Environmental Science and Pollution Research (2020) 27:10581–10598
https://doi.org/10.1007/s11356-019-06550-8

RESEARCH ARTICLE

“Modern agriculture” transfers many pesticides to watercourses: a case study of a representative rural catchment of southern Brazil

José Augusto Monteiro de Castro Lima[1] • Jérôme Labanowski[2] • Marília Camotti Bastos[3] • Renato Zanella[3] • Osmar Damian Prestes[3] • Jocelina Paranhos Rosa de Vargas[3] • Leslie Mondamert[2] • Eugenie Granado[2] • Tales Tiecher[4] • Mohsin Zafar[5] • Alexandre Troian[3] • Thibaut Le Guet[2] • Danilo Rheinheimer dos Santos[3]

Received: 28 May 2019 / Accepted: 16 September 2019 / Published online: 15 January 2020

Abstract

The total cultivated area in Brazil reached to 62 million ha in 2018, with the predominance of genetically modified soybean and corn (36 and 17 million ha, respectively) in no-tillage systems. In 2018, 5.3×10^5 Mg of active ingredient of pesticides was applied in cropfields, representing about 7.3 L of commercial product by habitant. However, the monitoring of water courses contamination by pesticides remains scarce and is based on traditional grab sampling systems. In this study, we used the grab (water) and passive sampling (Polar Organic Chemical Integrative Sampler—POCIS) to monitor pesticide contamination in the river network of a representative agricultural catchment of southern Brazil. We selected 18 sampling sites located in tributaries and in the main course of the Guaporé River, in Rio Grande do Sul State, with different land use predominance including forest, urban, and agricultural areas. Altogether, 79 and 23 pesticides were, respectively, analyzed in water and POCIS samples. The water of Guaporé River and its tributaries were highly contaminated by many pesticides, especially by four herbicides (2,4-D, atrazine, deethyl-atrazine, and simazine), three fungicides (carbendazim, tebuconazole, and epoxiconazole), and one insecticide (imidacloprid). The amount, type, and concentration of pesticides detected were completely different depending on the sampling technic used. POCIS was effective to discriminate the contamination according to the main land use of each sampling site. The monitored areas with the predominance of soybean cultivation under no-tillage tended to have higher concentrations of fungicide, while in the more diversified region, the herbicides showed higher values. The presence of five herbicides used in corn and grassland forage production was correlated with areas of integrated crop-livestock systems, in contrast to higher contamination by 2,4-D in areas of intensive production of soybean and winter cereals.

Keywords Environmental monitoring · Polar Organic Chemical Integrative Sampler · Water contamination

---

Responsible editor: Ester Heath

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11356-019-06550-8) contains supplementary material, which is available to authorized users.

✉ Tales Tiecher
tales.tiecher@ufgrs.br

[1] Instituto Federal de Alagoas, Rua Odilon Vasconcelos, 103, Maceió, AL 57035-350, Brazil

[2] Université de Poitiers, IC2MP, UMR CNRS 7285, 7 rue Marcel Dore, B16, 860073 Poitiers Cedex 9, France

[3] Universidade Federal de Santa Maria, Avenida Roraima, 1000, Santa Maria, RS 97105-900, Brazil

[4] Universidade Federal do Rio Grande do Sul, Bento Gonçalves, 7712, Porto Alegre, RS 91540-000, Brazil

[5] University of Poonch Rawalakot, Azad Jammu and Kashmir 12350, Pakistan

Introduction

In southern Brazil, there are more than 850,000 family farms. In this region, 20 million hectares is occupied by more than 2.3 million people working exclusively in rural activities and producing about 80×10^6 Mg of soybean, corn, rice, and wheat in 2017, representing 36% of Brazilian national production (IBGE, 2019). Even if soybeans as the main crop, there is a great diversity of production, including fruits and vegetables. Indeed, more than 90% of swine and poultry meat, approximately 50% of milk, and almost 100% of tobacco are produced in this macro-region. Approximately 143 Mg of active ingredients of pesticides is dispersed in a rural environment densely populated, even small towns which are surrounded by crops. This macro-region has one of the most important surface water reserves of South America, except for Amazon catchment. Furthermore, it has one of the largest aquifers in the world, Guarani Aquifer, which also involves part of Paraguay, Argentina, and Uruguay.

The transformation of natural biomes such as Pampa and Atlantic Forest in southern Brazil into cropfields tremendously decreases the infiltration of rainwater which results in increasing runoff and soil losses. The intensive land use combined with high intensity rainstorms makes this region one of the global erosion hotspots (Borrelli et al. 2017). Results obtained by using the fingerprinting approach to investigate sediment origin in southern Brazil revealed that about 90% of sediments present in Guaporé River (state of Rio Grande do Sul) come from cropfields, and the remaining from stream channels and unpaved roads (Tiecher et al. 2017). According to these authors, this occurs because of the high connectivity of erosive processes from hillslopes to the stream network in Guaporé River catchment, where there is a lack of mechanical runoff control strategies and absence of crop rotation. The main agricultural use is based in mono-cropping system of soybean in upper part and tobacco in middle/lower part of this catchment. There is also intensive integrated crop-livestock systems for milk production that results in lower soil cover by plant residues. Moreover, this region presents a rapid displacing of soil water by new rainfall events (Robinet et al. 2018). Accordingly, this scenario may result in high transfer the soluble and colloidal pesticides to the watercourses.

In southern Brazil, there is a great diversity of soil type and agricultural production systems. There are reports in the literature of studies that have focused on specific molecules in irrigated rice cultivation areas and the effect of pesticides used in rice fields on the oxidative stress of fish in a rice-fish system (Clasen et al. 2012; Clasen et al. 2018). Water and fish contamination in catchments with a predominance of tobacco cultivation (Bortoluzzi et al. 2006; Becker et al. 2009) as well as glyphosate contamination in areas with predominance of soy/corn/wheat cultivation under no-tillage has also been studied (Fernandes et al. 2018). However, the impact of pesticide contamination on more complex catchments with contrasting cultivation systems, such as the Guaporé River catchment, needs to be better understood in order to more holistically assess the effect of contamination generated by agricultural activities on aquatic systems. It is also important to evaluate a more diverse number of molecules and sampling strategies to generate information that can be used for river basin monitoring programs.

In 2018, 5.3×10^5 Mg of active ingredients of pesticides was applied in Brazil (IBAMA 2019). However, global estimates indicate that only 1% of applied amount reaches the target organisms. The remaining 99% of pesticides remains in the soil, water, and atmosphere, being eventually absorbed by non-target organisms (Zhang et al. 2011). The transport of pesticides from crops to other environmental compartments is mostly done by water through preferential flow and/or surface runoff. As a result, pesticides, especially polar and highly soluble ones, are found in surface and ground waters (Masiá et al. 2013).

The occurrence of pesticides in the aquatic environment has been reported worldwide (Fernandes et al. 2018; Schreiner et al. 2016; Michel et al. 2016; Masiá et al. 2013; Rabiet et al. 2010; Bortoluzzi et al. 2006 and Bortoluzzi et al. 2007). However, they are often found at concentrations below 1 $\mu g\ L^{-1}$, requiring the use of sensitive methods and equipment that achieve low detection limits (Terzopoulou and Voutsa 2016). Most analytical methods and grab water sampling techniques have limited ability to provide holistic assessment of exposure to pesticides (Petty et al. 2004). The monitoring of the Morcille stream (France) over a year confirmed that discrete sampling was not suitable for the accurate measurement of the level of exposure to pesticides in surface waters, stating that grab sampling largely underestimated pesticide concentrations and fluxes transiting through the stream (Rabiet et al. 2010).

An alternative is to employ passive sampling devices like the Polar Organic Chemical Integrative Sampler (POCIS). Theory and modelling about passive samplers have been largely described elsewhere (Alvarez et al. 2005; Huckins et al. 1993; Stuer-Lauridsen 2005; Vrana et al. 2005; Morin et al. 2012; Ibrahim et al. 2013; Bayen et al. 2014). There is evidence that the accumulation of target compounds by POCIS is a dynamic process, with adsorption and desorption on the sorbent occurring in response to ambient levels of the target compounds in water (Metcalfe et al. 2014). Hence, the POCIS is a passive sampling technology that has been developed to accumulate trace levels of pesticides to provide time-integrated average concentrations for individual compounds in water.

Metcalfe et al. (2019), using POCIS for monitoring the pesticides in several catchments in the Great Lakes in Ontario, make evident the relationship between frequency and concentration of many pesticides (2,4-D, atrazine, carbendazim, tebuconazole, and imidacloprid, especially) in watercourses and proportion of cropfields (soybean, corn, and wheat). The POCIS was more adequate than active sampling for pesticides present in very low concentration. Challis et al. (2018), also in Canada (Red River—Lake Winnipeg), showed that using POCIS was possible to estimate the main sources of pesticides (i.e., atrazine from the USA and neonicotinoid both from Canadian and the US agriculture fields) and signaled the time-scale concerning application and detection in surface water. Guibal et al. (2017), working in headwaters in two small catchments in France, aware to difficulty for monitoring the pesticides frequency and concentration fluctuation using active or passive sampling. They identified the three possible types of behavior (active >, =, and < POCIS) when compared grab and passive sampling in relation to pesticide concentration. We know that the time of concentration of agriculture hillslope catchment is very fast (from minutes to some hours) and the peaks of pesticide concentration occur only after a few days of the application time in the cropfields (Liess et al. 1999) and after, the pesticide concentration may be not detected in the water column. However, the use of POCIS allows the accumulation of compounds that persist at low concentrations in surface waters (Terzopoulou and Voutsa 2016; Metre et al. 2016). Moreover, it enables to decrease the high variability remaining when using grab sampling.

In this study, we compared the active and passive water sampling to evaluate the pesticides concentration in Guaporé River (Rio Grande do Sul State, Brazil) and its tributaries in order to understand the role of soil use and management on degree of contamination of surface water in the region.

Materials and methods

Catchment description

The Guaporé River catchment is located in the south of Brazil, Rio Grande do Sul State—between plane coordinates 420.900–366.400 mE and 6.874.286–6.772.536 mS, zone 22S. The Guaporé River, which is the main watercourse, is 153 km long and drains an area of 2,490 km^2. The average monthly flow rate was 31.3 m^3 s^{-1} in 2012 and 2013 (Scotto 2014). Sediment production in 2012 amounted to 390.2 Mg km^{-2} year^{-1}, and the average from 2000 to 2010 was estimated at 140 Mg km^{-2} year^{-1}, with runoff coefficient of up to 31% (Didoné et al. 2014).

The average annual temperature is 17.9 °C and average annual minimum and maximum temperatures are 12.6 and 24.7 °C, respectively (Cfa Köppen system). Average annual rainfall varies between 1,550 and 1,700 mm, but the annual minimum and maximum rainfall is 950 to 2,500 mm, respectively (BRASIL 1986). In this catchment, in previous studies conducted, it revealed that the rain events have high erosion potential (8,800 MJ mm ha^{-1} h^{-1} year^{-1}) (Didoné et al. 2014) with greater occurrence from July to November (INMET 2019). The main soil classes, in the FAO Classification, are Acrisols (14.8%), Ferralsols (33.8%), Luvisols (24.9%), Regosols (3.1%), and Nitosols (23.3%).

In the upper third of the catchment, where the relief is nearly level to gently sloping and predominated by Ferralsols, the farmers are practicing the no-tillage system from past two decades. There is a very direct relationship between soybean (*Glycine max* L. Merr.) cultivation, livestock/swine, and poultry production in the catchment in spring/summer. The animals reside in marginal non-cultivated areas, generally and along the watercourse. The farmers use high doses of herbicides and fungicides to soybean production, including the 2,4-D for resistant plant to glyphosate. The Nitosols covers almost 100% of the surface of Marau River tributary sub-catchment. In this area, family agriculture integrated to livestock, especially, production of corn silage in spring and summer and winter grasslands forage to milk production. In addition, almost all farmers have also swine and poultry production activities. In the Marau River tributary, there are 2.9 and 9.7 times corn and corn silage and − 1.3 times soybean density production (Mg km^{-2}) than in the source of Guaporé River.

In the other two-thirds (middle and lower) of the catchment, land use is more diverse and conventional soil management predominates in shallow soils with rocky surface (Luvisols, Acrisols, and Regosols). The cultivated surface is imbricated in landscape and the family farmers have less than 10 hectares. In this region, there are 1.3 and 1.6 times corn and corn silage and − 4.2 times soybean density production than in the upper third of the catchment. This region has the biggest density of tobacco (*Nicotiana* tabacum L.) and erva-mate (*Ilex paraguariensis* St. Hill) production of Brazil. There is also integrated poultry and pig farming systems as well as dairy farming. The main land use in this area is cropland (60.0%), natural forest (30.1%), pastureland (5.6%), forestry (3.1%), urban areas (0.6%), and water bodies (0.4%) (Fig. 1).

Sampling sites

Eighteen sampling sites were selected, located in the Guaporé River (G1, G2, G3, G4, G5, G6, G7, G8, G9, and G10), Marau Stream Tributary (M1, M2, M3, and M4), Lajeado Carazinho Stream Tributary (LC1, LC2, and LC3), and Carazinho Sream Tributary (C1). Descriptions of each site and locations are shown in Table 1 and Fig. 1, respectively.

Active water sampling

The water sampling was performed between 11 and 13 December 2014, after a high precipitation event (89 mm—INMET 2019). The soybean was in the V3 stage, the corn

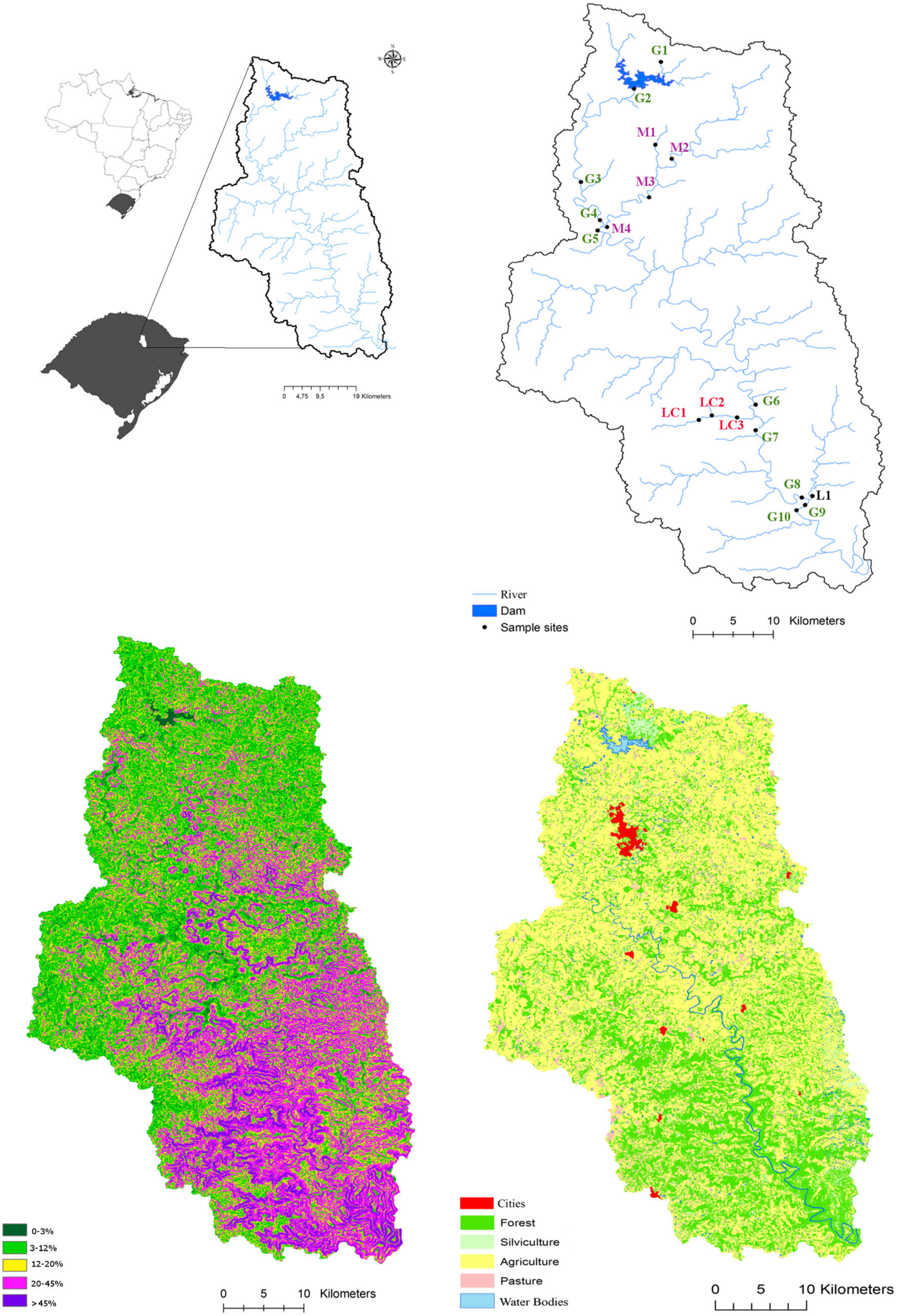


Fig. 1 Characteristics of area and location of the sampling sites in the Guaporé River and its tributaries (RS – Brazil)

Table 1 Catchment area, land use, and slope class at the different sampling sites in the Guaporé River and its tributaries

	Upper region								
Sample sites	G1	G2	G3	G4	G5	M1	M2	M3	M4
Catchment area (km^2)	1.3	123	201	267	542	13.4	165	227	256
Distance (km)	0	6	23	32	35	–	0	10	23
	Land use (%)								
Forest	100	28	24	23	22	22	20	21	22
Agriculture	0	64	69	71	70	72	74	72	72
Width riparian forest (m)	> 800	15–60	15	15	15	15	15	15	15
	Slope class (%)								
0–3%	5	10	9	8	7	6	7	6	6
3.1–12%	49	60	59	58	57	56	60	57	56
12.1–20%	35	22	23	23	24	25	23	24	24
20.1–45%	12	8	9	10	11	13	9	12	13
> 45%	0	0	0	0	1	0	0	1	1
	Middle/lower region								
Sample sites	G6	G7	G8	G9	G10	LC1	LC2	LC3	C
Catchment area (km^2)	1442	1505	1697	1850	1853	30	3.2	39	144
Distance (km)	85	90	106	108	110	0	–	3.2	0
	Land use (%)								
Forest	27	28	31	32	32	50	61	52	46
Agriculture	67	66	62	61	61	42	32	40	50
Width riparian forest (m)	15	> 60	> 100	> 100	> 100	> 100	15	> 100	> 100
	Slope class (%)								
0–3%	6	5	5	5	5	4	1	3	2
3.1–12%	47	45	42	41	41	34	10	28	23
12.1–20%	24	24	23	23	23	24	20	22	27
20.1–45%	21	22	24	26	26	29	53	34	43
> 45%	3	4	5	5	5	10	17	14	5

was in R1 stage, and the first leaf of flue cured tobacco was harvest. The bottles were cleaned with neutral detergent and HNO_3 10% for 12 h and after with osmotic water and methanol. One liter of water was stored in an amber bottle, maintained at 4 °C in thermic boxes, and transported to Pesticides Residues Analysis Laboratory of Federal University of the Santa Maria, in Brazil.

Passive sampling—Polar Organic Chemical Integrative Sampler

The samplers were made of 316 stainless steel with the following dimensions: 102 × 54 × 3 mm (outside diameter, inside diameter, and thickness); containing five 7-mm holes, two on the central axis, 6 mm from the inner edge, and three in the shape of an equilateral triangle with 67.5-mm sides. SUPOR® Polyethersulfone filtering membrane with 0.1-μm pores and 90-mm diameter (Petty et al. 2002) was used. The sorbent is consisted of 200 mg of OASIS® HLB resin (30-μm particle diameter) with hydrophilic and lipophilic balance.

Such devices were installed at the sampling sites in June 2015, fixed to be submerged during 15 days, and protected by an iron box with an aluminum screen to allow water flow and act as a physical barrier against branches and stones. After 14 days of exposure, the POCIS was collected, cleaned, packaged wrapped with aluminum foil, arranged in plastic bags in a cooler with ice, and transported to the laboratory. In this period, less than 1/5 of the total agricultural surface is cultivated with wheat, barley, and winter grasslands forage. There is a very low rate of pesticide application, comparatively to spring/summer season.

Analytical procedure

In the laboratory, the pesticides present in water samples were extracted on Solid-Phase Extraction using 200 mg of adsorbing Strata X cartridge. The pesticide determination was performed in an Ultra High-Performance Liquid Chromatography, tandem mass spectrometry Acquity UPLC® pump with the triple quadruple Xevo TQ® (Waters). The mass spectrometer was operating in selected reaction monitoring using an electrospray source positive ionization. Seventy-nine pesticides were monitored: 2,4-D, atrazine, azinphos-ethyl, azinphos-methyl, azoxystrobin, bentazone, bispyribac sodium, bitertanol, boscalid, bromoconazole, buprofezin, carbaryl, carbendazim, carbofuran, carborfuran-3-OH, carboxin, cianazin, chlorimuron, chlorpyriphos-éthyl, chlorpropham, diazinon, dichlofluanid, difenoconazole, dimethoate, epoxiconazole, fenpropathrin, fenpropimorph, fenarimol, fenthion, fipronil, fluquiconazol, fluroxypyr, flutolanil, imazalil, imidacloprid, iprovalicarb, linuron, malathion, mecarbam, mepronil, metalaxyl, metconazole, methiocarb sulfone, methiocarb sulfoxide, metsulfuron-methyl, mevinphos, myclobutanil, monocrotophos, monolinuron, oxamyl, paraoxon-ethyl, pendimethalin, pyraclostrobin, pyrazophos, pyrridiphention, pyrimethanil, pyrimicarbe, pirimiphos-methyl, profenofos, propiconazole, propyzamide, propoxur, quinclorac, quinoxyfen, simazine, tebuconazole, terbufos, tetraconazole, thiacloprid, thiamethoxam, thiodicarbe, tolclofos-methyl, triadimefon, triadimenol, triazofos, trichlorfon, trifloxystrobin, triflumizole, and vamidothion.

The POCIS adsorbent material was transferred to cartridges with the aid of ultrapure water, then dried first under vacuum in a SPE manifold with N_2 flow. Elution of the cartridges was done on a Thermo Scientific™ Dionex™ AutoTrace™ 150 Solid-Phase Extraction system with methanol. The extracts were evaporated under N_2 flow and then reconstituted in 500 μL of a methanol: water (10:90, v/v) mixture. This method has been successfully used for elution of POCIS in a previous study. For quantification purposes, the standard curve method was used with all the pesticides under examination at concentrations of 0, 5, 10, 15, and 20 $\mu g\ L^{-1}$ of the methanol:water (10:90; v/v) mixture.

The analysis was carried out on an ultra-high-performance liquid chromatography (UHPLC) system (Thermo) with an electrospray source coupled to a quadrupole-time-of-flight mass spectrometer (Q-TOF) (Brucker). Three injections of 20 μL in positive and negative mode for each extract were done. Data processing and treatment were done using Compass Data Analysis 4.2 and Target Analysis software. The presence of each compound was confirmed according to three criteria: the exact mass and the mass spectrum of the compound compared with the exact mass and the mass spectrum of a certified standard solution of this compound, and the retention time determined in the analytical conditions.

The concentration of pesticides adsorbed in POCIS resin was carried out by adjusting the linear model used between the concentration of the standards and the peak area of each injection for each compound detected. Detection limits were calculated from the standard derivation of calibration curves. Due to variability for each compound, an over evaluated value of 1 $\mu g\ L^{-1}$ was considered. A total of 23 compounds were analyzed, namely 2,4-D, atrazine, boscalid, carbendazim, chlorotoluron, chlorpyriphos-éthyl, deethyl-atrazine, dicamba, epoxiconazole, imidacloprid, iodosulfuron-methyl-sodium, isoproturon, MCPA, mesotrione, mesosulfuron-methyl, metconazole, nicosulfuron, prochloraz, prosulfuron, prothioconazole, simazine, tebuconazole, thifensulfuron-methyl. To evaluate the time average concentration of waters, Rs value from literature was used (Fauvelle and Mazzella 2014 (2,4-D = 0.08), Mazzella et al. 2010 (atrazine = 0.24; deethylatrazine = 0.17; simazine = 0.21), Ahrens et al. 2015 (carbendazim = 0.22; epoxiconazole = 0.17; imidacloprid = 0.18; thifensulfuron-methyl = 0.02; mesosulfuron-methyl = 0.06), Belles et al. 2013 (tebuconazole = 0.19; prosulfuron = 0.12), and Mazzella et al. 2007 (nicosulfuron = 0.04)). All data regarding development of analytical methods are available in supporting material.

Potential ecological risk

The predicted no effect concentration of each pesticide was calculated by dividing the concentration obtained in the literature responsible for causing some physiological damage or death of the standard species by an evaluation factor (EMEA 2006). In this study, we assess the potential ecological risk for two species: (i) *Daphinia magna*, which is a crustacean used worldwide in ecotoxicological tests because of its sensitivity to environmental changes, and (ii) silver catfish (*Rhamdia quelen*), a fish commonly found in rivers in the southern region of Brazil. For *Daphinia magna* M., the critical concentrations found in the literature were 2,4-D = 25.0 $mg\ L^{-1}$ (Toussaint et al. 1995); atrazine and deethyl-atrazine = 50.4 $mg\ L^{-1}$ (Moreira et al. 2014); simazine = 4.2 $mg\ L^{-1}$ (Arufe et al. 2004); carbendazim = 0.005 $mg\ L^{-1}$ (Silva et al. 2015); tebuconazole = 40.1 $mg\ L^{-1}$ (Sancho et al. 2009); and imidacloprid = 96.0 $mg\ L^{-1}$ (Loureiro et al. 2010). For silver catfish, the critical concentrations found in the literature were 2,4-D = 0.20 $mg\ L^{-1}$ (Glusczak et al. 2007); atrazine and deethyl-atrazine = 10.2 $mg\ L^{-1}$; simazine = 8.9 $mg\ L^{-1}$; tebuconazole = 4.8 $mg\ L^{-1}$ (Kreutz et al. 2008); carbendazim = 1.5 $mg\ L^{-1}$ (Sridhar and Joice 2012); imidacloprid = 78.0 $mg\ L^{-1}$ (Tyor and Harkrishan 2016). The evaluation factor values were set at 1000, according to the suggestion of the European Commission Technical Guidance Document and Guidelines for the Implementation of REACH (2006). The potential ecological risk (RQ_i) for each pesticide studied and potential ecological risk mix (RQ_{mix}) was quantified using the ratio between the measured environmental concentration and the predicted no effect concentration (Stehle and Schulz 2015; Di Lorenzo et al. 2018; Kienzler et al. 2019). The common risk ranking criteria are as follows: $0.01 < RQ < 0.1$ is considered low risk, $0.1 < RQ < 1$ is considered medium risk, and $RQ > 1$ is considered high risk (Hernando et al. 2006).

Statistical treatment

The Kolmogorov-Smirnov and Lilliefors tests were used to assess whether the concentrations of pesticides exhibited a normal distribution. As the results did not show normal distribution, the median was used as a measure of position, and the upper and lower quartiles, interquartile range, and maximum and minimum values as dispersion measures. The hypothesis that the systems of land use and management practiced in the northern and southern regions of the catchment contribute differently to the contamination of aquatic ecosystems by pesticides was statistically evaluated by the Mann-Whitney *U* nonparametric test.

Results and discussion

Grab water sampling

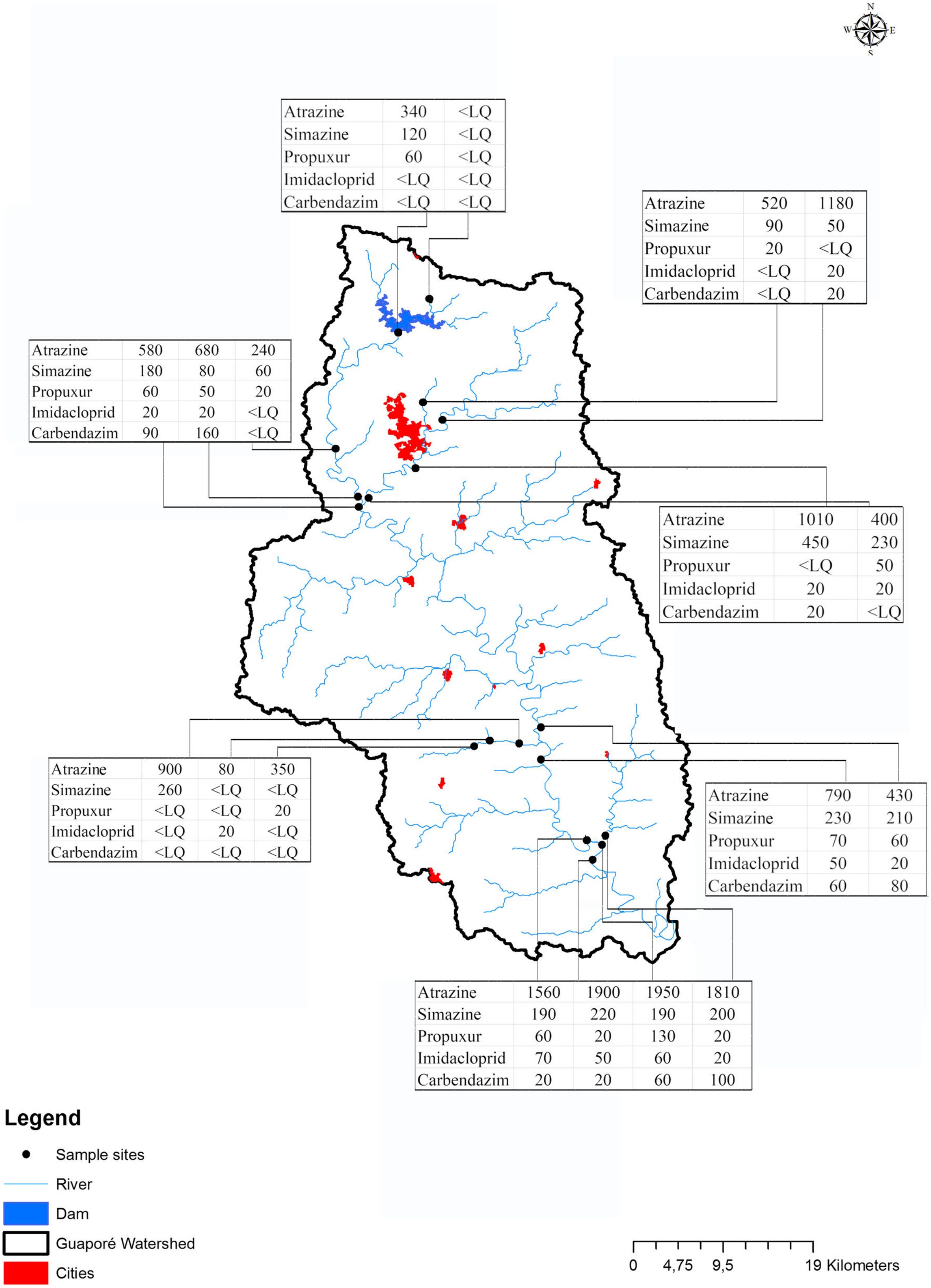
None of the water samples collected from the National Forest contained pesticide residues. However, all others 17 water samples were contaminated with at least one pesticide. Of the 79 monitored pesticides, 11 were detected in the water samples (atrazine, simazine, propoxur, imidacloprid, carbendazim, azoxystrobin, thiamethoxam, fipronil, propiconazole, tebuconazole, and carbofuran) (Fig. 2).

The two representative triazines pesticides (atrazine and simazine) were detected, respectively, in 94 and 89% of samples collected in Guaporé River and its tributaries (Table 2). It shows that this pesticides' class (high log K_{ow} 2.3–2.7 and low solubility 3.5–5.0 mg L^{-1}, Lewis et al. 2016) is systematically transferred to the superficial watercourses in Brazilian agroecosystems (Armas et al. 2007; Azevedo et al. 2010; Moreira et al. 2012) and can be persisted in the water and aquatic biota (Jablonowski et al. 2009; Bohn et al. 2011). These herbicides are, respectively, 3 and 6 most used in southern Brazil (IBAMA 2019). The 2,4-D was not detected despite its indiscriminate use (only surpassed by glyphosate) in Brazil and southern Brazil (57.4 and 14.8 Mg in 2017, respectively), due to its physicochemical properties (low K_{ow} − 0.82; high solubility 24.3 g L^{-1} and low half life time 4.4 days, Lewis et al. 2016). The 2,4-D transfer in the fluvial network is conditioned to the time of application and intensity of rainfall, which changes the speed and flow of rivers. The active sampling is more adequate to detect this type of pesticides (Silva et al. 2014).

The water of Guaporé River and its tributaries contain many insecticides (carbamates: propoxur and carbofuran; nicotinoids: imidacloprid and thiamethoxam; and pyrazole: fipronil). The neonicotinoids were detected in about 50% of water samples and confirm previous data published with superficial water monitored near to the Guaporé catchment (Bortoluzzi et al. 2006 and Bortoluzzi et al. 2007; Sequinatto et al. 2013). The neonicotinoid pesticides use increased in the last two decades in about 120 countries in order to replace the organophosphates and carbamates insecticides (Jeschke et al. 2010), in contrast to interdiction in European Union after 2018. The systemic pesticides replace the contact pesticides with very active periods within the plant and act against sucking insects, but also against beneficial insects such as bees. In southern Brazil, the imidacloprid consummation increased eight times between 2009 and 2017 (IBAMA 2019), and it has a very high potential for increased consumption because organophosphate is still seven times more consumed than neonicotinoids. Indeed, in 78% of water samples, we detected propoxur insecticide, which is recommended to use in animals' production. Moreover, the Guaporé catchment represents the highest concentration of swine and poultry in Brazil (FEE 2019). Its low capacity of adsorption to colloids ($K_{oc} = 30$ mL g^{-1} and log $K_{ow} = 0.14$), high solubility (1800 g L^{-1}), and high half life time (180 days) make the propoxur very disperse in surface watercourse.

The fungicides were detected in 11 monitored sites, especially those used in soybean production, such as the carbendazim (moderate $K_{oc} = 225$ L kg^{-1}, low $K_{ow} = 1.48$, and high half life time = 350 days). While Singh et al. (2016) warned that this insecticide was banned in developed countries (Australia and most European countries), in Brazil, its consumption is still extremely high (3.7 Mg in 2017—IBAMA 2019).

The highest pesticide concentration and variability between monitored sites were observed for pesticides with the highest frequency of occurrence in Guaporé River and its tributaries (Fig. 2). The median concentration of atrazine and simazine was the highest among the pesticides monitored (680 and 190 ng L^{-1}) and have also the highest spatial variability interquartile range (IQR of 1,000 and 150 ng L^{-1}), and with 75% of concentration higher than 380 and 90 ng L^{-1}, respectively. For carbendazim, propoxur, imidacloprid, and thiamethoxam, analyses showed that 75% of the concentration was lower than 80, 60, 50, and 15 ng L^{-1} for, respectively. According to Brazilian legislation (BRASIL 2005), the water from all monitored sites in Guaporé River catchment has been classified as "Special Class" and can be consumed by humans after a disinfection treatment. This classification allows the presence of glyphosate (65 μg L^{-1}), alachlor (20 μg L^{-1}), metolachlor (10 μg L^{-1}), 2,4-D (4 μg L^{-1}), atrazine (2 μg L^{-1}), and simazine (2 μg L^{-1}). Comparing pesticide concentrations obtained by grab sampling with the values allowed by the Brazilian legislation, all sites could be used as a source of water for a drinking water treatment station. However, this legislation is very permissive when compared with other countries, for



Atrazine	340	<LQ
Simazine	120	<LQ
Propuxur	60	<LQ
Imidacloprid	<LQ	<LQ
Carbendazim	<LQ	<LQ

Atrazine	520	1180
Simazine	90	50
Propuxur	20	<LQ
Imidacloprid	<LQ	20
Carbendazim	<LQ	20

Atrazine	580	680	240
Simazine	180	80	60
Propuxur	60	50	20
Imidacloprid	20	20	<LQ
Carbendazim	90	160	<LQ

Atrazine	1010	400
Simazine	450	230
Propuxur	<LQ	50
Imidacloprid	20	20
Carbendazim	20	<LQ

Atrazine	900	80	350
Simazine	260	<LQ	<LQ
Propuxur	<LQ	<LQ	20
Imidacloprid	<LQ	20	<LQ
Carbendazim	<LQ	<LQ	<LQ

Atrazine	790	430
Simazine	230	210
Propuxur	70	60
Imidacloprid	50	20
Carbendazim	60	80

Atrazine	1560	1900	1950	1810
Simazine	190	220	190	200
Propuxur	60	20	130	20
Imidacloprid	70	50	60	20
Carbendazim	20	20	60	100

Fig. 2 Pesticides concentration (ng L-1) in Guaporé River and its tributaries in a representative southern Brazilian catchment with grab sampling

example, France law. In France, the quality limits for raw water of any origin used for the production of water, intended for human consumption, are limited to 2 μg L^{-1} for individual concentrations and 5 μg L^{-1} for the sum of pesticides. Based on this, if these values were compared with the France legislation, the grab samples satisfied these criteria. Nevertheless,

Table 2 Frequency of pesticide detection (%) in Guaporé River and its tributaries using grab and passive (Polar Organic Chemical Integrative Sampler) water sampling

Active ingredient	Frequency of detection (%)	
	Grab sampling	POCIS
Herbicides		
2,4-D	0	100
Atrazine	94	100
Deethyl-atrazine	NA	100
Simazine	89	94
Mesotrione	NA	31
Thifensulfuron-methyl	NA	31
Nicosulfuron	NA	25
Mesosulfuron-methyl	0	19
Prosulfuron	NA	12
Fungicides		
Carbendazim	56	100
Azoxystrobin	33	NA
Propiconazole	17	NA
Tebuconazole	11	75
Epoxiconazole	0	50
Insecticides		
Imidacloprid	67	75
Propoxur	78	NA
Thiamethoxam	33	NA
Fipronil	28	NA
Carbofuran	6	NA

NA not analyzed

POCIS sampling exhibited that pesticide concentration values are largely above restrictive limits of French law.

Passive sampling—Polar Organic Chemical Integrative Sampler

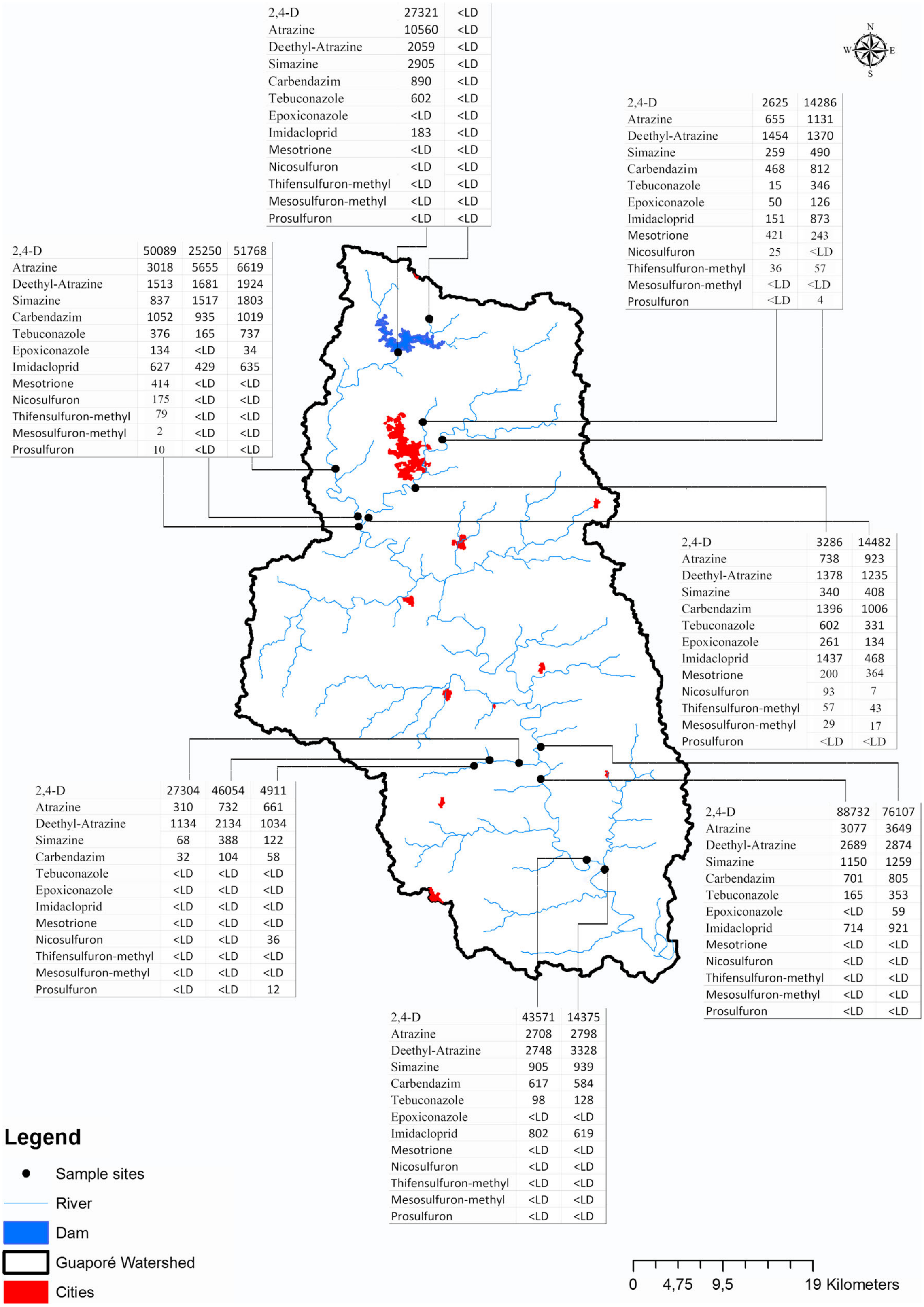
The use of POCIS enabled the detection of 2,4-D, atrazine, deethyl-atrazine, simazine, carbendazim, tebuconazole, epoxiconazole, imidacloprid, mesotrione, nicosulfuron, thifensulfuron-methyl, mesosulfuron-methyl, and prosulfuron in the waters of the Guaporé River and its tributaries (Table 2 and Fig. 3). All the sampling sites showed the presence of at least four of the 23 pesticides monitored, except in the National Forest site.

The uses of POCIS indicate that the pesticides, even months after their use, were transferred and detected in river ecosystems, in periods with low concentration. Therefore, the use of POCIS could avoid the problem of false negatives common in times of low pesticide use in agricultural fields, periods of low rainfall intensity, and/or high rate. The POCIS exposed for 14 days provided the accumulation of the pesticides present in the water of the Guaporé River and its tributaries to such an extent that it enabled its quantification active sampling. These results have been evidenced in several studies evaluating the occurrence of organic contaminants such as pesticides, polychlorinated biphenyls, flame retardants, and pharmaceuticals (Alvarez et al. 2005; Dalton et al. 2014; Schopfer et al. 2014; Martínez Bueno et al. 2016; Gonzalez-Rey et al. 2015). This displays the relevance of this tool for assessing the water quality compared to the traditional sampling system. The frequency of quantification of atrazine, deethyl-atrazine, azoxystrobin, epoxiconazole, imidacloprid, simazine, and tebuconazole in the waters was systematically enhanced with the use of POCIS (Poulier et al. 2014). These results suggest that the contamination of Brazilian waters is being underestimated when using “active” grab water sampling.

Among the herbicides, triazines (atrazine, deethyl-atrazine, and simazine), and aryloxyalkanoic acid (2,4-D), chemical groups were detected in 94 to 100% of the sampled sites, respectively (Table 2). After glyphosate (IBAMA 2019), the 2,4-D, atrazine, and simazine are the most widely used pesticides in southern Brazil and in the Guaporé River catchment. Fernandes et al. (2018) showed that epilithic biofilms occurring in Guaporé River catchment were impregnated by glyphosate (10 to 305 $\mu g\ kg^{-1}$) and metabolite AMPA (50 to 670 $\mu g\ kg^{-1}$) and are strongly influenced by the amount of herbicide applications. In general, the use of these compounds begins in June with the preparation of areas for the sowing of wheat and extends through January with the end of the corn and soybean planting season. The highest application volume is concentrated between the months of October and January, including for the other spring/summer cultures like tobacco and bean (*Phaseolos vulgaris* L.). Between January and June, the use of insecticides and fungicides is higher than the herbicide periods of vegetative and reproductive development of soybean and corn. The POCIS captured mesotrione, nicosulfuron, thifensulfuron-methyl, mesosulfuron-methyl, and prosulfuron only in the Marau tributary sites and upstream of the Lageado Carazinho tributary. These herbicides were recommended and used in corn and grasslands forage production.

The POCIS was also effective in detecting some fungicides in the Guaporé River network. Fungicides of the benzimidazole and triazole groups (in descendant order, carbendazim, tebuconazole, and epoxiconazole) are those with the highest occurrence (Fig. 3 and Table 2). However, anilide, imidazolecarboxamide, and triazolinethione groups were not detected.

Imidacloprid was detected in 75% of the sampling sites of the Guaporé River and its tributaries (Table 2). Conversely, chlorpyrifos (organophosphate) was not detected in the water of any of the sampling sites. This most likely happened due to its high octanol-water partition coefficient ($K_{ow} = 4.7$), which



2,4-D	27321	<LD
Atrazine	10560	<LD
Deethyl-Atrazine	2059	<LD
Simazine	2905	<LD
Carbendazim	890	<LD
Tebuconazole	602	<LD
Epoxiconazole	<LD	<LD
Imidacloprid	183	<LD
Mesotrione	<LD	<LD
Nicosulfuron	<LD	<LD
Thifensulfuron-methyl	<LD	<LD
Mesosulfuron-methyl	<LD	<LD
Prosulfuron	<LD	<LD

2,4-D	2625	14286
Atrazine	655	1131
Deethyl-Atrazine	1454	1370
Simazine	259	490
Carbendazim	468	812
Tebuconazole	15	346
Epoxiconazole	50	126
Imidacloprid	151	873
Mesotrione	421	243
Nicosulfuron	25	<LD
Thifensulfuron-methyl	36	57
Mesosulfuron-methyl	<LD	<LD
Prosulfuron	<LD	4

2,4-D	50089	25250	51768
Atrazine	3018	5655	6619
Deethyl-Atrazine	1513	1681	1924
Simazine	837	1517	1803
Carbendazim	1052	935	1019
Tebuconazole	376	165	737
Epoxiconazole	134	<LD	34
Imidacloprid	627	429	635
Mesotrione	414	<LD	<LD
Nicosulfuron	175	<LD	<LD
Thifensulfuron-methyl	79	<LD	<LD
Mesosulfuron-methyl	2	<LD	<LD
Prosulfuron	10	<LD	<LD

2,4-D	3286	14482
Atrazine	738	923
Deethyl-Atrazine	1378	1235
Simazine	340	408
Carbendazim	1396	1006
Tebuconazole	602	331
Epoxiconazole	261	134
Imidacloprid	1437	468
Mesotrione	200	364
Nicosulfuron	93	7
Thifensulfuron-methyl	57	43
Mesosulfuron-methyl	29	17
Prosulfuron	<LD	<LD

2,4-D	27304	46054	4911
Atrazine	310	732	661
Deethyl-Atrazine	1134	2134	1034
Simazine	68	388	122
Carbendazim	32	104	58
Tebuconazole	<LD	<LD	<LD
Epoxiconazole	<LD	<LD	<LD
Imidacloprid	<LD	<LD	<LD
Mesotrione	<LD	<LD	<LD
Nicosulfuron	<LD	<LD	36
Thifensulfuron-methyl	<LD	<LD	<LD
Mesosulfuron-methyl	<LD	<LD	<LD
Prosulfuron	<LD	<LD	12

2,4-D	88732	76107
Atrazine	3077	3649
Deethyl-Atrazine	2689	2874
Simazine	1150	1259
Carbendazim	701	805
Tebuconazole	165	353
Epoxiconazole	<LD	59
Imidacloprid	714	921
Mesotrione	<LD	<LD
Nicosulfuron	<LD	<LD
Thifensulfuron-methyl	<LD	<LD
Mesosulfuron-methyl	<LD	<LD
Prosulfuron	<LD	<LD

2,4-D	43571	14375
Atrazine	2708	2798
Deethyl-Atrazine	2748	3328
Simazine	905	939
Carbendazim	617	584
Tebuconazole	98	128
Epoxiconazole	<LD	<LD
Imidacloprid	802	619
Mesotrione	<LD	<LD
Nicosulfuron	<LD	<LD
Thifensulfuron-methyl	<LD	<LD
Mesosulfuron-methyl	<LD	<LD
Prosulfuron	<LD	<LD

Fig. 3 Pesticides concentration (ng L-1) in Guaporé River and its tributaries, a representative southern Brazilian catchment, obtained by Polar Organic Chemical Integrative Sampler

ensures higher retention of these compounds in nonpolar matrices, reducing its concentration in solution and consequently reducing its exposure to the POCIS and its detection in water samples. Therefore, chlorpyrifos was not sequestered in the POCIS because of the reduced exposure time of the POCIS in the field, since it is commonly used by farmers (IBAMA 2019). The uptake of less polar compounds (log $K_{ow} >$ 3.7) is strongly influenced by the exposure time of the POCIS (Silva et al. 2014). This characteristic, in addition to affecting the availability of the concentration in solution, also affects the diffusion of these pesticides between the two phases: from membranes with 0.1 μm porosity to the adsorbent.

In the box plots (Fig. 4), the median location in the interquartile range of the pesticides confirms the results obtained by the Kolmogorov-Smirnov and Lilliefors tests that the data is unlikely to present normal distribution. Therefore, they are presented with the median, quartiles, minimum, and maximum values.

The herbicide class showed a higher concentration in the Guaporé River waters. 2,4-D stands out for two reasons, such as (i) exhibited greater spatial variability between monitored points denoted in the IQR of 41,786 ng L^{-1} and (ii) the value of the first quartile was similar or higher than the values of the third quartile of other compounds analyzed in this study. Atrazine had a median of 1,905 ng L^{-1}, an IQR of 2,857 ng L^{-1}, and 75% of the observations were at concentrations below 655 ng L^{-1}, five times less than the values found for 2,4-D. The lowest values found were of simazine, which presented median, IQR, and first quartile values approximately 3 times lower than those of atrazine. The metabolite deethyl-atrazine showed similar behavior to simazine, but with higher amount accumulated in the POCIS sorbent.

Among the fungicides, the variability between compounds and between the sampling sites was lower compared to the herbicides (Fig. 4). For the median, IQR, and first quartile values, the highest concentrations of fungicide present in the waters of the Guaporé River and its tributaries were (in downward order) carbendazim, tebuconazole, and epoxiconazole. Contrary to the herbicides, 75% of the values for these three fungicides are below 994, 368, and 109 ng L^{-1}. The interquartile range of carbendazim was 792 ng L^{-1}, approximately 2.5 and 9.4 times than those of tebuconazole and epoxiconazole, respectively. Imidacloprid, the only representative of the insecticide class concentrated by the POCIS, was present in 75% of the sampled sites with concentrations below 786 ng L^{-1}, whose median was 548 ng L^{-1} and the maximum concentration was 1,429 ng L^{-1} in the Guaporé River catchment.

Although the use of the POCIS shows promise in improving the contaminant detection system in river waters, there are gaps of knowledge that must be overcome in order to obtain more realistic values of the concentration in the water derived from the amount sequestered, as well as for comparative purposes in each study and between studies. One of the issues is the lack of a method to satisfactorily correct *in situ* exposure conditions (water flow rates, temperature, pH, incrustation, etc.), which are known to affect the uptake rates of more polar compounds (Harman et al. 2011 and Harman et al. 2012). Another factor is related to the variability in the retention of pesticides in the membranes that protect the adsorbent. The study of Lissalde et al. (2014) showed that depending on the speed of water (3 to 13 cm s^{-1}) between the sampled rivers and the tested compound, the accumulation in the membrane may vary from 3 to 60% of the total concentration sequestered by the membrane/adsorbent.

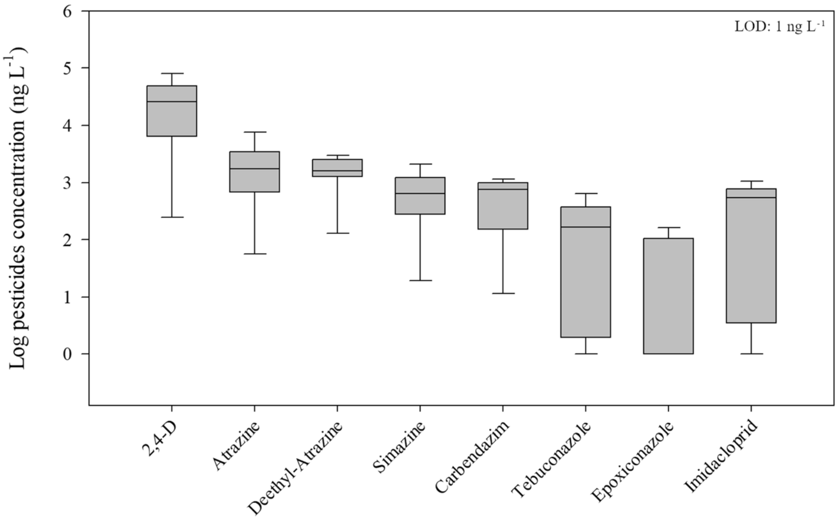


Fig. 4 Boxplot of the pesticide concentrations detected in the Guaporé River catchment. Median concentrations, interquartile amplitude (1st and 3rd quartile), and minimum and maximum values obtained using POCIS (n = 16)

For more nonpolar compounds (log $K_{ow} > 3$), these limitations were overcome using performance reference compounds. This was possible due to its dissipation following first order kinetics to the uptake kinetics and could therefore be used to estimate the sampling rates of target compounds *in situ* (Harman et al. 2011 and Harman et al. 2012; Booij et al. 1998). For the more polar compounds such limitations persist, there is a relationship between the flow rate and the reference compounds desorption, especially for speeds higher than 4 cm s^{-1} (Lissalde et al. 2014). However, the concentrations of 2,4-D, atrazine, carbendazim, simazine, imidacloprid, and tebuconazole were higher than the highest concentrations (Metre et al. 2016) reported in previous studies, except for deethyl-atrazine, which presented lower concentrations than those found by Lissalde et al. (2014).

If the interfering factors presented by Harman et al. (2011) are minimized, the higher intensity in pesticide use in southern Brazil associated with reduced adsorption of soil and water conservation practices will be the main differing factors among the reviewed studies. This hypothesis is based on soil and climate characteristics (high levels of soil organic matter and 2:1 clay mineral, and temperate climate) of the studied regions. Thus, reduced rates of physicochemical degradation of pesticides in the soil were expected, resulting in a higher pesticide load on water resources. In regard to deethyl-atrazine, Lissalde et al. (2014) presented neither justification for the high values found in comparison to other compounds or other studies, nor did they present sufficiently relevant environmental conditions to justify such behavior.

Table 3 Potential ecological risk for *Daphinia magnum* (M.) and *Rhamdia quelen* (Teleostei) by pesticides detected in Guaporé River and its tributaries

Site	*Daphinia magnum* (M.)			*Rhamdia quelen* (Teleostei)		
	RQ_{mix}	2,4-D	Carbendazim	RQ_{mix}	2,4-D	Carbendazim
Guaporé River						
G1	0.00	0.00	0.00	0.00	0.00	0.00
G2	179.97	1.09	177.92	138.30	136.61	0.01
G3	206.59	2.07	203.90	260.05	258.84	0.01
G4	188.54	1.01	187.01	127.19	126.25	0.01
G5	212.70	2.00	210.39	251.08	250.45	0.01
G6	164.53	3.04	161.04	381.41	380.54	0.01
G7	144.21	3.55	140.26	444.40	443.66	0.00
G8	125.45	1.74	123.38	218.53	217.86	0.00
G9	117.81	0.56	116.88	72.62	71.88	0.00
G10	93.72	0.10	93.51	13.37	13.13	0.00
Marau Tributary						
M1	163.09	0.57	162.34	71.82	71.43	0.01
M2	279.51	0.13	279.22	16.83	16.43	0.01
M3	202.03	0.56	201.30	72.75	72.41	0.01
M4	11.95	0.20	11.69	24.73	24.55	0.00
Lageado Carazinho Tributary						
LC1	22.77	1.84	20.78	230.59	230.27	0.00
LC2	7.63	1.09	6.49	136.67	136.52	0.00
LC3	22.77	1.84	20.78	230.59	230.27	0.00
Carazinho Tributary						
L1	7.63	1.09	6.49	136.67	136.52	0.00

Potential ecological risk

The surface water, generally, most of the sampling sites displayed low to medium ecological risk potential for the crustaceans *Daphinia magnum* and silver catfish by individual pesticides (Table 3). The 2,4-D and carbendazim concentrations could represent a huge risk of contamination than other pesticides, for silver catfish and crustaceans, respectively (RQ >>> 1, Hernando et al. 2006; Zeng et al. 2018). The access of these two pesticides can induce DNA damage and immobility and death to crustacean, respectively. Indeed, the 2,4-D can increase hepatic glycogen and reduce muscle glycogen (Glusczak et al. 2007) and carbendazim can cause the death of silver catfish (Sridhar and Joice 2012).

The cumulative potential risk (RQ_{mix}) for both species was null for watercourse in National Forest, and very low in the two tributaries monitored in middle/lower region of the catchment for crustaceans. In contrast, both Guaporé River and Marau tributary (upper region), the water represents a high ecological risk for the crustaceans and in all monitored site for silver catfish because of the high 2,4-D concentration. Becker et al. (2009), using juvenile silver catfish maintained in cage for 30 days in a high (high concentration in imidacloprid and clomazone) and low contaminated watercourse next to Guaporé catchment, showed that the plasma glucose and hepatic glycogen levels of fishes were lowered, but it increased the plasma K+ levels, values of hepatic glycogen, muscle lactate and protein of the kidney when exposed to water at the high than at low anthropic activity.

Generally speaking, sites with forests maintain a very low level of risk. For all other sites, the use of carbendazim exposes daphnia to a very high risk. For fish, the risk is associated with the presence of 2,4-D. However, as each species responds differently to a given molecule, it means that the ecosystem as a whole is threatened by the presence of pesticides in the water in Guaporé catchment due to the high anthropogenic pressure in the agricultural land.

Effect of agricultural use and management systems

It is known that in upper region prevails the transgenic soybean production in contrast to more diversified plant production in the middle/lower region (corn, tobacco, bean, etc.). In consequence, the type, doses, and period of pesticides application are different in these regions. However, there are no differences in the diversity and concentration of pesticides between the upper and middle/lower region of the Guaporé River catchment using grab sampling (Table 4). Punctual pulses of pesticides application are indeed detectable only at short period soon after its application. Moreover, the presence of natural barriers in the landscape will also be responsible for a decrease of pesticide transfer to river, because it reduces runoff connectivity to stream network. These combined phenomena may maintain the concentrations of pesticides in watercourses at levels that cannot be distinguished between the upper and the middle/lower region of the catchment.

Figure 5 presents the results of POCIS comparative analysis between the upper and middle/lower regions of the catchment by Mann-Whitney *U* test for each contaminant. No differences at $p < 0.06$ were found between the regions for 2,4-D, atrazine, deethyl-atrazine, simazine, epoxiconazole, and imidacloprid. However, we found that the distributions of the values of carbendazim, tebuconazole, and epoxiconazole are statistically different between the regions.

Nevertheless, the waters of the Guaporé River and its tributaries in the middle/lower region had the highest median concentrations for all herbicides (2,4-D, atrazine, deethyl-atrazine, and simazine) and lower concentrations for all fungicides (carbendazim, epoxiconazole, and tebuconazole) (Fig. 5). The variability of the median concentration between the two macro-regions was 30 to 120% for herbicides and 67 to 270% for fungicides. The highest values found of atrazine and simazine in the Guaporé River and its tributaries in the middle/lower region of the catchment are consistent with higher corn density (124 and 258% for grains and silage, respectively), compared to the upper region, where soybean predominates (300% more density). In general, herbicides (2,4-D, atrazine, deethyl-atrazine, and simazine) are more mobile in the environment (Lewis et al. 2016) and have higher concentrations in the waters of the river network compared to fungicides (carbendazim, epoxiconazole, and tebuconazole). This is due to the lower capacity of these herbicides to be adsorbed by colloids (low K_{oc} and low K_{ow} values), and therefore, they remain soluble in water and are easily transported during the occurrence of rainfall events of low to high intensity. They may even percolate into the soil profile and contaminate subsurface waters. Robinet et al. (2018), in a small sub-catchment in a Guaporé River catchment, showed that although the event rainfall is the main component for the surface runoff, and that the soil water is quickly displaced with new rainfall events in this agriculture catchment, there is also a significant contribution of deep groundwater to the streamflow.

Furthermore, the presence of five other herbicides (mesotrione, nicosulfuron, thifensulfuron-methyl, mesosulfuron-methyl, and prosulfuron) detected in the catchment was coherent with corn density. For example, Marau tributary and source of Guaporé River regions are neighboring, have even soil type, even relief, even soil management system, but differ sensibly in the soybean/maize ratio (191 and 870% more grain and silage corn density in Marau tributary) (FEE 2019).

In the upper region, the highest values of fungicides in the Guaporé River and its tributaries can be explained by conditions of agricultural use and management of the land. Soybean is the main crop in the spring/summer period, which preceded monitoring. The absence of crop rotation and the use of transgenic plants in 100% of the farms significantly increased the incidence of fungal disease and, consequently, the quantity and frequency of fungicide applications.

The discriminant function analysis was also used to verify which pesticides improve the discrimination of the established groups according to the predominant land use and soil

Table 4 Mann-Whitney *U* test for pesticides frequency in upper and middle/lower region in Guaporé River catchment (means and inter-quartile) with grab sampling

Pesticides	∑ Rank Upper	∑ Rank Middle/lower	U	Z	*p* level	Frequency Upper	Frequency Middle/lower
Atrazine	59.0	94.0	23.0	− 1.25093	0.2110	100	100
Simazine	71.5	81.5	35.5	− 0.04811	0.9616	100	100
Propoxur	67.0	86.0	31.0	− 0.48113	0.6304	75	78
Imidacloprid	56.5	96.5	20.5	− 1.49149	0.1358	62	78
Carbendazim	67.0	86.0	31.0	− 0.48113	0.6304	50	55
Azoxystrobin	73.5	79.5	34.5	0.14434	0.8852	37	33
Thiamethoxam	81.0	72.0	27.0	0.86603	0.3865	50	22
Fipronil	60.5	92.5	24.5	− 1.10659	0.2685	12	44
Propiconazole	68.5	84.5	32.5	− 0.33679	0.7363	12	22
Tebuconazole	64.0	89.0	28.0	− 0.76980	0.4414	0	22
Carbofuran	68.0	85.0	32.0	− 0.38490	0.7003	0	11

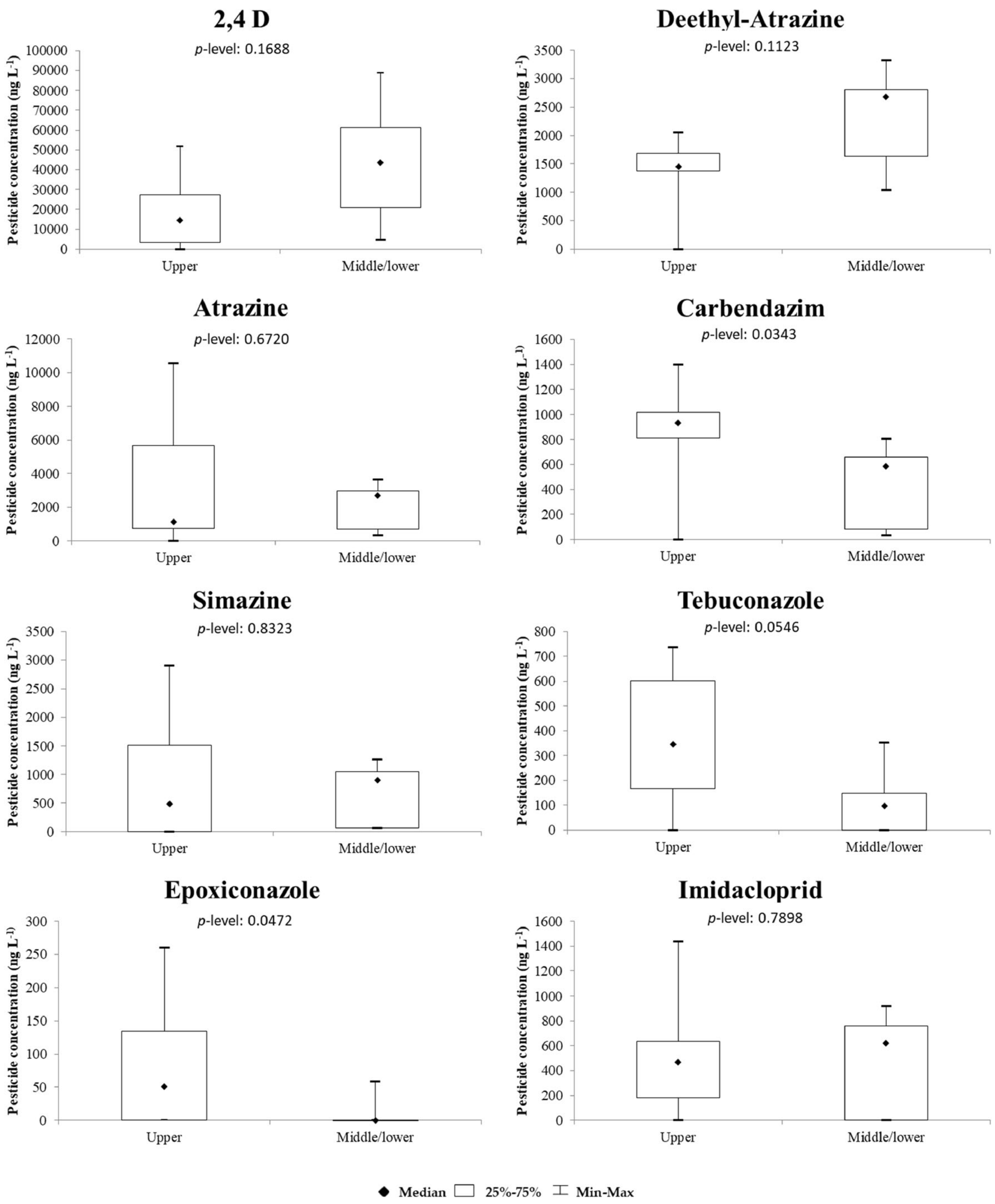


Fig. 5 Boxplot of the pesticide concentrations in the two regions of the catchment and results of the Mann-Whitney *U* test with Polar Organic Chemical Integrative Sampler

management systems. The eigenvalues and standardized coefficients for canonical variables are shown in Table 5. The calculated variance on the first and second axis was 100%, with eigenvalue of 7.7. Four variables were maintained in the model. However, only carbendazim (partial $\lambda = 0.19$, $F = 42.2$, and $p = 0.0001$), imidacloprid (partial $\lambda = 0.53$, $F = 8.9$, and $p = 0.0138$) followed by deethyl-atrazine (partial $\lambda = 0.68$, $F = 4.5$, and $p = 0.0593$) showed significant contributions (Table 5), and therefore, they confirm that the concentrations of these pesticides in the two regions were different. The values of tolerance (R^2) and 1-R^2 represent the correlation of the given variable with all other variables included in the model (Hair et al. 2009). Thus, the most informative variable is carbendazim ($R^2 = 0.14$). Samples from the upper region were well separated from middle/lower region samples along axis 1, and the average probability of uncertainty in the classification of the points was 0.31% and 0.00% in the upper and middle/lower regions, respectively. These results also indicate

Table 5 Results of the discriminant function analysis for regions, upper and middle/lower, in Guaporé River catchment

Pesticides	Wilks' lambda	Partial lambda	F- remove 1,10	*p* level	Tolerance 1- (R^2)	
	Variables in the model ($F_{4,10} = 19{,}256$)					
Carbendazim	0.600	0.191	42.217	0.0001	0.8563	
Deethyl-atrazine	0.167	0.688	4.526	0.0593	0.4332	
Imidacloprid	0.217	0.529	8.887	0.0138	0.8003	
2,4-D	0.140	0.823	2.149	0.1734	0.3367	
	Variables currently not in the model (Df for all *F* tests, 1.9)					
Atrazine	0.114	0.997	0.028	0.8699	0.6203	
Simazine	0.114	0.993	0.067	0.8020	0.6777	
Epoxiconazole	0.114	0.997	0.030	0.8666	0.7593	
Tebuconazole	0.115	0.998	0.020	0.8897	0.4954	
	Chi-square tests with successive roots removed					
Discriminant	Eigenvalue	Cum. prop	Canonicals roots	Wilks' lambda	Chi-sqr.	*p* level
Function 01	7.702	1.000	0.941	0.115	23.800	8.8×10^{-5}

that the molecules that most contributed to differentiate the regions were carbendazim, deethyl-atrazine, imidacloprid, and 2,4-D and, therefore, future studies on the impact of agricultural activities on pesticide contamination in southern Brazil should focus on these molecules.

In the upper region, 100% of the crops are conducted under no-tillage. However, these cropfields present conservationist efficacy compromised by the removal of physical barriers to surface water runoff, low addition of plant biomass, and insufficient soil cover. In this context, there is an increase in the susceptibility of contaminant transfer from terrestrial ecosystems to the aquatic ecosystem. Even if no-tillage reduces soil losses by more than 70%, water losses are practically similar to other soil cultivation systems (Londero et al. 2018). In this sense, several authors have emphasized the importance of resuming the adoption of terraces and increasing the density of soil cover for environmental conservation purposes (Cogo et al. 2003; Didoné et al. 2017; Merten et al. 2015). The distance between the crops and the river is very narrow (width riparian forest lower than 15 m). There is a high connectivity of erosive processes and the limited deposition of sediment in floodplains (Rheinheimer et al. 2017).

The least polar and highly persistent and reactive pesticides in the soil, such as tebuconazole and epoxiconazole, present in practically all monitored sites tend to be occasionally transported to water during rainfall events of high or low intensity. Longer distance and lower connectivity of crops with the river network are necessary conditions to maintain the quality of surface water, reducing the deposition of sediments and the water flow that drive the pesticides transport, both adsorbed and in solution, respectively. Catchment-scale connectivity is still a complex process of understanding and difficult to measure (Michaelides and Chappell 2009; Fryirs 2013; Koiter et al. 2013). However, it is known that in the middle/lower Guaporé catchment before reaching the water sources, the eroded sediments pass through successive processes of deposition and remobilization over time (Minella et al. 2014). Moreover, the small cultivated surface was imbricated in the landscape, and the watercourses were bordered by a great width riparian forest (60 to > 100 m), resulting an efficient barrier to sediment (Tiecher et al. 2017) and pesticides transfer to the surface water (Bortoluzzi et al. 2007), even of more accidently relief and conventional soil management.

Conclusions

Agriculture is a major sector of the Brazilian economy. One main priority of the Brazilian agricultural policy is to create conditions to increase production and improve the productivity of family farming. Consequently, the use of pesticides is widely favored to allow "modern intensive agriculture" also in rural areas. The results obtained in this study demonstrate that there is a high ecological risk of contamination with pesticides, indicating that the current agricultural production systems are contaminating the waters of the Guaporé River water and its tributaries, and highlighting that the current soil conservation practices are insufficient, even in the regions of the catchment where the use of no-till system predominates. The present work shows that the use of pesticides in rural catchments leads to the contamination of surrounding water resources. Thus, a very large variety of compounds was found in Guaporé River and its tributaries by grab or passive (POCIS) sampling, including 2,4-D, atrazine, simazine, deethyl-atrazine, carbendazim, epoxiconazole, tebuconazole, and imidacloprid. Furthermore, the sampling by POCIS highlighted that a discriminant role of land use (type of culture, slope of soils) on the pesticide contamination. Thus, flat areas grown with high soybean density in a no-till system had higher levels of fungicide. However, streams near fields with various agricultural plantations had a higher concentration of herbicides. The presence of five herbicides used in maize, grassland, and fodder production was linked to areas of integrated crop and livestock systems. In addition, the highest 2,4-D contamination was found in areas of intensive soybean and winter grain production. Facing the economic, social, sanitary, and environmental issues, reconciling growth and sustainability in Brazil's agricultural development model is more than ever needed to maintain agriculture and to preserve water resources.

Acknowledgements The authors acknowledge the following: Coordination for the Improvement of Higher Education Personnel (CAPES), Brazilian National Council for Scientific and Technological Development (CNPq), and Project "Mais Água" of FINEP/FEPAGRO/SEAPA-RS.

References

Ahrens L, Daneshvar A, Lau AE, Kreuger J (2015) Characterization of five passive sampling devices for monitoring of pesticides in water. J Chromatogr A 1405:1–11

Alvarez DA, Stackelberg PE, Petty JD, Huckins JN, Furlong ET, Zaugg SD, Meyer MT (2005) Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream. Chemosphere 61:610–622

Armas ED, Monteiro RTR, Antunes PM, Santos MAPF, Abakerli RB (2007) Diagnóstico espaço-temporal da ocorrência de herbicidas nas águas superficiais e sedimentos do rio Corumbataí e principais afluentes. Química Nova 30(5):1119–1127

Arufe MI, Arellano J, Moreno MJ, Sarasquete C (2004) Comparative toxic effects of formulated simazine on Vibrio fischeri and gilthead seabream (Sparus aurata L.) larvae. Chemosphere 57(11):1725–1732

Azevedo DA, Silva TR, Knoppersb BA, Schulz-Bullc D (2010) Triazines in the Tropical Lagoon System of Mundaú-Manguaba, NE-Brazil. J Braz Chem Soc 21(6):1096–1105

Bayen S, Segovia E, Loh LLLL, Burger DFDF, Eikaas HSHS, Kelly BCBC (2014) Application of Polar Organic Chemical Integrative Sampler (POCIS) to monitor emerging contaminants in tropical waters. Sci Total Environ 482:15–22

Becker AG, Moraes BS, Menezes CC, Loro VL, Rheinheimer DS, Reichert JM, Baldisserotto B (2009) Pesticide contamination of water alters the metabolism of juvenile silver catfish, Rhamdia quelen. Ecotoxicol Environ Saf 72:1734–1739

Belles A, Pardon P, Budzinski H (2013) Development of an adapted version of polar organic chemical integrative samplers (POCIS-Nylon). Anal Bioanal Chem 406(4):1099–1110

Bohn T, Cocco E, Gourdol L, Guignard C, Hoffmann L (2011) Determination of atrazine and degradation products in Luxembourgish drinking water: origin and fate of potential endocrine-disrupting pesticides. Food Addit Contam 28(8):1041–1054

Booij K, Sleiderink HM, Smedes F (1998) Calibrating the uptake kinetics of semipermeable membrane devices using exosure standars. Environ Toxicol Chem 17:1236–1245

Borrelli P, Robinson DA, Fleischer LR, Lugato E, Ballabio C, Alewell C, Meusburger K, Modugno S, Schutt B, Ferro V, Bagarello V, Van Oost K, Montanarella L, Panagos P (2017) An assessment of the global impact of 21st century land use change on soil erosion. Nat Commun 8(1):1–13

Bortoluzzi EC, Rheinheimer DS, Gonçalves CS, Pellegrini JBR, Zanella R, Copetti ACC (2006) Contaminação de águas superficiais por agrotóxicos em função do uso do solo numa microbacia hidrográfica de Agudo, RS. Rev Bra Engenharia Agríc Ambiental 10(4):881–887

Bortoluzzi EC, Rheinheimer DS, Gonçalves CS, Pellegrini JBR, Maroneze AM, Kurz MHS, Bacar NM, Zanella R (2007) Investigation of the occurrence of pesticide residues in rural wells and surface. Química Nova 30:1872–1876

BRASIL (1986) Projeto RADAMBRASIL, Folha SH. 22 Porto Alegre e parte das folhas SH. 21 Uruguaiana e SI. 22 Lagoa Mirim: geologia, geomorfologia, pedologia, vegetação, uso potencial da terra/ Fundação Instituto Brasileiro de Geografia e Estatística. IBGE, Rio de Janeiro, 796p

BRASIL (2005) Resolução do CONAMA nº 357, de 18 de março de 2005. Congresso Nacional, Brasília, DF

Challis JK, Cuscito LD, Joudan S, Luong KH, Knapp CW, Hanson ML, Wong CS (2018) Inputs, source apportionment, and transboundary transport of pesticides and other polar organic contaminants along the lower Red River, Manitoba, Canada. Sci Total Environ 635:803–816

Clasen BE, Loro VL, Cattaneo R, Moraes B, Lópes T, Avila AA, Zanella R, Reimche GB, Baldissertotto B (2012) Effects of the commercial formulation containing fipronil on the non-target organism *Cyprinus carpio*: implications for rice-fish cultivation. Ecotoxicol Environ Saf 77:45–51

Clasen BE, Loro VL, Murussi CR, Tiecher TL, Moraes B, Zanella R (2018) Bioaccumulation and oxidative stress caused by pesticides in *Cyprinus carpio* reared in a rice-fish system. Sci Total Environ 626:737–743

Cogo NP, Levien R, Schwarz RA (2003) Perdas de solo e água por erosão hídrica influenciadas por métodos de preparo, classes de declive e níveis de fertilidade do solo. Rev Bra Ciência Solo 27:743–753

Dalton RL, Pick FR, Boutin C, Saleem A (2014) Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS). Environ Pollut 189:134–142

Di Lorenzo T, Cifoni M, Fiasca B, Di Cioccio A, Galassi DMP (2018) Ecological risk assessment of pesticide mixtures in the alluvial aquifers of central Italy: toward more realistic scenarios for risk mitigation. Sci Total Environ 644:161–172

Didoné EJ, Minella JPG, Reichert JM, Merten GH, Dalbianco L, Barrros CAP, Ramon R (2014) Impact of no-tillage agricultural systems on sediment yield in two large catchments in Southern Brazil. J Soils Sediments 14:1287–1297

Didoné EJ, Minella JPG, Evrard O (2017) Measuring and modelling soil erosion and sediment yields in a large cultivated catchment under no-till of Southern Brazil. Soil Tillage Res 174:24–33

EMEA (2006) Guideline on the environmental risk assessment of medicinal products for human use CHMP/SWP/4447/00. The European Agency for theEvaluation of Medicinal Products, London

Fauvelle, V., Mazzella, N., 2014. Application du POCIS pour l'echantillonnage des pesticides acides dans les eaux de surface: proposition d'une resine echangeuse d'anions comme phase receptrice. Rapport Aquaref - ME-12-Echantillonnage passif des herbicides anioniques. 7p.

FEE. FUNDAÇÃO DE ECONOMIA E ESTATÍSTICA. 2019. Indicadores econômicos do agronegócio do Rio Grande do Sul. Disponível em: https://dados.fee.tche.br. Acesso em: 09 de abril de 2019.

Fernandes G, Aparicio VC, Bastos MC, Gerónimo E, Labanowski J, Prestes OD, Zanella R, Rheinheimer DS (2018) Indiscriminate use of glyphosate impregnates river epilithic biofilms in southern Brazil. Sci Total Environ 651:1377–1387

Fryirs K (2013) Connectivity in catchment sediment cascades: a fresh look at the sediment delivery problem. Earth Surf Process Landf 38:30–46

Glusczak L, Miron DS, Moraes BS, Simões RR, Schetinger MRC, Morsch VM, Loro VL (2007) Acute effects of glyphosate herbicide on metabolic and enzymatic parameters of silver catfish (Rhamdia quelen). Comp Biochem Physiol Part C: Toxicol Pharmacol 146(4): 519–524

Gonzalez-Rey M, Tapie N, Menach KLE, Dévier MH, Budzinski H, Bebianno MJ (2015) Occurrence of pharmaceutical compounds and pesticides in aquatic systems. Mar Pollut Bull 96:384–400

Guibal R, Lissalde S, Leblanc J, Cleries K, Charriau A, Poulier G, Mazzella N, Rebillard JP, Brizard Y, Guibaud G (2017) Two sampling strategies for an overview of pesticide contamination in an agriculture-extensive headwater stream. Environ Sci Pollut Res 25: 14280–14293

Hair JF, Black WC, Babin BJ, Anderson RE, Tatham RL (2009) *Análise multivariada dos dados*, 6rd. edn. Porto Alegre, Brasil, Bookman, 688p

Harman C, Brooks S, Sundt RC, Meier S, Grung M (2011) Field comparison of passive sampling and biological approaches for measuring exposure to PAH and alkylphenols from offshore produced water discharges. Mar Pollut Bull 63:141–148

Harman C, Allan IJ, Vermeirssen ELM (2012) Calibration and use of the polar organic chemical integrative sampler-a critical review. Environ Toxicol Chem 31:2724–2738

Hernando MD, Mezcua M, Fernandez-Alba AR, Barcelo D (2006) Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. Talanta 69:334–342

Huckins JN, Manuweera GK, Petty JD, Mackay D, Lebo JA (1993) Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. Environ Sci Technol 27:2489–2496

IBAMA – INSTITUTO BRASILEIRO DO MEIO AMBIENTE E RECURSOS NATURAIS RENOVÁVEIS. 2019. Boletins anuais de produção, importação, exportação e vendas de agrotóxicos no Brasil. Brasília, 2019. Disponível em: http://www.ibama.gov.br/phocadownload/qualidade_ambiental/relatorios/2014/os_dez_ias_vendidos_2014.xls. Acesso em: 25 março 2019.

IBGE – INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA. 2019. Censo Agropecuário 2017. Brasil. Brasília, 2019. Disponível em: https://censos.ibge.gov.br/agro/2017/templates/censo_agro/resultadosagro/agricultura.html. Acesso em: 25 março 2019.

Ibrahim I, Togola A, Gonzalez C (2013) Polar organic chemical integrative sampler (POCIS) uptake rates for 17 polar pesticides and degradation products: laboratory calibration. Environ Sci Pollut Res 20: 3679–3687

INMET – INSTITUTO NACIONAL DE METEOROLOGIA. 2019 Estações Automáticas. Disponível: http://www.inmet.gov.br/portal/index.php?r=home/page&page=rede_estacoes_auto_graf. Acesso em: 08 de abril 2019.

Jablonowski ND, Köppchen S, Hofmann D, Schäffer A, Burauel P (2009) Persistence of 14C-labeled atrazine and its residues in a field lysimeter soil after 22 years. Environ Pollut 157(7):2126–2131

Jeschke P, Nauen R, Schindler M, Elbert A (2010) Overview of the status and global strategy for neonicotinoids (dagger). J Agric Food Chem 59(7):2897–2908

Kienzler A, Bopp S, Halder M, Embry M, Worth A (2019) Application of new statistical distribution approaches for environmental mixture risk assessment: a case study. Sci Total Environ 693:133510

Koiter AJ, Lobb DA, Owens PN, Petticrew EL, Tiessen KHD, Li S (2013) Investigating the role of connectivity and scale in assessing the sources of sediment in an agricultural watershed in the Canadian prairies using sediment source fingerprinting. J Soils Sediments 13: 1676–1691

Kreutz LC, Barcellos LJG, Silva TO, Anziliero D, Martins D, Lorenson M, Marteninghe A, Silva LB (2008) Acute toxicity test of agricultural pesticides on silver catfish (Rhamdia quelen) fingerlings. Ciência Rural 38:1050–1055

Lewis KA, Tzilivakis J, Warner D, Green A (2016) An international database for pesticide risk assessments and management. Hum Ecol Risk Assess: Int J 22:1050–1064

Liess M, Schulz R, Liess MHD, Rother B, Kreuzig R (1999) Determination of insecticide contamination in agricultural headwater streams. Water Res 33:239–247

Lissalde S, Mazzella N, Mazellier P (2014) Polar organic chemical integrative samplers for pesticides monitoring: impacts of field exposure conditions. Sci Total Environ 488–489:188–196

Londero AL, Minella JPG, Deuschle D, Schneider FJA, Boeni M, Merten GH (2018) Impact of broad-based terraces on water and sediment losses in no-till (paired zero-order) catchments in southern Brazil. J Soils Sediments 18(3):1159–1176

Loureiro S, Svendsen C, Ferreira ALG, Pinheiro C, Ribeiro F, Soares AMVM (2010) Toxicity of three binary mixtures to Daphnia magna: comparing chemical modes of action and deviations from conceptual models. Environ Toxicol Chem 29(8):1716–1726

Martínez Bueno MJ, Herrera S, Munaron D, Boillot C, Fenet H, Chiron S, Gomez E (2016) POCIS passive samplers as a monitoring tool for pharmaceutical residues and their transformation products in marine environment. Environ Sci Pollut Res 23(6):5019–5029

Masiá A, Campo J, Vázquez-Roig P, Blasco C, Picó Y (2013) Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River Watershed (Spain). J Hazard Mater 263:95–104

Mazzella N, Dubernet JF, Delmas F (2007) Determination of kinetic and equilibrium regimes in the operation of polar organic chemical integrative samplers. J Chromatogr A 1154(1-2):42–51

Mazzella N, Lissalde S, Moreira S, Delmas F, Mazellier P, Huckins JN (2010) Evaluation of the use of performance reference compounds in an Oasis-HLB adsorbent based passive sampler for improving water concentration estimates of polar herbicides in freshwater. Environ Sci Technol 44(5):1713–1719

Merten GH, Araújo AG, Biscaia RCM, Barbosa GMC, Conte O (2015) No-till surface runoff and soil losses in southern Brazil. Soil Tillage Res 152:85–93

Metcalfe C, Hoque ME, Sultana T, Murray C, Helm P, Kleywegt S (2014) Monitoring for contaminants of emerging concern in drinking water using POCIS passive samplers. Environmental Science. Processes & Impacts 16(3):473–481

Metcalfe CD, Helm P, Paterson G, Kaltenecker G, Murray C, Nowierski M, Sultana T (2019) Pesticides related to land use in catchments of the Great Lakes basin. Sci Total Environ 648:681–692

Metre PC, Alvarez DA, Mahler BJ, Nowell L, Sandstrom M, Moran P (2016) Complex mixtures of Pesticides in Midwest U.S. streams indicated by POCIS time-integrating samplers. Environ Pollut 220: 431–440

Michaelides K, Chappell A (2009) Connectivity as a concept for characterising hydrological behaviour definitions of connectivity. Hydrol Process 522:517–522

Michel N, Freese M, Brinkmann M, Pohlmann JD, Hollert H, Kammann U, Haarich M, Theobald N, Gerwinski W, Rotard W, Hanel R (2016) Fipronil and two of its transformation products in water and European eel from the river Elbe. Sci Total Environ 568:171–179

Minella JPG, Walling DE, Merten GH (2014) Establishing a sediment budget for a small agricultural catchment in southern Brazil, to support the development of effective sediment management strategies. J Hydrol 519:2189–2201

Moreira JC, Peres F, Simões AC, Pignati WA, Dores EC, Vieira SN, Strüssmann C, Mott T (2012) Contaminação de águas superficiais e de chuva por agrotóxicos em uma região do estado do Mato Grosso. Ciência & Saúde Coletiva 17(6):1557–1568

Moreira RA, Mansano AS, Silva LC, Rocha O (2014) A comparative study of the acute toxicity of the herbicide atrazine to cladocerans Daphnia magna, Ceriodaphnia silvestrii and Macrothrix flabelligera. Acta Limnologica Brasiliensia 26(1):1–8

Morin N, Miège C, Coquery M, Randon J (2012) Chemical calibration, performance, validation and applications of the polar organic chemical integrative sampler (POCIS) in aquatic environments. Trends Anal Chem 36:144–175

Petty, J., Huckins, J., Alvarez, D., 2002. Device for sequestration and concentration of polar organic chemicals from water. U.S. Patent 6,478,961. U.S. Patent and Trademark Office, Washington, DC.

Petty JD, Huckins JN, Alvarez DA, Brumbaugh WG, Cranor WL, Gale RW, Rastall AC, Jones-Lepp TL, Leiker TJ, Rostad CE, Furlong ET (2004) A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants. Chemosphere 54(6):695–705

Poulier G, Lissalde S, Charriau A, Buzier R, Delmas F, Gery K, Moreira A, Guibaud G, Mazzella N (2014) Can POCIS be used in Water Framework Directive (2000/60/EC) monitoring networks? A study focusing on pesticides in a French agricultural watershed. Sci Total Environ 497–498:282–292

Rabiet M, Margoum C, Gouy V, Carluer N, Coquery M (2010) Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment–effect of sampling frequency. Environ Pollut 158(3): 737–748

REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), 2006. Regulation (EC) Nº 1907/2006. European Parliament and of the Council. Official Journal of the European Union. L 396/1 to 849.

Rheinheimer DS, Pellegrini A, Alvarez JW, Krolow IRC, Capoane V, Krolow DRV (2017) Flow Regularization and power dissipation in watershed in the center west region of Rio Grande do Sul state, Brazil. Geociências 36(3):521–530

Robinet J, Minella JPG, Barros CAP, Schlesner A, Lücke A, Ameijeiras-Mariño Y, Opfergelte S, Vanderborghta J, Govers G (2018) Impacts of forest conversion and agriculture practices on water pathways in Southern Brazil. Hydrol Process 32(15):2304–2317

Sancho E, Villarroel MJ, Andreu E, Ferrando MD (2009) Disturbances in energy metabolism of Daphnia magna after exposure to tebuconazole. Chemosphere 74(9):1171–1178

Schopfer A, Estoppey N, Omlin J, Udrisard R, Esseiva P, Alencastro LF (2014) The Use of Passive Samplers to Reveal Industrial and Agricultural Pollution Trends in Swiss Rivers. CHIMIA Int J Chem 68(11):778–782

Schreiner VC, Szöcs E, Bhowmik AK, Vijver MG, Schäfer RB (2016) Pesticide mixtures in streams of several European countries and the USA. Sci Total Environ 573:680–689

Scotto MAL (2014) Fluxos de fósforo em uma bacia hidrográfica sob cultivo intensivo no sul do Brasil. Dissertação (Mestrado em Ciência do Solo) - Universidade Federal de Santa Maria, Santa Maria

Sequinatto L, Reichert JM, Rheinheimer DS, Reinert DJ, Copetti ACC (2013) Occurrence of agrochemicals in surface waters of shallow soils and steep slopes cropped to tobacco. Química Nova 36(6):768–772

Silva, V.S., Poulsen, A., Tjeerdema, R., 2014. The Potential of POCIS and SPMD Passive Samplers to Measure Pesticides in California Surface Waters. Final Report Agreement No. 11-C0115. Department of Environmental Toxicology University of California, 47p.

Silva ARR, Cardoso DN, Cruz A, Lourenço J, Mendo S, Soares AMVM, Loureiro S (2015) Ecotoxicity and genotoxicity of a binary combination of triclosan and carbendazim to Daphnia magna. Ecotoxicol Environ Saf 115:279–290

Singh S, Singh N, Kumar V, Datta S, Wani AB, Singh D, Singh K, Singh J (2016) Toxicity, monitoring and biodegradation of the fungicide carbendazim. Environ Chem Lett 14(3):317–329. https://doi.org/10.1007/s10311-016-0566-2

Sridhar K, Joice PE (2012) Carbendazim induced histopathological and histochemical changes in liver tissues of common carp Cyprinus carpio. Int J Adv Life Sci 5(1):65–70

Stehle S, Schulz R (2015) Pesticide authorization in the EU—environment unprotected? Environ Sci Pollut Res 22:19632–19647

Stuer-Lauridsen F (2005) Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. Environ Pollut 136(3):503–524

Terzopoulou E, Voutsa D (2016) Active and passive sampling for the assessment of hydrophilic organic contaminants in a river watershed-ecotoxicological risk assessment. Environ Sci Pollut Res 23(6):5577–5591

Tiecher, T., Minella, J.P.G., Caner, L., Evrard, O., Zafar, M., Capoane, V., Gall, M.L, Rheinheimer, D.S., 2017. Quantifying land use contributions to suspended sediment in a large cultivated catchment of Southern Brazil (Guaporé River, Rio Grande do Sul). Agric Ecosyst Environ 237, 95–108.

Toussaint MW, Shedd TR, van der Schalie WH, Leather GR (1995) A comparison of standard acute toxicity tests with rapid-screening toxicity tests. Environ Toxicol Chem 14(5):907–915

Tyor AK, Harkrishan (2016) Effects of imidacloprid on viability and hatchability of embryos of the common carp (Cyprinus carpio L.). Int J Fish Aquat Stud 4(4):385–389

Vrana B, Allan IJ, Greenwood R, Mills GA, Dominiak E, Svensson K, Knutsson J, Morrison G (2005) Passive sampling techniques for monitoring pollutants in water. Trends Anal Chem 24(10):845–868

Zeng H, Xin F, Liang Y, Qin L, Mobc L (2018) Risk assessment of an organochlorine pesticide mixture in the surface waters of Qingshitan Reservoir in Southwest China. RSC Adv 8(8):17797–17805

Zhang W, Jiang F, Ou J (2011) Global pesticide consumption and pollution: with China as a focus. Proc Int Acad Ecol Environ Sci 1(2): 125–144