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RESEARCH ARTICLE

The environmental impact of informal and home productive arrangement in the jewelry and fashion jewelry chain on sanitary sewer system

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Abstract

The outsourcing informal home practices adopted in jewelry and fashion jewelry chain can cause toxic substance elimination in the effluents and raise a concern for its environmental impact. This study evaluates if this informal work alters the concentration of potentially toxic elements (PTEs: As, Cd, Cr total and Cr-VI, Cu, Hg, Ni, Pb, Sn, and Zn) in the sewage network. The sanitary sewage samples ($n = 540$) were collected in 15 manholes during two campaigns in three different areas of Limeira-SP, Brazil (industrial area, with informal work and without known industrial/informal activity). The sewage sludge ($n = 12$), raw ($n = 12$), and treated sewage ($n = 12$) were collected in two wastewater treatment plants (WWT: AS and TATU) operating with different treatment process. The PTE determination was performed by ICP-OES, direct mercury analysis, and UV–Vis spectroscopy. Cr-VI, Cu, Ni, and Zn were the only elements above the quantification limit. Four samples exceeded Cu or Zn values permitted to be discharged into sewage system; however, the concentration average was lower than that established by Brazilian legislation. A difference was found between values above and below the 75th percentile for campaign and total organic carbon values ($p < 0.015$). The AS-treated sewage presented low concentrations of Cu ($p < 0.05$), Zn ($p = 0.02$), and Ni ($p = 0.01$) compared to treated sewage from TATU. In the sludge samples, the Cu means exceeded the limits of the Brazilian legislation (1500 mg kg^{-1}) and the Zn results were very close to the limits (2800 mg kg^{-1}). The heterogeneity of the results can indicate the sporadic nature of the PTE's sanitary disposal. PTEs used in jewelry and fashion jewelry chain may precipitate on the sludge, where presented high concentrations of Cu and Zn which require controlled destination.

Keywords Environment impact · Metals · Sewage · Sludge · Contamination · Legislation

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Introduction

The practice of incorporating informal outsourced activities as part of an industrial process has been adopted in some sectors of the industrial economy, mainly on developing countries (Teare et al. 2015; Sikder et al. 2017). Since some activities are developed in the domestic domain and can be directly dumped into the sewage network, there is concern about environmental impact. The informal productive arrangement being researched on this study are included in jewelry and fashion jewelry production, with outsourced process as assembly, filing, polishing, embellishments, and electroplating (Vilela and Ferreira 2008).

The electroplating is a surface treatment that aims to provide the parts with characteristics of resistance to abrasion and corrosion (Chou et al. 2011). This stage is considered of high impact for environment due to the excessive use of chemical products, significant water consumption, and the elimination of toxic substances such as Pb, Cu, Ni, Zn, and Cr from baths and cleaning solutions with different types of acids (CETESB 2005; Ferreira 2005; Ahluwalia and Goyal 2007; Li et al. 2014; Benvenuti et al. 2015; Machado and Lansarin 2016).

The potentially toxic elements (PTEs) determined in this study can be used in electroplating or welding process in the production of jewelry or fashion jewelry (Azevedo and Chasin 2003; Ferreira 2005; Sikder et al. 2017). The high metal concentration, such as Cd, Pb, Ni, and Cu in jewelry content, has already been proven (Yost and Weidenhamer 2008; Weidenhamer et al. 2010, 2011; Guney and Zagury 2014a, b). The PTEs of this study will be represented by the following: As, Cd, Cr (total) and Cr-VI, Cu, Hg, Ni, Pb, Sn, and Zn. The PTE concentration in the environment generates concern for its toxicity, persistence, and non-degradability (Azevedo and Chasin 2003; Maanan 2007; Bacon and Davidson 2008; Zhou et al. 2008; Hill 2010). A significant part of these elements are discharged in sewage, and many of them are not effectively removed by conventional wastewater treatment (US EPA 2004; Baysal et al. 2013). Its accumulation in living organisms can impair metabolic pathways, alter the antioxidant balance, and cause toxic effects (Rehman et al. 2017). As, Cd, Cr-VI, and Ni compounds are classified by International Agency on Research Cancer (IARC 2012) as carcinogenic to humans and Pb (IARC 2006) and metallic Ni as possibly carcinogenic to humans (IARC 1990).

Due to the mobility and the bioavailability of some elements in the environment, the simple determination of their total concentrations in the sewage network is not sufficient to evaluate their constitution, being important to determine their concentrations after the treatment and in the main residue generated in the treatment, the sludge (Cai et al. 2007; Yang et al. 2017). Therefore, it is necessary to obtain information regarding the constitution of the urban sewage (liquid and solid) and compare the PTE concentration with legislation limits around the world. The main objective of this study was to evaluate if informal and domestic work with jewelry and fashion jewelry alters the concentration of sanitary effluents and impacts the environment.

Materials and methods

Study area

Limeira is located 154 km northwest of the city of São Paulo, in the Administrative Region of Campinas (PMSB 2013). Currently, the city has taken a prominent role in the Brazilian jewelry market with a significant concentration of jewelry companies (Lacorte et al. 2013). According to Limeira's jewelry association (ALJ 2014), there are 500 companies that produce about 50 t of pieces per month with national and international marketing channels. These sectors include cases of informality, exploitation of child labor, and improvised work at homes (Lacorte et al. 2013). A study conducted in 2005 found that some chemical elements related to the electroplating of jewelry and fashion jewelry appeared with high X-ray counting number in Limeira city's manholes compared to control area, reflecting the influence of the direct effluent disposal in the sanitary sewage network (Ferreira 2005).

The Limeira sewage system was under the responsibility of the Company "Odebrecht Ambiental" since 1995 until April 2017 (Odebrecht Ambiental 2014a). It is a separate system with 100% of sewage collected and treated and treatment efficiency of 55%. The TATU Wastewater Treatment Plant (WWT) receives the largest volume of sewage generated in the city (70%) and operates with the primary treatment process, with a treatment efficiency of approximately 40%. The AS WWT receives about 15% of the Limeira sewage and is the most modern and equipped in the city with anaerobic reactors followed by activated sludge and efficiency that exceeds 99% of the removal of the pollutant load (Odebrecht Ambiental 2014b). The final sludge disposal was made in landfill.

Sample collection and preparation

The sanitary sewage was collected in three areas of Limeira city (Fig. 1). The first area was an industrial area, including the presence of jewelry and fashion jewelry industries. The second area encompassed neighborhoods that presented a concentration of families inserted in the informal productive arrangement of jewelry and fashion jewelry of the city. The third area includes neighborhoods without known industrial activity and without reports of informal work. The

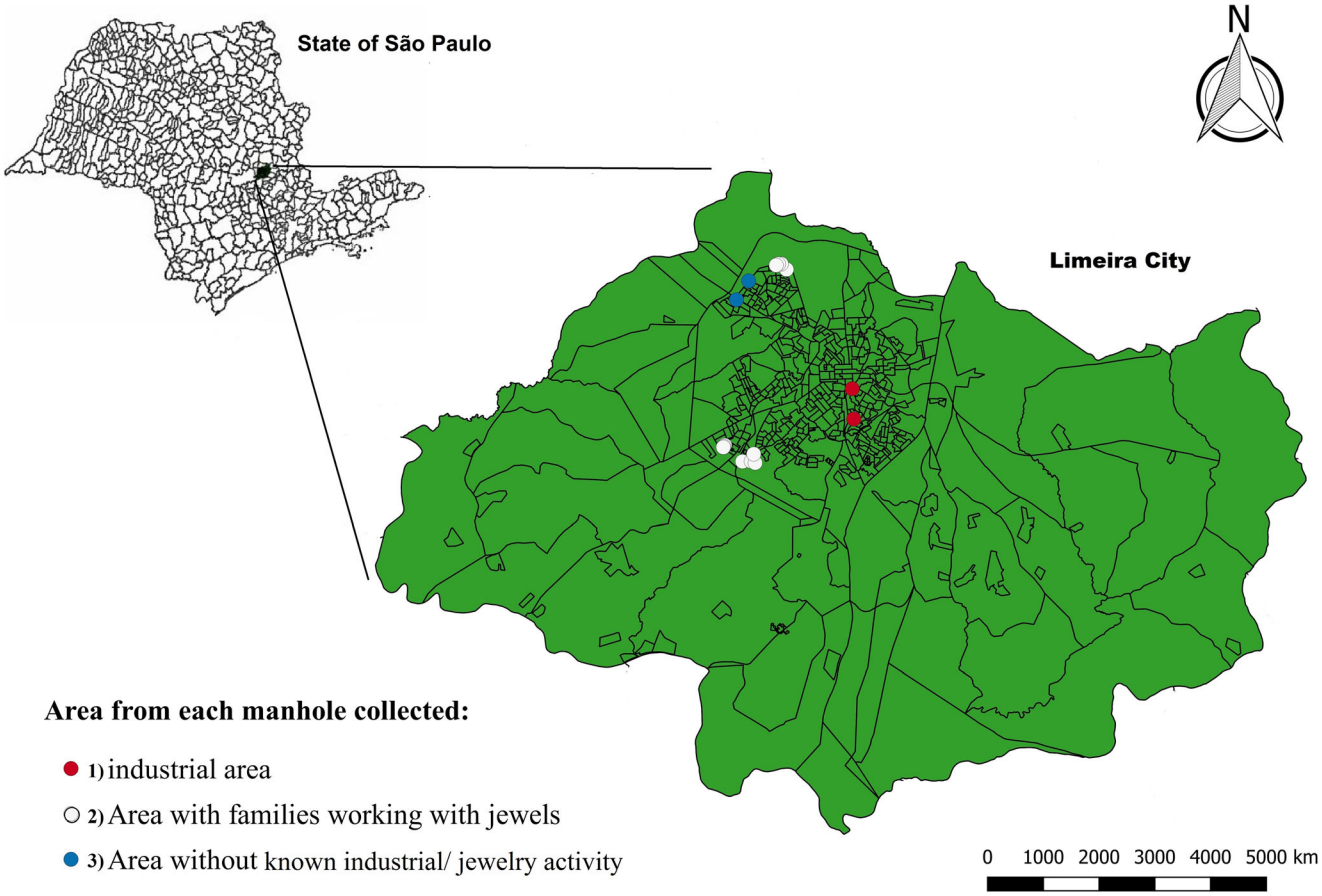

Fig. 1 Location of sanitary sewage collection in each manhole from three different areas of Limeira, SP, Brazil

differentiation between the areas 2 and 3 was confirmed by local observations, carried out in another ongoing study by our research group. Although informal activities are prevalent in area 2, it is impossible to attest their absence in area 3. There is no reliable and scientific information about location, processes, and substances used in informal work. For this reason, this study has an exploratory character and is pioneer in the region. Along with this work, other researches from our scientific group are being carried out in the region, enabling the evaluation of informal household activities and the investigation of their possible routes of exposure and health outcomes.

The sewage samples were obtained in manholes and WWTs, carried out with the support of Water and Sewage Company staff. The manhole selection was done with the aid of a complete map of the city's sewage network. There was concern that the selected manholes would offer representative sanitary sewage samples of the selected regions, without risk of interference of effluent from regions not selected for this study. In this way, it was assured that there were no collections in emissaries and in networks that receive contribution of sewage pumping stations. All the samples collected in the manholes represented only sanitary effluent that receives contribution of domestic and commercial activities, since the evaluation of the contribution of industrial activities is not the objective of this research. The set of manholes selected in each area receives all the effluent that passes through that neighborhood; therefore, the sanitary sewage of all the streets of that area will pass through one of the chosen manholes. Of the 15 manholes analyzed, 11 were in areas with informal work, 2 in industrial area, and 2 in areas without known industrial or informal activity.

The collections were carried out in two different campaigns of the year 2016, May/June and Oct/Nov. For three consecutive weeks, three weekly collections were made (Monday, Wednesday, and Friday). On each day of collection, samples from 15 manholes were collected in the morning (10 a.m.–12 a.m.). In the afternoon, we returned to collect samples in the same manholes (3 p.m.–5 p.m.). Especially on Fridays, in addition to the manholes collection, samples of raw and treated sewage and sludge were collected in the TATU and AS WWT. Thus, in each campaign, 270 samples of sanitary sewage were collected, 6 of raw sewage, 6 of treated sewage, and 6 of sludge, totalizing 540 samples of sanitary sewage, 12 samples of raw sewage, 12 of treated sewage, and 12 of sludge. Each manhole had a determined collection schedule, being at the same time on all days and months of collection, since a change in the sewage network

flow could occur depending on the time of the year, day of the week, number of inhabitants, and local characteristics related to the informality of work that generates a random flow of sewage discards.

All the materials used in this study underwent a cleaning procedure for metals at "Technological Research Institute of the State of São Paulo" (IPT). The materials were immersed in 10% (*v*/*v*) ultrapure nitric acid (HNO^3) from Merck (Darmstadt, Germany) for at least 24 h, subsequently rinsed with ultrapure water 18.2 MΩ cm at 25 °C (Milli-Q) from a Merck Millipore Advantage A10 system.

In each manhole, the contents of the 1 L pot were transferred to three containers of 125 mL; one for elemental, other for Cr-VI, and one for total organic carbon (TOC) determination. In the vessel for elemental determination, 1 mL of 1:1 (*v*/*v*) HNO_3 was added to pH < 2 for sample preservation. In the Cr-VI vessel, pH was adjusted to 9 with buffer solution plus 600 μL 5 N NaOH. In the container for TOC samples, 500 μL of 1:1 (*v*/*v*) sulfuric acid (H_2SO_4) was added to pH < 2. The vessels were transported in ice-boxes to Inorganic Chemistry Laboratory of State of São Paulo Environmental Company (CETESB), where they were refrigerated at 4 °C ± 2 °C until the chemical analyses (CETESB 2011). The same procedure was performed for raw and treated sewage collection. Approximately 500 g of sludge were collected from TATU and AS WWT and subsequently stored in decontaminated containers at 4 °C ± 2 °C (CETESB 2011).

Chemical analyses

All analytical procedures followed the standard operating procedures of the Brazilian Environmental Agency (CETESB), which are based on the methods of the US Environmental Protection Agency (US EPA) or Standard Methods for the Examination of Water and Wastewater (STM) and approved by Brazilian National Institute of Metrology, Quality, and Technology (INMETRO). According to the reference of Standard Methods for collection and preservation of samples (STM 2011d), we used laboratory blanks at the moment of analysis to verify the possible contaminations and during the collection, we preserved the samples in order to avoid analyte loss. The accuracy of the analytical methods was checked during the samples analysis using calibration curve, fortified matrix, and certified reference material analyses. The limits of quantification (LOQ) were calculated according the INMETRO orientation (CGA 2011); in this case, a standard solution diluted from the first point of the calibration curve was determined until the standard deviation began to lose its accuracy (values between replicates above 10%). Base on Student's t distribution, the LOQ was ten times the deviation value of at least seven replicates. In order to estimate the sewage dilution, the TOC determination was performed (Metcalf and Eddy 1991).

Arsenic, cadmium, chrome, copper, nickel, lead, zinc, and tin determinations in the sanitary sewage

The preparation of the samples was performed by acid digestion following the EPA 3015A (US EPA 2007a) method using microwave MARS 6 system (CEM Corporation, Matthews, NC, USA). The digestion method was carried out at "Nuclear and Energy Research Institute of the State of São Paulo" (IPEN). After being digested and cooled, the samples were diluted with ultrapure water to 50 mL, resulting in a dilution factor of 5 and a 10% of acidity. The samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) from Thermo Fisher Scientific (Waltham, MA, USA) according to method 6010C (US EPA 2007b). The relative standard deviation (RSD) was 25%; the method uncertainty was 5%. Each sample was analyzed in duplicate, and in case the deviations were above the uncertainty percentage of the method, the third sample was determined. Three reference materials were used: ICP-Sample 1 (Trace metals—QC1187 Sigma-Aldrich), SRM 1640a (Trace Elements in Natural Water—NIST), and TMDA 54.5 (Environment Canada). One sample per neighborhood was chosen, randomly, to the fortified matrix of samples, and the recovery value adopted was between 80 and 120% of the reference value. The LOQ were adjusted considering dilution factor and considered for analysis of the results.

Mercury determination

Mercury was determined by Direct Mercury Analyzer (DMA-80, Milestone, Sorisole, BG, Italy) according to method 7473 (US EPA 2007c). In each round, wastewater effluent certified reference material was used (ERM CA-713—trace elements in waste water), which contains a certified reference value for Hg (1.84 ± 0.11 μg L^{-1}). The recovery interval was considered between 80 and 120%.

Hexavalent chromium determination

Cr-VI was determined using 3500-Cr B colorimetric method (STM 2011a) based on the selective reaction between it and diphenylcarbazide. The samples were filtered on 0.45-μm acetate membrane filters and diluted five times in order to minimize the interference of suspended material. After 10 min of the diphenylcarbazide solution (0.250 g of 1.5-diphenylcarbazide in 50 ml of acetone) addition, triplicates were measured in the UV–Vis spectrophotometer (model DR/2010, Hach Company, Loveland, CO, USA) at 540 nm wavelength. The recovery interval was between 90 and 110%, the RSD between the

triplicates should be less than 10%, and the method uncertainty was 10%.

Total organic carbon determination

Samples from the first campaign were determined by the high-temperature combustion method on the Shimadzu brand analyzer according to the Standard Methods 5310 B (STM 2011b). The RSD was < 15% and recovery interval was 90–110%. In the second campaign, another instrument was used due to technical problems. However, the combustion technique was kept only with a different method. To standardize the methods, the accuracy was checked using fortified matrix and the same standard controls were used with the same known concentrations. The method for second campaign was Standard Methods Wet-Oxidation according to 5310 D (STM 2011c) performed using a Sievers InnovOx TOC Analyzer (GE Company). The recovery interval was 90–110%; method uncertainty was 10% and RSD 20%. In all analyses, the blank sample values were subtracted from the result.

Arsenic, cadmium, chrome, copper, nickel, lead, zinc, and tin determinations in the sludge

The sludge samples were dried at 40 °C until a constant weight to be reached. After this, each dried sample were macerated and homogenized. The sludge samples (0.5 g) were extracted following the 3051A method (US EPA 2007d) using microwave acid digestion with a MARS 6 system (CEM Corporation, NC, USA) at IPEN. At the end of the digestion process, volumes were completed with ultrapure water to 50 mL at an acidity of 20%. PTE concentrations were measured using Thermo Fisher Scientific ICP OES (Waltham, MA, USA). The certified reference material analysis for solid samples (CRM-049–trace metals–sandy clay 1) was carried out for all PTEs. The recovery interval was 80–120%; the calculated method uncertainty was 10% and the RSD 25%.

Statistical analyses

Stata Statistical Software 13.0 (StataCorp LLC, College Station, TX, USA) was used to analyze the data obtained from samples. PTE concentrations below and above the 75th percentile were considered dependent variables. The independent variables were three different areas (industrial, with informal work and without known informal or industrial activity), campaign (May/June and Oct/Nov), and sewage dilution (TOC values classified in three values: < 120, 120–225, > 225 mg L^{-1}). Data analysis included descriptive statistics and Mann-Whitney test for raw and treated sewage samples. The significance level adopted was 5%.

To deal with the large standard deviation and some results below the LOQ in the sewage samples collected in manholes, we decided to consider the 75th percentile of quantified PTE concentrations (0.1675 mg L^{-1} for Cr-VI, 0.0808 mg L^{-1} for Cu, 0.1992 mg L^{-1} for Zn, and 0.0354 mg L^{-1} for Ni). Multiple logistic regression models were used by calculating the odds ratio (OR), 95% confidence interval (95% CI), and p values. To compensate the influence of independent variables acting like confounding factors, all the models were adjusted for TOC values, campaigns, and area and adjusted odds ratio were calculated.

Results

Potentially toxic element concentrations in sanitary sewage

Most of the PTEs determined presented results below the LOQ, with the exception of Cr-VI, Cu, Ni, and Zn (Table 1). The LOQs (mg L^{-1}) considered for ICP OES were as follows: 0.003 for Cd; 0.02 for Cu, Ni, Zn, and Sn; 0.03 for Pb; and 0.05 for As and Cr. The LOQ for Hg was 0.1 ng L^{-1}, for Cr-VI was 0.004 mg L^{-1}, and for the COT was 0.38 mg L^{-1} in the first campaign, and 1 mg L^{-1} in the second.

Average concentrations were found to be within the limits of the state of São Paulo decree (São Paulo 1976). Among all 540 collected samples, four of them exceeded Cu or Zn values permitted to be discharged into sewage system (1.5 mg L^{-1} for Cu and 5.0 mg L^{-1} for Zn). The first sample that surpassed the legislation was collected in the second area with families working in the production of jewelry; the above results were 4.24 mg L^{-1} for Cu and 6.16 mg L^{-1} for Zn. The second sample was in the same local, and the result for Cu (1.52 mg L^{-1}) was exactly on the edge of the Brazilian legislation limit. The third sample was also collected in the second area and exceeded the Cu limit (2.21 mg L^{-1}). The fourth sample also exceeded the Cu limit (1.97 mg L^{-1}) and was collected in the first area with jewelry factories. These findings indicate the sporadic nature of PTE sanitary disposal derived from the informal productive arrangement of jewelry.

The difference between values above and below the 75th percentile for campaign, TOC, and area is seen in the Tables 2 and 3. The TOC results were classified into three different dilution ranges (< 120, 120–225, and > 225 mg L^{-1}). Samples with higher TOC values had a higher percentage of results above the 75th percentile for Cr-VI, Cu, Zn ($p < 0.05$), and Ni ($p = 0.001$) when compared to samples with lower TOC values. Samples from the second campaign also presented higher percentage of results for Cu, Zn, and Ni ($p < 0.05$) above the 75th percentile when compared to first campaign. The two different campaigns also obtained

Table 1 Median, minimum, maximum, and 75th percentile values of quantified potentially toxic elements (PTEs) in sanitary sewage compared with permissible values sets by State of São Paulo decree and median of the concentrations from other studies

PTEs	Sanitary samples from Limeira (mg L^{-1}) ($n = 540$[h])				State of São Paulo decree[g]		Median of sanitary samples (mg L^{-1}) (minimum–maximum)			
	Median	Minimum	Maximum	75th percentile	Article 18[a]	Article 19A[b]	Melbourne[c]	Stockholm[d]	Milwaukee[e]	Grand Nancy[f]
Cu	0.056	< 0.02	4.2425	0.0808	1.00	1.50	0.062 (0.035–0.097)	0.094 (0.047–0.162)	0.073 (uninformed)	0.059 (0.022–0.147)
Ni	< 0.02	< 0.02	1.3369	0.0354	2.00	2.00	0.004 (< 0.001–0.01)	0.011 (0.004–0.028)	0.011 (uninformed)	0.007 (0.004–0.013)
Zn	0.1516	< 0.02	6.1634	0.1993	5.00	5.00	0.169 (0.052–0.348)	0.295 (0.055–0.767)	0.164 (uninformed)	0.14 (0.05–0.272)
Cr-VI	0.122	0.009	1	0.1676	0.1	0.5	–	–	–	–

[a] Maximum concentration permitted in liquid effluents to be discharged into water bodies

[b] Maximum concentration permitted in liquid effluents to be discharged into sewage treatment networks

[c] Wilkie et al. (1996)

[d] Palmquist and Hanaeus (2005)

[e] Soonthornmonda and Christensen (2008)

[f] Houhou et al. (2009)

[g] São Paulo 1976

[h] Number of values below the limit of quantification by element = Cu ($n = 12$); Ni ($n = 287$); Zn ($n = 1$); Cr-VI ($n = 0$)

significant influence, being the second with more samples above the 75th percentile ($p < 0.001$). The only significant difference among the three different studied areas was Zn concentration, which presented a smaller result in the family workers area (22.2%) compared to the factories area (38.9%), considering the 75th percentile. The large standard deviations observed in these tables show the large variation between determined concentrations and support the argument that indicate the sporadic nature of PTE sanitary disposal.

Potentially toxic element concentrations in wastewater treatment plants

As well as in the manholes, most of the PTEs determined in WWTs presented results below the LOQ, with the exception of Cr-VI, Cu, Zn, and Ni, in which all values were above LOQ. Five raw sewage samples exceeded the amount of Cu permitted to be discharged into sanitary sewage treatment networks (1.5 mg L^{-1}), according to State of São Paulo decree (São Paulo 1976). Four of these samples were from the TATU WWT and the exceeded values were 3.01, 2.99, 7.23, and 2.87 mg L^{-1}; one of the samples was from AS WWT and the value was 2.86 mg L^{-1}. Taking into account the treated sewage, three samples from TATU WWT (1.42, 1.55, and 1.13 mg L^{-1}) exceeded the Cu concentration permitted in liquid effluents to be discharged into water bodies (1.0 mg L^{-1}).

Statistical difference observed between raw and treated sewage from each WWT are represented in Table 4. Between two WWT, there was no statistical difference in the raw sewage; however, the treated sewage from AS presented low concentrations of Cu ($p < 0.05$), Zn ($p = 0.02$) and Ni ($p = 0.01$) compared to treated sewage from TATU WWT.

Potentially toxic element concentrations in sludge

All the results for As, Cd, Cr, Ni, Hg, Pb, and Sn were within the limits of the Brazilian Environmental National Council's Resolution 375/2006 (CONAMA 2006). The total Cu average exceeded the legislation values (1500 mg kg^{-1}), and the total Zn results were very close to the Brazilian legislation value (2800 mg kg^{-1}) and surpass the Canadian legislation (1850 mg kg^{-1}). The Zn values exceeded the Brazilian legislation in two samples from AS WWT (3371 and 2926 mg kg^{-1}) and three samples from TATU WWT (3094, 3140, and 3150 mg kg^{-1}). All the samples collected in both WWT exceeded de Cu permissible legislation value. The LOQs (mg L^{-1}) considered for sludge samples were as follows: 1.6 for As, 0.16 for Cd, 3.88 for Cr, 4.18 for Cu, 0.28 for Ni, 1.21 for Pb, 0.44 for Zn, and 0.57 for Sn.

Table 2 Number and percentage of samples above the 75th percentile in sanitary sewage for Cr-VI and Cu and associations (odds ratio) between results above the 75th percentile and total organic carbon (TOC) values, campaigns, and areas

Variables	Potentially toxic elements (PTEs)					
	Cr-VI			Cu		
	> 75th percentile, *n* (%)	OR (95% CI) *p*	OR adj. (95% CI)[a] *p*	> 75th percentile, *n* (%)	OR (95% CI) *p*	OR adj. (95% CI)[a] *p*
TOC						
< 120 mg L^{-1}	7 (8.43)	1	1	11 (13.25)	1	1
120–225 mg L^{-1}	74 (23.49)	3.33 (1.47–7.55) 0.004*	3.31 (1.45–7.53) 0.004*	68 (21.59)	1.8 (0.9–3.59) 0.094	1.44 (0.69–2.97) 0.329
> 225 mg L^{-1}	54 (38.03)	6.66 (2.86–15.51) < 0.001*	6.86 (2.84–16.57) < 0.001*	56 (39.44)	4.26 (2.08–8.74) < 0.001*	2.12 (0.98–4.61) 0.057
Campaigns						
May/June	60 (22.2)	1	1	28 (10.37)	1	1
Oct/Nov	75(27.8)	1.35 (0.91–1.99) 0.137	0.91 (0.59–1.41) 0.686	107 (39.63)	5.6 (3.58–8.99) <0.05*	4.83 (2.97–7.85) <0. 05*
Area						
Industrial	14/72 (19.44) 14/540 (2.59)	1	1	22/72 (30.56) 22/540 (4.07)	1	1
Families working with jewelry	100/396 (25.25) 100/540 (18.52)	1.4 (0.75–2.62) 0.293	1.35 (0.71–2.56) 0.361	97/396 (24.49) 97/540 (17.96)	0.74 (0.42–1.28) 0.279	0.68 (0.38–1.23) 0.206
No industrial/no jewelry activity	21/72 (29.17) 21/540 (3.89)	1.71 (0.13–0.43) 0.176	1.54 (0.69–3.39) 0.285	16/72 (22.22) 16/540 (2.96)	0.65 (0.31–1.37) 0.258	0.57 (0.26–1.28) 0.175

[a] Adjusted values for TOC concentration, campaign, and areas

*Significant difference between groups ($p < 0.05$)

The arithmetic means for Zn and Cu in the AS WWT were, respectively, 2632 and 4829 mg kg^{-1}. In TATU WWT, the arithmetic mean for Zn was 2775 and 4715 mg kg^{-1} for Cu. In most cases, the total average also exceeded values allowed in the EU, the USA, and Canada (Table 5).

Discussion

Although the PTE results in the liquid sanitary sewage are below the limits established by the State of São Paulo decree, the presence of zinc and copper in the sludge above the allowed limits from agricultural use raises a concern. These two elements had a similar behavior in the liquid effluent, where they presented low concentration probably due to the diluted flow. However, during the treatment, they are adsorbed in organic matter, clay, or oxides and suffer precipitation; as a result, it is deposited in the sediments (Azevedo and Chasin 2003; Östman et al. 2017). The tin determination in the sewage sludge can represent the contribution of the jewelry production and calls our attention to the fact that there are no maximum values for it use in agriculture. Excessive levels of tin ingestion can cause gastrointestinal, hematological, or immunological effects (ATSDR 2005b) although it is not considered carcinogenic by IARC.

Another study in Limeira city (Ferreira 2005) pointed out an expressive and alarming result of PTEs in the urban area sewage. In this case, the X-ray counting number in sanitary effluent for Cu ranged 117 to 135 times above the control sample of Piracicaba, city that does not have the same jewelry productive arrangement. Zn presented values 100 times higher and Pb did not have such expressive results, but the X-ray counting was 2 to 6 times higher than the control. Nonetheless, unlikely what was observed in 2005 in the same region, our study did not indicate the same expressive results. The reason for these differences may be due to the increase of environmental agency surveillance in the last decade. In addition to the surveillance, CETESB also developed a technical guide for companies and formal workers with recognized value examples of cleaner production, pollution problems, and solutions (CETESB 2005). These actions can have caused a positive effect on the city's sanitary sewage constitution but are focused on the industrial sector. Informal domestic activities are still poorly monitored and investigated; there is no reliable and scientific information about processes and substances used on informal work. Currently, another study is being carried out in Limeira with the intention of evaluating the occupational exposure in the home environment and will be able to provide important and more detailed data about the productive process inside the residences. However, based on

Table 3 Number and percentage of samples above the 75th percentile in sanitary sewage for Zn and Ni and associations (odds ratio) between results above the 75th percentile and total organic carbon (TOC) values, campaigns, and areas

Variables	Potentially toxic elements (PTEs)					
	Zn			Ni		
	> 75th percentile, *n* (%)	OR (95% CI) *p*	OR adj. (95% CI)[a] *p*	> 75th percentile, *n* (%)	OR (95% CI) *p*	OR adj. (95% CI)[a] *p*
TOC						
<120 mg L^{-1}	15 (18.07)	1	1	13 (15.66)	1	1
120–225 mg L^{-1}	60 (19.05)	1.07 (0.57–1.99) 0.840	0.94 (0.49–1.80) 0.855	70 (22.22)	1.53 (0.8–2.94) 0.193	0.76 (0.31–1.88) 0.556
>225 mg L^{-1}	60 (42.25)	3.32 (1.73–6.39) <0.001*	2.40 (1.19–4.86) 0.015*	52 (36.62)	3.11 (1.57–6.16) 0.001*	0.62 (0.25–1.57) 0.317
Campaigns						
May/June	43 (15.93)	1	1	2 (0.74)	[b]	[b]
Oct/Nov	92 (34.07)	2.73 (1.81–4.12) <0.05*	2.09 (1.33–3.27) 0.001*	133 (49.26)	[b]	[b]
Area						
Industrial	28/72 (38.89) 28/540 (5.19)	1	1	23/72 (31.94) 23/540 (4.26)	1	1
Families working with jewelry	28/396 (22.22) 28/540 (16.30)	0.45 (0.26–0.76) 0.003*	0.4 (0.23–0.7) 0.001*	97/396 (24.49) 97/540 (17.96)	0.69 (0.4–1.19) 0.185	0.57 (0.28–1.17) 0.124
No industrial/ no jewelry activity	19/72 (26.39) 19/540 (3.52)	0.56 (0.28–1.14) 0.111	0.52 (0.25–1.11) 0.090	15/72 (20.83) 15/540 (2.78)	0.56 (0.26–1.19) 0.133	0.44 (0.17–1.12) 0.084

[a] Adjusted values for TOC concentration, campaign, and areas

[b] Values were not presented considering the low number of samples ($n = 2$) above the 75th percentile

*Significant difference between groups ($p < 0.05$)

the field work already performed, we know that most of the processes developed in the houses are related to the assembly and/or welding of the parts, which, probably, do not eliminate a large amount of PTEs in the effluent. The electroplating baths that would be responsible for the greater contribution of PTEs to the effluents have not yet been observed in residences. On this basis, the statistically similar results between the areas can be explained. We also have to consider that in the area without activity, we cannot attest that there are no families working with jewelry, and in the industrial area, companies are inspected and obliged to attend maximum concentrations allowed by the legislation; so, in some cases, pre-treatment is performed in the industry to decrease the concentration of PTEs discarded in the effluent.

In France, Houhou et al. (2009) collected sanitary sewage in manholes from Grand Nancy region and reported low means values of Cu, Pb, Zn, Cd, Ni, and Cr (0.02, 0.017, 0.058, 0.00007, 0.0064, and 0.0063 mg L^{-1}, respectively). Considering the French scenario, the authors discuss the presence of PTEs because of household activities such as kitchen, laundry, and bathroom, corrosion of water supply pipes, groundwater infiltration, and the influence of roof runoff in

Table 4 Mean and standard deviation of potentially toxic elements (PTEs) in raw and treated sewage from AS and TATU wastewater treatment plants (WWT) in Limeira, SP, Brazil

PTE	AS WWT (mg L^{-1})			TATU WWT (mg L^{-1})			Total (mg L^{-1})		
	Raw	Treated	*p*	Raw	Treated	*p*	Raw	Treated	*p*
Cr-VI	0.09 ± 0.05	0.02 ± 0.02	0.010*	0.06 ± 0.03	0.02 ± 0.01	0.006*	0.07 ± 0.04	0.02 ± 0.02	0.0002*
Cu	0.67 ± 1.08	0.08 ± 0.03	0.037*	2.86 ± 2.46	1.05 ± 0.39	0.149	1.77 ± 2.14	0.57 ± 0.57	0.106
Zn	0.88 ± 1.06	0.18 ± 0.11	0.055	0.99 ± 0.67	0.62 ± 0.35	0.262	0.93 ± 0.85	0.4 ± 0.34	0.065
Ni	0.12 ± 0.21	0.05 ± 0.02	0.408	0.33 ± 0.19	0.20 ± 0.12	0.201	0.22 ± 0.23	0.12 ± 0.12	0.171

*Significant difference between groups ($p < 0.05$)

Table 5 Mean and standard deviation of potentially toxic elements (PTEs) in sewage sludge from Limeira, SP, Brazil and maximum permitted concentration in sewage sludge or by-products (mg kg^{-1}, dry matter) for use in agriculture in the USA, EU, Canada, and Brazil

PTE	Legislation				Limeira		
	USA[a]	EU[b]	Canada[c]	Brazil[d]	Mean	SD	CI
Arsenic	41	–	75	41	2.9	1.1	2.2–3.6
Cadmium	39	20 to 40	20	39	7.6	4.8	4.5–10.6
Lead	300	750 to 1200	500	300	73	18	62–85
Copper	1500	1000 to 1750	–	1500	4772	987	4145–5399
Total chromium	–	–	–	1000	133	16	122–143
Mercury	17	16 to 25	5	17	0.74	0.13	0.66–0.83
Nickel	420	300 to 400	180	420	173	72	128–219
Zinc	2800	2500 to 4000	1850	2800	2704	464	2409–2999
Tin					77	14	68–85

[a] Law 40 CFR 503.13. Table 3: pollutant concentrations

[b] EU Council Directive 86/278/EEC

[c] T-4- 93 -Standards for Metals in Fertilizers and Supplements, 1997

[d] CONAMA Resolution 375/2006

combined sewer system. Considering the variability of sewer systems, the France mean values were similar to sewage from this study and other cities such as Melbourne (Wilkie et al. 1996), Stockholm (Palmquist and Hanaeus 2005), and Milwaukee (Soonthornnonda and Christensen 2008). Considering the scenario from Limeira with different socio-economic characteristics, with PVC water supply pipes and separate sewer system, we do not believe that only household activities are responsible for the disposal of PTEs; thus, the informal domestic work with jewelry and fashion jewelry can be one of the PTEs sources in sewage system.

The results showed that the sewage dilution factor directly influenced the concentration of toxic elements (Azevedo and Chasin 2003; Östman et al. 2017). Sanitary sewage samples with higher TOC values indicated a concentrated sewage, with a higher concentration of organic matter and PTEs. Rainfall data from Limeira measured by Campinas University (UNICAMP) indicated a mean of 9.9 mm of rain in the first campaign days and 1.5 mm in the second campaign. These precipitation values may have contributed to the sewage constitution and may be an explanation for the statistical difference observed for PTE concentrations between the campaigns. The influence of rainfall is not expected for dilution and roof runoff contribution in separate sewer system, such as Limeira's system (Gromaire et al. 2001; Houhou et al. 2009). However, US EPA (2016) affirms that separate sewer systems with fissures, faulty seals, and irregular connections can receive extra contribution of infiltration and inflow during rainy period.

Sewage sources that contribute to WWT effluents constitution are varied, including sanitary and industrial sources. Low PTE values in the raw and treated sewage were found in a study done in WWTs of the city of Campinas and Jaguariúna, which are near Limeira, considered industrialized cities, but without the jewelry chain (Souza et al. 2014). In this case, Ni, Cu, Zn, and Pb were determined by X-ray fluorescence and none showed higher concentration than allowed by legislation. Compared to this study, the result that draws more attention is the Cu mean concentration, which was more than three times higher in Limeira's raw sewage (1.77 mg L^{-1}) than in raw sewage from Campinas (0.43 mg L^{-1}) and Jaguariúna (0.53 mg L^{-1}). Also, some Limeira's WWT results were above the allowed limits stated by the Brazilian legislation, which was not observed in the nearby cities This comparison indicates the influence of the different activities developed in each city that can explain the effluent constitution. In our study, the TATU's treated sewage presented exceeded averages on random days. It is discharged into Ribeirão Tatu which is a tributary of Piracicaba River. Ribeirão Tatu is classified by Brazilian National Council resolution, n. 357 (CONAMA 2005) as class 4, which makes its waters indicated only for navigation and landscape harmony. In this case, both chemical and physical parameters analyzed are expected to be higher than other rivers and the CONAMA resolution does not regulate standard PTE values to class 4 rivers. The Piracicaba River is classified as class 2, which may be destined for human consumption, protection of aquatic communities, and recreation. The first CETESB's monitoring point in Piracicaba River, after the mouth of the Ribeirão Tatu, indicates some values in non-compliance with the Brazilian quality standards, among them dissolved oxygen, biochemical oxygen demand, dissolved P, Mn, and ammoniacal nitrogen (CETESB 2016). Even though the effluent released at the Limeira's WWT does not influence the class 4 river, they can influence the quality of the river and catchment points of downstream cities.

Probably, the difference between treated sewage of the present study from AS and TATU is due to the difference in sewage

treatment. AS is equipped with anaerobic reactors followed by activated sludge, and TATU operates with the primary treatment process (Odebrecht Ambiental 2014b). There are studies describing different methods for efficient metals wastewater removal, such as chemical precipitation, adsorption, ion-exchange, or reverse osmosis (Baysal et al. 2013); although, the secondary treatment performed in AS WWT seems to help to decrease Cu, Zn, and Ni concentrations, probably because of efficient organic matter removal. These data corroborate with our results indicating PTE precipitation due to higher concentrations in the sludge.

Souza et al. (2014) concluded that the sludge from Jaguariúna and Campinas could be directly used in agriculture because PTE concentrations were below the legislation. Sludge from the states of São Paulo and Minas Gerais presented Ni and Zn concentrations close to the maximum amount allowed for agricultural use and one sample exceeded the Cu value allowed (Braga et al. 2017). Sludge concentrations of Pb and Cd (1270 and 904 mg kg^{-1}, respectively), from a region with chemical plants in China, exceed the permitted values for agriculture use, while Cu and Zn concentrations (659 and 1106 mg kg^{-1}, respectively) were higher than in other regions but were below legislation (Chen et al. 2008). In sludge samples from Sweden, Cu (110 to 640 mg kg^{-1}) and Zn (396 to 1500 mg kg^{-1}) were found in higher levels in sludge than effluent, indicating metal sedimentation (Östman et al. 2017). In the same study, one sample exceeded the established limit for Cd and another for Hg, both related to localized pollution source and accidental release. A screening of sewage sludges from 15 European countries observed metal concentrations significantly lower; none of the samples exceeded the established limit by EU directive (Tavazzi et al. 2012). In South Africa, Zn and Cu concentrations were over the country guidelines (Shamuyarira and Gumbo 2014). Compared with the results of this study, none of the studies cited above presented higher Cu and Zn values than what we found, with the exception of one study performed in China that found 3649 mg kg^{-1} of Zn in sewage sludge during landfill, but does not discuss its source (Yang et al. 2017). Most of the values determined by other authors in the sludge were much lower than those of Limeira, the results that came closest to ours were from one city (1539 mg kg^{-1} of Cu and 2320 mg kg^{-1} of Zn), which also presented jewelry production (Braga et al. 2017). This comparison may be indicative of the influence of local jewelry industries on sludge constitution. Azevedo and Chasin (2003) state that the metal concentrations in effluents varied widely, and concentrations in urban sludge may increase considerably with the industrial sewage contribution.

Sludge inorganic contaminants, such as copper and zinc, which were quantified in excess in this study, can be bioconcentrated in the environment and be accumulated in the soil and in the food chain (Fijalkowski et al. 2017). Even considering non-carcinogenic adverse health effects, there are estimates of copper and zinc minimal risk levels considering acute, intermediate, and chronic exposures (ATSDR 2004; 2005a). Copper can cause liver and kidney damage, anemia, immunotoxicity, and developmental toxicity (ATSDR 2004; Kumar et al. 2016; Kalita et al. 2017). The gastrointestinal tract is the most sensitive to excessive levels of copper ingestion, considering human and animals studies, which reported nausea, vomiting, and/or abdominal pain (Araya et al. 2003; ATSDR 2004). Excessive levels of zinc ingestion can affect hematological or gastrointestinal system causing vomiting, abdominal cramps, and diarrhea (ATSDR 2005a).

The production of contaminated sewage sludge and its disposal or treatment has become expensive and with potential environmental risk (Ahluwalia and Goyal 2007). The disposal in landfills should be controlled and monitored to avoid environmental damages such as the infiltration of PTEs into the soil, leaching, and subsequent groundwater contamination. Fang et al. (2017) observed that the repeated application of sewage sludge in the soil can cause the release of Cd, Cr, Cu, Ni, and Pb, and consequent accumulation, but, not always, the release of PTEs means a significant increase in the leached concentration. Anyway, it is necessary to consider the long-term accumulation and the risks of leachate constituents.

The disposal of PTEs in the sludge in regions where electroplating occurs is proven, and some studies have discussed different methods of toxic metal removal from electroplating wastewater and sludge to avoid the leaching of toxic elements (Li et al. 2007; Sousa et al. 2009; Peng and Tian 2010; Wuana and Okieimen 2011; Chou et al. 2011; Zhuang et al. 2012; Huang et al. 2013). In Brazil, one of the alternatives used for final sludge disposal is the composting for agricultural (Krzyzanowski et al. 2014, 2016). The increase in PTE concentration in the soil and agricultural plants, after compost application, has been observed (Gonçalves et al. 2014; Grotto et al. 2015; Nascimento et al. 2015). Cai et al. (2007) observed that the compost concentrations increased by 12 to 60% for Cd, 8 to 17% for Cu, 15 to 43% for Pb, and 14 to 44% for Zn compared to those in sewage sludge. The PTE compost contents should also take into account parameters such as pH, temperature, decomposition, and organic matter content (Liu et al. 2007; Miaomiao et al. 2009). According to Fijalkowski et al. (2017), treatment sludge processes like anaerobic digestion, composting, and thermal carbonization do not guarantee the complete removal of contaminants.

Considering the compost process limitations, one of the most promising biological technologies for an environmentally safe alternative is the use of phytoremediation (Ali et al. 2013; Baysal et al. 2013; Ashraf et al. 2017; Ye et al. 2017). The method can use low-cost agricultural materials and can be coupled with the use of microbes or fungal biomass for the

removal of PTEs (Sud et al. 2008; Ashraf et al. 2017). These technologies can be applicable to treatment of dilute effluent with low concentrations of heavy metals originated from industrial activities (Ahluwalia and Goyal 2007). A bioremediation test performed with a fungal strain presented the ability to reduce 71, 56, and 100% of Cr, Cu, and Pb, respectively, in electroplating industry effluent (Mishra and Malik 2012).

Among the main limitations of the present study, we have the limited number of days and collection areas. The first intention of the authors was to increase the number of samples to have better evaluated the sporadic nature of the effluents discard, but the exponential growth of the samples number made their analysis impracticable and out of the our budget.

Conclusions

In sanitary sewage, probably, by the effect of the flow dilution, it was very difficult to quantify PTEs in concentrations above the LOQ, but this does not attest their absence in the sewage network and much less eliminate the risk of environmental impact. The heterogeneity of the results, observed on random days, can indicate the sporadic nature of the sanitary disposal of PTEs. The fact that no difference was found between the three areas and Cr-VI, Cu, Ni, and Zn have been quantified can be an indicator of household PTE disposal in the sewage. Considering the concentrations of PTEs in the sanitary effluent, it is not possible to confirm it as directly related to the production of jewelry but can indicate one suspect source. Furthermore, this evidence is reinforced by the high concentrations of Cu and Zn in the sludge, which were not observed in other cities of the region. The sludge from TATU WWT and AS WWT could not be used in agriculture without previous treatment. The presence of Zn and Cu in high concentrations in the sludge requires its controlled destination.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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