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Influence The USE of Pesticides in The Quality of Surface and Groundwater Located IN Irrigated Areas of Jaguaribe, Ceara, Brazil

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ABSTRACT: The irrigated area of Jaguaribe, Ceara, Brazil is considered important region of agribusiness of the country due to the installation of various fruit exporting companies. The present work has as main objective investigate twelve types of pesticides (molinate, atrazine, methyl parathion, malathion, chlorpyrifos, fenitrothion, pendimenthalin, triazophos, bentazone, azoxystrobin, propiconazole, difenoconazole) used in the region to assess the level of contamination of waters used for potable and irrigation. Analysis of pesticides were performed using chromatographic techniques (SPME-GC/MS and SPE-HPLC/DAD) through methodologies validated according to parameters recommended by ABNT. Among the 60 water samples, 48 were positive for at least one of the twelve active ingredients studied. Fungicides propiconazole and difenoconazole were detected more frequently. The total pesticide levels ranging from 0.11-17.30 µg/L were detected in the samples. The levels detected in surface and groundwater were lower than the limits established in Brazil, but 80% of the samples analyzed were above total pesticide levels established by the European Community (>0.5 µg/L). Prolonged exposure to pesticides can cause adverse effects to human health and the aquatic ecosystem

Keywords:Contamination, Pesticides, Surface water, Groundwater, Chromatography

INTRODUCTION

Brazilian agricultural modernization relies on the concept of maximum productivity, with intense exploitation of natural resources, generate new risks and environmental vulnerabilities.The pesticide consumption in Brazil has grown significantly in recent decades. Since 2008 the country is the largest consumer of pesticides in the world. In 2009, Brazilian companies traded a total of 1.06 million tons of agrochemicals. The soybean, corn, sugar cane, cotton and citrus consume 87% of total traded (Almeida *et al.*, 2009). The Irrigated Perimeter Jaguaribe-Apodi, Ceara, Brazil is a major area of horticulture and several companies exporting fruit are located in the area. The main crops produced in this region are bananas, pineapple, melon, rice, lemon, corn, papaya and sorghum. In recent years, expansion of agricultural production in the area has made people more vulnerable to exposure to pesticides (Milhome *et al.*, 2009). Pesticide drift has been significant environmental problem in rural areas, and it may result in damage to human health (Reimer and Prokopy, 2012). Increased incidence of cancer has been observed in the state of Ceara-Brazil during the 2000-2006 period and it may be associated with the intensive use of pesticides. High rates of leukemia, testicular and penis cancer were observed (Rigotto, 2010). Some studies have cited the problem of environmental contamination by pesticides residues and human health risk assessment. (Palma *et al.*, 2009; Leblank and Kuivila, 2008; Boer *et al.*, 2010; Vialle *et al.*, 2013; Toan *et al.*, 2013; Herrero-Hernández *et al.*, 2013). Varca (2012) showed that the water quality of Laguna de Bay, Philippines is threatened by agricultural activities. Malathion and profenefos were detected and exceeded the *World Health Organization -WHO* recommended level (0.1 µg/L for a single pesticide drinking water). Recently, Herrero-Hernández et al.(2013) detected forty compounds among fifty eight pesticides analyzed in water samples of the Spanish wine region. The herbicides terbuthylazine, its metabolite desethyl terbuthylazine, fluometuron and ethofumesate and the fungicides pyrimethanil and tebuconazole were the compounds most frequently detected in water samples (>60%). Monitoring

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program reported by Hermosin et al. (2013) studied the concentrations of 6 herbicides and two of its metabolites in surface water and evaluated the impact of olive crops in the basin of the Guadalquivir River, Spain. The average concentrations in surface water were found mostly above the WHO recommended limit (0.1 µg/L), but showed a decrease with time.

In Brazil, Armas et al. (2007) monitored the 12 herbicides and glyphosate in river basin Corumbataí, São Paulo. Ametrine, atrazine and simazine were present at higher levels, ranging from 0.7-2.9 µg/L, 0.6-2.7 µg/L, and 0.3-0.6 µg/L, respectively. Eight pesticides were found by Carbo et al. (2008) in samples of groundwater, located in Mato Grosso, Brazil. Endosulfan sulfate, atrazine and metolachlor showed high frequency of detection in water samples (surface, groundwater, rainfall and runoff) and sediment in studies by Casara et al. (2012).

In this context, the main relevance of the research is the identification and evaluation of environmental contamination, through the determination of twelve pesticide residues in surface water and groundwater situated in irrigated areas of Jaguaribe, Brazil used for supply. Moreover, the results obtained in this paper can be useful in developing strategies to minimize the impact of pesticides to humans and the environment.

MATERIALS & METHODS

The Irrigated Perimeter Jaguaribe-Apodi is located in the State of Ceara, between the cities of North Limoeiro and Quixere, as illustrated in Figure 1. The region has about 5,393.00 ha of irrigable area. The average temperature is around 28.5 ºC (minimum 22 °C and maximum 35 °C), with low annual variation and rainfall distribution very irregular during the year (average 772 mm). One of the main sources of water supply in the region is the "Pedrinhas" dam built in the derivation Jaguaribe River (Quixere River). The main pumping station of North Limoeiro city captures water from the dam and leads through the irrigation canal to reservoirs located in the Perimeter. The Canal has about 14.6 km long, 1.5 m diameter and 2.5 m deep and approximately 15 water reservoirs used for human supply and irrigation. The monitoring was conducted at 15 sampling points, 7 surface and 8 groundwater, located near the Irrigation Jaguaribe Apodi (according to Figure 1), during four quarters. Samples of surface water were collected with van Dorn bottle when needed. Groundwater samples were collected directly from the wells after pumping water for about 5 minutes. A 1 L of sample volume was collected and stored in amber bottles, and kept under refrigeration (4° C). The sampling and cleaning of the bottles and glassware was carried out as described by Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

Certified standards for pesticides studied (molinate, atrazine, parathion methyl, malathion, chlorpyrifos, fenitrothion, pendimentalina, triazophos, bentazone, azoxystrobin, propiconazole, difenoconazole) were purchased from Sigma-Aldrich (Brazil) and Dr. Ehrenstorfer (Brazil). Characteristics main and applications of the analyzed pesticides are showed in the table 1. All the standards had purities exceeding 97.0 %.Chromatographic grade methanol, acetonitrile, ethyl acetate, hexane, acetone, dichloromethane, were acquired from Merck (Brazil) and J. T. Baker (U.S).

Methods using *Gas chromatograph coupled to single quadrupole mass spectrometers* (GC-SQ/MS) and *Liquid Chromatography with a diode array detector* (HPLC-DAD) were used for analysis of 12 pesticides residues in water samples. The methodologies were validated according to ABNT NBR 14029 (2005).

The pesticides molinate, atrazine, parathion methyl, malathion, chlorpyrifos, fenitrothion, pendimethalin, triazophos were preconcentrate by solid-phase microextraction (SPME), using Fiber of polydimethylsiloxane (PDMS; 100 µm thickness). The conditioned fiber (1 h, at 250-300 °C) was immersed into 20 mL of the aqueous solution and maintained at the equilibrium time (15min) under stirring (150 rpm) at ambient temperature (28 ± 2 °C). After analyte extraction, the fiber was thermally desorbed during 15 min into the glass liner of the GC-SQ/MS (DSQII model, Thermo, USA) system injection port. Pesticides separations were accomplished on RTX-5ms column (30 m x 0.25 mm I.D. x 0.25 µm thickness). The temperature program was the following: initial temperature 100 ºC held for 1 min, and 10 $ºC.min^{-1}$ rate to 150 ºC, then 5 $ºC.min^{-1}$ rate to 230 ºC, and 30 $ºC.min^{-1}$ rate to 280 ºC. The injection temperature was 250 ºC, and 1 µL were injected in splitless mode. Helium was used as the carrier gas at a flow rate of 1 $ml.min^{-1}$. The mass spectrometer was operated in electron impact (EI) mode, ion source temperature 200ºC, MS Transfer Line 270 ºC, electron multiplier voltage 1295 V, scanning from m/z 50 to 600 at 2.0 s per scan; solvent delay 6.0 min. Quantitative analysis was performed using the Single Ion Monitoring (SIM), using three fragments (m/z_{Quan}, $m/z_{Qual1,}$ m/z_{Qual2}) and confirmed by the relative abundance.

The determination of the pesticides bentazone, azoxystrobin, propiconazole, difenoconazole was

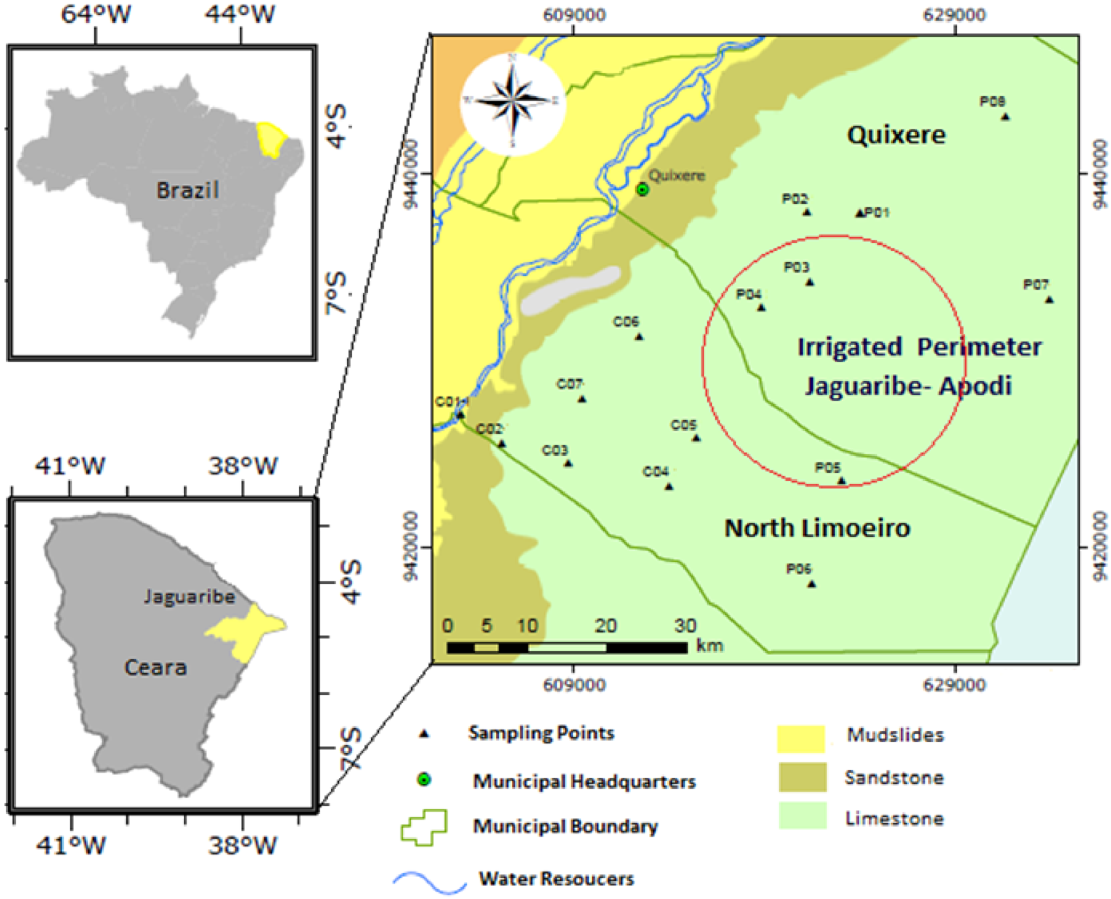

Fig.1. Location of sampling points for surface water (S1-S7) and groundwater (G1-G8) in the irrigated Jaguaribe-Apodi, Ceara, Brazil

Table 1. Characteristics main and applications of the analyzed pesticides

Active principle	Chemical group	Class	Toxicology classification	Environmental classification	Commodity
Atrazine	Triazine	H	III	III	pineapple, maize and sorghum.
Azoxystrobin	Strobilurin	F	III	II	cotton, banana, beans, watermelon, cantaloupe, maize, chili
Bentazone	Benzothiazinone	H	III	III	beans, maize
Chlorpyrifos	Organophosphate	I/F/ A	II	II	cotton, beans, corn, sorghum, banana
Difenoconazole	Triazole	F	I	II	banana, beans, papaya, watermelon, melon, pepper
Fenitrothion	Organophosphate	I	II	II	cotton
Malathion	Organophosphate	I/A	III	II	Cotton, beans, maize and sorghum
Molinate	Thiocarbamate	H	II	-	rice
Parathion methyl)	Organophosphate	I/ A	I	II	cotton, rice, beans, maize
Pendimethalin	Dinitroaniline	H	III	II	cotton, rice, beans, maize
Propiconazole	Triazole	F	II	II	Cotton, rice beans, banana, maiz
Triazophos	Organophosphate	I/ A /N	II	II	cotton, beans, maize

Fonte: MAPA (2013)

achieved by solid-phase extraction (SPE) using a Manifold System (Supelco, Brazil). C18 cartridges (500 mg/6 mL) were used. The SPE cartridges were conditioned with 10 mL methanol:water (80:20 v/v) and 10 mL methanol:water (30% v/v). Sample solutions (250 mL) were percolated through the cartridges at a flow rate of 2 mL/min. The analytes were eluted with 1 mL of methanol (concentration factor=250x) and the solution was injected in the HPLC-DAD (Shimadzu). The pesticide separation was performed on a Supelco C_{18} column (15 cm x 4.6 mm D.I. x 5 mm particle size) in the following chromatographic conditions: gradient system with mobile phase methanol - phosphoric acid (0.1% v/v): initially methanol- phosphoric acid at 50:50 v/v (flow 0.8 $mL.min^{-1}$), adding to 80:20 v/v, in 5 min (flow 1.0 $mL.min^{-1}$) and then dropping to 90:10 v/v in 14 min (flow 1.0 $mL.min^{-1}$) and then to 50:50 v/v in 20 min, at flow 0.8 $mL.min^{-1}$, detection at 220 nm and injection volume 20 µL.The quantification was performed by external calibration, with correlation coefficients greater than 0.99. Accuracy and precision of the method were obtained with recovery experiments, through samples spiked and determination of relative standard deviation (RSD, %).

RESULTS & DISCUSSION

The result of analysis of 60 water samples (surface and ground water) in the Irrigated Perimeter Jaguaribe-Apodi, CE, Brazil, showed the presence of atrazine, parathion methyl, triazophos, chlorpyrifos, difenoconazole, propiconazole, azoxystrobin, which it was belong to various chemical groups and different applications.

Surface water samples had at least one type of active principle in all samples analyzed. The total levels of pesticides detected in surface waters ranged from 1.1-17.3 µg/L, with higher concentrations in November, coinciding with the period of application (October-November) of pesticides in banana crop. About 62% of the groundwater samples showed the presence of pesticides at total levels ranging from nd-8.9 µg/L.

Table 2 shows the range of concentrations detected for each pesticide and frequency detection (%). Propiconazole was most frequently (82%) detected in surface water during the study period. Difenoconazole (43%), chlorpyrifos (54%) and atrazine (36%) also had high frequency of detection. Propiconazole and difenoconazole fungicides are usually used in the region Jaguaribe-Apodi to combat disease caused by *Mycosphaerella musicola Leach* in banana crop (Rigotto, 2010). Chlorpyrifos has been used mainly as an insecticide in Irrigated Agriculture Jaguaribe-CE (Milhome et al, 2009) Atrazine has been applied to controlling weeds in crops of maize, pineapple and sorghum. It is a herbicide which persistent moderately in the environment, and degrades in water within three months.

Table 2. Range of concentration (µg/L) and detection frequency (%) of the pesticides in surface and ground water samples. *n.d- not detected*

	Surface water		Groundwater	
Pesticide	Concentration (µg/L)	Nº of samples detected/ Detection Frequency (%)	Concentration (µg/L)	Nº of samples detected/ Detection Frequency (%)
Atrazine	n.d-0.96	10/36	n.d-1.45	8/25
Azoxystrobin	n.d-1.36	4/14	n.d-1.17	1/3
Bentazone	n.d	0/0	n.d	0/0
Chlorpyrifos	n.d-0.63	15/54	n.d	0/0
Difenoconazole	n.d-6.93	12/43	n.d-3.34	9/28
Fenitrothion	n.d	0/0	n.d	0/0
Malathion	n.d	0/0	n.d	0/0
Molinate	n.d	0/0	n.d	0/0
Parathion methyl	n.d-0.39	2/7	n.d	0/0
Pendimethalin	n.d	0/0	n.d	0/0
Propiconazole	n.d-10.14	23/82	n.d-6.19	9/28
Triazophos	n.d-6.91	4/14	n.d-7.74	2/6

Discrete contaminations of pesticides azoxystrobin, parathion methyl and triazophos were verified in surface water and there was no evidence of contamination by fenitrothion, molinate, malathion, pendimethalin and bentazone.

Regarding the analysis of groundwaters, pesticides difenoconazole (28%), propiconazole (28%) and atrazine (25%) were the most frequently detected. Triazophos (6%) and azoxystrobin (3%) showed a lower frequency of detection in these samples. The pesticides chlorpyrifos, fenitrothion, molinate, malathion, pendimethalin, parathion methyl and bentazone were not detected in this samples analyzed.

The wells studied are predominantly found in soils characterized by the presence of calcite and dolomite. In general, clay soils have low permeability, however, the natural flow of water promotes the formation of grooves or openings which facilitate water penetration, and may carry the contaminants to groundwater aquifers.Fig. 2 shows the Chromatogram illustrating a standard of pesticides (0.1 µg/L) after extraction by SPME and a sample of surface water contaminated with atrazine residue.

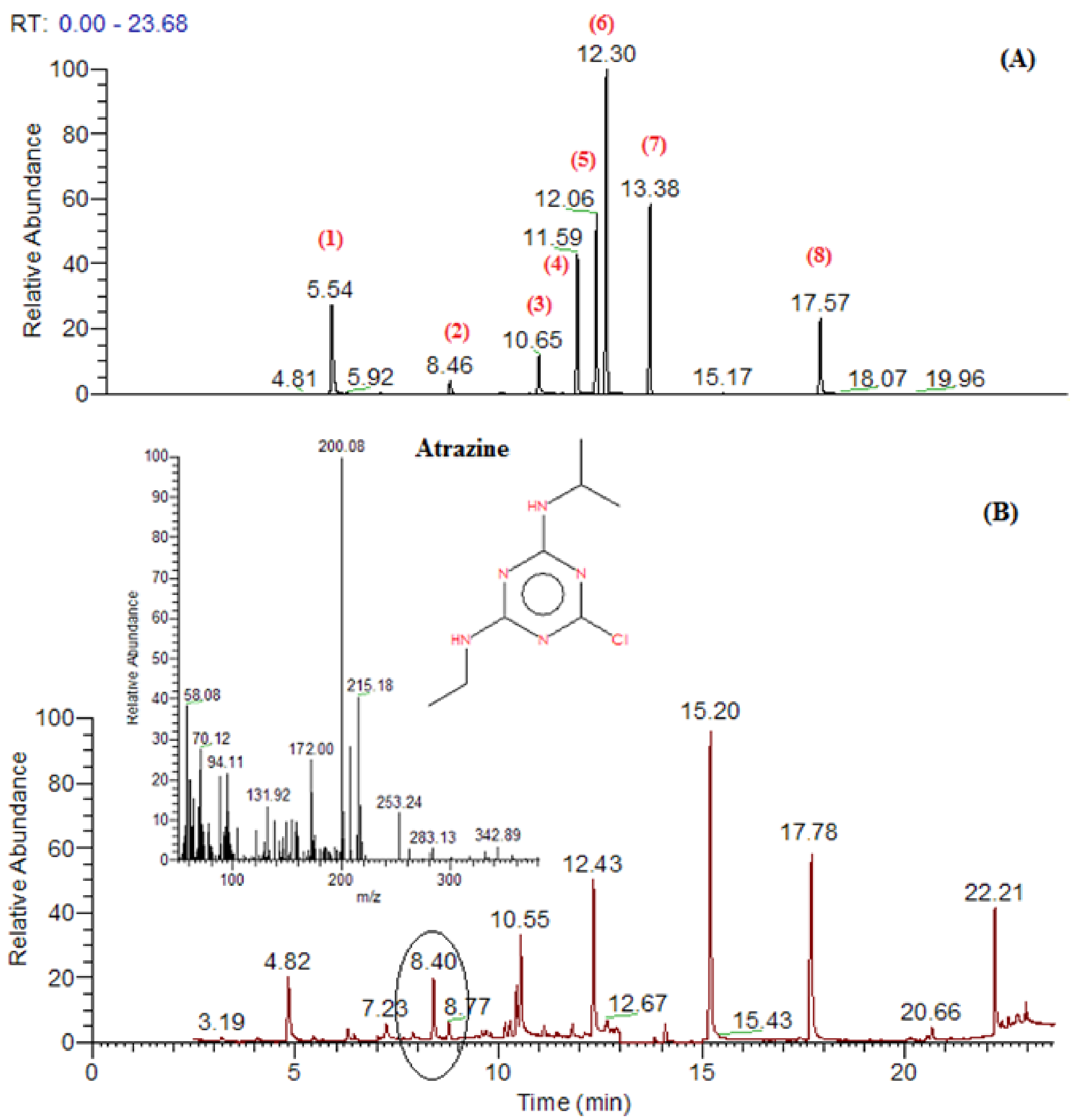

Fig. 2. Total Ion Chromatogram (TIC) obtained by GC-MS/SQ: (A) Standard of pesticides 0.1 µg.L^{-1} extracted by SPME *(1) Molinate, (2) Atrazine (3) Parathion methyl (4) Fenitrothion (5) Malathion (6) Chlorpyrifos (7) Pendimethalin (8) Triazophos;* (B) Sample of surface water containing atrazine residue

Pesticide residues have been detected in water resources in several research (Vryzas *et al.*, 2009). Atrazine is a pesticide widely applied worldwide and it has been frequently detected in aquatic environments (Vryzas *et al.*, 2009). Casara et al. (2012) found atrazine at maximum level of 28.3 µg/L in surface waters of the St. Lawrence River Headwaters, Mato Grosso, Brazil.

The pesticides applied to agricultural land can lead to contamination of surface water by means of fast transport processes as influenced by topography, soil properties, vegetation type, among others (Tang *et al.*, 2012).

Chlorpyrifos has been detected by Leblanc and Kuivila (2008) in surface water or associated with sediment. According Milhome et al.(2009) chlorpyrifos has low leachability, but it has high potential for contamination of surface waters through the transport associated with sediment or dissolved in water.

The quality of the waters is controlled by national and international standards. The European Community (EC, 1998) establishes limit of 0.1 µg/L of single pesticide and 0.5 µg/L for total pesticides detected. Table 3 shows the maximum residue limits-MRLs (µg/L) in water in according to laws established in Brazil and international agencies (Brazil, Canadá, EPA, WHO).

According to the results, about 80% of the samples (surface and groundwaters) were above pesticide levels established by the WHO, characterized as being unfit for human consumption (total level >0.5 µg/L). However, the individual levels of pesticides detected are below the limits established in Brazil and according to the standards required for surface water and groundwater (Table 3). Although the results show low levels of contamination, it is a great finding about the risks caused by prolonged exposure to these residues.

Table 4 shows values of acceptable daily intake (ADI), acceptable daily intake and mutagenicity and carcinogenicity of pesticides detected. According to data obtained, it appears that detectable levels in surface water (0.06 to 10.1 µg/L) and groundwater (0.09 to 7.74 µg/L) in the Irrigation Jaguaribe-Apodi showed below the maximum limits established for daily consumption acceptable. The pesticide chlorpyrifos showed contamination levels (average 0.3 µg/L) about 1,000 times lower than acceptable daily consumption in water. But this should not be regarded as a justification to allow the degradation of water quality for human consumption until these limits.

Organophosphates such as chlorpyrifos, parathion methyl and triazophos cause neurobehavioral disorders, including anxiety and depression which may even lead to suicide cases in individuals exposed to or poisoned by pesticides of this group. Parathion-methyl is considered highly toxic (ADI = 0.003 mg/kg), and it is possible carcinogen and acetylcholinesterase inhibitor (PPDB, 2013). Difenoconazole is a triazole, classified by EPA as Class I (highly toxic) and possible human carcinogen. Atrazine is considered moderately toxic to humans and other animals. Symptoms of poisoning triazines include abdominal pain, diarrhea, vomiting, eye irritation, irritation of mucous membranes and skin

Table 3. Maximum Residue Limits (MRLs) of pesticides in water (µg.L^{-1}), to the laws established in Brazil, Canada, EPA and WHO

Pesticide	Brazil MS 2914/2011	Brazil CONAMA 357/2005	Brazil CONAMA 396/2008	Canada	EPA	WHO
Azoxystrobin	-	-	-	-	-	-
Bentazone	-	-	300	-	-	-
Difenoconazole	-	-	-	-	-	-
Atrazine	2	2	2	5	3	2
Chlorpyrifos	30	-	30	90	-	-
Fenitrothion	-	-	-	-	-	-
Malathion	-	100	190	190	-	-
Molinate	6	-	6	-	-	6
Parathion methyl	9	-	-	-	-	-
Pendimethalin	20	-	20	-	-	20
Propiconazole	-	-	-	-	-	-
Triazophos	-	-	-	-	-	-

Table 4. Values of acceptable daily intake (ADI), acceptable daily intake and mutagenicity and carcinogenicity of pesticides detected

Pesticide	Acceptable daily intake-ADI (mg. kg^{-1})	Acceptable daily consumption in water* (µg. L^{-1})	Mutagenic	Carcinogenic
Atrazine	0.020	700.0	Not	Possible
Azoxystrobin	0.200	7,000.0	-	Not
Chlorpyrifos	0.010	350.0	Not	Not
Difenoconazole	0.010	350.0	-	Possible
Parathion methyl	0.003	105.0	Not	Possible
Propiconazole	0.040	1,400.0	-	Possible
Triazophos	0.001	35.0	-	Not

Fonte: PPDB (2013).*Considering: body weight (bw) =70 kg and daily water consumption =2L

reactions. Already pesticides as azoxystrobin, have lower acute toxicity (PPDB, 2013).

Beyond of the human contamination, regular use of pesticides in agriculture can cause their dispersal into the environment affecting other organisms in the ecosystem (Cid *et al.,* 2007). Several effects of pesticides in the aquatic environment have been reported in recent years (Sauco *et al.,* 2010).

Vryzas et al. (2009) show that triazine herbicides have toxic effects on aquatic plant communities. Atrazine shows acute toxicity to algae and macrophytes in concentrations of 3.0 µg/L. Aquatic invertebrates and fish are less sensitive to exposure by the compound. Ventura et al. (2008) found mutagenic effects in aquatic organisms exposed to atrazine. Most pesticides of the group of triazoles are considered of low toxicity to birds and bees, however difenoconazole has high toxicity to fish. Belden et al. (2010) showed that exposure of some fungicides such as propiconazole cause acute toxicity to amphibians. Low concentrations of group of organophosphate pesticides are able to affect aquatic invertebrates. Chlorpyrifos and parathion methyl exhibit toxicity level for zooplankton 0.05 and 0.002 µg/L, respectively, however with regard to phytoplankton show lower toxicity.

Therefore, it is important to assess that besides the occupational exposure of farmers and their families, through the consumption of water, fruits and vegetables with pesticide residues, it is possible that contamination is occurring aquatic ecosystem through contamination present in water, which represents an additional risk for local populations.

CONCLUSION

The present research indicates that pesticides used in agricultural activities in Jaguaribe region can be transported to the water consumed by the population. Most of the surface and ground waters at the Irrigated Perimeter Jaguaribe-Apodi are contaminated with pesticides propiconazole, difenoconazole, azoxystrobin, chlorpyrifos, parathion methyl, atrazine and triazophos Total pesticide levels of 80% of the surface and groundwater samples analyzed were above total pesticide levels established by the European Community (total level >0.5 µg/L), characterized as unfit for human consumption. But detected pesticides individual (0.09-10.14 µg/L) were fairly below as regulatory levels (Atrazine: 2 µg/L; Chlorpyrifos: 30 µg/L) established by Brazil. However chronic exposure to low levels of organophosphate pesticides are able to affect human health, aquatic invertebrates, etc. Therefore intensive use of pesticides causes acute and chronic effects to humans and the environment.

As the presence of pesticide residues in surface and groundwater is confirmed, it is necessary to control and continuous monitoring of the levels of these residues in waters used for human consumption in the region.

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