



Research article

Characterization of organic compounds and drugs in sewage sludge aiming for agricultural recycling

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ABSTRACT

The application of sewage sludge in soils can bring benefits to agricultural productivity, however, the risks arising from this application must be measured and carefully evaluated. Persistent organics compounds and drugs can be present in the sewage sludge and if applied to the soil, they can cause severe risks to the soil biota and contamination of groundwater. This work determined 174 persistent organic compounds and drugs in sludge samples from a wastewater treatment plant using chromatographic methods. The drugs ciprofloxacin, enrofloxacin and diclofenac were quantified, and values varied according to sampling period. For persistent organic compounds, cresols were the most abundant compounds in sewage sludge. With the analyses made of both the elutriate and the filtrate, it was possible to verify the potential for soil retention or leaching that each compound can present with the application of sewage sludge in the agriculture.

1. Introduction

The use of sewage sludge (SS) in agricultural soils is a practice that combines recycling of important nutrients, such as nitrogen (N) and phosphorus (P), and environmentally appropriate disposal of waste generated in large quantities. In addition, its use as a fertilizer in agricultural soils improves soil quality and increases productivity (Siebielec et al., 2018; Bai et al., 2017; Gonzaga et al., 2017; Fang et al., 2017; Hei et al., 2016; Hernández et al., 2016; Martins et al., 2016). The agricultural use of SS is a widespread practice, but it can be responsible for soil contamination affecting essential ecosystem services that maintaining and improve the quality of flora, fauna and human needs (Buch et al., 2017). According to Bondarczuk et al. (2016), a study by the European community revealed emerging risks related to the use of SS in the soil.

For a safe use of SS, it must be characterized in terms of its composition, as this residue may contain toxic compounds, causing environmental contamination. The risk of soil contamination due to the presence of metals, drugs and organic compounds has been detected in the SS (Ivanová et al., 2018; Konczak and Oleszczuk, 2018; Melo et al., 2018; Martins et al., 2016; Bouriou et al., 2015; Alvarenga et al., 2015).

The compounds that may be present in the SS are directly related to the sewage composition, and pharmaceutical and personal care products have attracted attention, not only due to their potential for ecotoxicological risk

but also due to their continuous release into the environment (Ivanová et al., 2018; Martín et al., 2015). Drugs reach the environment through different routes, but it is known that sewage is one of the main accessed routes, and these compounds have already been found in water, soil and waste around the world (Iranzo et al., 2018; Pino-Otín et al., 2017). According to Yang et al. (2017) drugs have been detected in organic crops that received SS as fertilizers and these compounds can have adverse cumulative effects on terrestrial and aquatic environments.

The presence of compounds, such as drugs in SS, has been drawing attention not only due to their potential for ecotoxicological risk but also due to the continuous release into the environment (Fijalkowski et al., 2017; Bondarczuk et al., 2016; Chen et al., 2015). Researches indicate the presence of aspirin, analgesics, diclofenac (Fijalkowski et al., 2017), the last being consumed on large scale and found in soils that received agricultural application of SS and that have a high toxicity potential (Chen et al., 2015). Legislation, such as the European Directive 86/278/EEC, have been revised so that more compounds can be evaluated, in addition to the commonly monitored organic and inorganic contaminants (Stiborova et al., 2017). Thus, characterizing the SS in terms of the presence of these compounds is extremely relevant, considering the possibility of reusing this residue and considering that there are not yet many studies evaluating these compounds in SS that are already in conditions to be applied on soils (Ivanová et al., 2018).

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Taking into account the potential for soil contamination, it is important to choose the most effective method to reduce the volume/weight of sludge and toxicity, especially when it comes from sludge that will be applied to agricultural soils.

Different sludge treatment methods can be used, such as biological, chemical, thermal, and thermochemical. [Teoh and Li \(2020\)](#) gathered studies that allowed to conclude that the biological sludge treatment methods, such as anaerobic digestion, compost and swamps, are the most effective to reduce organic compounds and medicines, but do not degrade heavy metals. Considering the SS life cycle, the same authors concluded that anaerobic digestion, pyrolysis and Supercritical Water Oxidation (SCWO) are the most effective treatments for both weight/volume reduction and toxicity reduction and still have less Global Warming Potential (GWP) in the SS degradation process.

Although anaerobic digestion has been considered one of the best treatments among the compared treatments, as it degrades about 30% of some drugs and reduces the level of Polychlorinated Biphenyls (PCBs) in SS by up to 32% in 21 days, this method does not reduce levels of metals in the soil. Pyrolysis was able to reduce Polychlorinated Dibenzo-p-dioxin and Dibenzofuran (PCDD/F) and metals, and SCWO reduced by 95% Chemical Oxygen Demand (COD) and 99% the metals chromium (Cr), copper (Cu), zinc (Zn) and iron (Fe) ([Teoh and Li, 2020](#)).

Considering that the presence of drugs and organic compounds has been increasing and that these compounds may be responsible for causing negative impacts on the environment, this research had the main objective to make an extensive evaluation of a SS of a Wastewater Treatment Plant (WWTP) to identify and quantify the presence of organic compounds and drugs, having been evaluated the crude SS, elutriates and elutriate filtration residues to verify the presence of these compounds for agricultural use of this residue.

2. Material and methods

2.1. Sewage sludge sampling

Two samples of SS were collected at a WWTP in the Metropolitan Region of Campinas - SP (22°52' 22°43'S, and 47°06' 46°L), with the capacity to treat the effluents of an average population of 250000 inhabitants and that operates with a nominal flow of 650 L/s to 800 L/s, of sewage in an Upflow Anaerobic Reactor and Sludge Mantle, followed by post-treatment by chemical flocculation and flotation by dissolved air. The sludge generated in the biological treatment and the physical-chemical treatment is directed to the sludge equalization tank, and then it is dehydrated through two centrifugal pumps. The centrifuged sludge has a humidity of around 0.7–0.8 g/g, and the daily production of SS is approximately 19000 kg (dry basis).

The SS samples were collected with a stainless-steel shovel directly from the container that received the residue after centrifugation, and the volume collected was made in stainless-steel trays (approximately 20 kg) and transferred to non-toxic plastic bags, according to Brazilian legislation ([Brazil, 2006](#)). The containers containing the sample were transported inside a thermal box under refrigeration below 10 °C, without freezing, as proposed by [ABNT 15469 \(ABNT, 2007\)](#). The samples were stored in a specific refrigerator, under the same conditions (refrigeration below 10 °C, without freezing) until the end of the tests.

The collections were carried out with an interval of 10 months, being called collections A and B, respectively. Both samples were considered stable as the Sludge Stability Index (Volatile Total Solids/ Total Solids) was greater than 0.7, complying with the legislation for agricultural use ([Brasil, 2006](#)). The results of the chemical characterization of the sludge samples are shown in [Table 1](#) and the analyses were performed according to the methodology proposed by [APHA \(2012\)](#).

2.2. Sample preparation

The preparation of the aqueous extract followed the Brazilian legislation ([ABNT, 2007](#)) item 5.9.2, with adaptation concerning centrifugation speed, due to the characteristics of the sample, as it had a high content of sediment, suspended solids, and turbidity. Thus, the centrifugation speed used was 14.000 rpm, which enabled greater clarification of the aqueous extract. The centrifugation process occurred at approximately 4 °C to minimize the degradation or chemical reactions in the samples that may occur due to the heat generated in the centrifugation process. The extract was prepared to simulate the elutriate, which represents the leaching of SS through the soil. Thus, the elutriate enables verification of the presence of contaminants and consequent groundwater contamination.

2.3. Instrumental analysis of organic compounds

The organic compounds monitored in the sludge and the elutriate are presented, together with the respective methodologies in [Tables 2 and 3](#). [Table 2](#) shows the organic compounds considered volatile analyzed via "Head Space" and Gas Chromatography coupled to Mass Spectrometry (GC-MS). An aliquot of these samples was transferred to a 20 mL vial, 10 mL of water, and 0.5 g of sodium sulfate were added to promote the "salting out" effect, sealed with aluminum and placed to be heated by 30 min at 60 °C before being injected.

Analytical methods used in the dosages of the compounds were USEPA 8081B ([EPA, 2007](#)) by Gas Chromatography coupled to Electron Capture Detector (GC-ECD) for Organochlorine and Aroclor Pesticides, and USEPA 8270B ([EPA, 2014](#)) by GC-MS for the other tested compounds. The semi-volatile organic compounds evaluated in the studied SS and elutriate are shown in [Table 3](#).

The extractions of the solid samples were performed by ultrasound with power control, using Hexane-Dichloromethane solvent (1: 1 v/v), followed by concentration with the aid of a TurboVap evaporator and a nitrogen jet, swelling the final extract to 1 mL. Then, each extract was filtered at 0.45 µm and injected. The liquid samples were extracted by liquid-liquid extraction with Hexane-Dichloromethane (1: 1 v/v), 2 × 100 mL with pressure relief between each partition, followed by evaporation and swelling identical to the solid samples. [Table 4](#) shows the characteristics of the organic compounds detected as well as the retention time of the compounds under operational conditions using the gas chromatography method.

2.4. Instrumental analysis of drugs

The drugs enrofloxacin, ciprofloxacin, and diclofenac were chosen as they are commonly consumed by the human population and for animal health.

The raw SS, the filtrates and the elutriate from collections A and B were analyzed. The separation of the elutriate and SS (elutriate filtrate) was carried out by ultracentrifugation with refrigeration at 10 °C, avoiding heating of the samples with potential degradation of the drugs of interest. The analysis of filtered elutriate was performed only for the drugs under study, in order to allow knowing the total load of these contaminants (filtrate + elutriate) and simulate leachate that can contaminate groundwater.

The drugs analyzed followed the methodology of [Fornazari \(2015\)](#), using Ultra Performance Liquid Chromatography coupled to Mass Spectrometry and Positive Electrospray Ionization (UPLC-ESI-MS/MS). The samples of raw SS were submitted to extraction with methanol and the elutriate sample was extracted with n-Hexane, the solvent was changed to methanol in formic acid. After extraction, the samples were filtered at 0.45 µm and injected into the equipment. The characteristics of the drugs are presented in [Table 5](#), such as the chromatographic retention times of the compounds and their respective most abundant fragments, through the applied methodology, used in the quantification step.

Table 1. Results of Physico-chemical parameters in the two samples of sewage sludge.

Parameters	Collection A	Collection B
Organic Carbon (g kg ⁻¹)	384	709
Chloride (mg kg ⁻¹)	2342	1905
Nitrate Nitrogen (mg kg ⁻¹)	265	91.9
Nitrite Nitrogen (mg kg ⁻¹)	4.87	1.0
Ammoniacal Nitrogen (mg kg ⁻¹)	4311	1079
Nitrogen Kjeldahl (mg kg ⁻¹)	20678	32367
Total Nitrogen (mg kg ⁻¹)	20948	32460
pH in water (1:10)	7.33	7.62
Total Solids (TS) (%)	24.4	20.4
Volatile Total Solids (VTS) (%)	13.4	24.6
Sludge Stability Index	0,55	0,59
Humidity (%)	75.6	79.6

2.5. Quality assurance and quality control

For technical support of the results, Analytical Quality Control (QC) data were generated, which are divided into Laboratory White Samples, Fortified White Samples and Tracers (Organic Analysis). Laboratory White Samples provide information about the operational conditions in which the analysis is being performed and results below the Limit of Quantification (LOQ) of the method in question, indicating that the analytical system is in full condition to be used. For Fortified White Samples, the sample is fortified with a known quantity of the analyte (s) of interest. Then, the complete analytical method is performed and recovery of this added fraction is expected as close to 100% as possible. A typical recovery range can be 70%–130% of the fortified quantity. In this work the recovery ranged between 102% and 119% for volatile organic compounds (LOQ < 4 µg kg⁻¹) and between 97% and 86% for semi-volatile organic compounds (LOQ < 20 µg kg⁻¹ for phenolic compounds and aromatic polycyclic hydrocarbons). The tracers allow to evaluate any deviation that may occur during sample manipulation and would impact the result of the analysed chemical agent (s). Therefore, a selected chemical agent is added, different from those to be analysed, which acts as a tracer. The addition of an aliquot of the tracer 4-Bromofluorbenzene (BFB) in this works samples, for volatile organic compounds' analysis, showed a 100% recovery, for phenolic compounds the tracer O 2,4,6-Trichlorophenol (TCF) was used with a recovery of 92%.

3. Results

The analyses carried out on the raw SS and elutriate evaluated a total of 108 semi-volatile compounds, 66 volatile compounds, and 3 drugs. The results were grouped according to the main chemical characteristics and compared with CONAMA 375 (Brasil, 2006) and, when relevant, with CONAMA 420 (Brasil, 2009), which provides guiding values for contaminated areas.

3.1. Concentration profile of organic compounds

Of the 174 organic compounds analyzed, 7 were detected in at least one of the 2 samples, in the SS or the elutriate. In both collections, volatile organics were detected while for collection B, phenolic compounds were also found and toluene was present in the two samples analyzed. Table 6 shows all organic compounds that were quantified in the analyzed samples.

Some of the concentrations of organic compounds varied between the two collections, with an emphasis on cresols, phenol, and toluene, as shown in Table 6. This variation can be attributed to the heterogeneity of the sewage and the sample, throughout the operation of the WWTP. According to Yu et al. (2015) and Ramalho et al. (2020), cresols are commonly used in the production of disinfectants, with creolin and lysol being their most common derivatives. Also, Yu et al. (2015) state that biological treatment has a low level of cresols' removal. Therefore, a possible justification for the high concentration of cresols in collection B is the presence of a soap and glycerin production industry (responsible for 33% of all product sales in the national market) close to the WWTP where the studied SS was collected.

Regarding the phenolic compounds detected, emphasis should be given to the mixture of cresols (ortho, meta, and para-cresol) and phenol in collection B, since toluene remained below the maximum limit established for the evaluated legislation. In collection A, tetrachloroethane and toluene were detected, while pentachlorophenol was detected in collection B, all below the maximum allowed by CONAMA 375 (Brasil, 2006) and CONAMA 420 (Brasil, 2009). In the research by Byliński et al. (2019) high concentrations of cresol were also detected, which varied from $47.7 \times 10^2 \pm 6.9 \times 10^2$ ng g⁻¹ of sludge, and according to the authors, the presence of this compound can also be related to the action of microorganisms and the presence of tryptophan, an amino acid present in plant and animal cells.

USEPA classified the cresol group as a class C pollutant, possibly carcinogenic to humans (González-Blanco et al., 2015; Zhou and Nemati, 2018). Bright and Healey (2003) evaluated the SS from several regions of

Table 2. Volatile organic compounds analyzed in sewage sludge and elutriate using USEPA8260B method (EPA, 1999).

1,1-Dichloroethane	Bromoform	cis-1,2-Dichloroethane	Trichloroetene
- 1,1-Dichloroethene	Bromomethane	cis-1,3-Dichloropropene	Trichlorofluoromethane
1,1-Dichloropropene	1,2-Dichlorobenzene	Vinyl chloride	1,3,5-Trimethylbenzene
1,1,1-Trichloroethane	1,2,3-Trichlorobenzene	Chlorodibromomethane	1,4-Dichlorobenzene
1,1,1,2-Tetrachloroethane	1,2,3,4-Tetrachlorobenzene	Chloroethane	2-Chlorotoluene
1,1,2-Trichloroethane	1,2,3,5-Tetrachlorobenzene	Chloroform	4-Chlorotoluene
1,1,2,2-Tetrachloroethane	1,2,4-Trichlorobenzene	Chloromethane	Bromobenzene
1,2-Dibromo-3-chloropropane	1,2,4-Trimethylbenzene	Dibromomethane	Chlorobenzene
1,2-Dibromoethane	1,2,4,5-Tetrachlorobenzene	Dichlorodifluoromethane	Hexachlorobenzene
1,2-Dichloroethane	1,3-Dichlorobenzene	Dichloromethane	Pentachlorobenzene
1,2-Dichloropropane	1,3,5-Trichlorobenzene	Hexachlorobutadiene	n- Propylbenzene
1,2,3- Trichloropropane	Benzene	Hexachloroethane	o- Xylene
1,3- Dichloropropane	Styrene	Carbon tetrachloride	p- Isopropyltoluene
2,2- Dichloropropane	Ethylbenzene	Tetrachloroethene	sec- Butylbenzene
Bromochloromethane	Isopropylbenzene	trans-1,2- dichloroethene	tert-Butylbenzene
Bromodichloromethane	m + p- Xylene	trans-1,3- Dichloropropene	Toluene

Table 3. Semi-volatile organic compounds analyzed in sewage sludge and elutriate using USEPA 8270D (EPA, 2014) and USEPA 8081B (EPA, 2007).

Monoaromatics	Organochlorine Pesticides	Phenolics
1,2- Dichlorobenzene	Chlordane (isomers)	2- Chlorophenol
1,2,3- Trichlorobenzene	DDT (isomers)	2,3,4,5- Tetrachlorophenol
1,2,3,4- Tetrachlorobenzene	Pentacyclodecane dodecachlor	2,3,4,6- Tetrachlorophenol
1,2,3,5- Tetrachlorobenzene	Heptachlor	2,3,5,6- Tetrachlorophenol
1,2,4- Trichlorobenzene	Lindano (g-HCH)	2,4- Dichlorophenol
1,2,4- Trimethylbenzene	Toxafen	2,4,5- Trichlorophenol
1,2,4,5- Tetrachlorobenzene	Aldrin	2,4,6- Trichlorophenol
1,3- Dichlorobenzene	DDT-DDD-DDE	2,6- Dichlorophenol
1,3,5- Trichlorobenzene	Dieldrin	4-Chlorine-3-methylphenol
1,3,5- Trimethylbenzene	Endrin	Pentachlorophenol
1,4- Dichlorobenzene		2-Methylphenol (o-cresol)
2- Chlorotoluene	Amines	2,4- Dimethylphenol
4- Chlorotoluene	1- Naphthylamine	2,4- Dinitrophenol
Bromobenzene	2- Naphthylamine	3-Methylphenol (m-cresol)
Chlorobenzene	4- Aminobiphenyl	4-Methylphenol (p-cresol)
Hexachlorobenzene	4- Chloroaniline	Cresols
Pentachlorobenzene	p- Dimethylaminoazobenzene	Phenol
Nitro Compounds	Polycyclic Aromatic Hydrocarbons	Ethers
2- Nitroaniline	1- Chloronaphthalene	4- Bromophenyl Phenyl Ether
2,4- Dinitrotoluene	2- Chloronaphthalene	4- Chlorophenyl Phenyl Ether
2,6- Dinitrotoluene	2- Methylnaphthalene	Bis (2-Chlorisopropyl) ether
3- Nitroaniline	3- Methylchlorantrene	Bis (2-Chloroethyl) ether
4- Nitroaniline	7,12 -Dimethylbenzo (a) anthracene	
4- Nitrophenol	Acenaftene	Others
Nitrobenzene	Acenaftilene	3,3-Dichlorobenzidine
Pentachloronitrobenzene	Anthracene	2-Picolino
	Benzo (a) anthracene	Acetophenone
Nitrous Compounds	Benzo (a) pyrene	Benzoic acid
N- Nitrosodi-n-butylamine	Benzo (b) fluoranthene	Benzylic alcohol
N- Nitrosodi-n-propylamine	Benzo (g, h, i) perylene	Bis (2-Chloroethoxy) methane
N- Nitrosodiphenylamine	Benzo (k) fluoranthene	Dibenzofuran
N- Nitrosodimethylamine	Dibenzo (a, h) anthracene	Diphenylamine
N- Nitrosopiperidine	Dibenzo (a, j) acridine	Ethyl Methanesulfonate
	Phenanthrene	Phenacetin
Phthalates	Fluoranthene	Isophorone
Bis (2-Ethylexyl) phthalate	Fluorene	Pronamide
Phthalates	Indene (1,2,3-cd) pyrene	
Butylbenzylphthalate	Naphthalene	Aroclor
Di-n-Butyl Phthalate	Pyrene	Aroclor 1242
Di-n-Octil Phthalate		Aroclor 1254
Diethyl Phthalate		Aroclor 1260
Dimethyl Phthalate		

Canada and found levels of o-cresol, m-cresol, and p-cresol between 50–70 $\mu\text{g kg}^{-1}$, 50–460 $\mu\text{g kg}^{-1}$ and 1300–940000 $\mu\text{g kg}^{-1}$, respectively. Ramalho et al. (2020) evaluated SS from six different WWTPs and found cresol levels between 105.5 and 677.7 $\mu\text{g kg}^{-1}$. In the present study, up to 15545 $\mu\text{g kg}^{-1}$ and 15620 $\mu\text{g kg}^{-1}$ were found for o-cresol and m-cresol, respectively, however, p-cresol was not detected.

The concentration of phenol found by Bright and Healey (2003) was between 200 $\mu\text{g kg}^{-1}$ and 43000 $\mu\text{g kg}^{-1}$, while in the present work 28705 $\mu\text{g kg}^{-1}$ were found. Phenol results of collection B exceeded almost six times the maximum allowed for use in agricultural soil, which would strongly impact the use of this SS for agricultural purposes.

Considering that SS, once applied or incorporated into agricultural soil can generate an aqueous fraction under rain and/or irrigation (Wang and Shizong Wang, 2016), it is understood that this aqueous fraction has similar characteristics to the elutriate generated in the present study. Thus, it was decided to compare the elutriate with the limits established

for organic compounds in groundwater, following CONAMA 420 (Brasil, 2009) as reference. Except for total cresols, all other organics are below the maximum permitted values (Table 7).

For collection A, no concentrations of the evaluated pollutants were detected. For collection B, the concentration of cresols exceeded the limit established for groundwater by Brasil (2009). The concentration of cresols in the elutriate was 603 $\mu\text{g L}^{-1}$ and this value may indicate a risk of contamination of the area that receiving the SS for soil fertilization. Organic pollutants such as polycyclic aromatic hydrocarbons, cresol, and others analyzed are not included in the standards established by the European Union and the United States regarding the application of SS in soil intended for agriculture (EC, 1986; EPA, 1995). According to Hudcová et al. (2019) Directive 86/278/EEC needs to be updated according to the current risks associated with SS application in agricultural soil, with the possibility of using ecotoxicological tests to assess the risks.

Table 4. Characteristics of compounds quantified via SIM/GC-MS (EI +).¹

Compound	CAS	RT ² (min)	SIM Ions (m/z)
Ortho -cresol	95-48-7	5.76	108
			79
Meta-cresol	108-39-4	5.58	108
			79
Para-cresol	106-44-5	5.76	107
			77
Phenol	108-95-2	5.24	94
			66
			39
2- Chloro-Phenol	95-57-8	5.93	128
			64
Bis-2- ethyl-Hexyl Phthalate	117-81-7	12.35	149
			167
Butylbenzyl Phthalate	85-68-7	12.03	91
			149
			206
Toluene	108-88-3	11.13	91
Tetrachloroethene	127-18-4	11.38	166
			131
			94

¹ SIM – Single Ion Monitoring/Gas Chromatography mass Spectroscopy (Positive Electron Impact).

² RT = Retention time.

Table 5. Characteristics of quantified compounds via UPLC-ESI-MS/MS.

Compound	CAS	RT (min)	Precursor Ion (m z ⁻¹)	Transitions (m z ⁻¹)	Collision energy (eV)
Diclofenac	15307-79-6	1.48	296.1	214.10 ³ 250.10	30 13
Enrofloxacin	93106-60-6	1.89	360	342.00 ³ 245.00 316.00	25 25 20
Ciprofloxacin	85721-33-1	1.86	332	314.00 ³ 240.00 288.00	23 24 20
Levofloxacin ¹	100986-85-4	1.86	362	261.00	27
Piroxicam ²	36322-90-4	0.94	332.2	95.00	25

¹ Internal Standard of Enrofloxacin and Ciprofloxacin.

² Diclofenac internal standard.

³ Ions used for quantification.

3.2. Concentration profile of drugs

SS can act as the main reservoir for some drugs, such as fluoroquinolones (FQ), due to their high affinity with solids, which favors the sorption of SS (Arun et al., 2020). Consequently, the use of SS as fertilizer can intensify the strong adsorption of FQ and its persistence in agricultural soil, which may modify soil microbiology and resistance of microorganisms (Arun et al., 2020). Enrofloxacin and ciprofloxacin are antibiotics in the FQ class. Also, diclofenac is a nonsteroidal anti-inflammatory drug, which is widely used, has also been detected in sewage and SS and can leave residues in the environment (Chen et al., 2015).

In this research, concentrations of enrofloxacin, ciprofloxacin, and diclofenac were analyzed in two periods of the same WWTP. In the first collection (A) concluded in August, diclofenac and enrofloxacin showed results below the detectable limits for this methodology. However, in collection B, undertaken in June of the following year, the three drugs were detected, as shown in Table 8.

Results indicate variations in drug concentrations between collection A and collection B. In collection A only ciprofloxacin was detected in the SS in high concentrations. In collection B, the concentration of ciprofloxacin was much lower, and diclofenac and enrofloxacin were both detected. Many variables can justify the different concentrations of drugs in the SS. According to Wang and Shizong Wang (2016), this variation

may be related to the seasonality of consumption of the population and the variation of sewage's characteristics throughout the day. These concentrations and detections can also vary by regions and/or countries in quantities and variety and can also be explained by the different prescription practices related to economic and health development, in addition to the difference related to the biodegradation of the compound and the consumption of these drugs in different periods (Chen et al., 2013).

Environmental factors also influence variations in drug concentrations in the SS. Temperature plays an important role in the processes of drug sorption or degradation (Fernandez-Fontaina et al., 2012; Chen et al., 2013). At lower temperatures, the presence of drugs in environmental compartments increases mainly due to increased consumption and decreased speed of biodegradation because of the lower temperature (Martín et al., 2012; Wang and Shizong Wang, 2016), which corroborates with the present study in which for the coldest period (collection B) higher concentrations of diclofenac and enrofloxacin were observed.

Ciprofloxacin was detected in both collections; however, collection A showed the highest concentration when compared with the other two drugs evaluated. According to Clarke and Smith (2011) and Yang et al. (2017), ciprofloxacin is commonly found in sewage and SS, and for Lachassagne et al. (2015), ciprofloxacin was the antibiotic that had the highest concentration in SS and the authors also confirm the high affinity of FQ for SS. In the study by Arun et al. (2020), high levels of FQ were

Table 6. Values obtained for organic compounds in the sewage sludge samples, compared with CONAMA 375 (Brasil, 2006) and CONAMA 420 (Brasil, 2009).

Organic Pollutants	Results of SS		Maximum value	
	Collection A	Collection B	Brasil (2006)	Brasil (2009)
	(µg kg ⁻¹)			
Phenols				
2- Chlorophenol	<20	<20	na	500
2-Methylphenol (o-cresol)	<20	15545	na	na
3-Methylphenol (m-cresol)	<20	15620	na	na
4-Methylphenol (p-cresol)	<20	<20	na	na
Cresols	<20	31170	160	6000
Phenol	<20	28705	na	5000
Pentachlorophenol	<20	135	160	350
Volatile Solvents				
Tetrachloroethene	270	<2	na	4000
Toluene	1041	116	na	30000
Phthalates				
Bis (2-Ethylexyl) phthalate	<20	<20	1000	1200
Di-n- Butylphthalate	<20	<20	700	na
Dimethylphthalate	<20	<20	250	500
Polychlorinated biphenyls	<20	<20	na	10

na = no applicable.

Table 7. Results of the organic compounds identified and quantified in the elutriate of sewage sludge samples and maximum values allowed from CONAMA 420 (Brasil, 2009).

Organic Pollutants	Results		Maximum value Brasil (2009)
	Elutriate A	Elutriate B	
	(µg L ⁻¹)		
Cresols	<10	603	175
Phenol	<20	<20	140
Pentachlorophenol	<20	<20	9
2- Chlorophenol	<20	<20	10.5
Tetrachloroethene	<2	<2	40
Toluene	<4	22.6	700
Bis (2-Ethylexyl) phthalate	<20	14.5	1200
Dimethylphthalate	<20	<20	14
Polychlorinated biphenyls	<20	<20	3.5

Table 8. Values obtained for drugs in the elutriate and filtrate samples of sewage sludge.

Drugs	Collection A		Collection B	
	Filtered	Elutriate	Filtered	Elutriate
	(µg kg ⁻¹)			
Ciprofloxacin	112.1	46.3	5.4	5.5
Diclofenac	<2.5	<2.5	41.7	3.3
Enrofloxacin	<5	<5	8.2	5.1

found, with ciprofloxacin being the most abundant and present in all samplings carried out in the study. Its presence is due to its wide use in humans in addition to veterinary use (Martín et al., 2015) and because it is an antibiotic prescribed worldwide (Barceló et al., 2009).

Ciprofloxacin values in this study were 158.4 and 10.9 µg kg⁻¹ (filtrate + elutriate) which are relatively lower than those found in other countries. In the United States, 778 µg kg⁻¹ of ciprofloxacin was detected in SS samples, 4.8 µg kg⁻¹ in Switzerland and 230 µg kg⁻¹ in Austria (Barceló et al., 2009). Martín et al. (2015) evaluated 22 pharmaceutical compounds present in different types of SS as primary sludge and digested and composted secondary sludge, in Cadiz and Seville/Spain

regions and detected ciprofloxacin concentrations in the range of 30.3–2759 µg kg⁻¹. A study by Clarke and Smith (2011) evaluated 72 drugs in 84 samples of SS in the United States and ciprofloxacin was detected in all samples, ranging from 10.5 to 2.35 mg kg⁻¹ of dry SS.

Enrofloxacin was not detected in collection A, while in collection B the concentration was 13.3 µg kg⁻¹ (filtrate + elutriate). Ekpeghere et al. (2017) found in Korea 0.065–11.56 mg kg⁻¹ of enrofloxacin, whereas ciprofloxacin was not detected in SS as it is not a widely used drug in the country. The concentrations detected by the mentioned authors were much higher than the concentrations detected in collection B. The authors justify these results due to the extensive production of veterinary

medicine and high adsorption capacity in the SS. In the research by Ikem et al. (2017), this antibiotic was detected in a sewage treatment system in different samples, in concentrations below 15 ng L⁻¹.

Diclofenac was detected in collection B with 45 µg kg⁻¹ (filtrate + elutriate). A bibliographic review by Sillanpää and Vieno (2014), regarding diclofenac and its metabolites content, showed maximum values detected in urban sewers in Europe, China, South Korea, and the USA of 7.1 µg L⁻¹, and in the outlets of WWTP from these regions, the values reached 4.7 µg L⁻¹. This is equivalent to 240 mg per 1000 inhabitants, not counting the metabolites. Other diclofenac detections in SS were found to be 424 µg kg⁻¹, 35 µg kg⁻¹, and 23 µg kg⁻¹ in Spain, Japan, and the USA, respectively (Barceló et al., 2009). Martín et al. (2015) quantified a range of 18.7–35.3 µg kg⁻¹ in a sample of secondary sludge in Spain and Ivanová et al. (2018), 300 ng g⁻¹. Therefore, the range of values found in raw SS in the mentioned countries corroborates with the concentration of diclofenac found in one of the collections for this study. In addition, according to Yang et al. (2017), some analgesics and anti-inflammatories, such as diclofenac, were detected in groundwater in concentrations up to mg L⁻¹, which reinforces the need for this monitoring. The assessment of the presence of drugs in the elutriate, simulating potential groundwater contamination is extremely important.

In this study, the proportion of each drug in the elutriate and the filtrate also allowed the identification of how much of the drug can be retained in the soil and how much can be in the solution. The more soluble the drug is, the greater the concentration of the drug in the elutriate (E) compared to its value in the filtrate (F). Therefore, if the E:F ratio is calculated, greater fraction will indicate greater solubility, due to the drug's greater concentration in the aqueous phase, increasing the risk of groundwater contamination if SS is applied to the soil.

The results obtained in collection A showed that ciprofloxacin was distributed in the elutriate and the filtrate of the SS in a ratio of approximately 3:7 (E:F), and for collection B this ratio was 1:1. This difference in proportionality can be explained when compared to the high concentration of ciprofloxacin in collection A, making solubilization difficult due to saturation, which implies a high retention rate of this particular drug on soil. For enrofloxacin, the proportion for collection B was 2:3 (E:F), which demonstrates high solubility, unlike diclofenac in collection B, which presented ratio of 7:93 (E:F), as it tends to remain trapped in the superficial layers of SS because of its low solubility. Accordingly, it can be stated that ciprofloxacin has a significant migration capacity to the aqueous phase (29% in the collection A concentration and 50% in the collection B). In addition, Arun et al. (2020) claim that FQ, like ciprofloxacin and enrofloxacin, has low mobility in the soil, decreasing the risk of leaching in groundwater, although its persistence in the soil for a longer time cannot be neglected.

The present work reinforces the importance of an extensive chemical SS evaluation before allowing its agricultural use. Also, this research supports the need to evaluate the presence of drugs and organic compounds, aiming not to cause environmental contamination.

It is important to emphasize that constant monitoring in areas that may receive this type of waste is essential, as well as the performance of other types of tests. Thereby, a complete analysis enables verification of possible risks of SS use to the soil and consequent problems in relation to the ecosystem services provided through that environmental compartment.

4. Conclusions

The studied SS from both collections could be applied in agricultural soils considering its nutritional potential, and the SS from collection A showed no other restrictions. However, cresols and phenol were found above the limit concentrations established by Brazilian legislation for collection B, which prevents its disposal for agricultural purposes. Also, the high concentration of ciprofloxacin detected in the elutriate highlights the need of studies on the quantification and behavior of organic compounds on SS and soil, and therefore, a probable update in the

current legislation might be needed. In addition, it is recommended further evaluation of cresols and ciprofloxacin behavior in the soil and its impacts in the ecosystem, as well as the effects of these compounds accumulation in the environment.

Declarations

Author contribution statement

J. M. Santana: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

S. V. B. Fraga: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

M. C. K. Zanatta: Analyzed and interpreted the data; CWrote the paper.

M. R. Martins: Analyzed and interpreted the data; Wrote the paper.

M. S. G. Pires: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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