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RESEARCH ARTICLE

Determination of pharmaceuticals, personal care products, and pesticides in surface and treated waters: method development and survey

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Abstract Water is fundamental to the existence of life since it is essential to a series of activities, such as agriculture, power generation, and public and industrial supplies. The residual water generated by these activities is released into the environment, reaches the water systems, and becomes a potential risk to nontarget organisms. This paper reports the development and validation of a quantitative method, based on solid-phase extraction and liquid chromatography tandem mass spectrometry, for the simultaneous analysis of 18 pharmaceuticals and personal care products (PPCPs) and 33 pesticides in surface and drinking waters. The accuracy of the method was determined by calculating the recoveries, which ranged from 70 to 120 % for most pesticides and PPCPs, whereas limits of quantification ranged from 0.8 to 40 ng/L. After the validation step, the method was applied to drinking and surface waters. Pesticides and PPCPs were found in concentrations lower than 135.5 ng/L. The evaluation of different water sources with regard to contamination by pesticides and PPCPs has been quite poor in southern Brazil.

Keywords Pesticides · PPCPs · LC-MS/MS · Environmental waters

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Introduction

Population growth together with industrial and agricultural activities results in an increased demand for water and more generation of wastewater. Nowadays, a wide range of pollutants which pose risks to human health can be found in water sources (Lapworth et al. 2012). Among the compounds that can be found in the aquatic environment, pesticides, and pharmaceutical and personal care products (PPCPs) have been frequently detected (Xu et al. 2011; Basaglia and Pietrogrande 2012; Iglesias et al. 2012).

A great diversity of pesticides is used in agriculture in order to improve productivity and enhance the quality of products since producing food to assure the increased demand is a global problem, especially in developing countries (Caldas et al. 2011). According to the National Health Surveillance Agency, Brazil stands out in the world as one of the largest consumers of pesticides (IBGE 2008).

Since last decade, PPCPs have been classified as the most common organic contaminants detected in the aquatic environment, due to constant anthropogenic inlet (Richardson 2009). In different continents, studies of material collected in rivers, lakes, groundwater, and seawater have shown concentrations around nanograms per liter and micrograms per liter (Capdeville and Budzinski 2011; Bono-Blay et al. 2012; Iglesias et al. 2012).

PPCPs are released into the aquatic environment in their original form or as metabolites. The main route of environmental contamination is through the sewage treatment system, hospital wastewater, industries, and the discharge of solid waste (Buchberger 2007). Some pesticides and PPCPs persist long in the environment while others do not, but, since they are continuously released into the environment, they may cause overwhelming impact on the aquatic ecosystem and, therefore, on human health (Daughton and Ternes 1999; Calza et al. 2012). Thus, proper assessment of the quality of surface water requires the identification of such pollutants.

The analysis of these residues in water is difficult to perform, since these compounds have different physicochemical properties and occur in extremely low concentrations when there are high concentrations of interfering compounds (Demoliner et al. 2010). However, progress in the development of analytical methods for the analysis of PPCPs residues has happened due to the fact that there is considerable expertise in the analysis of pesticide residues. Strategies used for the routine analysis of pesticide traces can be directly applied to pharmaceutical residues (Fent et al. 2006; Primel et al. 2012).

For the extraction of pesticides and PPCPs from environmental samples, the solid-phase extraction (SPE) is the most common and well-established technique because it has acceptable accuracy and precision when compounds that belong to several different classes are being investigated. The determination of these compounds has been carried out mostly by liquid chromatography tandem mass spectrometry (LC-MS/MS) (Caldas et al. 2010; Primel et al. 2012).

Since the contamination of different environmental compartments involves severe threat to the environment and to human health, it is important to know these compounds and their concentrations so that these data can support the implementation of safety measures and mitigating factors. The aim of this study was to assess the quality of surface and treated waters through the identification of pesticides, pharmaceutical, and personal care products. Eighteen PPCPs and 33 pesticides were investigated. It is worth mentioning that Brazilian data on the contamination of waters by emerging contaminants are still scarce (Bila and Dezotti 2007; Sodré et al. 2010; Locatelli et al. 2011) and that only 55 % of the Brazilian cities have sewage drainage and only about 29 % have sewage treatment (IBGE 2011).

Materials and methods

Chemicals and reagents

High purity (>90 %) analytical standards of pesticides were purchased from Sigma-Aldrich (São Paulo, Brazil), whereas pharmaceuticals and personal care products were purchased from Fiocruz (Fundação Oswaldo Cruz, Rio de Janeiro, RJ, Brazil). The list of compounds under analysis is in Table 1.

The individual standard solutions were prepared in methanol at the concentration of 1,000 μg/mL. The working standard solutions were prepared at 100 μg/mL by mixing the appropriate amounts of the individual standard solutions and diluting them with methanol. All solutions were kept at −18 °C. All solvents were HPLC grade from Mallinckrodt (Phillipsburg, NJ, USA), and all the other reagents were of analytical grade. Ultrapure water was obtained by Direct Q UV3® water purification system (Millipore, Bedford, MA, USA). SPE extraction tubes were Chromabond C18 EC (octadecyl-modified silica phase) (Macherey-Nagel, Düran, Germany).

Sampling site and sample collection

Sampling was carried out fortnightly at Companhia Riograndense de Saneamento (CORSAN), the water treatment station in *Morro Redondo*, from October 2010 to March 2011, totaling ten samples.

Morro Redondo is a small town (244,645 km^2) located in Rio Grande do Sul State, in the south of Brazil, with 6,227 inhabitants. The economy of the city is practically based on agriculture, whose main cultures are peach, orange, grape, fig, guava, apple, and tangerine.

Samples of drinking water (after treatment) and surface water (before treatment) were collected directly in their water sources. Water to be treated comes from *Arroio do Carvão*, which is a stream that gets organic wastes from urban and agricultural areas. One liter of the sample was collected in an amber glass bottle rinsed with acetone and baked at 100 °C. Before sampling, bottles were rinsed with the same water of the sample. Samples were stored at 4 °C until analysis, which was performed on the same day.

Solid-phase extraction

Before the SPE, the samples were filtered by a Sartorius cellulose acetate filter (Biolab Products, Goettingen, Germany). Due to the diversity of target analytes with a broad range of pK_a values, it was difficult to find an optimal pH value for all analytes (Wick et al. 2010). Therefore, to ensure reproducible recoveries, two different pH values were used. The samples were divided into two subsamples: one of them had the pH adjusted to 3 and the other one had no pH adjustment. Subsamples were extracted in duplicate and injected three times. The samples were extracted by SPE tubes with 500 mg C18 whose average particle size was 45 μm. After the SPE procedure, the analytes were eluted with 2 mL (1,000+1,000 μL) methanol. The final organic extracts were directly analyzed by LC-ESI-MS/MS with injection volume of 10 μL.

Table 1 MRM conditions for the PPCPs under study

PPCPs	ESI mode	Transition (*m/z*)	Cone (V)	Collision (eV)	t_R (min)
Atenolol	+	267>145[a]	15	30	1.1
		267>190.2	25	25	
Avobenzone	+	310.4>135[a]	20	30	21.1
		310.4>161	20	30	
Benzophenone	−	307.1>211.1[a]	55	35	8.7
		307.1>182.2	55	35	
Caffeine	+	195.3>110	25	20	3.4
		195.3>138[a]	25	20	
Carbamazepine	+	236.9>194.1[a]	26	12	11.5
		237.4>167.4	35	40	
Chlorpropamide	+	277>175[a]	27	22	11.4
		277>110.9	27	29	
Diclofenac sodium	−	293.6>250.2[a]	20	10	16.6
		294>214	20	25	
Eusolex 6300 (methybenzylidene camphor)	+	255.4>157.2	25	20	19.2
		255.4>105	25	30	
Gemfibrozil	−	249>121	20	30	18.3
Furosemide	−	328.8>284.9	30	15	9.9
		328.8>205[a]	30	20	
Glibenclamide	+	494>369	30	18	16.4
		494>169[a]	30	38	
Mebendazole	+	296.2>264.2	35	30	12.6
		296.2>104.9[a]	35	30	
Methylparaben	+	151>135.9	35	15	8.0
		151>91.6[a]	35	20	
Nimesulide	−	307>229	33	20	13.3
		307.2>198.1	30	25	
Miconazole nitrate	+	417.1>161	45	25	16.7
		417.1>159[a]	45	30	
Propylparaben	−	179.1>137.1	30	15	12.7
		179.1>91.8[a]	30	20	
Triclocarban	−	313>160.1[a]	30	20	18.3
		315>125.7	30	15	
Triclosan	−	289>35	18	7	18.4
		287>35	18	9	
2,4-D	−	219>161[a]	15	20	11.7
		219>89	15	30	
3,4-DCA	+	162>127	35	15	11.5
		162>109[a]	25	25	
3-Hydroxycarbofuran	+	238>163[a]	25	15	6.2
		238>135	25	20	
Atrazine	+	216>174	33	20	12.3
		216>146	35	22	
Azoxystrobin	+	404>372[a]	20	20	14.6
		404>329	15	30	
Bentazone	−	239>132[a]	35	25	9.5
		239>197	35	20	
Bispyribac sodium	+	453>297[a]	35	25	14.8
		453>275	35	22	
Carbendazim	+	192>160	28	28	3.0
		192>132[a]	28	29	
Carbofuran	+	222>165	20	25	10.3
		222>123	20	25	
Cyproconazole	+	292>125	35	20	15.4
		292>70[a]	35	20	
Clomazone	+	240>125[a]	30	20	13.6
		240>219	26	20	
Difenoconazole	+	406>251[a]	31	32	17.9
		406>337	32	20	
Diuron	+	233>72[a]	28	20	12.9
		233>160	28	25	
Epoxiconazole	+	330>123	27	30	16.1
		330>121[a]	27	30	
Fipronil	−	435>330[a]	30	15	16.7
		435>250	25	26	
Imazapic	+	276>231[a]	40	20	7.4
		276>185	40	30	
Imazethapyr	+	290>230	40	20	9.4
		290>177[a]	40	20	
Iprodione	+	330>101[a]	20	33	15.9
		330>143.2	20	21	
Irgarol	+	254>108	30	30	15.2
		254>198	30	19	
Malathion	+	331>199	24	30	15.1
		331>127[a]	24	10	
Methalaxyl-M	+	280>220	16	17	12.8
		280>192[a]	16	17	
Metsulfuron-methyl	−	380>139[a]	30	15	10.9
		380>214	30	10	
Molinate	+	188>126[a]	25	10	14.7
		188>83	25	20	
Penoxsulam	−	482>109	35	40	12.1
		482>179[a]	35	25	
Pyrazosulfuron-ethyl	−	413>232	35	15	15.6
		413>154	35	26	
Pirimiphos-methyl	+	306>136	40	33	17.3
		306>108[a]	40	20	
Propanil	+	218>127	25	28	14.1
		218>162[a]	30	14	
Propiconazole	+	342>159[a]	32	22	16.9
		342>69	30	20	
Quinclorac	−	240>196	15	6	7.6
Simazine	+	202>132[a]	35	18	10.1
		202>124	35	18	
Tebuconazole	+	308>70	40	20	16.9
		308>125	28	22	
Tiabendazole	+	202>131	47	25	4.6
		202>158	47	25	
		202>175	30	34	
Trifloxystrobin	+	409>206	35	15	18.2
		409>145[a]	25	40	

[a] Quantification ions

Acidified subsample SPE procedure

A subsample was acidified to pH 3 with phosphoric acid. Afterwards, it was passed through an SPE tube that had been previously conditioned with 3 mL methanol, 3 mL purified water, and 3 mL purified water pH 3.0. Then, the samples were well mixed and passed through the SPE tubes at 10 mL min^{-1}.

Non-acidified subsample SPE procedure

The pH of the non-acidified treated and surface subsamples was measured in each sampling; values ranged from 6.4 to 6.9.

The SPE column was conditioned by passing consecutively 6 mL methanol and 6 mL purified water. Afterwards, the samples were well mixed and passed through the SPE tubes at 10 mL min^{-1}.

Liquid chromatography coupled to mass spectrometric analysis

Analyses were performed by a Waters Alliance 2695 Separations Module HPLC, equipped with a quaternary pump, an automatic injector, and a thermostatted column compartment (Waters, Milford, MA, USA). The chromatographic separation was performed by a Kinetex C18 (3.0 mm×50 mm i.d., 2.6 μm film thickness) column Phenomenex (Torrance, CA, USA). The mobile phase components are (A) ultra-pure water with 0.01 % acetic acid and (B) pure methanol, with elution in the gradient mode. The initial composition was 20 % B, which increased linearly to 90 % in 20 min, held it until 23 min and, then, returned to the initial composition (20 % B) in 0.5 min and held it for 6.5 min, totaling a 30-min analysis. The injection volume was 10 μL.

A Quattro micro API (triple quadrupole) mass spectrometer, equipped with a Z-spray electrospray ionization source, from Micromass (Waters, Milford, MA, USA) was used. Drying gas, as well as nebulizing gas, was nitrogen, generated from pressurized air in a NG-7 nitrogen generator (Aquilo, Etten-Leur, NL). The nebulizer gas flow was set to 50 L h^{-1} and the gas flow desolvation to 450 L h^{-1}. For operation in the multiple reaction monitoring (MRM) mode, collision gas was Argon 5.0 (White Martins, Rio Grande do Sul, Brazil) with pressure of 3.5×10^{-3} mbar in the collision cell. The optimized values were: capillary voltages, 4.5 kV; extractor voltage, 2 V; source temperature, 100 °C; desolvation temperature, 450 °C; and multiplier, 650 V.

Optimization of the MS-MS conditions, choice of the ionization mode, identification of the parent and product ions, and selection of the cone and collision voltages which were most favorable for the analysis of the target analytes were performed with direct infusion of each standard solution in the concentration of 1 μg/mL. Analytical instrument control, data acquisition, and treatment were performed by software MassLynx, version 4.1 (Micromass, Manchester, UK).

Quality control and quality assurance

Calibration was performed over concentration range between the limit of quantification (LOQ) and 1 μg/mL. Given the complexity of analyzing compounds in trace concentrations due to background contamination, the analytical performance was continuously checked by analyzing extraction solvents and by performing blank analysis and quality controls in each extraction batch.

Accuracy was evaluated by means of recovery experiments, i. e., the analysis of tap water spiked at 4.0, 8.0, 40.0, 80.0, and 400 ng/L levels. Each compound, according to the LOQ, was evaluated in, at least, two different levels. Each fortification level was extracted in triplicate and injected three times (n=9). Blank analysis was performed with HPLC water. The LOQ of the method was determined by the signal-to-noise ratio of 10. The precision of the method was evaluated in terms of repeatability, which was studied with nine determinations.

Results and discussion

Method performance

After the optimization of the collision cell energy of the triple quadrupole, two different MRM transitions were selected for each compound: one for quantification and one for qualification. These ions were monitored under time-scheduled MRM conditions.

The multiresidue LC-MS/MS led to the determination of 51 compounds within less than 30 min (Fig. 1). Each compound was identified, whenever possible, at two transitions (Table 1), besides retention time, to ensure unequivocal identification.

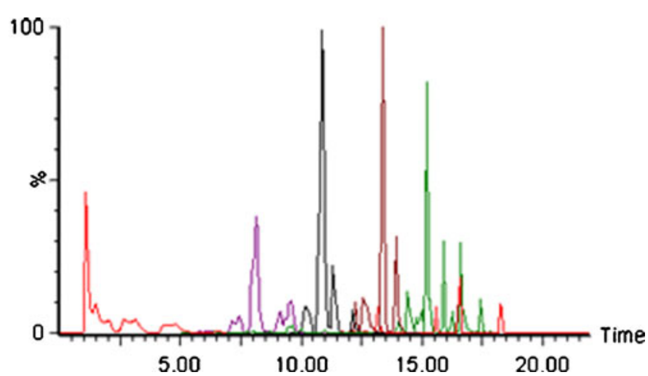

Fig. 1 Overlay of the total ion chromatograms in the determination of 51 compounds (0.1 μg/mL)

The linearity of the method, evaluated from LOQ to 1 μg/mL, with three replicate injections per concentration, had correlation coefficient $r>0.99$, a value within the validation guidelines.

Since the compounds under study are expected to be found at very low concentration in water samples, the method was optimized to detect low nanogram per liter levels. Table 2 shows the LOQs which varied from 0.8 to 80 ng/L.

Recoveries are shown in Table 2. For the PPCPs, values from 49 to 128 % were obtained. Pesticides were recovered from 67 to 132 %. Recoveries in 80 ng/L, the closest level to 100 ng/L, which is regarded the maximum for individual pesticides in water for human consumption in Europe, ranged from 72 to 123 % for PPCPs and pesticides with RSD values lower than 20 %. It provides evidence that the method is highly repetitive and adequate even for the extraction of a series of compounds belonging to several chemical classes.

These results show an advantage the optimized method has. A prerequisite for multiresidue analysis of different PPCPs is to reach enough accuracy in the same extraction conditions. In this study, acceptable recoveries and precision were obtained when C18 cartridges were used. They are usually cheaper than polymeric ones, which had been chosen for the preconcentration of both polar and nonpolar compounds (Primel et al. 2012).

Distribution of pharmaceuticals, personal care products, and pesticides in source waters

In this study, pesticides, pharmaceuticals, and personal care products were detected in water sources which are located near either urban or agricultural areas. It is worth emphasizing that only ten samples were collected and that the main objective of this study was to carry out a survey of PPCPs that were reaching these waters. Since they were detected, the reasons why these compounds may have been found were discussed.

Residues, mostly pesticides, were found throughout all the sampling period (Table 3). Atrazine, bentazone, carbendazim, carbofuran, clomazone, diuron, epoxiconazole, irgarol, pirimiphos-methyl, and tebuconazole were detected. However, clomazone, diuron, epoxiconazole, and tebuconazole were the most common compounds detected in the water.

Azole compounds, classified into triazoles and imidazoles, have been widely used as fungicides in agriculture. Biocides have been added to several products and antifungal agents have been used in human and veterinary pharmaceuticals. Some azoles have also been prescribed for cancer therapy (Zarn et al. 2003).

Tebuconazole was detected in the surface water in concentrations ranging from 2.5 to 60.6 ng/L and, in treated water, between 4.1 and 76.7 ng/L. Tebuconazole had been previously detected in industrial water (Huang et al. 2010), streams (Battaglin et al. 2011), groundwater (Caldas et al. 2010), and surface water (Demoliner et al. 2010).

Diuron (*N*-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea) is a herbicide which belongs to the phenylamide family and to the subclass phenylurea. It represents an important class of contact herbicides that have been used worldwide for more than 40 years. Diuron has been used to control a wide variety of annual and perennial broadleaf and grassy weeds, as well as moss. It has also been applied to non-crop areas, such as roads and garden paths, besides many agricultural crops, such as fruit, cotton, sugar cane, and wheat. Moreover, diuron has been used as an antifouling paint booster biocide (Cabrera et al. 2010).

Diuron was detected in all samples in a study carried out by Munaron et al. (2012) in estuarine and coastal waters in concentrations ranging from 1 to 222 ng/g of sorbent. Köck-Schulmeyer et al. (2012) have also found diuron in surface waters, in average concentrations between 2.4 and 460.6 ng/L. Struger et al. (2011) found diuron in 38.7 % of the sampling sites, 55.2 ng/L on average. In this study, diuron was detected in more than 50 % of the samples, in concentrations ranging from 7 to 123.5 ng/L.

Carbendazim was detected in concentrations below the LOQ. Pareja et al. (2012) determined pesticides in 59 paddy field water samples collected in different regions: 33 in Spain and 26 in Uruguay. The most common pesticide in Uruguayan samples was the fungicide tebuconazole even though carbendazim was also detected in the samples. The compounds found in the samples were the pesticides that were widely used in rice crops. The concentration of the individual pesticides found in the samples under analysis was 1–70 times higher than the standard of 100 ng/L allowed for individual pesticides in water.

Bentazone has been frequently detected in considerable concentrations in surface waters in Brazil (Marchesan et al. 2010) and European countries (Bach et al. 2010). In this study, it was detected in concentrations below the LOQ.

Carbofuran was also found in the samples. Chowdhury et al. (2012) report the presence of carbamate residues in 24 surface water samples and five groundwater samples in Pirgacha Thana, Rangpur District, Bangladesh. Some samples of surface water from paddy fields were found to contain, for instance, carbofuran, at concentrations ranging from 0 to 3,395 ng/L. Carbofuran was found in surface water in lakes at concentrations ranging from 949 to 1,671 ng/L. In this study, the average concentration in treated samples was 13.3 ng/L, and in surface waters, it was 2.8 ng/L.

Regarding pharmaceuticals, cimetidine was always detected in concentrations below the LOQ in more than 50 % of the samples. This compound had been found in samples that were analyzed in other studies. Pinhancos et al.

Table 2 Method limit of quantification, recoveries, and relative standard deviation

Compound	LOQ (ng/L)	R% 4 ng/L	RSD	R% 8 ng/L	RSD	R% 40 ng/L	RSD	R% 80 ng/L	RSD	R% 400 ng/L	RSD
PPCPs											
Atenolol[b]	40	n.e.		n.e.		84	14	63	14	49	8
Avobenzone[a]	40	n.e.		n.e.		76	6	69	12	59	5
Benzophenone[b]	40	n.e.		n.e.		93	7	91	16	86	7
Caffeine[b]	40	n.e.		n.e.		125	8	114	14	100	5
Carbamazepine[b]	4	104	20	116	20	112	8	124	9	119	2
Chlorpropamide[a]	40	n.e.		n.e.		96	13	88	6	81	6
Diclofenac sodium[b]	8	n.e.		119	18	77	15	101	13	80	8
Eusolex 6300[a]	40	n.e.		n.e.		86	12	69	8	64	9
Gemfibrozil[b]	8	n.e.		83	16	87	16	97	13	84	5
Furosemide[a]	40	n.e.		n.e.		96	18	69	22	61	13
Glibenclamide[b]	40	n.e.		n.e.		108	17	105	13	89	4
Mebendazole[b]	8	n.e.		128	12	97	12	94	12	100	7
Methylparaben[b]	8	n.e.		115	21	62	20	60	26	52	4
Nimesulide[b]	4	113	33	118	13	122	4	113	15	125	10
Miconazole nitrate[b]	8	n.e.		87	20	64	8	82	11	64	7
Propylparaben[a]	8	n.e.		100	19	92	16	115	14	76	15
Triclocarban[b]	0.8	81	5	97	12	81	5	88	3	84	6
Triclosan[b]	80	n.e.		n.e.		n.e.		76	20	84	16
2.4-D[a]	40	n.e.		n.e.		96	17	88	19	78	8
3.4-DCA[a]	40	n.e.		n.e.		83	23	87	19	83	17
3-Hydroxy-carbofuran[b]	80	n.e.		n.e.		n.e.		122	10	114	10
Atrazine[b]	4	120	10	115	23	106	6	116	2	108	5
Azoxystrobin[a]	40	n.e.		n.e.		100	7	98	5	97	16
Bentazone[a]	8	n.e.		87	30	67	11	95	11	72	5
Bispyribac-sodium[b]	8	n.e.		120	15	112	11	123	6	108	3
Carbendazin[b]	8	n.e.		110	32	105	4	116	2	105	4
Carbofuran[b]	8	n.e.		98	6	132	9	115	2	120	6
Cyproconazole[a]	8	n.e.		119	19	109	10	98	7	97	11
Clomazone[b]	40	n.e.		n.e.		102	20	120	5	124	19
Difenoconazole[a]	8	n.e.		119	9	102	10	90	4	91	12
Diuron[a]	40	n.e.		n.e.		102	25	120	11	104	16
Epoxiconazole[a]	40	n.e.		n.e.		125	10	102	5	87	8
Fipronil[a]	0.8	82	20	85	15	96	5	88	8	81	12
Imazapic[b]	8	n.e.		106	20	113	5	94	2	64	2
Imazaphyr[b]	8	n.e.		110	32	94	9	115	6	111	3
Iprodione[a]	40	n.e.		n.e.		116	11	111	20	90	9
Irgarol[b]	4	87	9	115	10	108	5	111	2	103	2
Malathion[b]	4	99	17	97	20	84	19	89	13	78	4
Methalaxyl-M[b]	4	100	25	83	10	99	15	104	7	102	7
Metsulfuron-methyl[b]	40	n.e.		n.e.		71	16	72	12	78	10
Molinate[b]	8	n.e.		111	22	114	18	115	17	109	5
Penoxsulan[b]	40	n.e.		n.e.		92	14	93	7	96	5
Pyrazosulfuron-ethyl[b]	4	120	20	87	14	97	13	94	9	96	5
Pirimiphos-methyl[b]	8	n.e.		77	11	91	18	92	16	86	12
Propanil[b]	8	n.e.		116	35	101	16	101	13	81	7
Propiconazole[b]	4	121	24	116	10	110	13	109	7	100	6
Quinclorac[a]	80	n.e.		n.e.		n.e.		102	20	67	19

Table 2 (continued)

Compound	LOQ (ng/L)	R% 4ng/L	RSD	R% 8ng/L	RSD	R% 40ng/L	RSD	R% 80ng/L	RSD	R% 400ng/L	RSD
Simazine[b]	4	98	9	129	17	103	8	123	11	101	2
Tebuconazole[a]	40	n.e.		n.e.		103	6	117	7	89	6
Thiabendazole[b]	8	n.e.		101	20	102	7	101	4	99	4
Trifloxystrobin[a]	8	n.e.		89	11	108	8	81	13	73	7

n.e. not evaluated

[a] Extraction in acidified conditions

[b] Extraction with no acidification

(2011) found some pharmaceuticals in tap water and bottled water. Cimetidine was detected in tap water in the range from 200 to 300 ng/L. Choi et al. (2008) detected cimetidine in surface waters in concentrations ranging from <20 to 1,338 ng/L. Nimesulide was detected in only one sample at a concentration of 12.0 ng/L.

Alkyl esters of 4-hydroxybenzoic acid (called parabens) have been widely used in food, cosmetic, and pharmaceutical industries due to their antimicrobial activity, low toxicity, and low cost. They often serve as food additives and preservatives in cosmetics and are common constituents of shampoos, moisturizers, deodorants, antiperspirants, shaving gels, lubricants, and toothpaste. Their bactericidal and fungicidal properties have also been employed in topical and parenteral pharmaceuticals (Kroflič et al. 2012). In this study, methylparaben was found on almost all sampling dates in concentrations always below the LOQ. Propylparaben was detected in two samples, and the highest concentration was 128.3 ng/L. In a study conducted by Pedrouzo et al. (2009), some parabens were determined in three kinds of matrices (river water, effluent, and influent wastewater). The levels found in river waters were considerably lower than the ones found in wastewater because the sewage waters become diluted when they are released into the environment. Methylparaben and propylparaben were found in the Ebro and Llobregat Rivers at levels below the limit of quantification. In waters from sewage treatment plants, methylparaben and propylparaben were within the commonest

Table 3 Summary of PPCPs and pesticide concentrations for the surface and treated waters

PPCPs and pesticides	Treated water						Surface water				
	N	N<LOQ	N>LOQ	Min (ng/L)	Max (ng/L)	Mean (ng/L)	N<LOQ	N>LOQ	Min (ng/L)	Max (ng/L)	Mean (ng/L)
Atrazine	10	1	1	92.3	92.3	–	1	0	–		<LOQ
Bentazone	10	1	0	–	–	–	5	1	88	88	–
Carbendazim	10	0	0	–	–	–	4	0	–	–	–
Carbofuran	10	1	3	8.9	23.8	16.0	3	0	–	–	–
Cimetidine	10	6	0	–	–	–	5	0	–		<LOQ
Clomazone	10	6	4	40.0	123.9	63.3	7	2	46.5	47.2	46.9
Sodium diclofenac	10	1	0	–	–	–	3	0	–		<LOQ
Diuron	10	5	1	95.8	95.8	–	4	1	123.5	123.5	–
Epoxiconazole	10	6	2	46.7	83	64.9	5		–	–	–
Irgarol	10	0	1	7.2	7.2	7.2	2	2	7.7	15.9	11.8
Mebendazole	10	0	1	18.5	18.5	–	0	1	14.3	14.3	–
Methylparaben	10	9	0	–	–	–	10	0	–		<LOQ
Nimesulide	10	0	0	–	–	–	1	1	12.0	12.0	–
Pirimiphos-methyl	10	1	0	–	–	–	1	0	–	–	–
Propilparaben	10	0	1	135.5	135.5	–	1	1	128.3	128.3	–
Tebuconazole	10	8	2	53.0	76.7	64.9	9	1	60.6	60.6	–

N number of samples studied, *N<LOQ* number of compounds detected below the LOQ, *N>LOQ* number of compounds detected above the LOQ, *Min* minimum, *Max* maximum, *Mean* concentration (in nanograms per liter) of each compound compounds in the influent waters. Methylparaben ranged from 4,427 to 1,658 ng/L and propylparaben from 1,945 to 77 ng/L. The authors arrived at some conclusions regarding the removal of these compounds by the wastewater treatment and stated that, although it had not been an exhaustive study of the removal of PPCPs by sewage treatment plants (STPs), the tendency was that the STP process would eliminate PPCPs. It was clearly confirmed when the high concentrations of parabens in influents were severely reduced in effluents.

Conclusions

A rapid and sensitive analytical method employing SPE and LC-MS/MS for the determination of 51 PPCPs and pesticides belonging to several different classes was developed in this study.

Surface and treated waters have been reached by several pollutants which can cause an impact on health and on the environment. In this research, the first survey of pesticides, pharmaceuticals, and personal care products was carried out in the south of Brazil. Pesticides and PPCPs were found in concentrations below 135.5 ng/L. In most cases, concentrations were lower than the parametric values set by the European Union, which is one of the most restrictive organizations in the world. It means that water sources have been affected by domestic sewage that has been produced and by agricultural activities that have been developed all over the region.

Additional research into the fate of PPCPs in Brazilian environments may shed light on how these compounds have reached the environment and how this situation may affect the environment and human health.

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