Hormones and antibiotics associated with intensive pig production in a river basin

Hormônios e antibióticos em rio de uma bacia hidrográfica com intensa criação de suínos

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ABSTRACT: In recent years, the use of pharmaceutical substances, mainly hormones and antibiotics, in agriculture has increased. The combined use of these pharmaceutical substances both in animals and humans has led to serious concerns related to the environment and human health due to potential adverse effects on the endocrine system and bacterial resistance. These substances are usually transported by runoff processes to rivers, modifying the quality of aquatic ecosystems. The aim of this study was to evaluate the occurrence of hormones (estradiol, 17α-estradiol, 17β-estradiol, 17α-ethinylestradiol, estrone, norgestrel, progesterone and mestranol) and antibiotics (oxytetracycline, doxytetracycline, tetracycline, chlortetracycline, toltrazuril and sulfamethazine) in surface waters in the Coruja river basin, which has a drainage area of 48.79 km². This catchment area is one of the leading regions of pig production in southern Brazil. Samples were collected over a 15-month period from four stream water sites corresponding to sub-basins 1, 2, 3 and 4. The chemical analysis was performed by High Performance Liquid Chromatography (HPLC). Antibiotics and hormones were detected in 4,82 and 4,04 % of the samples respectively but only antibiotics were detected above the limit of quantitation. The samples with the largest analyte concentrations and highest occurrence were collected in January and February. The largest occurrence and highest concentrations of analytes was in sub-basin 2, which had the largest number of pigs. Chlortetracycline was the most frequently detected and also the most frequently detected analyte at quantifiable concentrations. These detectable and quantifiable levels of antibiotics represent an environmental risk, reducing the quality of surface waters.

KEYWORDS: Emerging pollutants, water quality, agricultural residues.

RESUMO: O uso de fármacos no setor agropecuário tem aumentado significativamente nos últimos anos, destacando-se as classes dos hormônios e antibióticos. O uso compartilhado destes fármacos tanto em animais como em humanos tem acarretado em grandes preocupações com a saúde humana e ao meio ambiente, podendo provocar alterações no sistema endócrino e de resistência às bactérias. Os fármacos, normalmente são transportados pelo escoamento superficial aos corpos hídricos, provocando a degradação do ecossistema aquático. Assim, este estudo visa avaliar a ocorrência de moléculas de homônimos e de antibióticos em águas superficiais na bacia hidrográfica do rio Coruja, cuja área de drenagem é de 48,79 km². Esta bacia é uma das principais produtoras de suínos na região sul do Brasil. Foram realizadas coletas mensais, durante 15 meses, em quatro seções fluviométricas, caracterizando as sub-bacia 1, 2, 3 e 4. As análises químicas foram realizadas em Cromatógrafo Líquido de Alta Eficiência (HPLC). Observou-se que as moléculas analisadas apresentaram concentrações detectáveis e quantificáveis, sendo o maior número ocorrido nos meses de janeiro e fevereiro. A sub-bacia 2 apresentou o maior número de moléculas quantificadas. Esta sub-bacia possui o maior número de suínos. Para os antibióticos, a molécula clortetraciclina foi quantificada o maior número de vezes, e as moléculas de hormônio não foram encontradas com concentrações quantificáveis. Conclui-se que nesta bacia, os antibióticos contidos nos dejetos líquidos suínos constituem risco de degradação da qualidade das águas superficiais.

PALAVRAS-CHAVE: Poluentes emergentes, qualidade de água, resíduos agropecuários.

INTRODUCTION

In recent years the use of pharmaceutical substances in the agricultural sector has expanded, particularly in swine production. According to Kummerer (2009) the use of antibiotics as growth promoters is considered one of the most prevalent applications of such substances, due to the increase of confined animal production processes. As growth promoters, hormones, also known as endocrine disruptors, act on the central immune system and may inhibit or alter regular functions of the organism (KIDD et al., 2007).

The restriction of the use of these substances varies in each country according to specific legislation. In Brazil, the regular use of hormonal substances in animal production is prohibited, but they are permitted for therapeutic purposes via veterinary prescription. However, in October 2010, ANVISA (Brazilian National Health Surveillance Agency) published a new resolution restricting the sale and prescription of antibiotics in Brazil (BRASIL, 2010).

The increased use of chemicals in swine production is mainly used and prophylaxis for disease control. Most of these substances are only partially metabolized, thus, active forms are excreted in urine and feces by the animal (KUMAR et al.; 2005). According to Kwon et al. (2011) around 90% of antibiotics used as prophylaxis are released to the environment through feces and urine. Thus, animal manure can constitute an important source of these chemicals in the environment.

Several studies have confirmed the presence of chemical substances in aquatic and terrestrial environments (KUMMERER; HENNINGER, 2003; YANG; CARLSON, 2003; PEI et al., 2006; AUST et al., 2008; KARCI; BALCIOGLU, 2009; MARTINEZ-CARBALLO et al., 2007; TAMTAM et al., 2008; ZOU et al., 2011). Inputs of chemical substances to the environment through the application of organic fertilizers produced from animal manure are becoming one of the major sources of terrestrial pharmaceutical pollution (KIM et al., 2012). Once applied to the soil these chemicals are transported to water bodies through water runoff (AWAD et al., 2014) and they have become the important pharmaceutical contamination source of surface and subsurface waters (KAY et al., 2005; BURKHARDT et al., 2005; KREUZIG et al., 2005; DAVIS et al., 2006). In Germany, Wiegel et al. (2004) detected high concentrations of human pharmaceuticals in a river close to an urban area. In Slovenia, Kosjeka et al. (2005) found non-steroid anti-inflammatory drugs (NSAIDs) in human drinking water samples and Boleda et al. (2011) also reported the occurrence of pharmaceutical drugs in water destined for human consumption. Jurado et al. (2012) detected pharmaceuticals in deep groundwater in Barcelona, Spain. Kim et al. (2009), investigated pharmaceuticals in the River Makyung (South Korea) and reported higher concentrations of these products downstream of a sewage treatment plant. In France, pharmaceuticals in concentrations of ng L^{-1} were found in surface waters that supply a water treatment plant (VULLIET et al., 2009). In addition to surface and subsurface waters, drugs have also been found in atmospheric particulate material (CECINATO; BULDUCCI, 2007).

In developing countries, such as Brazil, studies on the detection and mobility of hormones and antibiotics in surface water, groundwater and soil are scarce. Most researchers have evaluated the occurrence of pharmaceuticals in urban areas due to sewage discharge into receiving waters (JONES et al., 2005; PETROVIC et al., 2005, LARSSON et al., 2007). Antibiotics have also been reported in effluents originating from a sewage treatment plant, hospitals and milk production systems (BROW et al., 2006). Langford et al. (2011) registered the occurrence of human pharmaceutical products in sediment and sewage sludge. In Brazil, the presence of antipyretic, anti-inflammatory and analgesic compounds has been observed in Billings reservoir (ALMEIDA; WEBER, 2005).

The aim of this study was to evaluate the presence of hormones and antibiotics in the Coruja river basin located in southern Brazil, in a region with the presence of Atlantic Forest along with intense swine production.

MATERIALS AND METHODS

The study was performed in the Coruja river basin (Figure 1), located in the town of Braço do Norte, State of Santa Catarina, southern Brazil. The climate in the region is predominantly humid mesothermal with temperatures ranging between 15 and 35°C and annual rainfall of around 1300 to 1600 mm (THOME et al., 1999). The soil of the basin is classified, according to Embrapa (2006), as Dystrophic Argisoil and Dystrophic Oxisol.

The Coruja river basin has a total area of 48.79 km² and of this total 48.6% is grassland, 25.3% is forest, 9.2% is used for agriculture, 9.0% is given over to reforestation, 7.7% is comprised of urban areas, 0.1% is undergoing native forest regeneration and 0.1% is exposed soil.

The basin was divided into four sub-basins (sub-basins 1, sub-basin 2, sub-basin 3 and sub-basin 4). The sampling plots were located close to the spring of the Coruja river (sub-basin 1), along the course of the river (sub-basins 2 and 3) and at the outflow (sub-basin 4) at the river mouth. Table 1 describes the distribution of the land use in these areas.

According to a survey of the pig breeders in this basin, there are 52 pig farmers, divided into stages of breeding, rearing, fattening, finishing and complete cycle, comprising a total of 52,659 animals. In addition to the pig farmers, the basin has 11 slaughter and processing plants which are also potential sources of river pollution. Table 2 shows the total number of swine farms and the number of animals in each sub-basin and Figure 1 gives the location of each pig farm.

Monthly sampling events were carried out in the stream water sites in the period of June 2012 to September 2013. During this period the total rainfall was 2086 mm (Figure 2). The highest rainfall was recorded in August 2013 (450.4 mm) and the lowest in August 2012 (14.4 mm).

River water samples were collected at a depth of 0.5 m. The sampled water was stored in polyethylene bottles with a capacity of 50 mL and maintained at an average temperature of 4°C in a polystyrene box with ice and then sent to the laboratory for further analysis.

Concentrations of hormones and antibiotics were determined by high performance liquid chromatography (HPLC) on a Dionex Ultimate 3000 LC system. The antibiotics investigated were oxytetracycline, doxytetracycline, tetracycline, chlortetracycline, toltrazuril and sulfamethazine and the hormones were estradiol, 17α-estradiol, 17β-estradiol, estrone, 17α-ethinylestradiol, norgestrel, progesterone and mestranol.

For the estradiol, 17α-estradiol, 17β-estradiol, 17α-ethinylestradiol, estrone, mestranol, norgestrel and progesterone and toltrazuril molecules the determination was performed with the adapted method described by Almeida and Nogueira (2006), using HPLC with diode array detection (DAD) in direct injection mode. The mobile phase consisted of an aqueous solution of 10% acetonitrile (v/v) and

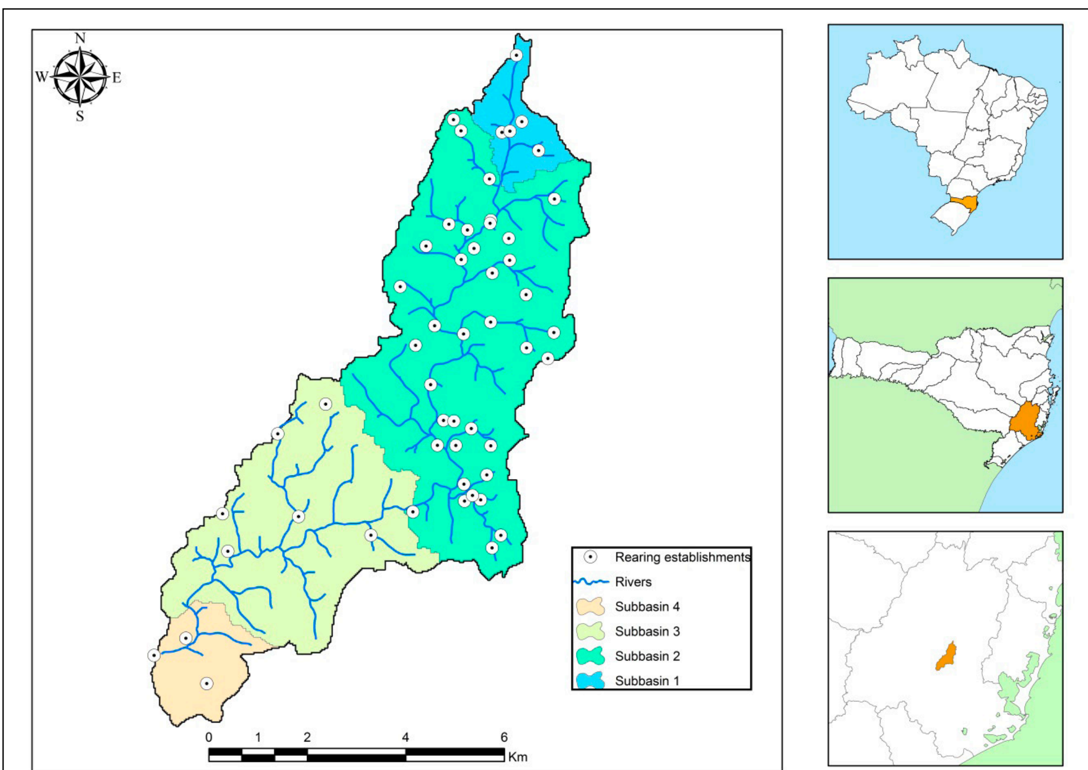

FIGURE 1. Coruja river basin and location of pig rearing establishments.

TABLE 1
Sub-basin land use (ha)

Land use	Sub-basin 1	Sub-basin 2	Sub-basin 3	Sub-basin 4	Total	
					ha	%
Grassland	176.89	1.281.69	716.06	198.24	2.372.88	48.6
Native forest	33.70	740.82	447.86	11.15	1.233.53	25.3
Agriculture	47.66	361.47	34.51	4.34	447.97	9.2
Reforestation	12.42	214.77	198.65	12.57	438.41	9.0
Urban area	13.20	12.88	209.87	139.10	375.05	7.7
Forest regeneration	0.00	7.09	0.00	0.00	7.09	0.1
Exposed soil	0.00	0.00	4.87	0.00	4.87	0.1

TABLE 2.
Distribution of pig farms and animals in the sub-basins

	Sub-basin 1	Sub-basin 2	Sub-basin 3	Sub-basin 4	Total
No. of pig farms	5	38	6	3	52
No. of animals	7,754	35,167	4,718	5,020	52,659

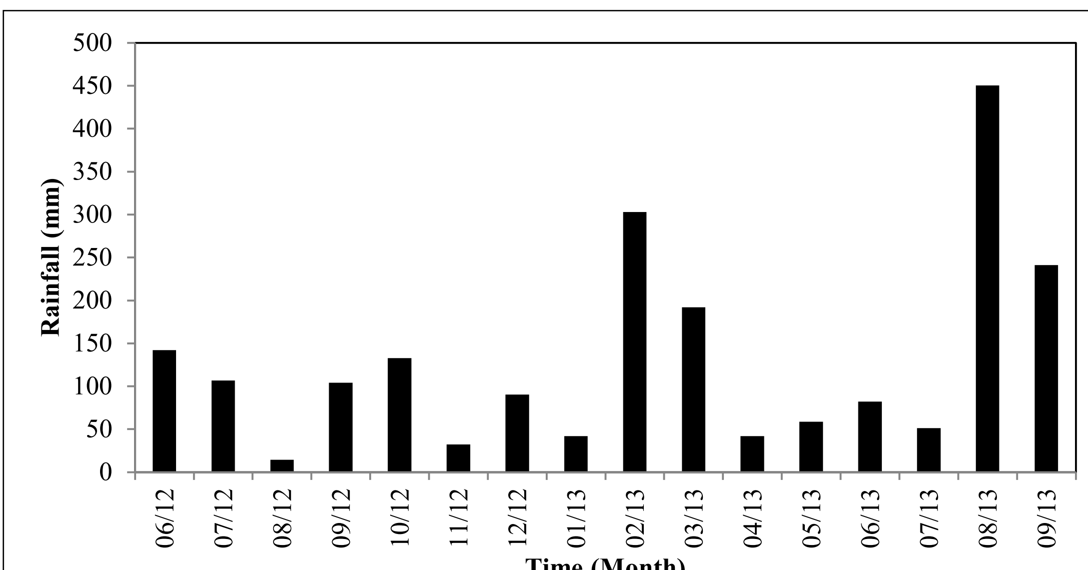

FIGURE 2. Temporal (monthly) distribution of rainfall

acetonitrile P.A. applying a gradient of 0 to 100% acetonitrile P.A. over 60 min and a flow rate of 1 ml min^{-1}. The column used was a C18 (150 mm x 4 mm, 5μm) and the detection wavelengths were 200 nm for estradiol, 17α-estradiol, 17β-estradiol, 17α-ethinylestradiol, estrone and mestranol, 240 nm for norgestrel and progesterone and 280 nm for toltrazuril. Cyclins were determined by the method Dionex #76, Tetracyclines in pork (DIONEX, 2010). The reagents used were acetonitrile and phosphoric acid (0.15%, pH 2.15). Elution started with 10% acetonitrile and 90% phosphoric acid with a flow rate of 1 ml min^{-1}, followed by 45% acetonitrile and 55% phosphoric acid with a flow rate of 1.2 ml min^{-1} for 14 min. The analysis time was around 17 min and the wavelength for all molecules was 370 nm. For sulfamethazine the method adapted by Santos et al. (2007) was employed, using acetonitrile and water in a ratio of 30:70 and a flow of 0.250 ml min^{-1}. The analysis time was 18 min and the wavelength was 270 nm. In both analysis procedures the column temperature was maintained at 25°C and the injection volume was 200 μl min^{-1}.

The evaluation of the results was divided into quantitated, detected and not detected: 'quantitated' relates to cases where the concentration was higher than the quantitation limit defined by the calibration curve; 'detected' indicates that the molecule was detected but in a concentration that could not be quantitated; 'not detected' indicates that the molecule could not be detected employing the chromatographic technique. The quantitation and detection limits were determined from the slope of the standard calibration curve multiplied by 10 and by 3.14, respectively, as recommended by Ribani et al. (2004). Table 3 shows the quantitation and detection limits obtained for each molecule investigated.

RESULTS AND DISCUSSION

Table 4 shows the number of determinations and the distribution of the results (quantitated, detected and not detected). Of the 389 determinations, 2.06% of the results corresponded to 'quantitated' and 2.31 % to 'detected', while 95.63% of the results fell into the category of 'not detected' by the equipment.

Table 5 shows the monthly results for the samples. Seasonally, the highest number of 'quantitated' results was obtained for samples collected in January (6 out of 44 samples analyzed) which was one of the months with the lowest rainfall rate (42.1 mm). In January corn is harvested for silage production, which also marks the beginning of the soil preparation for the pig manure application on pasture land. This result is in agreement with that reported by Awad et al. (2014), who evaluated antibiotics in a Korean river and observed a higher detection frequency in the months with lower rainfall. This finding can be explained by the fact that with higher precipitation the chemical species may be diluted in the soil, water or in other environmental compartments.

In the study region, January (summer) is associated with high temperatures, in contrast to the results reported by Kim and Carlson (2007b). The authors observed higher antibiotic concentrations in water and sediment samples during the winter, when the microbial activity is lower due to low temperatures.

Table 6 shows the results of the analysis for each sub-basin (SB). A variation, of an irregular nature, between upstream and downstream samples was observed. Arikan et al. (2007) also report this trend in the Choptank River Watershed, along the Delmarva Peninsula of Chesapeake Bay, USA.

Sub-basin 1 showed no quantitation of the molecules analyzed. This result reinforces the expectation that the presence of pig farming activities promotes the trasport of these contaminants into the environment, since Sub-basin 1 was the less developed basin with a low presence of pig production. A similar result was reported by Pei et al. (2006) who did not detected antibiotics in rivers with low anthropogenic influence.

In sub-basin 2 the highest number of quantitated molecules occurred, reaching 4.81% of the total number of samples analyzed, possibly due to the greater number of animals, pasture areas and agricultural areas where manure applications are mostly performed. In this sub-basin there were 38 pig farms, totalizing 35,167 pigs (Table 2). According to Yang and Carlson (2003, 2004), along a river the presence of chemicals increases with an increase in urban and agricultural activity.

In sub-basin 3, only one quantitation occurred (representing 0.90% of the samples analyzed) and in sub-basin 4 two quantitations were obtained (representing 2.60% of the samples analyzed). Sub-basin 4 is located close to the outflow of the Coruja river, that is, downstream of the urban area.

In Table 7 the total number of samples of the different analyte groups is detailed. Analysis were conducted on 166 and 223 samples for antibiotics

TABLE 3
Quantitation and detection limits (ng L-1) for molecules investigated

Group	Molecules	Detection	Quantitation
Antibiotics	Oxytetracycline	12.99	29.40
	Doxytetracycline	9.71	10.29
	Tetracycline	17.22	21.90
	Chlortetracycline	17.39	20.06
	Toltrazuril	8.70	28.90
	Sulfamethazine	9.70	32.20
Hormones	Estradiol	28.40	94.80
	17α-Estradiol	1.28	3.89
	17β-Estradiol	2.18	6.62
	17α-Ethinylestradiol *	18.40	61.20
	17α-Ethinylestradiol *	0.86	2.60
	Estrone	36.50	121.70
	Norgestrel	4.09	12.37
	Progesterone	1.37	4.16
	Mestranol	1.70	5.16

* The column was changed and the quantitation/detection limit was reduced.

TABLE 4
Total number of determinations

Result	Total	%
Total number of determinations	**389**	**100**
Quantitated	**8**	**2.06**
Detected	**9**	**2.31**
Not Detected	**372**	**95.63**

TABLE 5
Temporal distribution of samples and molecules determined

Month/ year	Samples Analyzed	Quantitated	Detected	Not Detected	Concentration max. (ng L^{-1})	Molecule
06/2012	27	0	0	27	-	-
08/2012	27	0	0	27	-	-
09/2012	27	0	0	27	-	-
12/2012	16	0	0	16	-	-
01/2013	44	6	2	36	452.60	Chlortetracycline
02/2013	44	2	7	35	16.20	Doxytetracycline
03/2013	20	0	0	20	-	-
05/2013	20	0	0	20	-	-
06/2013	20	0	0	20	-	-
07/2013	32	0	0	32	-	-
08/2013	56	0	0	56	-	-
09/2013	56	0	0	56	-	-

TABLE 6
Distribution of results for the sub-basins (SBs).

Session	Samples analyzed	Quantitated	%	Detected	%	Not Detected	%	Concentration $_{max.}$ (ng L^{-1})	Molecule
SB 1	104	n.d*	-	3	2.88	101	97.12	-	-
SB 2	104	5	4.81	1	0.96	98	94.23	452.60	Chlortetracycline
SB 3	104	1	0.96	3	2.88	100	96.15	81.80	Chlortetracycline
SB 4	77	2	2.60	2	2.60	73	94.81	372.40	Doxytetracycline

*n.d – not detected.

TABLE 7
Total number of determinations per substance group.

Parameters	Antibiotics	%	Hormo-nes	%
Samples analyzed	166	100	223	100
Quantitated	8	4.82	0	-
Detected	0	-	9	4.04
Not Detected	158	95.18	214	95.96

and hormones, respectively, but only antibiotics were quantitated. This result corroborates those of Carballa et al. (2004), who noted that antibiotics are easier to detect in water because they typically remain in the aqueous phase, while hormones are mostly adsorbed by soil or sediment.

Antibiotics were detected at concentrations greater than the quantitation limit in 4.82 percent of the 166 samples analyzed. Hormones were detected below the quantitation limit in 4,04 % of the 223 samples that were analyzed. A similar result was encountered by Arikan et al. (2007) in a study on the Choptank River, Northeastern, U.S., where hormones were practically absent from the samples, being below the detection limits at various points of the river. According to Ying et al. (2002) and Sumpter and Johnson (2008), hormones have short half-life times and rapidly degrade in river water. This is consistent with the findings of Ho et al. (2013), who reported that 99% of the hormones and antibiotics investigated were removed within only 40 days of composting.

Table 8 provides details of the determination of the antibiotics, showing the maximum and minimum concentrations. Only sulfamethazine and toltrazuril were not quantitated. The toltrazuril molecule did not even present trace levels. This result is in contrast with that of Choi et al. (2008), who reported high concentrations of sulfamethoxazole (also of the sulfa group) in surface waters collected from sewage treatment plants. The non-occurrence of sulfamethazine may be linked to its rapid degradation. In a study by Selvam et al. (2012) on swine manure composting, sulfadiazine was completely removed within 3 days. Another important factor in relation to the result obtained for sulfamethazine is photochemical degradation. According to Boreen et al. (2004), photochemical reactions are involved in sulfonamide reduction. In a study with four sulfonamides, Lai et al. (2011) concluded that these molecules degraded more quickly on exposure to natural light.

Of the antibiotic molecules investigated, oxytetracycline, tetracycline and doxytetracycline were the most frequently detected in the samples. This result is in agreement with that of Kim and Carlson (2007a), who found high concentrations of chlortetracycline and oxytetracycline in sediments in the Cache la Poudre River, northern Colorado (USA). The high occurrence of chlortetracycline can be explained by the fact that these molecules have a high half-life of more than 400 days in water (SOEBORG et al., 2004). In a study to determine the effects of composting animal manure, Bao et al. (2009) concluded that within 42 days only 27% of the chlortetracycline had been eliminated from swine manure.

Doxytetracycline is one of most frequently detected molecules in the analysis, but at the same time this is the molecule with the lowest maximum concentration (88.60 ng L^{-1}). This result may be linked to its rapid degradation. Ho et al. (2013), studied bird manure composting and demonstrated that doxytetracycline was degraded in only 13 days of composting, with low concentrations being present after this time.

The quantitation rate for chlortetracycline was 10.34 % (Table 8), a value close to that found by Arika et al. (2008), that is, 19% for chlortetracycline. However, for oxytetracycline the value of 3.45% was below that found by the same author, that is, 15% for oxytetracycline.

Oxytetracycline was quantitated in only one sample (3.45 % of the samples analyzed), which is similar to the result reported by Winckler et al. (2004), that is, 5.1% for oxytetracycline. This result may have been influenced by two fac-

TABLE 8

Results for antibiotics determination

Molecule	Samples analyzed	Quantitated	%	Detected	%	Not Detected	%	Concentration $_{max.}$ (ng L^{-1})
Oxytetracycline	29	1	3.45	n.d	-	28	96.55	120,00
Doxytetracycline	29	2	6.90	n.d	-	27	93.10	88,60
Chlortetracycline	29	3	10.34	n.d	-	26	89.66	452,60
Tetracycline	29	2	6.90	n.d	-	27	93.10	238,20
Sulfamethazine	29	n.d*	-	n.d	-	29	100	-
Toltrazuril	21	n.d	-	n.d	-	21	100	-

*n.d – not detected

TABLE 9

Results for hormone determination

Molecule	Samples analyzed	Quantitated	%	Detected	%	Not Detected	%	Concentration $_{max.}$ (ng L^{-1})
Estradiol	25	n.d*	-	n.d	-	25	100	-
17α-Estradiol	28	n.d	-	n.d	-	28	100	-
17β-Estradiol	28	n.d	-	n.d	-	28	100	-
Estrone	25	n.d	-	n.d	-	25	100	-
17α-ethinylestradiol	41	n.d	-	6	14	35	85	-
Norgestrel	20	n.d	-	n.d	-	20	100	-
Progesterone	28	n.d	-	3	10.71	25	89.29	-
Mestranol	28	n.d	-	n.d	-	28	100	-

*n.d – not detected

tors: soil adsorption or degradation due to the high temperature of the water. According to Allaire et al. (2006), sandy soils quickly adsorb chlortetracycline and Rose et al. (1996) noted that oxytetracycline is rapidly degraded in warmer waters, indicating a higher rate of abiotic degradation. In a composting study, Arikan et al. (2008) confirmed a 95% reduction in the oxytetracycline levels after 35 days of composting.

The tetracycline and doxytetracycline quantitation rate for the samples was 6.90% for each molecule (Table 8). This result is close to that reported by Arika et al. (2008), that is, 4% for the same molecules. According to Qiao et al. (2012) tetracycline is one of the most commonly used antibiotics in swine production.

Chlortetracycline had a maximum concentration of 452.60 ng L^{-1}, a result similar to that reported by Aust et al. (2008), where the surface water concentrations in two Canadian feedlots where antibiotics were used reached 400.00 ng L^{-1}.

Table 9 provides the total results for the determination of the hormones. In the river water samples the hormones presented lower incidence compared to the antibiotics. In fact, in this study, there was no quantitated result for the hormones, all most concentrations were below the detection level. A hypothesis for the absence of these molecules was proposed by Sarmah and Northcott (2008), who studied hormone degradation in river water and concluded that hormone concentrations decreased by more than 90% over a period of 2 to 4 days.

Although hormones do not present a direct risk to the environment, according to Sumpter and Johnson (2008), even at low concentrations hormones can cause endocrine disruption in species present in the environment. Furthermore, in combination with other substances their estrogenic effect can be enhanced (BRIAN et al., 2005).

17α-ethinylestradiol presented occurrence, which may be linked to its rapid degradation. Sarmah and Northcott (2008) concluded that 17α-ethinylestradiol is degraded by over 90% within 2 to 4 days, significantly decreasing thereafter. This result is in agreement with the findings of Jiang et al. (2012), who evaluated surface water resources and noted that the 17α-ethinylestradiol concentrations were below the quantitation limits, being partially detected. Following a study on hormones in drinking water in the USA, Benotti et al. (2008) reported that the maximum concentrations of 17α-ethinylestradiol reached 1.40 ng L^{-1}. Hohenblum et al. (2004) carried out a study on surface waters in Austria and found concentrations of 0.33 ng L^{-1} while Zuo et al. (2006) reported concentrations of 4.17 ng L^{-1} in the USA.

Progesterone was detected in three samples. This result is similar to that of Arika et al. (2008), who identified progesterone as one of the most frequently occurring molecules, which was present in high concentrations in their analysis.

Estradiol was not quantitated or detected in any of the sub-basins, confirming its non-occurrence in these river water courses. A similar result was found by Arika et al. (2008), with no estradiol detected in the river sub-basins studied.

17β-estradiol was also one of the molecules that did not occur in quantifiable levels. This result is in agreement with that reported by Jiang et al. (2012), who studied estrogens in a major river in China, concluding that concentrations of 17β-estradiol were below the quantitation limits. In several studies, low concentrations of 17α-estradiol have been found in surface water bodies. Lu et al. (2010) reported a maximum concentration of 0.97 ng L^{-1} in a river in China, Zuo et al. (2006) found a surface water concentration of 0.83 ng L^{-1}, Dorabawila and Gupta (2005) determined concentrations ranging from 1.90 to 6.0 ng L^{-1} in surface water bodies in the U.S, Hohenblum et al. (2004), determined a maximum concentration of 1.2 ng L^{-1} in superficial waters in Austria and Cargouet et al. (2004), also in surface waters in Austria, determined concentrations ranging from 1.40 to 3.00 ng L^{-1}. Jacobsen et al. (2005) and Snow et al. (2010) concluded that 17α-estradiol is strongly adsorbed by organic carbon present in the soil.

Estrone showed no occurrence, in other words, concentrations were below the detection limit of 35.50 ng L^{-1} for this molecule. Similar results were encountered in China by Jiang et al. (2012), where low concentrations of estrone were present, varying between 0.16 and 2.98 ng L^{-1}. In the Yangtze River, Lu et al. (2010) found a maximum concentration of 3.8 ng L^{-1}. In the USA, Zuo et al. (2006) found a concentration of 1.20 ng L^{-1} and Cargouet et al. (2004) reported surface water concentrations ranging from 1.10 to 3.00 ng L^{-1}. According to Lopes de Alda and Barcelo (2001), under favorable conditions the completed degradation of estrone can occur within a few days. According to Kashian and Dodson (2004) and Brennan et al. (2006), even estrone levels below 5.00 ng L^{-1} can be harmful to aquatic organisms.

CONCLUSIONS

The occurrence of hormones and antibiotics was observed in the Coruja river basin, this being mainly related to swine manure applied to agricultural fields as fertilizer. The molecules investigated presented low mobility and their presence was focused mainly in sub-basins 2 and 3, areas with the highest occurrence due to their release from soils treated with animal manure. Sub-basin 2 has the largest areas of fields, farms and animal rearing and sub-basin 3 has the largest urban area.

Oxytetracycline, tetracycline and chlortetracycline molecules were the antibiotics most frequently detected, and these were associated with more intense swine culture. The highest antibiotic concentration occurred in the case of chlortetracycline, with a value of 452.60 ng L^{-1}.

The results of this study verify that swine farming waste products and manure are a source of hormones and antibiotics in aquatic ecosystems, including water destined for domestic use or industrial and agricultural activities.

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