Pesticide Levels in Ground and Surface Waters of Primavera do Leste Region, Mato Grosso, Brazil

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Abstract

Residues of the herbicides simazine, metribuzin, metolachlor, trifluralin, atrazine, and two metabolites of atrazine, deisopropylatrazine (DIA) and deethylatrazine (DEA), are surveyed in the surface and groundwater of the Primavera do Leste region, Mato Grosso, Brazil during September and December 1998 and April 1999. Different water source sampling stations of groundwater (irrigation water well, drinking water well, and water hole) and surface water (dam and river) are set up based on agricultural land use. A solid-phase extraction procedure followed by gas chromatography–nitrogen-phosphorus detection is used for the determination of these compounds. All compounds are detected at least once in water samples. A temporal trend of pesticide contamination is observed, with the highest contamination frequency occurring in December during the main application season. Metribuzin shows the highest individual detection frequencies throughout the monitoring period, followed by metolachlor, simazine, and DEA. The maximum mean concentrations of pesticides in this study are in the range from 0.14 to 1.7 µg/L. We deduct that the contamination of water resources is predominantly caused by non-point pollution of pesticides used in intensive cash-crop cultures of the Cerrado area. Therefore, a continuous monitoring of pesticide concentrations in water resources of this tropical region is necessary to detect the longer term contamination trends and developing health risks.

Introduction

Pesticide use in modern agriculture is necessary to reduce the pressure of weeds and insects in monoculture cropping systems. Because of their widespread use, pesticides and their metabolites are detected in various environmental compartments, such as soil, water, and air in temperate regions. As result of their agricultural application and substance-specific physical and chemical properties, several pesticides (e.g., atrazine and metolachlor) have been shown to be common pollutants of soil and water resources (1,2).

However, from tropical regions only a few published studies exist on pesticide occurrence in water samples, and many of them are focused mainly on organochlorine pesticides, which have been banned from use in most countries (3,4). Yet, several recent monitoring studies on currently used pesticides show the relevance of these contaminants to the aquatic environment in tropical and subtropical regions (5–10). The Primavera do Leste region (Mato Grosso state, Central-Western Brazil) is characterized by intensive farming with monoculture plantations, whose production has expanded greatly since their start 30 years ago. After their application, pesticide residues may persist in the crops, soil, and natural water, and thus pose an environmental risk because of their toxicity.

Lanchote et al. (11) analyzed atrazine, simazine, and ametryn, herbicides largely used in sugar cane, in potable water in São Paulo State. From 250 samples, ametryn was detected in 17, however at concentrations above the European Union (EU) limit in only two of them (0.17 and 0.23 µg/L).

Filizola et al. (12) analyzed trifluralin, endosulfan, lambda-cyhalothrin, dicofol, captan, parathion-methyl, chlorotalonil, and chlorpyrifos in surface and groundwater in Guairá region, in São Paulo State. Chlorotalonil, endosulfan sulfate, captan, and lambda-cyhalothrin were detected in surface water, all in concentrations above the EU limit. With the exception of endosulfan sulfate, these pesticides are unlikely to contaminate groundwater due to either high sorption to soil particles or low persistence. In Mato Grosso State, 29 pesticides and 3 metabolites were determined in surface water of the northeastern Pantanal region (13). Triazines (atrazine, simazine, and ametryn), acetanilides (alachlor and metolachlor), trifluralin, and endosulfan were detected in high frequency.

Glyfosate and its main metabolite were studied in water from a rice-growing area in Brazil (14). However, no information on pesticide residue levels in groundwater in the Cerrado area of Mato Grosso state has yet been published.

Therefore, the objective of our work was to evaluate the contamination of ground and surface water resources with five herbicides (atrazine, simazine, metolachor, metribuzin, and trifluralin) and two metabolites of atrazine (deisopropylatrazine [DIA] and deethylatrazine [DEA]) in Primavera do Leste region, Central-Western Brazil.

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Material and Methods

Study area

The study area was located in Primavera do Leste (Mato Grosso State) in Central-Western Brazil (Figure 1). The agricultural use is dominated by intensive farming with soybean, cotton, rice, and maize as the main cash crops.

The pesticides selected for this study were the most frequently used in this agricultural area and those which present high potential for surface or groundwater contamination, as reported previously by Dores and De-Lamonica-Freire (15). In addition, pesticides needed to be applicable to an analysis via gas chromatography (GC) with nitrogen-phosphorus specific detector (NPD).

Sampling and sample preparation

In total, 108 water samples were collected from different water sources in the Primavera do Leste region (Central-Western Brazil between 15 32'S to 15 34'S and 54 17'W to 54 19'W). The water samples were collected at three different periods: end of dry season (September 1998), middle of rainy season (December 1998) corresponding to the main application period for herbicides, and end of rainy season (April 1998). In each period, between 33 and 39 water samples were collected from different water sources.

The sampling sites were drinking water wells (n = 23) (sites 1 to 23 in Figure 1), water holes (open wells) (n = 6) (sites 24 to 29), irrigation wells (n = 4) (sites 36 to 39), dam (n = 3) (sites 30 to 32), and "Cabeceira dos Bois" stream (n = 3) (sites 33 to 35). The irrigation and drinking water well depth ranged from ten to thirty-nine meters, while the open wells were up to 15 meters deep. Except for the irrigation wells, all the other sampling points correspond to water used for human consumption localized either in the urban area or in its surroundings. The sampling site in the "Cabeceira dos Bois" stream corresponded to a site where the city Council was planning to abstract water for distribution to the urban region of Primavera do Leste.

Before groundwater samples were collected, each well was mechanically pumped until clear water and constant field measured values of pH, temperature, electrical conductivity, and dissolved-oxygen concentration were obtained. Electrical conductivity, pH, turbidity, and dissolved oxygen were measured using portable meters (Water Checker U-10 HORIBA Instruments Ltd, UK). For superficial waters, water was collected at a depth of 30 cm. Duplicate water samples were collected from each sampling location for pesticide measurement. The containers were carefully filled to the brim, without passing air through sample or trapping air bubbles in sealed containers.

The ground and surface water samples were collected in 1000-mL amber glass bottles pre-rinsed with acetone and methanol. After filling, the bottles were sealed with Teflon-lined screw caps and transported on the same day to the laboratory in refrigerated conditions. After transportation to the laboratory, samples were stored at 4°C, and extraction was normally done within 48 h. Before the solid-phase extraction (SPE) procedure, water samples were filtered using a 0.45 µm cellulose nitrate membrane filter, pH was adjusted to 6.5–7.5 with 1 mol/L HCl p.a. and NaCl p.a. was added to increase the ionic strength (17.5%, w/v).

Analytical methodology

A Bakerbond C_{18} cartridge (1 000 mg) (J.T. Baker, Grossgerau, Germany) was placed on top of a vacuum chamber (system spe-12G, J.T. Baker), and conditioned with 10 mL of methanol followed by 10 mL of water before applying the sample. An aliquot of 500 mL water was transferred to the cartridge at a flow-rate of ca. 5 mL/min. Vacuum was maintained for 30 min after water extraction to dry the SPE cartridges. The herbicides were eluted with 2 × 10 mL of ethyl acetate at a flow-rate of ca. 1 mL/min. The combined fractions of ethyl acetate were concentrated in a rotary evaporator and the residue was redissolved in 1 mL of ethyl acetate for GC–NPD analysis (16).

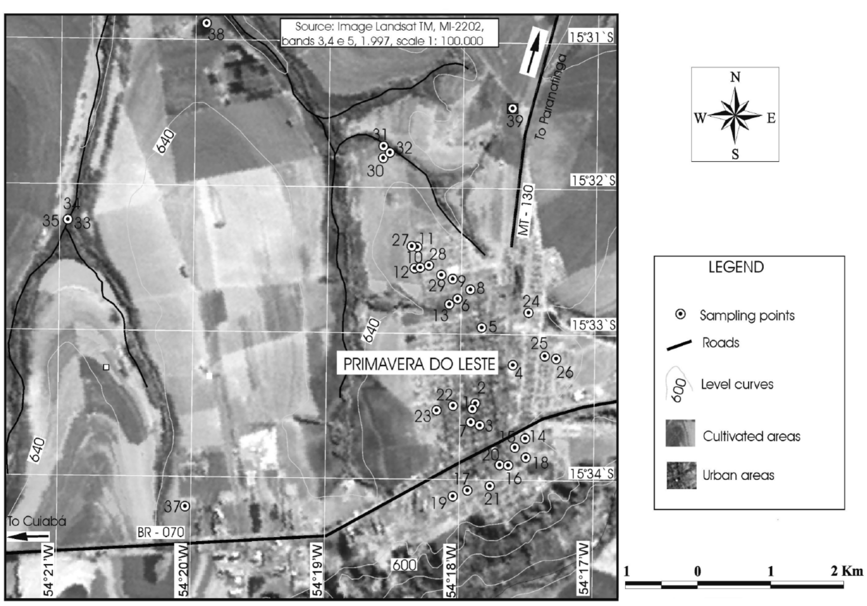

Figure 1. Sampling locations in Primavera do Leste region, Mato Grosso, Center-West Brazil.

GC–NPD conditions

A Hewlett-Packard 6890 GC equipped with a split/splitless injector and a nitrogen-phosphorus detector was employed. A DB-5 fused-silica capillary column (30 m × 0.32 mm i.d., 0.25 µm; J&W Scientific, Folsom, CA) was used, with nitrogen (purity 99.999%) as carrier at flow-rate of 1 mL/min. Detector gases: hydrogen 3 mL/min, air 60 mL/min, and make up gas (nitrogen) 7 mL/min. The injector temperature was set at 240ºC and the detector temperature was 300ºC. The oven temperature was programmed as follows: 70ºC for 1 min, increased to 150ºC at 20ºC/min, then to 180ºC at 3ºC/min, and followed by a final ramp to 240ºC at 10ºC/min (hold for 1 min). The data were acquired and processed by HP Chemstation software. Aliquots of one µL of the water extracts, standards, and blanks were injected in the splitless mode into the GC–NPD system.

Analytical quality controls

All data were subject to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analyzed. None of the target compounds were detected in the procedural blanks for deionized water.

Method performance was assessed using spiked water samples (spiking levels from 0.05 to 8.0 µg/L in six replicates), and the method was shown to have good precision and high recoveries. Average recovery, relative standard deviation, and limit of detection (LOD) of the analytical method applied were 72–110% of spiked amount; 2–19%; and 0.023–0.088 µg/L, respectively, except for DIA and trifluralin, for which lower recoveries (25% and 56%, respectively) were measured. Further details of the method have been previously published (16).

The low recovery of trifluralin was probably due to either glassware adsorption and/or volatilization and of DIA was due to breakthrough during sample pre-concentration in the cartridges. Lower recoveries of DIA and trifluralin have been reported in the literature by different authors (13,17–19).

The difference between the results for duplicate analysis of water samples was never greater than 10%, and results were reported as the arithmetical mean of the two values.

Results and Discussion

Herbicide residues in water samples

The contamination of water resources with pesticides in the region of Primavera do Leste was evaluated using a sampling scheme which was also aimed at identifying the seasonal variation of pesticide levels.

The pesticides chosen from those currently in use in the study area were atrazine and its metabolites DEA and DIA, simazine, metribuzin, metolachlor, and trifluralin. Except for trifluralin, all studied pesticides present low adsorption to soil, high water solubility, and high environmental stability, which causes them to be a potential contamination of ground and surface water. Trifluralin was included in the present study due to its frequent use, and our aim to evaluate the occurrence of a hydrophobic substance in comparison to highly hydrophilic ones.

Table I. Occurrence of Herbicides in Water samples Collected in Primavera do Leste region (Central-Western Brazil) in 1998/1999

Sampling site	Pesticide occurrence					
	September 1998		December 1998		April 1999	
	n_t*	%†	n_t	%	n_t	%
Ground water	32	53	28	75	31	55
Surface water	6	0	5	60	5	20
Pesticides						
atrazine	38	0	33	12	36	0
DEA		13		18		8
simazine		10		18		0
metribuzin		26		49		44
trifluralin		3		6		0
metolachor		13		12		11

* n_t = number of samples analyzed.
† % = percentage of positive detection.

The sampling dates were chosen considering the application periods of pesticides by farmers and rainfall events during the following months: September and December 1998, and April 1999.

The results of the water sample analysis showed the presence of herbicide residues, which are summarized in Table I. Significant variation on herbicide detection in the sampling periods were observed. All analyzed compounds were detected at least once during the study in higher concentrations and frequency during the application period, indicating that the presence of herbicides in the surface and groundwater could be attributed to the agricultural use. The increase in percentage of positive detections in surface waters in December was greater than in groundwater, indicating the higher vulnerability of surface water to contamination during the application period. However, due to the slower dynamics of groundwater systems and reduced pesticide half-life in sub-surface, once contaminants reach these waters it tends to be more persistent.

Metribuzin was the herbicide detected with the highest frequencies of 26%, 49%, and 44% in September and December 1998, and April 1999, respectively, followed by DEA, simazine, atrazine, and metolachlor. Metribuzin use in crops would account for its high frequency of detection; it is favored by its relatively high polarity and water solubility. On the other hand, trifluralin was the herbicide detected in lower frequency, as expected by its low polarity and water solubility.

Table II presents the minimum, maximum, and median of the detected concentrations of herbicide in water sources during sampling periods. A seasonal variation of atrazine ($p < 0.01$), DEA ($p < 0.05$), and metribuzin ($p < 0.01$) detection frequencies was observed in these sampling periods using an χ^2 test. Besides, there was an increasing detection of these compounds at the second sampling during rainy season (October/March).

Metolachlor was the herbicide detected in the highest amounts, up to 1.732 µg/L. Atrazine was only detected at the second sampling (December 1998), while simazine was detected at the first (September 1998) and second samplings (December 1998). These data were compared using Friedman test for paired data between sampling periods, which showed that there were significant differences between atrazine ($p = 0.018$), simazine ($p = 0.040$), and metribuzin ($p = 0.009$), with highest concentrations in the beginning of the rainy season. In the analyzed samples, pH for superficial water varied from 5.0 to 5.8 and for groundwater from 3.6 to 5.4. These values may have contributed to the degradation of the triazines, like atrazine and simazine, which are only stable in neutral pH (1), while metribuzin persists longer in acidic conditions (20). The detection of some pesticides like metolachlor and metribuzin over the whole period of study indicates persistent pollution, as observed by Carabia-Martínez et al. (21) in Spain.

Herbicide concentrations in water samples did not exceed the guidelines for drinking water established by different organizations such as EPA, (22) World Health Organization (23), and Brazilian Health Ministry (24). However, the more strict EU guidelines (0.1 µg/L for individual pesticides) were occasionally exceeded.

Among the groundwater samples analyzed from the agricultural area, all samples contained at least one of the herbicides. Although the amount of trifluralin used in the region was comparable to that of atrazine, that herbicide was detected at lower concentrations in groundwater samples. Because trifluralin has low water solubility and tends to sorb to organic matter from soil, it is less inclined to be released from soil. However, due to its high volatilization tendency, it is probable that this compound moves significantly by diffusion in the gas phase of the soil, as reported by Reichenberger et al. (25). Moreover, these authors concluded that preferential flow is likely to be an important mechanism of pesticide movement downward the soil profile in Oxisols, which explains the occurrence of trifluralin in the groundwater samples.

Few studies investigated groundwater contamination by pesticides in Brazil. Laabs et al. (26) studied the leaching of herbicides, such as atrazine, simazine, metolachlor, and trifluralin, in soil in an area in Mato Grosso near Primavera do Leste. They observed that the accumulated amount of leached pesticide during the first 30 days after application accounted for more than 60% of the total leached amount during the studied period. After 30 days, polar pesticides still exhibited substantial leaching but in lower concentrations. These observations may explain the increase in pesticide concentration in the beginning of the rainy season, the period when the herbicides atrazine, simazine, metolachlor, and metribuzin are applied in Primavera do Leste (October/November).

In Southwestern Brazil, in Rio de Janeiro, Correia et al. (27), when studying the dynamics of atrazine in an Ultisol reported that considerable atrazine leaching was measured in microcosms and atrazine was detected in field experiments at depths of 50 cm; which, under regional conditions of intensive tropical rain is a threat to groundwater quality. A monitoring study in São Paulo, Southern Brazil, investigated the possible contamination of the Guarani Aquifer by several pesticides, among them trifluralin, which was not detected during a 2.5 year monitoring period. The absence of water contamination was interpreted in relation to the structural characteristics of the soils like thickness, grain size, and field capacity (12).

Recent studies in several countries have also detected the studied pesticides in groundwater. The detection frequency of herbicides in groundwater samples in Primavera do Leste region was lower than reported in studies from the United States (28,29). In their studies, atrazine and its metabolites were detected in higher concentrations, and simazine and metribuzin in similar concentrations. In Germany, atrazine and simazine were detected in higher frequency than Primavera do Leste region (30). In the Gaza Strip, Shomar et al. (9) determined high concentrations of atrazine (average 3.5 µg/L) in 18 out of 94 groundwater wells. In Axios, Greece, atrazine and propanil were the most frequently detected pesticides in the phreatic horizon in concentrations above 0.1 µg/L in several samples, while simazine was detected in only one sample (8). The smaller half-life of pesticides generally found in tropical environments (31)

Table II. Detection Frequency, Minimum and Maximum Concentrations of Pesticides Detected in Water Samples in Primavera do Leste, Mato Grosso, Central-western Brazil, in 1998/1999

		September 1998				December 1998				April 1999			
Sampling site	Pesticides	%*	median† (µg/L)	minimum‡ (µg/L)	maximum (µg/L)	%	median† (µg/L)	minimum‡ (µg/L)	maximum (µg/L)	%*	median† (µg/L)	minimum‡ (µg/L)	maximum (µg/L)
Drinking water well (23)	atrazine	–§	–	–	–	5	0.063		0.063	–	–	–	–
	DEA	22	0.055	0.048	0.690	25	0.066	0.055	0.078	13	0.354	0.049	0.415
	simazine	26	0.076	0.047	0.138	10	0.052	0.042	0.061	–	–	–	–
	metribuzin	35	0.134	0.085	0.340	65	0.198	0.098	0.351	48	0.122	0.070	0.882
	trifluralin	4	0.182		0.182	5	< 0.102		< 0.102	–	–	–	–
	metolachlor	17	0.348	< 0.206	0.836	5	< 0.206		< 0.206	13	< 0.206	< 0.206	< 0.206
Waterhole (6)	metribuzin	17	< 0.106		< 0.106	20	< 0.106		< 0.106	20	< 0.106		< 0.106
	metolachlor	17	0.825		0.825	60	0.672	< 0.206	1.732	20	0.631		0.631
Irrigation water well (3)	atrazine	–	–	–	–	100	0.152	0.078	0.856	–	–	–	–
	DEA	–	–	–	–	33	0.206		0.206	–	–	–	–
	simazine	–	–	–	–	67	0.080	0.075	0.085	–	–	–	–
	metribuzin	33	0.129		0.129	–	–	–	–	–	–	–	–
	trifluralin	–	–	–	–	33	< 0.102		< 0.102	–	–	–	–
River (3)	simazine	–	–	–	–	67	0.046	0.045	0.047	–	–	–	–
Dam (3)	metribuzin	–	–	–	–	50	0.138		0.138	–	< 0.106	< 0.106	< 0.106

* % = detection frequency.
† When the pesticide was detected in only one sample, median was reported as equal to this one value.
‡ When pesticides were detected with concentrations above LD but lower than LQ, concentrations were reported as < LQ. Blank cells for minimum values means that the pesticide was detected in only one sample.
§ Not detected.

may account for the less frequent detection of pesticides than other countries found in our study.

Regarding surface waters, in Brazil, Laabs et al. (13), in a monitoring study, found lower concentrations of metolachlor and metribuzin in superface water samples from Pantanal region, Mato Grosso state. However, these authors detected these pesticides with higher frequency. In a sugar cane area in Sao Paulo State, atrazine and simazine were not detected in potable water (11), while in Rio de Janeiro State, high concentrations of atrazine (maximum of 100 µg/L) were detected in the Paraiba do Sul river, associated with the first rainfall after application. The level of atrazine in river water varied seasonally with the highest concentrations found in the spring and summer months (32).

On the other hand, Pereira et al. (33) and Squillace and Thurman (34) found higher concentrations of atrazine and metolachlor in surface water samples of the Cedar River and the Mississipi River in United States, respectively.

In Portugal, in a monitoring study of surface waters, the herbicides more frequently detected were atrazine (64%), simazine (45%), and alachlor (25%), with maximum concentrations of 630 ng/L for atrazine and 294 ng/L for simazine (32).

In our study, only simazine and metribuzin were detected in surface waters in concentrations up to 0.047 µg/L for simazine and 0.138 µg/L for metribuzin, values that are, in general, smaller than those found in other countries.

Risk scenario in the study region and water contamination

Primavera do Leste region presents some important characteristics which should be considered when the vulnerability of water resources to contamination by pesticides is under analysis. First of all, Primavera do Leste region is located in an aquifer recharge area, which is vulnerable to contamination as discussed by Cohen et al. (35).

This region is characterized by a high percentage of cropped land and only thin buffer strips of natural vegetation between fields and streams/rivers, and there is frequent aerial application of pesticides which favors pesticide drift. These characteristics render the surface water vulnerable to contamination by run-off from the planted areas (35). Laabs et al. (13) found high levels of metolachlor in rain water in the Pantanal, which is distant from agricultural areas, confirming the importance of drift as a mechanism of surface water contamination.

Soils are predominantly Oxisols, which are well drained and have medium permeability in the region of Primavera do Leste, a situation which favors leaching (15). Preferential flow is likely to occur in Oxisols, as identified by Reichenberg et al. (25) which allows the infiltration of even less polar substances in soil such as trifluralin.

Foomsgaard (36) in a review about pesticide degradation in soils in sub-surface (below 30 cm from surface), reported that atrazine, metolachlor, and metribuzin showed almost no degradation in sub-soil after 91 days, demonstrating that once pesticides reach undergroundwater the pollution may be persistent.

The climate plays an ambiguous role, as the high mean air temperatures (monthly means from 22 to 27°C) favor pesticide degradation, but also enhance pesticide dispersion by volatilization. Solar radiation also intensely favors the decomposition of some molecules by photolysis. Moreover, soil temperature can reach extremely high values on the top layer (up to 65°C) as verified in a meteorological station localized in Primavera do Leste, which also favors degradation and volatilization. Paraíba et al. (37) have shown the importance of soil temperature effect on pesticides leaching. Laabs et al. (38) reported that the half-life of some molecules can be up to five times lower in tropical than in temperate environment.

Rainfall events are intense in the months from October to March, which coincide with pesticide application in temporary crops. Intense rains just after pesticide application are likely to occur in this region; thus, pesticides transport is intensified by run-off and leaching (35).

The combination of the intensive pesticide use with the vulnerable soils and high-intensity rainfalls during the application season make a non-point pollution of surface water with several pesticides highly probable in our study region (15). This statement is now confirmed by our first results from groundwater and surface water monitoring.

Conclusions

The monitoring of surface and groundwaters of the agricultural area from Primavera do Leste region, Central-Western Brazil, showed the studied pesticides are common ground and surface water pollutants in the tropical Brazil as well as in temperate regions, presumably from non-point sources in agriculture. The main pollutants in our study are metribuzine (frequency, concentration) and metolachlor (concentration); in comparison, simazine and atrazine are of lesser concern. Even the non-polar trifluralin is found in groundwater resources, which calls for further research for this compound regarding leaching studies.

Pesticide maximum values in drinking water resources exceed the EU guidelines values by a factor of up to 17. Further monitoring of water resources is therefore needed and also more long-term research about pesticide leaching in tropical agriculture in Brazil.

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