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Quantitation of Pesticide Residue in Water and Food in Louisiana, USA

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Abstract

Pesticides can remain in the environment for decades and contaminate surface water that is used for irrigation of produce. This study examined pesticide residues in some surface waters and foods in Louisiana. Samples of 8 foods (tomato, corn, rice, blueberry, cucumber, cabbage, wheat and melon) and 35 surface waters were studied using a QuEChERS extraction method for food samples and liquid-liquid extraction method for the water samples. Gas chromatography-mass spectrometry was used to analyze water and food samples. Nine pesticides were detected in the surface water samples and 5 in the food samples. Pesticides detected in foods were below FDA tolerance limit but 0.18 ppm cypermethrin found in tomato was within 90% of the FDA limit (0.2 ppm). Four water samples had atrazine levels that were above the FDA limit for potable water. This study suggests the need to intermittently monitor pesticide contamination in our food and water.

Keywords

Gas Chromatography, Mass Spectrometry, QuEChERS, Cypermethrin, Atrazine, Pesticide, FDA

1. Introduction

Food and water are among the basic necessities of life and must therefore be consumed in a contamination-free manner in order to maintain a healthy diet. Cereal grains, vegetables and fruits are vital components of human daily balanced diets. Use of pesticides in agriculture has improved the quality of produce and requires less labor in maintaining field crops; however, lack of caution in pesticide handling could make an environment vulnerable and desolate, as some pesticides, once applied, take ages to degrade

thereby constituting an impediment to life and subsequent agricultural practice in such environment [1]. Since pesticide application is a potential source of environmental pollution [2], a regular quantitation of pesticide residue in food and water from an environment where pesticide application is routine should be considered. The use of QuEChERS (quick, easy, cheap, effective, rugged and safe) as a precise method of extraction of pesticides from food matrices is recommended [3] [4] particularly in the detection of pesticides in food especially fruits and vegetables [5]. Extraction of pesticides from water samples has been carried out by the United States Environmental Protection Agency. Analytical methods such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) have been used in the past but were not confirmatory in their output results. This was mainly due to the type of detectors routinely used namely electron capture, flame photometric, nitrogen phosphorus in GC and ultraviolet and fluorescence detectors in HPLC [6]. These detectors are not well suited to dealing with complex matrices and the interference encountered at lower detection limits. The addition of MS to GC has solved the problem of the shortfalls inherent to the traditional single dimension detectors. However, while MS detection has succeeded delivering low level detection using selected ion monitoring (SIM) mode for quantitation, full scan spectral data is still required for quantitative confirmation. Although complex matrices still pose a challenge for some residues in full scan mode, full scan data is necessary to prevent the reporting of false positives [7]. The combination of GC-MS provides analysis of trace amounts of pesticide residues in diverse samples ranging from biological fluids [8] [9], waters [10] [11], or fruits and vegetables [12] [13]. In this study, pesticide residues in surface waters and selected food samples (corn, rice, wheat, cucumber, tomato, cabbage, melon and blueberry) were evaluated. Walther studied pesticide residue in Louisiana water and found atrazine as most prevalent [14]. Wijnja *et al.* confirmed dependence of pesticide detection in surface waters in some suburban surface waters of Massachusetts on their usage [15]. Atrazine has been reported to be found in ground water in the UK [16]. This study seeks to quantitate possible pesticide residue in surface waters and some food crops in Louisiana in attempt to enhance our environmental and health management.

2. Experimental

2.1. Sample Storage and Preparation

Surface water and food samples were collected from different locations in Louisiana. Samples were placed on ice upon collection prior to delivery to the lab. These were sourced from a pool of samples being routinely submitted to the Pesticide Laboratory of the Agricultural Chemistry department, Louisiana State University through the Louisiana State Department of Agriculture and Forestry (LDAF). As outlined in **Table 1**, there were samples of 6 tomatoes (*Lycopersicon esculentum*), 3 sweet corns (*Zea mays*), 2 each for blueberries (*Vaccinium spp.*) and wheat (*Triticum aestivum*), and 1 each for melon (*Cucumis melo*), cucumber (*Cucumis sativus*), cabbage (*Brassica oleracea*) and rice (*Oryza sativa*). All the food samples were received in June 2015 except rice that was

delivered in August 2015. All the 35 waters were received in May 2015. Water samples and their sources are listed in Table 2. All water samples were stored at 4˚C and food samples stored at −20˚C until each was analyzed.

2.2. Pesticide Residue Extraction of Surface Water

Water sample was allowed to warm up to room temperature having been stored in a cooler at 4˚C. Five hundred ml of surface water samples were measured and transferred to a 1-liter separatory funnel. Seventy five ml of methylene chloride was added to the surface water sample. The surface water samples were capped and shaken for 1.5 minutes, with occasional release of pressure every 15 - 20 seconds to prevent breakage. A large funnel was prepared for each sample by plugging the stem with a small amount of rinsed glass wool in the bowl and filling approximately a quarter full with petroleum-ether

Table 1. Food samples collected from different locations in Loiuisana.

Food	Amount	Source	Food	Amount	Source
Melon	1	Breaux Bridge	Cucumber	1	Pollock
Cabbage	1	Lafayette	Wheat	2	Deridder (2)
Rice	1	Eunice	Blueberries	2	Franklinton, Ringgold
Corn	3	Alexandria, Winsboro, Dixie			
Tomato	6	Amite (2), Boyce, OakGrove, Epps, Coushatta			

Table 2. Surface water samples collected from different locations in Loiuisana.

Water	Source	Water	Source
BPH	Bayou Pierre, Hwy 1 S of Powha	BTH2	Bayou Tigre Hwy 404 T11S-RSE
CRH	Cane River, Hwy 1, 1 mile N. Gal	BRH2	Blind River Hwy 61 T11S-RSE
CLC	Chatlin Lake Canal, Hwy 457 T2N	HRH	Houston River Hwy 27, 2 MI N.O
CDG	Coulee Des Grues, hwy 115-SW	BDC	Bayou De Cannes, Hwy 98 2 MI, W
BCH	Big Creek Hwy 80 at Holly Ridge	BPH2	Bayou Plaquemine Hwy 98 4 MI
LTC	Little Turkey Creek, Hwy 128 T1	EBL	East Bayou Lacassine 1/2 Mile W
LBT	Lake Bruin T12N R12E S29	MRH	Mermentau River Hwy 90 at Merme
TRH2	Tensas River Hwy 15 at Clayon	BLH	Bayou Lacassine Hwy 14 T11S R5
CBS	Cross Bayou-S of Hwy 84 T7N R8E	BSM	Bayou Serpent at Manuel Road
BTI	Bayou Teche I-10 Breaux Brid	BPH2	Bayou Pierre Hwy 530 2 MI. E. Foley AL 36,535
BPI	Bayou Portage I-10 at Henderson	BGT	Bayou Grosse Tete at Frisco Hwy
BDP	Bayou Du Portage Hwy 679 T10S R	VRH	Vermillon River Hwy 14 at Abbev
LCH	Lasalle Coulee Hwy 182 at Cade	BTG	Bayou Terrebonne at Gray T16S-Port Barre
BTH	Bayou Tech Hwy 87 Olivier	BBH	Black Bayou Hwy 530 2 MI. E. Foley AL 36,535
BGT2	Bayou Grosse Tete at I-10 at GR	BLR	Bayou Lafourche at Raceland T1 Port Barre
BRH	Boeuf Rv Hwy2 T2 IN R8E S25 Eunice	TRH	Tensas River Hwy 80 at Tendal, Eunice, LA
BMH	Bayou Macon Hwy134 Pov POI Eunice	BQD	Bayou Queue De Turtue Hwy 13 T Metairie
GBH	Grand Bayou Hwy 70 T12S-R13E Washgton		

rinsed sodium sulfate. The bottom layer of methylene chloride was drained from the separatory funnel through the prepared funnel into a 400 ml beaker. The sample was extracted with methylene chloride two more times with the bottom layer drained into same 400 ml beaker. The collected extract was placed in a water bath at 35˚C, and was evaporated to about 1 ml volume. Hexane (2 - 3 ml) was added into the evaporated sample, and returned to the water bath for further evaporation until about 1 ml volume remained. Sample extract was transferred from 400 ml beaker into a graduated centrifuge tube through a glass wool plugged funnel containing petroleum ether rinsed sodium sulfate using 12 ml of Hexane to completely rinse beaker into tube. The hexane was evaporated off by nitrogen in a water bath that was set to 35˚C. Sample tubes were left in the water bath until the sample volume was concentrated to slightly below 1 ml. Hexane was added to make the final sample volume to the 1 ml mark. Surface water samples, positive and negative controls, solvent and matrix standards were prepared in vials for GC-MS (gas chromatography-mass spectrometry) analysis.

2.3. Sample Preparation, Pesticide Residue Extraction and Cleanup of Food Samples

Each food sample was retrieved from the freezer and kept overnight in the cooler (4˚C) to allow for thawing. Having mixed the grain samples very well to ensure homogeneity, 100 g was measured of wheat and rice separately and each blended into powder using a Magic Bullet (MB1001, Magic Bullet, China). Representative samples were selected from samples with high moisture content like tomato, blueberry, corn, cucumber, cabbage, and honeydew and chopped with a knife into small bits that could fit into the cup of the blender. Each sample was blended into puree using a Robot Coupe (RS12V, Robot Coupe USA Inc, Ridgeland, Mississippi). Each prepared sample was labeled separately, poured into glass quart jars, and stored at −20˚C until ready for extraction.

The extraction technique used was a modified QuEChERS method [5]. Both the extraction and cleanup stages were modified. In the extraction process, 12 g magnesium sulphate ($MgSO_4$) was added and no sodium chloride included. During the dSPE cleanup, upper layer (acetonitrile extract) was carefully added to a 15 ml centrifuge vial containing dSPE 150 mg $MgSO_4$, 50 mg PSA, 50 mg C18 and 50 mg GCB.

Ten grams of each food sample was measured into 50 ml plastic centrifuge tube. A reagent blank sample, which was the negative control, was prepared by pipetting 10 ml of milliQ water into a 50 ml centrifuge tube. Immediately after weighing, spike samples, which were the positive controls, were sorted out, labeled separately and spikes (a low, medium and high spike) added to each of them accordingly. All spiked samples were mixed with a vortexer and allowed to sit for 30 minutes. For grain samples, 10 ml of milliQ water was added, vortexed and allowed to sit another 30 minutes. With an auto dispenser, 10 ml of solvent (acetonitrile) was added to each of the samples. Samples were hand shaken, and once again vortexed. One pack of an extraction salt of QuEChERS containing 1200 mg magnesium sulphate ($MgSO_4$), 400 mg primary and secondary amine (PSA), 400 mg carbon 18 (C18) and 400 mg graphitized carbon black (GCB) was added to each sample. Salted samples were hand-shaken, after which they were centri-

fuged for 10 minutes at 3500 rpm for 15 minutes. Coming out of the centrifuge, separate layers were formed distinctly, and using a Pasteur pipette, the upper layer (acetonitrile extract) was carefully separated into a 15 ml centrifuge tube containing dSPE 150 mg $MgSO_4$, 50 mg PSA, 50 mg C18 and 50 mg GCB. These were each vortexed and centrifuged for 1 minute at 3500 rpm. With Pasteur pipette, supernatant was taken and syringe-filtered using 0.2 µm filter into clean sample vials before analyzed in GC-MS.

2.4. Analysis

Gas chromatography-mass spectrometry was used to analyze the pesticides. The GC component was an Agilent 6890 (HP6890 C1530A, Agilent, USA) while the MS was Agilent 5975C quadrupole (63170A, Agilent, USA). An autosampler 6890 series was used to inject sample extracts and standards into the GC-MS. The column was a Restek 35 GC-MS column of 30 m length, 0.25 mm internal diameter and 0.25 µm film thicknesses. For the instrument control and quantitative data analysis, the software used was Agilent ChemStation. The injection volume was 2 µl with pulsed splitless at 20 psi pressure pulse for 0.74 minutes. The injector temperature was 250˚C with transfer line temperature of 280˚C. Helium gas was the carrier mobile phase with a constant flow at 1.5 ml/min. The column temperature was programmed with an initial temperature set to 120˚C and held for 2 min after which it was elevated to 340˚C at 30˚C/min rate prior to the final hold of 2 minutes. The total run based on these settings was 12.33 minutes. The mode at which the MS was operated was electron impact ionization (EI) with MS ion source at 230˚C and the quadrupole at 150˚C. Electron multiplier was set at 200 V above the calibration standard using PFTBA (Perfluorotributylamine) auto-tuned setting. Selected ion monitoring (SIM) mode was used for screening and quantitative analysis of targeted pesticides. The initial identification of a pesticide in the sample was based on the detection of its characteristic ion peaks and their relative abundances as well as the comparison of its retention time with those observed in the analytical standard. The particular retention times and quantitation ions for the SIM mode analysis of the pesticides is as shown in Table 3. Full-scan (50 - 450 m/z) MS analyses were conducted to confirm the pesticide's detection by comparison to mass spectral libraries from both commercial sources and internally generated spectra. This comparison was automated using the NIST (National Institute of Standards and Technology) AMDIS (Automated Mass spectral Deconvolution and Identification System) software. Retention time confirmation against the analytical standard in full-scan MS mode was also required for confirmation. Pesticides with multiple peaks were summed for quantification.

Matrix matched (>95% matrix) standards were used to calculate all spike recoveries (positive controls) as well as any positive samples. The concentration needed for matrix matched standards was determined by the expected on column concentration of spikes. The efficiency of the methodology was determined by comparing the concentration recovered in the spikes including the amount of sample represented to the actual spiking rate. Efficiency at a minimum of 60% was considered acceptable in this study.

Table 3. Retention time and quantitation ion for target compounds and their degradation products.

Compound	t_R (min)	Q_{ion} (m/z)	Compound	t_R (min)	Q_{ion} (m/z)
Acephate	5.62	136	Fipronil	7.35	367
Acetochlor	6.87	223	Hexazinone	9.01	171
Alachlor	6.95	188	Malathion	7.20	173
Atrazine	6.50	200	MB45950fm	7.29	420
Azoxystrobin	11.51	344	MB46136fm	7.80	383
Bifenthrin	8.57	181	MB46513, Fip. met.	6.76	388
Bromacil	7.50	207	Metalaxyl	7.10	249
Captan	7.80	79	Methamido	4.45	141
Captan deg.	5.67	79	Methyl Parathion	7.16	263
Carbaryl	5.84	144	Metolachlor	7.22	162
Carbofuran	6.65	164	Metribuzin	7.18	198
Carbofuran deg.	4.08	164	Molinate (Ordram)	5.57	126
Chlorpyrifos	7.26	197	Norflurazon	8.76	303
Clomazone	6.53	125	Pendameth	7.50	252
Cyanazine	7.57	225	Permethrin I	9.53	163
Cyfluthrin 1	9.69	206	Permethrin 2	9.57	163
Cyfluthrin 3	9.76	206	Prometone	6.34	225
Cypermet 1	9.88	181	Propicon 1	8.56	259
Cypermet 2	9.95	181	Propicon 2	8.59	259
DesEthylAtrazine		6.24	172	Prometryn	7.05
DesIsopropylAtz	6.28	173	Propanil	7.10	161
Diazinon	6.40	137	Tebupirimiphos	6.42	261
Dimethenamid	6.91	154	Tefluthrin	6.17	177
Endosulfan I	8.18	237	Terbacil	6.93	161
Endosulfan II	8.79	195	Terbufos	6.40	231
Endosulfan SO_4	9.08	272	Thimet	6.17	75
Eptam	4.24	128	Trifluralin	5.60	306
Esfenvalera 1	10.36	167	λ-cyhalot 1	8.91	181
Esfenvalerate	10.45	167	λ-cyhalot	8.99	197
Etridiazole	5.04	183			

λ = lambda; DesIsopropylAtz = desisopropylatrazine; MB46136fm = MB46136, Fip. met.; MB45950 = MB45950, Fip. met. Pendameth = Pendamethalin; Propicon 2 = Propiconazole 2; Propicon 1 = Propiconazole 1; λ-cyhalot 1 = Lambda-cyhalothrin 1; λ-cyhalot = Lambda-cyhalothrin; Cypermethrin 1 = cypermet 1; cypermethrin 2 = cypermet 2. Esfenvalerate 1 = Esfenvalera 1; Methamido = methamidiphos.

2.5. Trends of Some Pesticide Residues in the Surface Water Samples

From the database of the pesticide lab of agricultural chemistry dept. of LSU, data for the recent past 4 years (2012-2015) from the results of analysis of pesticide residues in some surface waters was accessed. Water samples collected each year was done in

summer in the month of May. In order to show the trends of either an increase or reduction in the levels of pesticide residues detected from the same sources year-in year-out, selected water samples studied included BPH, CLC, BBH, BRH, BCH, TRH2, BPI and CDG.

3. Results and Discussion

3.1. Pesticides in Surface Waters

Different pesticides were found in the 35 water samples. The total number of pesticides that were detected across the 35 surface waters was 9. Since there is no threshold set for pesticide residues in surface water, the closest way to interpret the possible impact of the pesticide levels detected in this study was to compare them with the threshold set for potable waters by the EPA. However, the EPA has thresholds published for selected pesticides like atrazine, glyphosate and 2, 4-D. The limit is 3 ppb for atrazine, 70 ppb for 2, 4-D and 700 ppb for glyphosate. As outlined in **Table 4**, in comparison to these standards, 4 waters (6.48 ppb in CLC, 6.2 ppb in BRH, 6.24 ppb in BCH, and 11.88 ppb in CBS) were above the atrazine limit.

The lowest among the 4 samples that were over the threshold of Atrazine was from a sample collected from BRH and it was 107% higher than the EPA limit for potable waters (**Table 5**). The highest above threshold sample was collected from CBS at 296% above the EPA limit. Results obtained in this study were similar to previous reports of atrazine in surface water. In 2003, 37.5 ppb atrazine was detected in Iberville water district surface water in Upper Terrebonne Basin of Louisiana [14]. This was 1150% above EPA tolerance limit of 3 ppb and was far above the range value obtained in this study. Atrazine was found in ground water in the United Kingdom to have exceeded potable water limit (0.1 ppb) in more than 10% of the analyzed samples [16]. Exposure of amphibians [17], fish [18], reptiles and human cell [19] to atrazine could result in endocrine

Table 4. Surface waters with high Atrazine.

Pesticides	Sample source & PR detected (ppb)				Pesticides	Sample source & PR detected (ppb)			
	BCH	CBS	CLC	BRH		BCH	CBS	CLC	BRH
Atrazine	6.24	11.88	6.48	6.20	Clomazone	ND	ND	ND	2.4
AMPA	ND	ND	ND	ND	Metribuzin	0.36	ND	ND	0.34
Glyphosate	ND	ND	ND	ND	Trifluralin	ND	ND	ND	ND
Quinclorac	ND	ND	ND	4.3	Triclopyr	ND	ND	ND	ND
Desethatz	0.54	1.22	0.74	0.62	Dicamba	ND	ND	ND	ND
Metolachlor	3.9	3.96	1.08	17.2	Bromacil	ND	ND	ND	ND
Fluometuron	ND	ND	ND	1.4	2, 4-D	ND	ND	ND	ND
Diuron	ND	ND	ND	ND	Acifluorfen	ND	ND	ND	0.22
Acetochlor	0.28	ND	ND	ND					

PR = Pesticide residue; ND = Not detected. Desethatz = Desethylatrazine; BCH = Big Creek Hwy; CBS = Cross bayou-S of Hwy; CLC = Chatlin Lake Canal; BRH = Boeuf Ry Hwy.

disruption [21]. Amphibians are said to be more sensitive to atrazine even at a low concentration of 0.1 ppb [20]. Demasculinisation (feminization) [21] and hermaphroditism was reportedly observed to be associated with exposure of male frogs to water-borne atrazine contamination in parts of the US [22].

3.2. Pesticide in Food

Pesticide residues were found in tomato, melon and rice while no pesticide was found in corn, wheat, blueberry, cucumber, and cabbage (**Table 6**). Out of the 6 tomatoes

Table 5. Percentage of Atrazine above limit when surface water is compared with portable water EPA limit.

Sample	Atrazine detected in surface water (ppb)	Potable water EPA limit for atrazine (ppb)	% above limit
CLC	6.48	3.00	116
BRH	6.20	3.00	107
BCH	6.24	3.00	108
CBS	11.88	3.00	296

CLC = Chatlin Lake Canal; BRH = Boeuf Ry Hwy; BCH = Big Creek Hwy; CBS = Cross bayou-S of Hwy.

Table 6. Pesticides detected in food collected from different locations in Louisiana.

Food sample	Sample number	Pesticide detected	Amount (ppm)	Tolerance (ppm)
Tomato	1	None	-	-
Tomato	2	Sevin	0.110	5.000
Tomato	3	None	-	-
Tomato	4	Cypermethrin	0.180	0.200
Tomato	5	None	-	-
Tomato	6	Cyfluthrin	0.110	0.200
Corn	1	None	-	-
Corn	2	None	-	-
Corn	3	None	-	-
Blueberry	1	None	-	-
Blueberry	2	None	-	-
Cucumber	1	None	-	-
Melon	1	Azoxystrobin	0.057	0.300
Cabbage	1	None	-	-
Wheat	1	None	-	-
Wheat	2	None	-	-
Rice	1	Propiconazole	0.031	7.000
Rice	1	Azoxystrobin	0.027	5.000

*Sample number = serial number assigned to each sample.

analyzed, 3 of them, samples 2, 4 and 6 contained sevin (carbaryl), cypermethrin and cyfluthrin respectively. Concentration of the carbaryl was 0.110 ppm, while that of cypermethrin and cyfluthrin were 0.180 and 0.110 ppm respectively. The FDA tolerance threshold [23] in tomatoes was 5.000, 0.200 and 0.200 ppm for carbaryl, cypermethrin and cyfluthrin respectively. Azoxystrobin was found in melon at the level of 0.057 ppm. The FDA tolerance rate was 0.300 ppm in melon. The rice variety contained 0.031 ppm propiconazole and 0.027 ppm azoxystrobin. Tolerance rate in rice as provided by the FDA was 7 ppm for propiconazole and 5 ppm for azoxystrobin. The 3 pesticides detected in tomato namely carbaryl, cypermethrin [24] [25] and cyfluthrin [26] are insecticides used in its cultivation. Sevin is used to control cutworm, stinkbugs and thrips; Cypermethrin is used to control hornworm; and Cyfluthrin is used against thrips, leafminer and stinkbug [27]. Cypermethrin level of 0.180 ppm detected in tomato is very close to its 0.200 ppm ceiling level as set by the FDA. However, cypermethrin is acid-labile as it degrades with increasing level of acidity. Cypermethrin level in tomato decreases by 30% within 12 days at 5˚C in tomato paste pH of 4.3 [29]. The degradative product of cypermethrin is 3-Phenoxybenzaldehyde whose health effect is yet unknown but an *in-vitro* study carried out confirmed some endocrine activity associated with cypermethrin breakdown [29]. Azoxystrobin and propiconazole are fungicides. Azoxystrobin detected in melon and rice in this study is used in melon to control gummy stem blight [30], and in rice to control sheath blight [31]. Propiconazole serves the same purpose of controlling sheath blight in rice farming [32]. While pesticides found in the foods products were below tolerance limits as set by the FDA, those levels detected in surface waters were above the tolerance for atrazine in 4 samples. Since the amount of pesticide residue in water is a function of its usage [15] [28], in addition to our results, the ground water samples and produce from those 4 locations should be monitored for atrazine after which the respective authorities and the users of atrazine in the regions could be advised to take caution.

3.3. Trends of Some Pesticide Residues in Surface Water Samples

In 2012 through 2014 for samples collected in the month of May, no atrazine was detected in sample BPH (**Table 7**). There was a steady increase in atrazine level in the samples collected from CLC from 0.4 ppb in 2012, 2.26 ppb in 2013, 4.62 ppb in 2014 and 6.48 ppb in 2015. In the samples collected from BBH, atrazine content also was on the increase starting at 0.2 ppb in 2012, 0.66 ppb in 2013, ND (no detection) in 2014 and finally 1.78 in 2015. A fluctuation was observed in the atrazine levels in sample BCH as the level was 6.24 ppb in 2013, dropped to 1.38 ppb in 2014 and finally back to 6.24 ppb in 2015. No atrazine was found in 2012. Another fluctuation was in BPI atrazine level that was 1.16 ppb in 2012, dropped to 0.7 ppb in 2013, increased to 2.32 ppb in 2014 and dropped back to 0.72 ppb in 2015. Atrazine level in 2012 in BRH sample was at 2.36 ppb; while there was no detection in both 2013 and 2014, year 2015 experienced an increase to 6.2 ppb.

In sample TRH2, there was no detection in 2013 and 2014; but the 2012 atrazine level

Table 7. Pesticide residue (ppb) detected in surface waters 2012 through 2015 from different locations in Louisiana.

Source	PR	2012	2013	2014	2015	Source	PR	2012	2013	2014	2015
BPH	Metolachlor	ND	ND	1.72	0.16	BRH	Atrazine	2.36	ND	ND	6.2
CLC	Atrazine	0.4	2.26	4.62	6.48		Clom	3.96	2.48	1.96	2.4
	Dese	ND	ND	ND	0.74		Dese	5.7	ND	ND	0.62
	Bifethrin	ND	ND	ND	0.02		Metri	ND	1.96	0.2	0.34
CDG	Metolachlor	0.84	ND	ND	0.84		Meto	3.26	40	4.56	17.2
BBH	Atrazine	0.2	0.66	ND	1.78		Propa	ND	ND	ND	0.08
	Metolachlor	0.2	ND	ND	1.16		Metal	ND	ND	ND	0.08
LBT	Dese	ND	ND	ND	0.22		Dimet	ND	ND	0.2	0.16
BCH	Atrazine	ND	6.24	1.38	6.24	TRH2	Atrazine	1.28	ND	ND	0.38
BPI	Atrazine	1.16	0.7	2.32	0.72		Dese	ND	ND	ND	0.26
	Metalaxyl	ND	ND	ND	0.12		Azoxy	ND	ND	ND	0.06
	Azoxy	ND	ND	ND	0.06		BDC	None	ND	ND	ND

ND = not detected; PR = pesticide residue; Dimet = Dimethenamid; Clom = clomazone; Dese = desethylatrazine; metri = metribuzin; propa = propanil; metal = metalaxyl; dimet = dimethenamid; azoxy = azoxystrobin; BPH = Bayou Pierre Hwy; CLC = Chatlin Lake Canal; CDG = Coulee Des Grues; BBH = Black bayou Hwy; LBT = Lake Bruin T1; BCH = Big Creek Hwy; BPI = Bayou Portage I-10.

was 1.28 ppb and a decrease to 0.38 ppb in 2015 was observed. Metolachlor in sample BPH was not detected in 2012 and 2013, but its level which was 1.72 ppb in 2014 dropped to 0.16 ppb in 2015. In the sample CDG, there was no detection for metolachlor levels in 2013 and 2014; but incidentally the same level of 0.84 ppb recorded in 2012 reoccurred in 2015. Metolachlor level in 2012 sample of BBH was 0.2 ppb and increased in 2015 to 1.16 ppb; there was no detection in consecutive years 2013 and 2014. Metolachlor also fluctuated greatly in sample BRH as it was 3.26 ppb level in 2012, increased to 40 ppb in 2013, went down to 4.56 ppb in 2014 and rose to 17.2 in 2015. There were mild fluctuations observed in sample BRH as clomazone was 3.96 ppb in 2012 dropped to 2.48 ppb in 2013, further dropped to 1.96 ppb in 2014 but on the increase in 2015 up to 2.4 ppb. Changes in pesticide level in the environmental surface water is a function of their usage level as confirmed by this data, and similarly by the result of a study [15]by Wijnja *et al.* where they compared pesticide levels in Massachusetts suburban surface waters between 1999 and 2010 and concluded that changes in pesticide usage directly correlated with changes in the pesticides detected.

4. Conclusion

Despite the closeness of insecticide (cypermethrin) detected in tomato to the tolerance level, all the pesticides found in the food samples were below threshold value. Cypermethrin may remain harmless to consumers of tomato products considering its degrading potential at an acidic pH level. High atrazine level in the surface waters in certain

locations of Louisiana call for further study of both surface and ground waters in such locations. Inclusion of ground waters in those areas will be necessary in order to know how much infiltration of surface water contamination is going into ground waters. Weather anomalies resulting in wild winds, storms, heavy rain falls, erosion and flood may be the main reason why fluctuations are so rampant in the 3 pesticide residue levels observed in some water samples across a consecutive period of 4 years. A quantitation study for pesticides in food and water is important because the information will help the government and communities manage the environment better. This study in general serves as a reminder of the need to regularly monitor the pesticide residue in our foods and waters. On the part of the users, an immediate application of the results of this study may include scaling down on the use of pesticides like atrazine and cypermethrin considering their high level detected in the designated water and/or food in this study.

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