngml⁻¹, 50 ngml⁻¹, 20 ngml⁻¹ and 10 ngml⁻¹) were prepared from the stock solution using dilution technique. All the stock and working solutions of 36 pesticide standards were stored under refrigerated condition (-4°C), protected from sun light.

Sample preparation:

The conventional liquid-liquid extraction (LLE) method was used for water samples using three different solvent mixtures namely S_1 (EA:DCM 8:2), S_2 (Hexane:DCM 8:2) and S_3 (100% DCM) to check and compare the % recovery (Fig. 3). Collected water samples were filtered through whatman glass fibre filter (GF/F, 0.45 mm) to remove suspended particles before extraction. Sample (750 ml) was taken in separatory funnel (1 litre), NaCl (150 g) was added to separatory funnel and mixed properly, extracted thrice with 70, 40 and 40 mL of each solvent mixture (S_1 , S_2 and S_3) using separating funnel shaker @ 210 rpm and allowed 15 min to settle down for clear solvent phase separation. Altogether 150 ml (= 70 + 40 + 40) of organic solvent layer was collected in a conical flask after passing over anhydrous Na_2SO_4 . The collected solvent was evaporated to dryness in a rotary vacuum evaporator at 40°C and the volume was made up with 5 mL hexane. It was taken in tarbo-vap tube for evaporation to dryness using Turbo Vap LV. The volume was reconstituted in 1 mL acetone. After vortexing for 30s and sonication for 5 min., the acetone was transferred to 2ml vial for Gas Chromatography-Mass Spectrometric (GC-MS) analysis with proper filtration using syringe filter.

Instrumental analysis:

The final extracts were analyzed using GC-MS, QP 2010 Plus (Shimadzu Corp., Kyoto, Japan), with a mass selective detector (MSD). The oven conditions were: initial temperature of 40°C (hold for 1 min), raised @ 25°C/min to 130°C, then @ 12°C/min to 180°C, and finally @ 3°C/min to 280°C, with a hold time of 7 min. The injector temperature was 250°C. Helium was used as a carrier gas with purity-99.999%. The ion source temperature was 250°C. The interface temperature was 280°C. The instrument was operated in the spit mode with split ratio of 1:10. The injection volume was 2 μL . The MS conditions include solvent delay of 6 min; scan rate of 0.50/s and scanned mass range of 50–500 m/z. All samples were analyzed in the Selected Ion Monitoring (SIM) mode (Fig. 4). Data were acquired and processed by GC-MS Lab Solution Software (version 4.45). The compound specific retention times, m/z ions and molecular mass for the identification, confirmation and quantification are represented in (Table 1). Pesticides were identified based on their retention times, quantification and identification transitions.

Method validation:

The method was validated following SANTE/11813/2017 guidelines with linearity, limit of detection (LOD), limit of quantification (LOQ), specificity, accuracy (% recovery) and precision (% RSD) (SANTE 2017). LOD was determined based on signal to noise ratio (S/N) 3:1 whereas S/N ratio of 10:1 was used to determine the LOQ. The five-point (10, 20, 50, 100 and 250 ng mL^{-1}) calibration curve of mix-standard solution was prepared for checking linearity with the regression coefficient (R^2). A comparative recovery experiment in three replicates was carried out spiking blank water sample with the working mix-standard solution at fortification levels of LOQ, 2 $\times$ LOQ, and 5 $\times$ LOQ. The precision and trueness of the results, expressed as %RPD was also calculated using $\text{RPD} = (\text{M}/\text{N}) \times 100$ where $\text{M} = \text{A} + \text{B}$ and $\text{N} = (\text{A}-\text{B})/2$, A = Inter assay recovery and B = Intra assay recovery (Tripathy et al. 2019).

Risk assessment:

Risk Quotient (RQ) was assessed and curtailed following EPA's Level of Concern (LOC) for aquatic animals (e.g., fish and invertebrates), for presuming the potential risk associated with the presence of pesticide residues in the aquatic environment (USEPA 2017a). RQ was calculated as follows: $\text{RQ} = \text{EEC}/\text{LC}_{50}$ or $\text{EEC}/\text{EC}_{50}$ or EEC/NOAEC where, EEC = Estimated Environmental Concentration (i.e. detected pesticide level in environmental water); LC_{50} and EC_{50} = Median Lethal and Effective Concentration, respectively (for estimation of acute toxicity) and NOAEC = No Observed Adverse Effect Concentration (for estimation of chronic toxicity). Pesticide Properties Data Base (PPDB 2020) was used for the collection of all eco-toxicological (LC_{50} or EC_{50} or NOAEC) data (Table 2).

Table 2
Risk presumption in water ecosystem of river and pond.

Aquatic animals										
Pesticides	River Water					Pond Water				
	EEC ^a	LC ₅₀	NOAEC	RQ		EEC	LC ₅₀	NOAEC	RQ	
				Acute	Chronic				Acute	Chronic
T-HCH	1.26	2.9	2900	0.43448	0.0004344	0.11	2.9	2900	0.0379	0.000037
T-DDT	1.11	2510	130	0.0005	0.0085384	0.18	2510	130	0.000071	0.000062
T-Endosulfan	0.59	2	0.0001	0.295	5900	0.03	2	0.0001	0.015	0.000017
Phorate	0.005	13	-	0.000384	-	0.005	13	-	0.000385	-
Parathion-methyl	0.031	2700	-	0.000011	-	0.031	2700	-	0.000011	-
Malathion	0.015	18	91	0.00083	0.00016483	-	-	-	-	-
Chlorpyrifos	0.075	25	0.14	0.00301	0.53571428	0.13	25	0.14	0.0052	0.928571
Quinalphos	0.023	5	-	0.0046	-	0.083	0.005	-	16.6	-
Profenophos	0.015	0.08	0.002	0.1875	7.5	-	-	-	-	-
Butachlor	0.025	441	-	0.000056	-	0.047	441	-	0.000107	-
Semi-aquatic plants										
	EEC	EC ₅₀	NOAEC	RQ		EEC	EC ₅₀	NOAEC	RQ	
				Acute	Chronic				Acute	Chronic
T-HCH	1.26	2500	1900	0.000504	0.0006631	0.11	2500	1900	0.000044	0.000057
T-DDT	1.11	-	-	-	-	0.18	-	-	-	-
T-Endosulfan	0.59	2150	-	0.0002744	-	0.03	2150	-	0.0000139	-
Phorate	0.005	1300	-	0.0000038	-	0.005	1300	-	0.0000038	-
Parathion-methyl	0.031	1300	-	0.0000238	-	0.031	1300	-	0.0000238	-
Malathion	0.015	13000	-	0.0000011	-	-	13000	-	-	-
Chlorpyrifos	0.075	480	43	0.0001562	0.0017441	0.13	480	43	0.000271	0.003023
Quinalphos	0.023	-	-	-	-	0.083	-	-	-	-
Profenophos	0.015	-	-	-	-	-	-	-	-	-
Butachlor	0.025	210	-	0.00011904	-	0.047	210	-	0.000224	-
^a EEC: Estimated Environmental Concentration; LC ₅₀ or EC ₅₀ or NOAEC represent ecotoxicological data; - (dash) represents that the data have not been found in PPDB, 2021										

Meteorological Parameters:

Meteorological data (temperature, relative humidity and rain fall) were also collected from Department of Agricultural Meteorology and Physics, BCKV, Kalyani, for entire study period (Fig. 1). These data was used to correlate and discuss on the seasonal variation of occurrence of pesticide residues in environmental water samples.

Results And Discussion:

Method standardization:

Different binary solvent mixtures and single solvent system were used for extraction of water samples. Extraction of pesticide residues having different polarities depends on the polarity of extraction solvent (Allen et al. 2015). To standardize the extraction solvent, three solvent mixtures were considered for extraction namely S_1 (EA:DCM 8:2), S_2 (Hexane:DCM 8:2) and S_3 (100% DCM). Among these three solvent mixtures, highest % recovery (77.85 to 110.5) was achieved in case of S_1 solvent mixture at fortification level of 0.10 ng mL^{-1} . At the same fortification level other two solvent mixtures (S_2 and S_3) could not extract all pesticides. Even these solvent mixtures showed average percent recovery from 11.52 to 258.03 (Fig. 3). Sibali et al. (2008) used hexane (100%), DCM:Methanol (1:1), DCM:Hexane (1:1) and DCM (100%) as extraction solvent mixtures. The researcher and his team found 100% DCM as the best extraction solvent giving recoveries above 70%. Using the standardized extraction solvent mixture S_1 (EA:DCM 8:2), the method was validated following SANCO/11813/2017 guidelines. The LOQ of individual pesticide was determined and found within the range $0.011\text{--}0.087 \text{ ng mL}^{-1}$. A common LOQ of 0.1 ng mL^{-1} was fixed for all 36 pesticides to study average percent recovery. The same is prescribed as standard value by EC (2016) and accordance with Govt. of India (Sankararamakrishnan et al. 2005; Raghuvanshi et al. 2014). Average percent recovery found at fortification levels of LOQ (0.1 ng mL^{-1}), 2xLOQ (0.2 ng mL^{-1}) and 5xLOQ (0.5 ng mL^{-1}) were in the range 70.67–118.15. This data matched the criteria (70–120) of SANTE guideline. %RPD were calculated for individual pesticide and found satisfactory ($\leq 20\%$). The highest % RPD was found in case of β -cyfluthrin (18.65) and the least was for fenvalerate (1.46) (Table 1).

Monitoring of pesticide residues and effect of Seasonal variation:

A total eighteen out of 36 pesticides were detected irrespective of seasons during the study. These 18 pesticides are organochlorine insecticides [α -HCH, β -HCH, γ -HCH and δ -HCH (total HCH), endosulfan, α -endosulfan and β -endosulfan (total endosulfan), p,p' -DDE, p,p' -DDT, o,p' -DDD and p,p' -DDD (total DDT)], organophosphate (OP) insecticides (phorate, parathion-methyl, malathion, chlorpyrifos, quinalphos and profenophos) and chloroacetanilide herbicide Butachlor. River water samples were found contaminated with all 18 pesticides except profenophos in summer. The water samples of pond were reported with residues of 16 pesticides except p,p' -DDD (winter), α -endosulfan (in summer) and β -endosulfan (in summer and winter seasons). Chlorpyrifos and butachlor residues were detected in tubewell water samples irrespective of seasons. No residues of other pesticides under study were detected in any of the environmental water samples irrespective of seasons.

Seven out of ninety six tube-well water samples were contaminated only with 2 pesticides (chlorpyrifos and butachlor) and others samples detected pesticide residues below limit of quantification (LOQ) of 0.1 ng mL^{-1} for every season. The river water was contaminated with 18 pesticides including 11 organochlorines in spite of the restricted use (UNEP 2003) and low water affinity (Singh et al. 2012) of organochlorines (OCs).

The mean concentration of Total organochlorines (T_{OC}) = Total HCH + Total DDT + Total endosulfan) detected in river water (2.96 ng mL^{-1}) (Table. 2) despite the low water affinity (Singh et al. 2012) of OCs in water. These values were higher compared to those reported in other Indian rivers viz. Yamuna (Kaushik et al. 2008), Kuano (Singh and Mishra 2009) but lower than reported T_{OC} level in Sembrong lake basin in Malaysia (Sharip et al. 2017). In this study, DDT isomers were detected more frequently in river water in contrary to other water sources. Although DDT is banned for use in agriculture, presence of its residues in river water may be indicated the use of DDT in National Malaria Eradication Programme (NMEP, Govt. of India) in India (NVBDCP 2016). Values of Total HCH (sum of HCH isomers) in the river system indicates non-point source of contamination. It is assumed as an old source of contamination due to isomer's least reactivity and the most persistent nature among HCH isomers (Wang et al. 2007).

Remarkably, OP pesticides were predominant in pond and tubewell water located in neighboring places within 1 km radius in contrary to the abundant presence of OC insecticide residues in river water system. A mean concentration of chlorpyrifos (0.13 ng mL^{-1}) was found and the insecticide was frequently detected in pond water irrespective of season. In tube-well water, it was the second most found pesticide next to butachlor irrespective of season. The residues of OPs in pond water probably due to contamination from agricultural pesticides used nearby cultivated land (Reddy and Reddy 2010; Lari et al. 2014). The mean concentration of T_{OC} was much lower in pond water (0.32 ng mL^{-1}) compared to river water throughout all seasons. Interestingly, residues of no synthetic pyrethroid (SP) insecticide were detected in any water throughout the study period. This is probably due to the photo instability of synthetic pyrethroids (Kocourek et al. 1987).

Seasonal residual data showed huge influence of environmental parameters (rain fall, temperature and relative humidity). Variation of environmental parameter in study period showed in Fig. 1. In monsoon season, mean rain fall (50.9 mm) was three times higher of summer and average residue found in different aquatic system also showed the highest. In tube-well water sample, insecticide chlorpyrifos (0.157 ng mL^{-1}) and the herbicide butachlor (0.065 ng mL^{-1}) were detected in monsoon period predominantly. In river and pond water samples, pesticides was found in winter comparatively lower than summer, because average temperature of summer was expectedly higher than winter. Although winter season is major agricultural period of Bengal, this scenario also designates some non-point source of

contaminations. Contamination by agricultural pesticides in neighboring pond water system may be endorsed to run-off during monsoon water from subsequent agricultural land (Reddy and Reddy 2010; Lari et al. 2014). Intensive agricultural practices performing in the neighborhood of water system was also the probable causes of recommended OP pesticides contamination in pond water (Agrawal et al. 2010) but banned OCs (PPQS 2020) residues leads to unknown sources of contamination. Seasonal variation of detected average residues of OP and OC pesticides in aquatic system (Fig. 5) showed different behavior (Fig. 6). Abundances of OC pesticides in river water higher than pond water while OPs were predominate in pond water. But both were getting rise in monsoon season. Nguyen and his coworkers, 2019 also reported maximum OC pesticide concentration in Dong Nai River at rainy season in their study. Rising of OCs' contamination in river water was related to run-off rain water to river but sources were not specific. Moreover, OCs has an affinity to gather in the river sediments due to their hydrophobic nature and high octanol-water partition coefficient (Yang et al. 2005; Masiá et al. 2013)

Most of the study areas consist of a well-drained sandy-loam soil and the ground water levels are 35–50 ft deep from surface. This ground water (Tube-well sample) showed seasonal contamination due to rapid transport of soil holding pesticides in monsoon (butachlor and chlorpyrifos) with low water solubility and high Log K_{ow} (octanol-water partition coefficient) (Yang et al. 2005; Masiá et al. 2013). Table 3 lists the physicochemical properties of the pesticides inspected.

Table 3
Physicochemical properties of the target pesticides.

Compound	Molecular formula	Solubility in water (mg L ⁻¹)	Log D (pH 7.4)	Vapor pressure (mPa)	Log K _{oc}
4-Br-2-Cl- phenol	C ₆ H ₄ BrClO	-	-	0.000308	-
Trifluralin	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	0.221	4.6	9.5	3.940
Phorate	C ₇ H ₁₇ O ₂ PS ₃	50	3.6	112	3.370
α-HCH	C ₆ H ₆ Cl ₆	2	3.82	5.99	3.456
Atrazine	C ₈ H ₁₄ ClN ₅	35	2.2	0.039	2.000
β-HCH	C ₆ H ₆ Cl ₆	0.2	3.82	4.06	3.456
Lindane	C ₆ H ₆ Cl ₆	8.52	3.82	4.4	3.456
Chlorothalonil	C ₈ Cl ₄ N ₂	0.81	3.12	0.076	3.075
δ-HCH	C ₆ H ₆ Cl ₆	31.4	3.82	-	3.456
Dimethachlor	C ₁₃ H ₁₈ ClNO ₂	2300	2.63	0.64	2.806
Alachlor	C ₁₄ H ₂₀ ClNO ₂	240	2.99	2.9	3.002
Parathion-methyl	C ₈ H ₁₀ NO ₅ PS	55	2.94	0.2	2.977
Heptachlor	C ₁₀ H ₅ Cl ₇	0.056	5.54	53	4.389
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	148	2.76	3.1	2.878
Chlorpyrifos	C ₉ H ₁₁ Cl ₃ NO ₃ PS	1.05	4.78	1.43	3.979
Aldrin	C ₁₂ H ₈ Cl ₆	0.027	5.91	8.6	4.589
Pendimethylene	C ₁₃ H ₁₉ N ₃ O ₄	0.33	4.83	3.34	4.005
Quinalphos	C ₁₂ H ₁₅ N ₂ O ₃ PS	17.8	3.3	0.346	3.160
Butachlor	C ₁₇ H ₂₆ ClNO ₂	20	4.09	0.24	3.605
α- Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	0.32	2.6	8.3	4.060
Profenophos	C ₁₁ H ₁₅ BrClO ₃ PS	28	4.4	2.53	3.770
p,p-DDE	C ₁₄ H ₈ Cl ₄	0.0265	6.46	-	4.890
o,p-DDD	C ₁₄ H ₁₀ Cl ₄	0.06764	5.84	0.18	4.553
Ethion	C ₉ H ₂₂ O ₄ P ₂ S ₄	2	4.94	0.2	4.063
p,p-DDD	C ₁₄ H ₁₀ Cl ₄	0.09	5.84	0.18	4.553
β-Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	0.32	2.6	8.3	4.030
p,p-DDT	C ₁₄ H ₉ Cl ₅	0.025	6.22	-	4.760
Endosulfan sulphate	C ₉ H ₆ Cl ₆ O ₃ S	0.32	3.87	0.83	3.481
Spiromesifen	C ₂₃ H ₃₀ O ₄	0.13	5.25	0.007	4.233
Bifenthrin	C ₂₃ H ₂₂ ClF ₃ O ₂	0.001	6.93	0.0178	5.146

Compound	Molecular formula	Solubility in water (mg L ⁻¹)	Log D (pH 7.4)	Vapor pressure (mPa)	Log K _{oc}
Fenpropathrin	C ₂₂ H ₂₃ NO ₃	0.33	5.82	0.76	4.544
Lamda-cyhalothrin	C ₂₃ H ₁₉ ClF ₃ NO ₃	0.005	6.32	0.0002	4.815
β-cyfluthrin	C ₂₂ H ₁₈ Cl ₂ FNO ₃	0.0019	6.13	0.000028	4.712
Cypermethrin	C ₂₂ H ₁₉ Cl ₂ NO ₃	0.01	6.05	0.00023	4.670
Fenvalerate	C ₂₅ H ₂₂ ClNO ₃	0.001	6.28	0.0192	4.791
Deltamethrin	C ₂₂ H ₁₉ Br ₂ NO ₃	0.0002	6.12	0.0000124	4.705
Data predicted with www.chemspider.com and PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/), -(dash) represents that the data have not been found in PPDB, 2021					

Although, in summer there is some reduction of water volume in river and pond for rising of temperature, (Sharip et al. 2017; Kaushik et al. 2012) total-pesticide concentration was much higher in monsoon than summer and winter period (Fig. 5). Tanabe et al. (2001) reported maximum residue in Shinano River in the month of May when most applications were conducted.

Risk assessment:

Aquatic as well as humans ecosystem is very much scarring due to the biotransformation (Le Du-Lacoste et al. 2013) and bioaccumulation (Luna-Acosta et al. 2015) of pesticide residues in aqueous system.

In India, due to persistence nature in the environment of DDT (since 1993) and HCH (since 1997) restriction was imposed in their agricultural (UNEP 2003; PPQS 2020) as well as human health use (UNEP 2003; NVBDCP 2016). Remarkable presence of these non-agricultural pesticides in water moiety is very alarming in spite of their restrictions. These pesticides were also key suppliers of global persistent organic pesticide (POP) circulation (Yadav et al. 2015). Mankind directly depends on these water and aquatic life, so the risk connected with the contaminated water system was evaluated in terms of humans (EC 2016) and aquatic health (USEPA 2017a).

EC limit for single pesticide in drinking water is 0.10 ngmL⁻¹ (EU 1998). Interestingly more than 50% monsoon samples has exceeded the threshold for both pond and river water. Conversely tube-well water was safe for drinking as it was below the total pesticides limits irrespective of season.

To evaluate the possible ecological risk (acute and chronic) associated with the pesticides contaminated river and pond water risk quotient (RQ) was used (Table.2). The RQ level of concern (LOC) of semi-aquatic (e.g., marimo and algae) plants was 1, so the RQ values (< 1) showed no possible risk on the aquatic ecosystems. But in case of T-HCH (RQ = 0.434) in river aquatic animals (e.g., fish; *Oncorhynchus mykiss*), estimated RQ value was very closer to the limiting marks of EPA's LOC for acute toxicity in terms of Acute High Risk (0.500). Chen et al. 2020 also indicated OC pesticides as a moderate risk group in their study at Shanghai river, China. Significantly RQ of total endosulfan (0.295) crossed acute toxicity in river fish in terms of Acute Endangered Species (LOC = 0.050) and showed very high risk in chronic toxicity RQ = 5900 compared to LOC = 1. Kapsi et al. (2018) and his team also reported α-endosulfan as medium risk in their study at Louros river, Greece. Profenofos also indicated chronic toxicity threat in river water unlike others OPs. However, in pond water system there was no ecological hazard (RQ < 1) for total-HCHs, total-DDTs and total-Endosulfan. In this study showed, the borderline RQ value of chlorpyrifos (0.928) comparing the LOC for Chronic Risk (1.0) in pond water fish, indicating future risk. Ccanccapa et. al. (2016) also reported that chlorpyrifos is the most frequent occurring pesticide in Ebro river water. Subsequently, the outcomes of this study are originated very serious for aquatic habitat around the study area.

Conclusion

In this study, an effective and profound method involving liquid-liquid extraction (LLE) and GCMS detection was standardized for determination of selected 36 pesticides in surface and ground water. EA and DCM (8:2, v/v) solvent system for LLE showed to be the best compared to other solvent systems. Method was validated according to EC guidelines and applied for observing of 36 pesticide residues (OCs, OPs and others) in different aquatic systems with seasonal variations. Different residues distribution of OPs and OCs was evaluated in river and pond water system with changes of environmental conditions. Comparatively higher concentration of pesticide residues

occurred during monsoon period compared to summer and winter. Despite the restricted use of persistent OCs, river water samples were found to be contaminated with high OC residues which reflect non-point sources of contaminations.

In most of the samples, the pesticide residue levels spotted were higher than EC recommended drinking water quality standards. Risk assessment in the aquatic system was assessed where the potential risk on aquatic bionetwork in terms of acute and chronic toxicity was also observed for OC pesticides in river aquatic ecosystem. Therefore, this study initiates reference line data for possible execution of pollution control and governing decision-making policies in Barrackpore and Kalynai, West Bengal.

Declarations

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Compliance with ethical standards

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Figures

Figure 1

Agro-meteorological data [Temperature, Relative humidity (RH) and rainfall] during the entire study period (48 weeks)

Figure 2

Study area (Sampling sites of the experiment)

Figure 3

Chromatogram showing peaks identified by retention time (min) and chemical name:

Retention Time (min)	Chemical Name
9.0	Phenol, 4-hydroxy-2-chloro-
13.506	Trifluoromethoxybenzene
14.188	Phenol, 4-hydroxy-2-chloro-
14.424	alpha-HCH
15.134	Atrazine
15.254	beta-HCH
15.584	gamma-HCH
16.147	Chlorobenzene
16.635	delta-HCH
17.551	Dimethylsiloxane
18.506	Hepachlor
19.091	Parathion-methyl
19.599	Methachlor
19.912	Chlorpyrifos
20.136	Aldrin
21.522	Permethrin
22.196	Quinolphos
23.669	Dieldrin
23.896	alpha-Etothion
24.892	Profenofos
25.091	beta-Etothion
25.442	gamma-Etothion
27.091	beta-Etothion
27.244	Etothion sulfate
29.558	gamma-Etothion
31.435	Spiromethion
32.552	beta-Etothion
33.113	Etothion sulfate
35.789	lambda-Cyhalothrin
40.086	lambda-Cyhalothrin
41.178	Permethrin
41.587	Permethrin
41.635	Permethrin
44.178	Permethrin
44.558	Permethrin
47.147	Dimethylsiloxane

GC-MS Chromatogram of thirty six selected pesticide standards

Figure 5

Seasonal average concentration of pesticide residues in pond and river water (ng ml⁻¹)

Figure 6

Frequency of occurrence of pesticides in River and Pond water with three seasons