RESEARCH ARTICLE

Occurrence of pesticides in waters from the largest sugar cane plantation region in the world

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Abstract

In this study, a multi-residue method was used to analyze 13 pesticides and 1 degradation product in surface and groundwater in the region with the largest sugar cane production in the world. The potential effects of individual pesticides and their mixtures, for aquatic life and human consumption, were evaluated. For the surface water, 2-hydroxy atrazine, diuron, carbendazim, tebuthiuron, and hexazinone were the most frequently detected (100, 94, 93, 92, and 91%, respectively). Imidacloprid (2579 ng L^{-1}), carbendazim (1114 ng L^{-1}), ametryn (1101 ng L^{-1}), and tebuthiuron (1080 ng L^{-1}) were found at the highest concentrations. For groundwater, tebuthiuron was the only quantified pesticide (107 ng L^{-1}). Ametryn, atrazine, diuron, hexazinone, carbofuran, imidacloprid, malathion, carbendazim, and their mixtures presented risk for the aquatic life. No risk was observed for the pesticides analyzed in this work, alone or in their mixtures for human consumption.

Keywords Surface water · Groundwater · Risk assessment · Mixture toxicity · PCA · Human consumption

Introduction

The growing demand for clean energy to replace non-renewable sources has caused a great expansion of the production and consumption of biofuels in the world (Diouf 2008). In Brazil, government programs to encourage the production and processing of sugar cane, popularization of the so-called flex-fuel engines and international investments in the sector, made the country the second largest producer of biofuels and the largest producer of sugar cane in the world (Lourenzani and Caldas 2014; Gilio and de Moraes 2016; OECD/FAO 2019; FAO 2020).

Brazil is considered one of the biggest pesticide markets in the world and currently 332 active ingredients are authorized for agricultural use (Albuquerque et al. 2016). São Paulo state accounts for more than half of the sugar cane production of Brazil and in 2018 was responsible for 15% of the total amount of pesticides commercialized in the country (MAPA 2019; IBAMA 2020).

After application, different mechanisms of transport and degradation describe the fate of pesticides in the environment and their respective risk for the non-target organisms. It is expected to find pesticides contamination in different environmental matrices, such as air (Meire et al. 2016; Tominaga et al. 2016; Silvério et al. 2017; de Guida et al. 2018; Nascimento et al. 2018a, b), soil (Rissato et al. 2006; Kemmerich et al. 2015; Nascimento et al. 2018c) and water (River et al. 2004; de Armas et al. 2007; Dores et al. 2008; Jacomini et al. 2011; Casara et al. 2012; Caldas et al. 2013; Montagner et al. 2014). In fact, according to Pimentel and Burgess (2012), less than 50% of the total amount applied by farmers gets to the target organism.

The soil is the main route for pesticides to contaminate groundwater (leaching) and surface water (runoff, direct application, spray drift, aerial spraying or erosion) (Beitz 1994; Arias-Estévez et al. 2008; C. Turgut 2014). When these compounds reach the water bodies, they can pose risk to aquatic biota and indirectly to human health (Ippolito and Fait 2019).

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According to Schulz ([2004](#)), it is estimated that the loss of pesticide from the field to the water body is between 1 and 10% of the total applied.

Pesticides are considered a global threat for the ecological integrity of aquatic ecosystems (Stehle and Schulz [2015](#)). One simple way to evaluate the risk of pesticide in environmental samples is to use the risk quotient (RQ) approach. Exposure data is divided by a selected water quality criteria (WQC) (Evans et al. [2015](#)) defined for specific uses of water (e.g. agricultural, recreational, livestock, aquatic life protection, human consumption) (CCME [2001](#); Health Canada [2019](#)).

This work aims to investigate the occurrence of 13 pesticides widely used in sugar cane cultivation and 1 degradation product in surface and groundwaters from the largest sugar cane plantation region in the world, and to evaluate their potential risk to aquatic life and human health.

Experimental

Characterization of the study area

The agricultural catchment located between latitude 22° 44′ 16″ and 19° 47′ 7″ S and between longitude 46° 29′ 21″ and 51° 29′ 33″ W, lies within the Atlantic rainforest and the Savanna (Cerrado) biomes where approximately 12 million people live (Fig. [1](#)). The sugar cane is the predominant crop in this area, responsible for 54% of the entire Brazilian production (MAPA [2019](#)). All sample sites and coordinates are available at Table S1 in the supplemental material.

Selection of pesticides

The pesticides selected in this work are among the top 30 active ingredients commercialized in Brazil and in the southeast region, which includes São Paulo state, from 2010 to 2014 among the 112 approved for use in sugar cane plantation in Brazil (IBAMA [2020](#); MAPA [2020](#)). The choice of the target compounds was made based on their chemical characteristics and suitability of the multi-residue method developed in this work. Some highly consumed pesticides in sugar cane plantations, such as fipronil, 2,4-D, and glyphosate, were not able to be included in the multi-residue method applied in this work because of their chemical properties. Atrazine is one of the most commercialized pesticides in the world (Ackerman [2007](#)). The 2-hydroxy atrazine was included in the multi-residue method as an example of one of the several atrazine's transformation products.

Reagents and materials

High purity standards of 14 pesticides were purchased from Sigma-Aldrich. For a representative multi-residue method, all
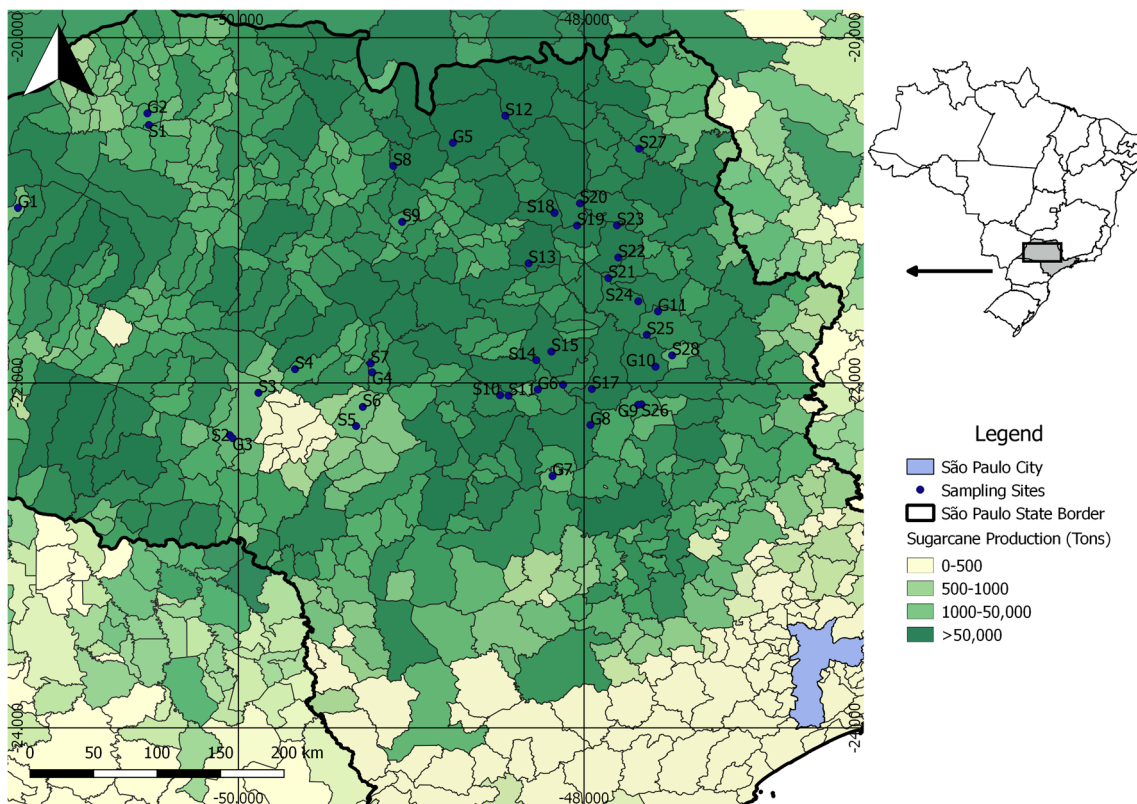

Fig. 1 Sampling sites, denoted as S, for surface water and G, for groundwater in mask for São Paulo state sugar cane production areas

the pesticides selected must be allowed for sugar cane use and must be adequate for a single multi-residue method (MAPA 2020). The selected pesticides cover three different classes: insecticides, fungicides and herbicides. The physico-chemical properties of the selected pesticides are presented in Table S2 in the supplemental material.

The stock solution of 2-hydroxy atrazine was prepared in methanol:0.1 M HCl, 80:20 (v/v). The other compounds' stock solutions, mixtures and further dilutions were prepared in methanol. Calibration standard solutions were dissolved in water:methanol, 70:30 (v:v).

Chromatographic grade methanol and acetonitrile were acquired from Merck (Darmstadt, Germany). Formic acid (98%) from Fluka (Ottawa, Canada). Ultrapure water was obtained from a water purification system (Synergy, Millipore). Solid phase extraction (SPE) cartridges Oasis HLB 500 mg/6 cc were acquired from Waters (Milford, MA, USA).

Sampling and sample preparation

Samples were collected following the *National guide for collection and preservation of samples* (ANA and CETESB 2011). A total of 196 samples were collected in 3 aquifers and 11 different sites. Surface water samples were collected every month from October 2015 to October 2016, in 19 rivers and 28 different sites. Groundwater samples were collected from deep bore wells, used as a source for public supply and before any water treatment, with depth ranging from 17 to 36 meters between October/ November 2015 and March/April/May 2016.

Samples were immediately extracted after their arrival in the laboratory. Half liter of the water samples was passed through 1.2 µm pore size glass fiber filters (Sartorius, Germany). The filtered samples were extracted by SPE cartridges in a lab-made extraction system (Sodré et al. 2010). The cartridge was conditioned by using 5 mL of methanol followed by 5 mL of ultrapure water. The extraction was carried out at a flow rate of 8 mL min^{-1}. After the extraction, the cartridges were dried under vacuum for 20 min. The target compounds were recovered with 4 mL of methanol and 4 mL of acetonitrile. The elution step was carried out using a 12-port Prep Sep vacuum manifold (Fisher Scientific, Fair Lawn, USA). Solvents were evaporated to dryness with a gentle flow of nitrogen and the target compounds were re-suspended to a final volume of 500 µL in a solution of water:methanol, 70:30 (v/v). All extracts were kept at refrigeration (− 18 °C) until the LC-MS/MS analysis.

Instrumental analysis

The quantification of the target compounds was carried out by Liquid Chromatography couple to Triple Quadrupole Mass Spectrometer (LC-MS/MS) using a multi-residue method which allowed the simultaneous determination of them with nanogram per liter level of detectability.

The LC-MS/MS analyses were performed using an Agilent 1200 system coupled to an Agilent 6410 triple quadrupole mass spectrometer with an electrospray ionization source (ESI). All instruments were controlled by Mass Hunter Acquisition software, version B.02.01 (Agilent Technologies, Palo Alto, USA).

The chromatographic separation was performed in a thermostatted column compartment (TCC G1316A) at 25 °C, using a Zorbax SB-C18 column (2.1 x 30 mm, particle size of 3.5 µm) from Agilent Technologies. The separation was carried out with gradient elution methanol and ultrapure water (0.1% formic acid as additive). The gradient elution was programmed at a flow rate of 0.3 mL min^{-1}, increasing the organic solvent concentration from 30 to 60% in 3 min and followed by an increase to 67% in 10 min. After re-adjusting to the initial condition, the system was re-equilibrated for 5 min. The injection volume was 10 µL.

After the chromatographic separation, the pesticides were ionized using an ESI source operating in the positive ion mode. To maximize all compounds ionization, the following parameters were adjusted: drying gas flow rate of 10 L min^{-1}, drying gas temperature of 350 °C, nebulizing gas pressure at 50 psi and capillary voltage of 3000 V. The electron multiplier voltage was set at 300 to increase the abundance at the detector. Nitrogen (99.998%) was used as drying and collision gas. For the quantification and confirmation of all target compounds, the multiple reaction monitoring (MRM) transitions were employed.

The analytical method was adapted from Montagner et al. (2014) and data on linearity, recovery, intraday precision and breakthrough volume are available at Table S3. Concentrations of the target compounds in the water samples were determined using external calibration curves. The limit of detection (LOD) was defined as the smallest concentration that could be recognized as a chromatographic peak with a signal-to-noise (S/N) ratio of 3. The limit of quantification (LOQ) was calculated using S/N ratio of 10.

Multivariate analysis

A principal component analysis (PCA) was performed using the software The Unscrambler X10.4 (Camo, Norway). For this, the algorithm SVD (singular value decomposition) was used. A total of 7 compounds were selected due to their frequency of detection above 80%. The concentration values for all pesticides obtained were auto scaled, i.e., centered in the mean and divided by the standard deviation. An array with 167 samples (rows) and 7 compounds (columns) was built.

We performed the PCA only for surface water samples. Besides the concentration of the 7 selected compounds, the other components of the PCA were, site classification (urban

and non-urban) and seasonality (rainy and dry). We considered as urban the samples collected within cities surroundings in the supplemental material (Table S1).

Risk assessment

Risk assessment was performed separately for surface water and groundwater. For surface water, we considered aquatic life protection and human consumption, if used without any treatment. For groundwater, only human consumption was considered.

We selected the risk quotient approach to evaluate the potential risk of pesticides concentrations found in the water samples. The risk quotient was obtained dividing the minimal and maximum measured concentration for each compound by the respective water quality criteria (WQC). Risk quotient greater than 1 represents risk to the intended use. To evaluate the overall risk of the 14 compounds analyzed, we used the sum of each risk quotient (Evans et al. 2015).

Aquatic life protection

The WQC for aquatic life protection was selected for each pesticide using the lowest predicted no effect concentrations (PNECs), or Environmental Quality Standard (EQS) or Guideline Value (GV) calculated based on chronic exposure published in the peer review literature as well in health and environmental agencies of different countries. This approach is based on the one adopted by Albuquerque et al. (2016).

Human consumption

The WQC for human consumption were selected based on the maximum allowed value of the current Brazilian regulation (MS 2017). Several pesticides are not included in cited regulation; therefore, we calculated them using Acceptable Daily Intakes (ADIs) from other agencies/countries (Table 2) using 20% of allocation factor, 60 kg of body weight and consumption of water of 2 liters a day (WHO 2017).

Results and discussion

Surface water occurrence

The occurrence of pesticides in surface water is shown Table S1 and summarized in Table 1 and Fig. 2.

All target compounds were detected in at least one sample. The herbicides had the highest detection frequencies, followed by fungicides and insecticides (73, 53 and 42%, respectively) which corresponds to the same pattern found in literature (Kreuger 1998; Moschet et al. 2014). Concentrations above 1000 ng L^{-1} were quantified 0.5% of the time, 8% between 1000 and 100 ng L^{-1}, 79.5% between 100 and 10 ng L^{-1}, and 12% below 10 ng L^{-1} (Fig. 2; Table S1).

Table 1 Summary of the occurrence of the 14 target compounds in the analyzed surface and groundwater samples

Pesticide	LOD (ng L^{-1})	LOQ (ng L^{-1})	Surface water			Groundwater		
			Concentration range (ng L^{-1})	Detection frequency (%)	N	Concentration range (ng L^{-1})	Detection frequency (%)	N
2-Hydroxy atrazine	2.2	6.7	7.3–289	100	175	-	24	21
Ametryn	1.7	5.2	5.7–1101	81	175	-	0	21
Atrazine	1.7	5.2	5.2–516	56	175	-	9	21
Clomazone	2.1	6.9	7–90	58	175	-	0	21
Diuron	1.1	3.4	4–279	94	175	-	9	21
Hexazinone	1.4	4.1	5.7–225	91	175	-	0	21
Simazine	2.7	8.3	15–29	8	175	-	0	21
Tebuthiuron	2	6	7.1–1080	92	175	61–107	9	21
Carbofuran	1.6	4.9	5.3–142	39	175	-	5	21
Imidacloprid	2.1	6.8	6.7–2579	86	175	-	14	21
Malathion	1.8	5.3	60.7–110	1	167	-	0	21
Azoxystrobin	1.9	5.7	6–7.5	24	167	-	0	21
Carbendazim	0.9	2.8	3–1114	93	167	-	9	21
Tebuconazole	1.6	4.8	5–199	41	167	-	0	21

LOD limit of detection, *LOQ* limit of quantification, *N* samples analyzed, - below LOD

Fig. 2 Distribution of the target compounds' concentrations in the analyzed surface water samples
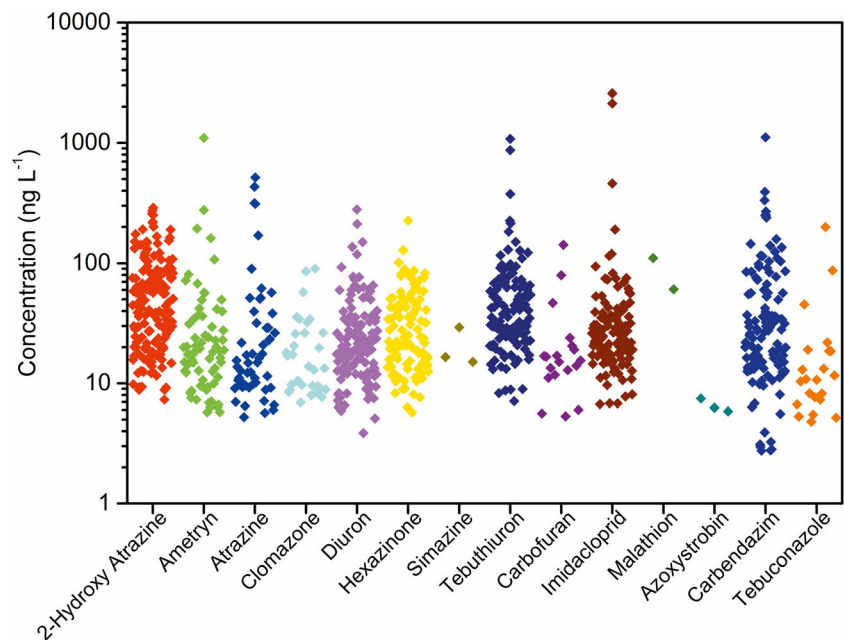
The only compound that was detected in all samples analyzed was the 2-hydroxy atrazine. The main route of degradation of atrazine to 2-hydroxy atrazine occurs in the soil, and its water solubility is lower than atrazine, it would not be expected in waters (Lerch et al. 1995, 1998; Carabias-Martínez et al. 2002). The presence of this compound in all samples could be the result of constant soil runoff/erosion process(es). More studies should be conducted to verify its importance as a surface water contaminant.

Malathion was detected in only 1% of the samples, the lowest detection frequency in the study. A reason for his low frequency may be because of its relatively low half-life (Liu et al. 2020) or an indication that it has not necessarily widely applied in sugar cane plantations.

The maximum concentration of imidacloprid was the highest among all target compounds, followed by carbendazim, ametryn, tebuthiuron and atrazine. Imidacloprid was quantified in similar concentrations in the southern of Brazil (380–2180 ng L^{-1}) (Bortoluzzi et al. 2006) and China (10.9–1886.9 ng L^{-1}) (Peng et al. 2018) and higher than in Portugal (1–8 ng L^{-1}) (Gonzalez-Rey et al. 2015), Canada (1.2–11 ng L^{-1}) (Montiel-León et al. 2019), and Spain (1.6–14.9 ng L^{-1}) (Ccanccapa et al. 2016). The maximum concentration of diuron was 80 times lower than previously quantified in Costa Rica (Carazo-Rojas et al. 2018) and higher than reported in Portugal (15 ng L^{-1}) (Gonzalez-Rey et al. 2015), Spain (31.1 ng L^{-1}) (Proia et al. 2013) and China (107.2 ng L^{-1}) (Peng et al. 2018).

Clomazone, hexazinone, simazine, atrazine and ametryn were also found in the Corumbataí river, located in a sugar cane region in São Paulo state, and all concentrations were higher than those found in our study (de Armas et al. 2007).

Groundwater occurrence

All the 21 samples of groundwater studied presented at least one of the target compounds investigated (Table S1). Imidacloprid and 2-hydroxy atrazine were positively identified in 14 and 24% of samples analyzed while tebuthiuron was the only one quantified (Table 1). For imidacloprid and tebuthiuron, these results agree with their high leaching potential, according to their Groundwater Ubiquity Score index, between 3.69 and 5.36, high water solubility, between 610 and 2500 mg L^{-1}, and their widespread application in the area. However, for 2-hydroxy atrazine, this may be related to the type of soil/lithology in the region. The sampling sites G1, G2, G4, G9 and G10, where the atrazine degradation product was detected, are located in regions where the Vale do Rio do Peixe geological formation (G1, G2, and G4) and the Pirambóia formation (G9 and G10) emerge. The Vale do Rio do Peixe formation is characterized by fine sandstone levels of good selection interspersed with siltstones (Fernandes and Coimbra 2000). The Pirambóia formation is composed as a sequence of fine to medium sandstones, in a dune field environment (Chang and Wu 2003). As these are sedimentary formations with a predominance of sandstones, generally well selected, the soils from these formations tend to facilitate the leaching of compounds, including 2-hydroxy atrazine.

Some of the pesticides investigated in this work were also found in agricultural regions around the world, such as United States, where 11 pesticides were quantified and, among them, simazine (140 ng L^{-1}), atrazine (34 ng L^{-1}), and azoxystrobin (1 ng L^{-1}) (Reilly et al. 2012). In South Korea, carbofuran (116 ng L^{-1}) was quantified (Lee et al. 2019). In Catalonia,

Spain, researchers found simazine (1690 ng L^{-1}), atrazine (756 ng L^{-1}), diuron (178 ng L^{-1}), and malathion (87 ng L^{-1}) (Postigo et al. 2010). The depth of the wells, climate, land use, type of soil, hydrogeological conditions, and nature of the pesticides are important variables to determine the susceptibility of groundwater to pollution via soil (Arias-Estévez et al. 2008).

Our data highlights the contamination of the studied aquifers under the influence of sugar cane plantation, therefore a program should be implemented to monitor temporal and spatial concentrations as well the need of mitigation measures.

Multivariate analysis

Principal Component Analysis (PCA) is used to show the similarities and differences in a set of samples and verifying how the variables influence them. PCA performs the grouping of information contained in all constituents of a sample and projects this information on a new coordinate system of the few principal components (PC), which allows an easy visualization of complex data. The results from PCA are shown in score and loading graphics, in which the scores are the representation of the samples and the loadings of the variables on the PCs (Wold et al. 1987; Bro and Smilde 2014).

Figure 3 shows the PCA for 167 samples divided in two groups, non-urban and urban. In Fig. 3a, the scores show the projection of these two groups in the PC-1 and PC-2. In Fig. 3b, the loadings show the projections of the 7 compounds present in the samples over the PC-1 and PC-2. These principal components accumulated 59% of the variance present in

the samples. PC1 has 38% and PC2 21%. The graphs of score and loadings for the other PCs are presented in Fig. S1.

The samples were separated into two categories according to the proximity of the sampling sites classified as non-urban and urban. These samples were then subjected to an exploratory analysis to check for possible differences in the predominance of a given compound or even by the difference between the concentration levels of these compounds in the samples. However, regardless of the region where the samples were collected, they were randomly scattered close to the origin of the PCA. There is no significative difference between these two groups of samples, demonstrating that the composition is equally affected in both regions (urban and non-urban). Hoffman et al. (2000) obtained a similar result after analyzing 8 urban streams in the United States and found that the patterns of occurrence of pesticides were similar to the agricultural profile of the surrounding area. In Fig. 3b, we observe the formation of two groups: the first one with a positive weight on PC-1, being diuron, ametryn, tebuthiuron, hexazinone, and 2-hidroxy atrazine, and the second group with negative weight on PC-2, being imidacloprid and carbendazim. However, although present, this grouping is not characterized by any type of effective correlation that can be used to interpret these data.

In the scores plot, we also observe the insertion of the ellipse of the Hotelling's T^2 statistic with 95% confidence (Wold et al. 1987; Bro and Smilde 2014). The limit calculated for Hotelling's T^2 is generally used to assess the presence of outlier samples in the PCA

Fig. 3 Principal components analyses, **a** scores and **b** loadings. In A, two categories of the samples are presented in blue and red, non-urban (127 samples) and urban (40 sample), respectively. It is also present the ellipse of Hotelling T^2 that indicates the confidence interval of 95%. In B, the 7 compounds that were qualified in the samples are presented
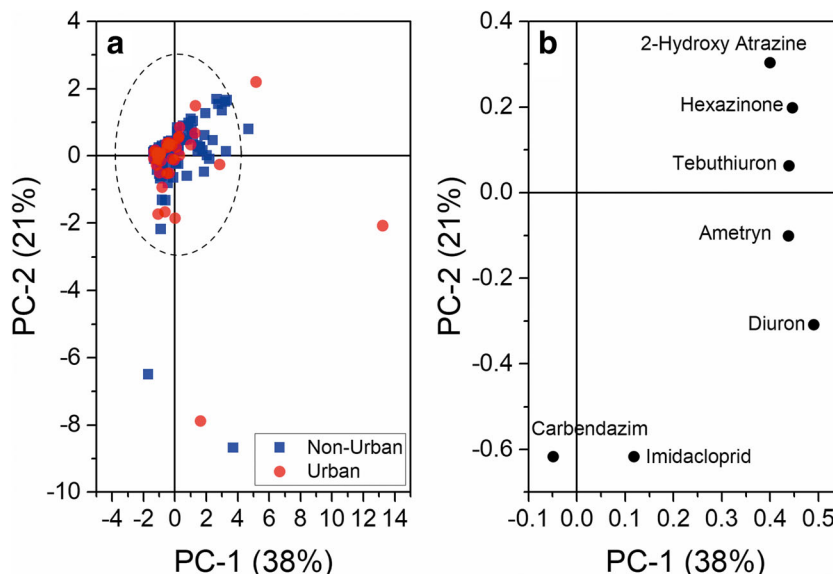
(Galaverna et al. 2018). We found that there are 6 samples outside their limits, which represents about 3.6% of the samples. In cases of monitoring processes, for example, these samples would be considered out of control. However, as these samples are from very large region that was monitored over a wide period of time, they may present a greater variance than the average of the samples. Here, we decided to keep these samples in the model, but we also built another model without these samples (Fig. S2). We observed that there is a little impact on the loadings plot and, on the variance explained by the PCs, without any changes in the PCA interpretations.

We also classified the samples according to dry and rainy season. October to March is considered rainy season, and from April to September as dry season. The PCA graphs are presented in Fig. S3. Again, the samples are distributed randomly, without any separation, according to their constituents or even the concentration levels of the constituents, suggesting an annual cycle of pesticides reaching the rivers.

Risk assessment for surface water

The LOQs (Table 1) of the method applied in this study were considered adequate for the risk evaluation, except for ametryn, whose value for aquatic life protection is lower than the limits of the method. Table 2 lists the

WQC adopted in this study for aquatic life protection and their sources. Only atrazine, simazine and malathion are included in the Brazilian regulation in which aims to protect aquatic life at the chronic exposure level (long term) (MMA 2005). For atrazine and simazine the values are 2000 ng L^{-1} and for malathion, 100 ng L^{-1} which are greater than the lowest WQC found in the literature (Table 2).

The risk assessment for the aquatic life posed by the quantified pesticides was evaluated. Comparing all the selected water quality criteria, with the range of every pesticide quantified, allowed us to determine the RQs (Fig. 4). From the three types of pesticides analyzed, insecticides showed greater risks, followed by herbicides and then fungicides. Results from this study are similar with ones found by Albuquerque et al. (2016) that assessed the risk of pesticides to aquatic life in Brazil.

Ametryn, diuron, hexazinone, imidacloprid, and carbendazim presented RQ higher than 1 with detection frequencies higher than 85%, indicating the worst scenario for aquatic life protection. Carbofuran also presented risk, but it was less frequently detected (39%). The sum of the lowest RQs (20,8) is mainly driven by malathion, which was detected only in 1% of the samples. If we do not consider malathion in the analysis, the minimum risk would be 2.5, which also represents risk to the aquatic life.

Table 2 Water quality criteria for aquatic life protection and drinking water quality criteria adopted in this work and their respective sources

| Target compounds	Aquatic life protection		Human consumption		
	Water quality criteria (ng L^{-1})	References	Water quality criteria (ng L^{-1})	Acceptable daily intake (mg/kg body weight/day)	References
2-Hydroxy atrazine	600	OJEU (2013)	240,000	0.04	Diouf (2007)
Ametryn	4.2	von der Ohe et al. (2011)	400,000	0.072	U.S. EPA (2005)
Atrazine	600	OJEU (2013)	2000		MS (2017)
Clomazone	2000	INERIS (2020a)	240,000	0.04	ANVISA (2020a)
Diuron	70	Oekotoxzentrum (2020)	90,000		MS (2017)
Hexazinone	6.8	von der Ohe et al. (2011)	300,000	0.05	ANVISA (2020b)
Simazine	1000	OJEU (2013)	2000		MS (2017)
Tebuthiuron	1600	CCME (1999)	420,000	0.07	U.S. EPA (1988)
Carbofuran	20	INERIS (2020b)	7000		MS (2017)
Imidacloprid	13	Oekotoxzentrum (2020)	300,000	0.05	ANVISA (2020c)
Malathion	6	INERIS (2020c)	1,800,000	0.3	ANVISA (2020d)
Azoxystrobin	200	Oekotoxzentrum (2020)	120,000	0.02	ANVISA (2020e)
Carbendazim	150	INERIS (2020e)	120,000	Not informed	MS (2017)
Tebuconazole	240	Oekotoxzentrum (2020)	180,000	Not informed	MS (2017)

Fig. 4 Risk assessment for aquatic life protection: minimum and maximum quotients calculated for each pesticide. The sum of the quotients is also presented to represent a scenario where the organisms are chronically exposed for the 14 compounds analyzed
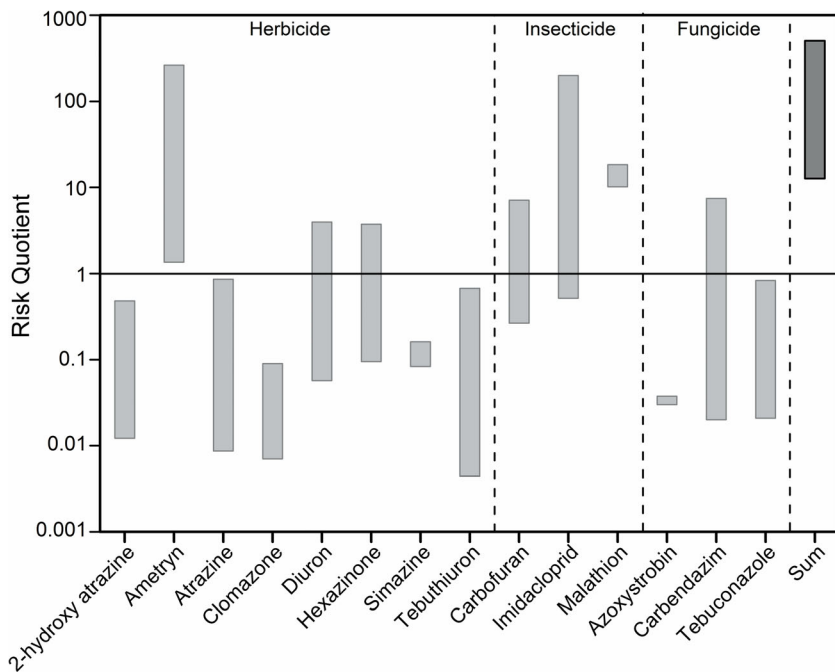
For human consumption, no risk was observed for any of the pesticides alone or their sum. Atrazine presents the RQ closest to 1 and is driving the RQ's sum, which is between 0.1 to 1 (Fig. 5). The European Union (EU) establishes maximum limits for pesticides in drinking water based on pragmatic values and the non-compliance with these standards does not necessarily offer risk to humans, based on a risk assessment approach. EU considers as maximum concentrations, 100 ng L^{-1} for each pesticide and 500 ng L^{-1} for their sum (EC 1998). In our study, 31% of the samples showed at least one pesticide in concentration above 100 ng L^{-1} (Table S1). This can be viewed as an early warning and actions for the mitigation of the contamination should be taken based on the precautionary principle.

Fig. 5 Drinking water risk assessment: minimum and maximum quotients calculated for each pesticide and the sum of the quotients for the 14 compounds analyzed
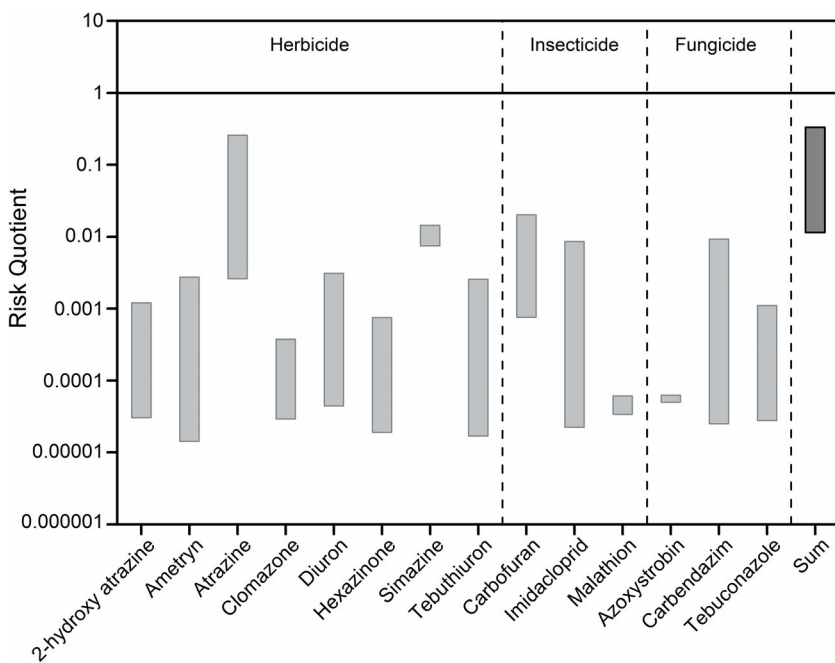
Risk assessment for groundwater

Only the use considered for groundwater risk assessment was human consumption. Atrazine and its degradation product (2-hydroxy atrazine), diuron, tebuthiuron, carbofuran, imidacloprid, and carbendazim were detected in at least one sample. Tebuthiuron was the only pesticide quantified, in concentrations of 61 and 107 ng L^{-1}. Those value are almost 7000 to 4000 times lower than the considered drinking water criteria adopted in this study (Table 1). However, according to EU standards (EC 1998), the sample with the highest value exceeded the maximum allowed concentrations (100 ng L^{-1}).

Conclusion

The applied multi residue method was appropriate for the detection of the selected compounds providing quantification limits suitable for human consumption risk assessment and aquatic life protection, except for ametryn and malathion for the latest use of the water.

In surface water, all the 14 target compounds were detected at least in one sample. The detection frequencies varied from 1 to 100%. The herbicides, diuron, hexazinone, tebuthiuron, 2-hydroxi atrazine and the fungicide carbendazim were the most prevalent compounds with detection frequencies above 90%.

In groundwater, atrazine and its degradation product (2-hydroxy atrazine), diuron, tebuthiuron, carbofuran, imidacloprid, and carbendazim were detected in at least one sample but only tebuthiuron was detected in concentrations above LOQ.

No correlation of occurrence of pesticides in the dry and rainy season or among pesticides and land use (urban or non-urban) were found in the dataset provided in this study.

In surface water, ametryn, diuron, hexazinone, imidacloprid, carbendazim, carbofuran, and malathion presented possible risk to aquatic life. Therefore, actions to reduce the levels of pesticides in the aquatic environment under the influence of sugar cane plantation should be considered. No risk was observed for the pesticides analyzed in this work, alone or in their mixtures for human consumption.

The level of the only pesticide detected in groundwater does not seem to be a concern for human consumption. Risk for aquatic life was not evaluated for this type of water.

This study highlights the need of actions to reduce the amount of pesticides used in crops, including in sugar cane plantation in São Paulo state to protect the aquatic life and the implementation of a comprehensive monitoring program to protect surface and groundwater resources for human consumption.

Compliance with ethical standards

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