

THE HEAVY METAL COPPER IN THE SEWAGE SLUDGE OF MARINGÁ, PR, BRAZIL

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ABSTRACT

Human wastes are a permanent challenge to the environment. Current research has evaluated the amount of copper metal in the sewerage and in the sludge of the Sewerage Treatment Stations (STSs) of Maringá PR Brazil. Sample collection was undertaken at the STSs and samples were digested with nitric acid at reduced volume. Biosolid samples, previously dried and ground, at constant weights, were digested by aqua regia. Determination of metal concentrations was made by atomic absorption spectrometry. The pH, nitrogen, carbon and organic matter (OM) values were determined by the respective classical methods. Total average were: a) Cu in affluent sewerage 0.077 and effluent sewerage 0.058 $\mu\text{g mL}^{-1}$. b) biosolid: Cu = 0.74 mg g^{-1} ; pH = 3.38; N = 3.24 %; C = 24.5 % e OM = 42.1 %. Variance analysis of the experimental values, and taking into consideration the variation sources of STSs and collection time, showed that no significant difference between the values of copper concentration, N (%), C (%) and organic matter (%) respectively existed in both variation sources. Total average rate of copper concentration of STSs is higher than the international world average value found in the relating literature. Amounts of organic matter and the C:N (carbon:nitrogen) proportions of sewage sludge are appropriate for soil application.

Key words: sewerage, biosolid, heavy metals, nutrients, environmental pollution, organic matter.

RESUMO

Os resíduos da ação antrópica são um permanente desafio ambiental. Neste sentido, este trabalho teve como objetivo avaliar o metal pesado Cu no esgoto e lodo das ETEs de Maringá. As amostras de esgoto foram digeridas em meio ácido nítrico com redução de volume, as de biossólido foram digeridas com água régia. As leituras das concentrações de cobre foram feitas pelo método de espectrometria de absorção atômica. O pH, o N e o C foram determinados pelos respectivos métodos clássicos. Os resultados em valor médio global foram os seguintes, respectivamente: a) Cu em $\mu\text{g mL}^{-1}$, para o esgoto afluente 0,077 e para o esgoto efluente 0,058. b) para o biossólido: Cu = 0,74 mg g^{-1} ; pH = 3,38; N = 3,24 %; C = 24,5 % e MO = 42,1 %. Pelos resultados conclui-se que, o esgoto efluente está conforme a legislação e o lodo das ETEs: apresenta valores médios de pH; concentração de cobre, N, C e MO, que, em nível de 5%, não têm diferença significativa entre si, tanto nas estações de tratamento quanto no tempo das coletas, respectivamente. O biossólido apresenta um valor médio global de cobre mais elevado que o apresentado por lodos de esgoto em nível internacional. O teor de matéria orgânica e as relações C:N dos lodos das três ETEs são recomendáveis para o uso agrícola.

INTRODUCTION

Human society produce a type of refuse, the result of daily activities, which may be called urban residue or waste^{1,2}. Home sewage, the type of waste proper to urban centers, is frequently placed untreated in the environment, endangering water sources, health, the environment and the quality of life³.

For centuries man has been aware of the relationship between poor health situations and public health problems. As far as 1840, owing to fear of epidemics, European communities have made mandatory the application of technologies in waste and sewage treatment. They started to dispose sewage in the soil and drastically reduced epidemic-caused mortality⁴.

Treatment of urban sewage produces sewage sludge whose final disposition is highly problematic for Sewerage Treatment Stations (STSs). Without previous analysis of its physical, chemical and biological composition, inadequate disposition of untreated sewage sludge may pollute the soil and water sources. It may also alter their physical, chemical and biological characteristics, besides being an aesthetic problem and, worse still, a threat to the environment and public health^{5,6}.

Since copper is a heavy metal⁷, it has been and still is very important in the development of civilization and in the recent past has been among the five metals most used in the world⁸. Copper may be found naturally (Cu) and as a mineral, cuprite [Cu₂O], malachite [Cu₂(CO₃)(OH)₂], chalcocite [Cu₂S], chalcocopyrite [CuFeS₂], azurite [Cu₃(CO₃)(OH)₂], and others⁹. Mean rate of copper in rocks of the earth's crust is close to 55 µg g⁻¹¹⁰. Since copper is relatively available and movable in the soil¹¹, it has variable concentrations in the latter, frequently at toxic rates for biota¹². It is also a contaminating element carried through the air¹³ and in water¹⁴. In the largest rivers it is found at interval rates of 0.830 - 152 µg L⁻¹^{15, 16, 17}.

Several copper derivatives are toxic and even highly toxic¹⁸. Although used as a fungicide in vineyards and coffee plantations¹⁹, it is one of the micronutrients necessary for animal and vegetative life²⁰. Actually its presence in protein and enzymes makes it an essential element²¹.

Decree No. 20 of the Brazilian Council for the Environment (CONAMA), published in June 1986, reads that a disposable effluent, such as the case of treated sewage sludge, should contain a maximum copper concentration rate of 1 mg L⁻¹. In the case of fresh water maximum concentration limits recommended are 20 µg L⁻¹ (Class 1 and 2 water) and 50 µg L⁻¹ (Class 3 and 4 water)²².

Although several dispositions, among which may be mentioned its application in the soil, have been conjured up for the biosolid, none is completely safe. As a general rule, sludge is rich in organic matter, nitrogen, phosphorus and micronutrients and its use as a fertilizer in agriculture has great advantages^{23, 24, 25, 26}. However, risks exist, particularly those proper to heavy metals and pathogenic agents²⁷.

Several studies have been undertaken on the application of sewage sludge in agriculture. The problem has been tackled from several angles especially on the mineralization and the availability of nutrients^{28, 29, 30, 31}, absorption of ions made available by plants³², production yield of vegetations^{33, 34, 35}.

Owing to possible environmental impacts caused by the application of sewage sludge, studies have been undertaken not only at international²⁶ and national²³ levels to establish usage criteria²³. Even the state of Paraná has tackled the problem²⁴.

Recycling of sewage sludge in agriculture is a natural trend worldwide, as may be surmised from the themes and conferences given at the I Mercosur Seminar on Administration of Biosolids³⁶. In the wake of analyzing sludge application, current research is concerned with copper, which has been used for many years and is still used in the Maringá region as a fungicide in vineyards and on coffee shrubs^{37, 38}. There has surely been an accumulation of the heavy metal in the environment during so many years of usage. In spite of the fact that copper concentration dilutes in natural systems, it may reach urban sewage through food and the water system. Concern with the sewage sludge at such concentrations and rates is becoming high.

The present research evaluates the concentration of the heavy metal copper in sewage and in sewage sludge of the Sewerage Treatment Stations of Maringá (STS-1, STS-2 and STS-3).

MATERIALS AND METHODS

Biosolid: collection and first preparation of samples

Sewage treatment in Maringá is done by anaerobic reactors (Anaerobic Reactor of Fluidized Sludge, RALF). Samples of sludge were collected by technicians of the Water Works Department of the state of Paraná (SANEPAR) at STS-1, STS-2 and STS-3.

At the lab sludge samples were dried at room temperature, ground, sieved and taken to a 60°C buffer till they reached constant weight. They were then stored in polyethylene bags for analysis.

Biosolid: analysis of the heavy metal

A mass of dry sludge, weight 2.0000 g, was transferred to a 125-mL Erlenmeyer glass with emery rim. 2 to 3 mL of distilled and de-ionized water were added to the mass to make it turn into paste. Aliquots of 7.5 mL of concentrated chloridic acid and 2.5 mL of concentrated nitric acid were added for each gram of sludge. Flasks were covered and left to rest during a 12-hour period, at night, at room temperature. Flasks were then heated in a 40cm-high reflux condenser system, during 2 hours. Solution of digested matter was filtered and collected in a 100-mL volumetric balloon. Care was taken to wash the condenser, Erlenmeyer glass and the filter paper and residue with portions of nitric acid 2 mol L⁻¹³⁹. Control and analytic curve standards underwent the same process. Determinations of copper concentrations were done by atomic absorption spectrometer Varian, model Spectr AA 10 PLUS, flame mode⁴⁰. Method had a detection limit of $(c_L) = 0.027 \mu\text{g mL}^{-1}$, with 99% confidence level⁴¹.

Biosolid: analysis of organic matter

A sample of 30.0 mg of dry sludge was transferred to a 250-mL Erlenmeyer glass; 10mL of potassium dichromate 0.1667 mol L⁻¹ and 20mL of concentrated sulfuric acid were added respectively; solution was shaken well and left to rest for 20 – 30 minutes. It was then diluted to 100 mL with distilled and de-ionized water; 3 to 4 drops

of ortho-phenanthroline were added and completed with hexahydrated ferrous sulfate 1.0 mol L^{-1} . Percentage of C determined the percentage of organic matter⁴².

Biosolid: analysis of total nitrogen

After 0.1000 g of the sample has been placed in each 25x250mm-glass tube, 1 mL of H_2O_2 at 30% and 3 mL of concentrated sulfuric acid were added and left to cool for 15-20 minutes. Afterwards, 0.7 g of digesting mixture were added and flasks were taken to the digester SARGE, temperature was raised every 15 min till it reached 330°C and maintained for 2 h. After cooling, the samples were placed in flasks for distillation of NH_3 , with 30 mL of de-ionized water and 30 mL of NaOH at 40%. Condensed vapors of NH_3 were collected in 10 mL of boric acid with indicator. After collecting 30 to 35 mL of the distilled solution, it was completed with sulfuric acid 0.05 mol L^{-1} ⁴³.

Biosolid: pH

Determination of pH was undertaken as from 15 mL of dry sample in a test-tube and placed in a 125-mL Erlenmeyer glass. Aliquot of 25 mL de-ionized water were then added⁴⁴, the mixture was shaken, and the pH of supernatant was measured by a pH-meter after decantation.

Sewage: collection and initial preparation of samples⁴⁵

Sewage samples were also collected by technicians of the Water Works Department – Maringá Section, at STS-1, STS-2 and STS-3. Two liters of the compound sample of affluent sewage that arrived at each STS and 2 liters of compound sample of effluent sewage that came out of each STS were stored in clean plastic flasks^{46,47}, and preserved at $\text{pH} < 2$ by adding concentrated HNO_3 . They were stored at 3°C till the respective analyses, which were done immediately^{48,49}.

Sewage: digestion of samples and analysis of the metal

Samples were prepared to calculate total concentration of copper. After homogenization of the sample, 500 mL of each sample were transferred to their respective beakers, labeled and covered with glass, in duplicate, and 5 mL of concentrated HNO_3 were added. The solution was slowly warmed till almost dried and repletion was done when necessary so that sample could be digested. Residue was dissolved by portions of the $\text{HCl } 5 \text{ mol L}^{-1}$ solution, and transferred to a 50-mL volumetric flask with distilled and de-ionized water till completion of marked volume. The sewage sample was thus ready for copper concentration contents.

Copper concentrations were read by atomic absorption spectrometer Varian, Spectr AA 10 Plus model, flame mode, according to recommendations by Handbook and by Welz and Sperling⁴⁰. Although the method's detection limit (c_L) was $0.027 \mu\text{g mL}^{-1}$, samples were concentrated ten times (500 mL of in natura sample were reduced to 50 mL of prepared solution). This means that the sample of the original sewage, concentration $0.0027 \mu\text{g mL}^{-1}$, would produce an analytic signal of the sample at 99% reliability after a 10 fold concentration. Sewage with copper concentrations less than

$0.0027 \mu\text{g mL}^{-1}$, done with the same technique, would not produce any reading analytic signal.

Statistical analysis

Results underwent variance analysis and Tukey's test with SANEST.

RESULTS AND DISCUSSION

Sewage

SANEPAR-Maringá Technical Data (1997)⁵⁰ shows that the sewage system in Maringá is formed by three basins. Main basins direct the collected sewage to STS-1, STS-2 and STS-3 operating with anaerobic reactor systems of fluidized sludge (RALF).

Sludge from the south basin is collected by STS-2 which services downtown Maringá, the old districts (zones 2, 3, 4 and 5) and the most recent districts close to the above.

The northern region has two big basins. Both concentrate the sewage from STS involving Maringá Stream (STS-1) and the other involving Morangueira Stream (STS-3).

Sewage treatment in Maringá is based on the anaerobic stabilization process of organic matter. Pre- and first treatments are traditional, whereas the second treatment is done by Anaerobic Reactors of Fluidized Sludge (Figure 1).

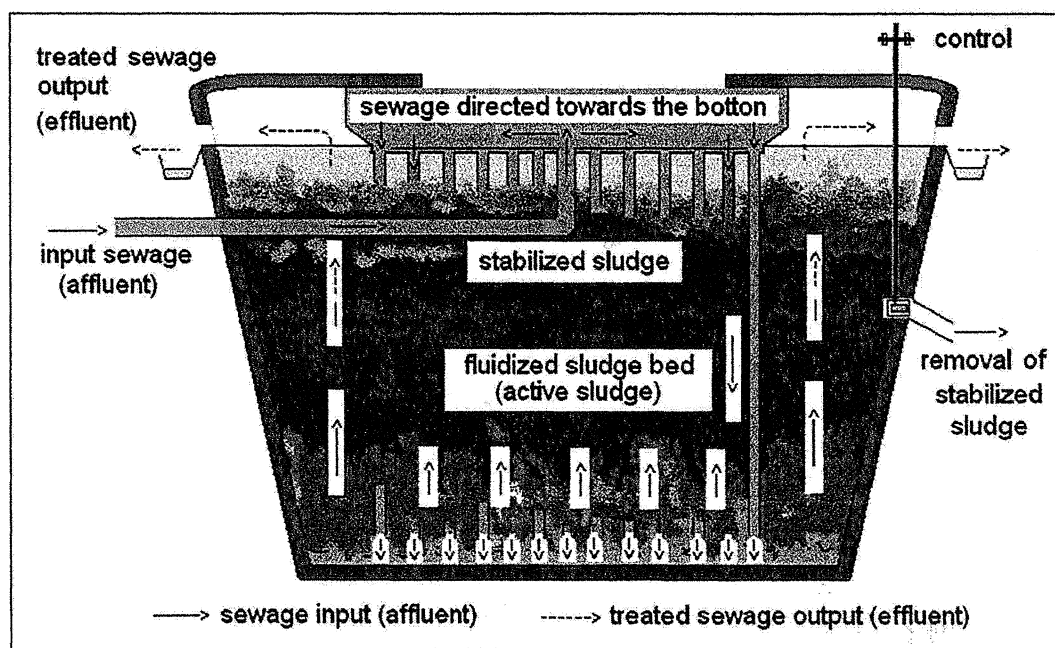
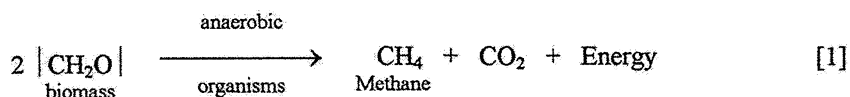
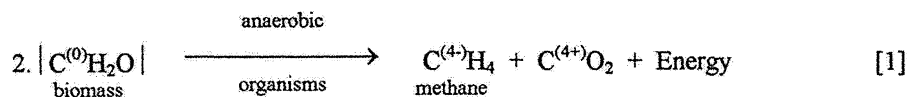
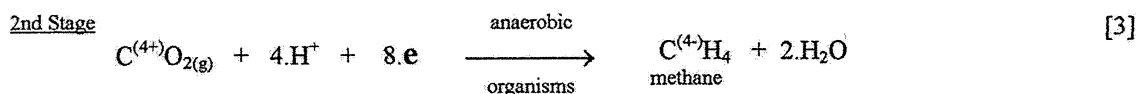
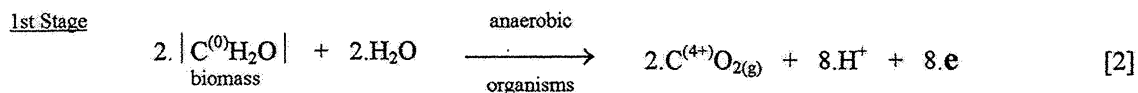


Figura 1. Cross-section and processing of an Anaerobic Reactor of Fluidized Bed (RALF)⁵².

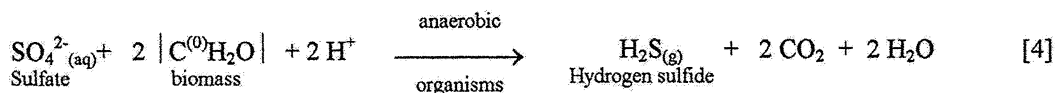
Figure 1 shows that no air (or oxygen) exists in the descent of sewage to the reactor's bottom. Oxygen in the fluidized sludge is practically zero, or rather, a hypoxia environment is created which may be called anoxia due to the complete lack of oxygen. Chemical species in this environment are reduced to a minimum, or rather, to an environment with electron availability, called a reducing environment. Two factors may explain this: (a) the lack of the oxidant agent oxygen; (b) the biota in this environment causes fermentation [1] in its quest for energy and a reduction reaction⁵¹ too.



Equation [1] shows reaction with two stages, given in [2] and [3] which, when added together, reproduce equation [1]. In the two reactions, oxidation status was indicated (in Arabic numerals) for the key element involved in the oxidation-reduction reaction, on the upper right side.



Reduction reactions are processed in the fluidized bed of the reactor (Figure 1) and may be perceived in stage [2] in which 8 electrons are released by fermentation. This is due to the passing of carbon from the biomass's oxidation status 0 ($\text{C}^{(0)}$) to carbon with oxidation status 4+ ($\text{C}^{(4+)}$) of CO_2 . Released electrons of the latter may also reduce other species, such as CO_2 to CH_4 , in which $\text{C}^{(4+)}$ of CO_2 becomes $\text{C}^{(4-)}$ in CH_4 . In the case of other species, sulfate (SO_4^{2-} , with S^{6+}) [4] releases hydrogen sulfide gas (H_2S , with S^{2-}) causing the bad smell.



It may be observed that in anaerobic processes, or rather, those that occur in the absence of air, albeit with oxygen, there is a 'release' or an 'availability of electrons' in the environment. The latter becomes a reducing environment with greater electronic activity.

Table 1 shows analytic results of mean concentrations of copper in the sewage input at the STS (affluent sewage) and the sewage output from the STS (effluent sewage), in each unit and total averages.

Total data of Table 1 show that the interval in mean concentrations, in $\mu\text{g mL}^{-1}$, in input sewage of all STSs is $(0.40-45.8)10^{-2}$, mean rate 0.0773, whereas that in output sewage of all STSs is $(0.40-56.4)10^{-2}$, mean rate 0.0576.

Table 1 shows a 25.5% retention of copper in STSs when total averages of Cu input and output are compared. Consequently, STSs are efficient in copper retention, which will be found in the sewage sludge.

Table 2 shows variance analysis of copper concentrations in sewage input of the place (3 STSs) and time (collection period), analyzing the phenomenon's temporality, as variation sources, with possible significant difference. Experimental results fail to give any significant difference, at 5% level, between copper concentration rates that arrive at STSs.

Table 1. Efficiency Evaluation of STS of Maringá in Retention of Copper (Cu).

Month	Year	STS - 1		STS - 2		STS - 3	
		Input ($\mu\text{g mL}^{-1}$)	Output ($\mu\text{g mL}^{-1}$)	Input ($\mu\text{g mL}^{-1}$)	Output ($\mu\text{g mL}^{-1}$)	Input ($\mu\text{g mL}^{-1}$)	Output ($\mu\text{g mL}^{-1}$)
Sept	1999	5.70×10^{-2}	2.70×10^{-2}	6.90×10^{-2}	3.20×10^{-2}	4.00×10^{-2}	1.20×10^{-2}
Oct	1999	7.20×10^{-2}	2.40×10^{-2}	7.70×10^{-2}	3.20×10^{-2}	3.50×10^{-2}	2.80×10^{-2}
Nov	1999	4.40×10^{-2}	2.20×10^{-2}	7.30×10^{-2}	4.00×10^{-2}	4.70×10^{-2}	2.20×10^{-2}
Jan	2000	4.80×10^{-2}	1.50×10^{-2}	3.10×10^{-2}	2.70×10^{-2}	5.80×10^{-2}	2.70×10^{-2}
Mar	2000	2.70×10^{-2}	2.70×10^{-2}	4.20×10^{-2}	2.70×10^{-2}	4.10×10^{-2}	1.20×10^{-2}
May	2000	2.90×10^{-2}	0.40×10^{-2}	0.90×10^{-2}	2.60×10^{-2}	2.40×10^{-2}	1.70×10^{-2}
Aug	2000	36.5×10^{-2}	6.50×10^{-2}	2.20×10^{-2}	2.00×10^{-2}	10.9×10^{-2}	2.10×10^{-2}
Oct	2000	15.5×10^{-2}	56.4×10^{-2}	45.8×10^{-2}	20.5×10^{-2}	12.4×10^{-2}	23.9×10^{-2}
May	2001	0.90×10^{-2}	0.80×10^{-2}	1.80×10^{-2}	0.40×10^{-2}	0.40×10^{-2}	0.80×10^{-2}
Data for STS							
Interval:		0.0090- 0.365	0.0040- 0.564	0.0090- 0.458	0.0040- 0.205	0.0040- 0.124	0.0080- 0.239
Mean:		8.95×10^{-2}	8.40×10^{-2}	8.88×10^{-2}	4.59×10^{-2}	5.36×10^{-2}	4.29×10^{-2}
Standard Deviation:		11.1×10^{-2}	18.1×10^{-2}	14.1×10^{-2}	6.05×10^{-2}	3.89×10^{-2}	7.39×10^{-2}
Median:		4.80×10^{-2}	2.40×10^{-2}	4.20×10^{-2}	2.70×10^{-2}	4.10×10^{-2}	2.10×10^{-2}
Total Data		Input		Output			
Total Interval:		$(0.40-45.8) \times 10^{-2}$		$(0.40-56.4) \times 10^{-2}$			
Mean \pm s:		$(7.73 \pm 10.1) \times 10^{-2}$		$(5.76 \pm 11.5) \times 10^{-2}$			
Median:		4.40×10^{-2}		2.60×10^{-2}			

STS-1 – Sewage Treatment Station in the districts of Mandacaru, Jardim Universitário and Zone 7; STS-2 – Sewage Treatment Station of South Region (central region, zones 2, 3, 4, 5 and new districts of Maringá); STS-3 – Sewage Treatment Station of districts Jardim Alvorada and Ribeirão Morangueira, s – Standard Deviation. Note: concentration rates lower than the Limit of Detection ($c_L = 0.0027 \mu\text{g mL}^{-1}$) were maintained for statistical calculations since there may be a 1% chance of being verified.

Results seem to show that, at 5% significance level, no dangerous refuse containing copper occurred in the sewage network during this specific period.

Art. 21 of Law 20/1986 of the CONAMA reads:

Effluents from any polluting source may be released directly or indirectly into water sources under the conditions below:

g) maximum rates permitted of the following compounds: Cadmium, 0.2 mg L⁻¹; Lead, 0.5 mg L⁻¹; Copper, 1.0 mg L⁻¹; Hexavalent Chromium, 0.5 mg L⁻¹; Trivalent, 2.0 mg L⁻¹; Soluble iron, 15.0 mg L⁻¹; Manganese, 1.0 mg L⁻¹ and Zinc, 5.0 mg L⁻¹.

Effluent from STSs lies within the legal conditions of the above law when the highest interval value (0.564 µg mL⁻¹) for copper are taken into consideration.

When average and higher interval values of output concentrations of some metals into the environment are analyzed, it may be seen that they are below the limits established by CONAMA. Table 3 shows that, since rates are within the CONAMA limits, the respective effluents may be deposited into the environment.

Table 2. Data Variance Analysis of Mean Values of Copper Concentrations in the Affluent Sewage to STS of in µg mL⁻¹.

Causes of variation	F.D.	S.S.	M.S.	Rate of F	Prob > F
Place	2	76.1163	38.0581	0.4799	0.63241
Time	8	1430.7162	178.8395	2.2549	0.07901
Residue	16	1268.9837	79.3115		
Total	26	2775.8162			

General Mean = $7.73 \cdot 10^{-2}$

Variation Coefficient = 115.215 %

F.D. – Freedom Degree; S.S. – Sum of Squares; M. S. – Mean Square; $F_{\text{place}} = \sigma^2_{\text{(place)}} / \sigma^2_{\text{(Residue)}}$ e $F_{\text{Time}} = \sigma^2_{\text{(Time)}} / \sigma^2_{\text{(Residue)}}$.

Table 3. Total Mean Concentrations of Some Metals in the Affluent and Effluent Sewage of STSs of Maringá and Their Respective Sewage Sludge in the Period 1999–2000.

Total Metal Concentration of Metals from STS-1, STS-2 and STS-3					
Metal	Sewage				Sewage sludge ($\mu\text{g g}^{-1}$)
	Affluent Sewage from STSs		Effluent Sewage from STSs		
	Mean ($\mu\text{g mL}^{-1}$)	Interval ($\mu\text{g mL}^{-1}$)	Mean ($\mu\text{g mL}^{-1}$)	Interval ($\mu\text{g mL}^{-1}$)	
Cu	0.091	0.0040-0.46	0.058	0.0040-0.56	410.9
Pb	0.089	0.0060-0.46	0.070	0.020-0.13	357.7
Zn	0.25	n.d. – 0.62	0.17	n.d. –0.69	1,517
Mn	0.11	0.055-0.22	0.10	0.060-0.17	144.8
Fe	2.87	0.22-9.88	2.20	0.11-6.77	53,066
Cd	n.d.	n.d – 0.0080	n.d	n.d – 0.0020	2.74
Cr	0.0057	n.d. – 0.037	0.0059	n.d. – 0.037	67.5

STS-1 – Sewage Treatment Station of districts Mandacaru, Jardim Universitário and Zone 7; STS-2 – Sewage Treatment Stations of South region (central region, zones 2, 3, 4, 5 and new districts in Maringá); STS-3 – Sewage Treatment Station of districts Jardim Alvorada and Ribeirão Morangueira. n.d. – not detected by method, concentration less than Detection Limit (c_L).

Sewage sludge (or biosolid)

After a certain period, varying between 2 to 4 months, depending on the physical, biological, physical and chemical characteristics of the reactor, non-consumed organic matter (OM) is stabilized (Figure 1). It turns into particled flakes that make up the sewage sludge or biosolid, which is removed from the reactor as 'fluid material'. Or rather, organic matter dispersed in water with many lyophilic chemical groups. It is generally spread in a thin film on protected soil surfaces and then left to dry or to release most of its water. The sewage sludge is actually the solid with particle agglomerates.

Table 4 shows pH values, mean concentration values of copper per STS, and total rate of copper concentration (0.74 mg g^{-1}) from August 1997 to March 2000.

Table 4. Concentration of Heavy Metal Copper in Sewage of Sewage Treatment Stations (STS) of Maringá.

Sample (n.)	Month and Year	STS-1		STS-2		STS-3	
		pH	Cu (mg g^{-1})	pH	Cu (mg g^{-1})	pH	Cu (mg g^{-1})
1	08.97	3.29	0.35	4.40	1.66	3.25	1.57
2	11.97	4.01	0.32	3.30	0.59	3.90	1.09
3	03.98	3.43	0.51	3.45	0.61	3.15	3.71
4	05.98	3.73	0.60	4.15	0.92	3.67	1.42
5	06.98	3.56	0.48	3.06	0.68	2.89	0.53
6	08.98	3.32	0.33	3.41	0.87	2.82	0.14
7	10.99	3.45	0.45	3.06	0.51	2.92	0.27
8	01.00	3.56	0.30	3.26	0.40	2.72	0.19
9	03.00	3.67	0.55	3.10	0.62	2.80	0.40
Mean \pm s:		3.56	0.43	3.47	0.76 ± 0.37	3.12	1.04 ± 1.14
Intervals:		3.29-	0.30-0.61	3.06-4.40	0.40-1.66	2.72-3.90	0.19-1.57

Total Rates of 3 STSs

	Copper (mg g^{-1})	pH
Mean \pm s:	0.74 ± 0.70	3.38 ± 0.41
Interval:	0.19 – 1.66	2.72 – 4.40

STS-1 – Sewage Treatment Station of districts Mandacaru, Jardim Universitário and Zone 7; STS-2 – Sewage Treatment Station of South region (central region, zones 2, 3, 4, 5 and new districts of Maringá); STS-3 – Sewage Treatment Station of districts Jardim Alvorada and Ribeirão Morangueira; s – standard deviation; analyses were done in triples.

Table 5 shows the variance analysis of results of copper concentration in the biosolid with two possible causes for variation: place (STSs) and time (sampling period) that reveals the phenomenon's temporality. No significant difference exists, at 5% variance analysis, between copper concentrations of the three STSs, throughout the collection period.

Table 6 exhibits mean world rate and the respective rate interval of heavy metals for sewage sludge and for arable soil. Sewage sludge in Maringá (Table 4) has 7.2%

copper more than mean world rate and 66.0% higher with regard to mean interval rates. This copper rate has already been detected in STS-2⁵³ and in STS-2 and STS-3⁵⁴.

Since sewage sludge is a sewage residue, indirectly revealing the composition of water, food, environmental refuse, human behavior and others, it seems that copper concentration has been caused by fungicides on coffee shrubs^{37, 38} and vines. In fact, the region of Maringá has been a large coffee plantation for many years in which copper fungicides were extensively used, similarly to what happens at present with regard to vineyards in the same region. Further, RALF process of the STSs retains 25.5% of the copper input from home sewage. It seems, therefore, that the high rate is due to copper use as an agricultural defense factor in the entire region, confirming Lavoisier's law that in Nature nothing is lost, nothing is created, but everything is transformed.

Table 5. Variance Analysis of Data for Mean Rates of Copper Concentrations in Sewage Sludge of STS in Maringá, in mg g⁻¹.

Causes of variation	F.D.	S.S.	M.S.	Rate of F	Prob > F
Place	2	1.643	0.821	1.856	0.187
Time	8	4.485	0.561	1.267	0.326
Residue	16	7.082	0.443		
Total	26	13.210			

General Mean = 0.74 mg g⁻¹

F.D. – Freedom Degree; S.S. – Sum of Squares; M. S. – Mean Square; $F_{Place} = \sigma^2_{(Place)} / \sigma^2_{(Residue)}$ and $F_{Time} = \sigma^2_{(Time)} / \sigma^2_{(Residue)}$.

Table 6. Mean Concentrations and Interval Concentrations of Metals in the Soil and in Sewage Sludge in World Level, and in Acceptable Maximum Concentrations, AMC*,¹² in agricultural soil, in the literature.

Metal	Type of material	Mean (µg g ⁻¹) ¹¹	Interval of rates (µg g ⁻¹) ¹¹	Interval of rates (µg g ⁻¹) ⁵⁶	AMC ¹² (µg g ⁻¹)	
					Interval ¹²	Median
Cu	Sludge	690	100 – 1,000	
	Soil	30	2.0 – 250	6.0 – 80	23 – 140	100
Zn	Sludge	2,250	1,000 – 10,000	
	Soil	90	1.0 – 900	17 – 125	70 – 400	265
Mn	Sludge	1,980	60 – 3,600	
	Soil	1,000	20 – 10,000	80 – 1,300	1,500–3,000	1,500
Pb	Sludge	1,832	136 – 7,627	
	Soil	20	2.0 – 200	10 – 84	20 – 500	100
Cr	Sludge	1,221	20 – 40,615	
	Soil	40	10 – 150	7 – 221	50 – 600	100
Cd	Sludge	74	2.0 – 1,100	
	Soil	0.35	0.010 – 2.0	0.060 – 1.1	3.0 – 8.0	3.0

* - Acceptable Maximum Concentrations, terminology by KABATA-PENDIAS, PENDIAS (1992)¹²; ... - non-calculated rates by authors above.

Mean pH values of sludge in STS-1, STS-2 and STS-3 may be found in Table 4. Total averages of each STS are 3.56; 3.47 and 3.12 respectively, with 3.38 as total average. There is no significant difference in average rates of the three STSs throughout the sampling period, according to variance analysis and Tukey's test, at 5% significance level. Low pH rates are favorable for the release of copper.

Since biosolids are applied to agriculture, relationship C:N and rate of organic matter, given by the product of (% of C) \times 1.72⁵⁵ (Table 7), were also analyzed.

Table 7 shows concentration rates of organic matter in the 3 STSs which lie within the interval between 28.0% and 55.6%, with 42.1% as total average. There is no significant difference, at 5% level, between rates for STSs and periods of sludge collection.

Table 7. Ratio C:N and Organic Matter (OM) in sludge of the Sewage Treatment Stations (STSs) of Maringá.

(Sample) Month/Year	STS-1			STS-2			STS-3		
	N (%)	C (%)	C:N	N (%)	C (%)	C:N	N (%)	C (%)	C:N
(1) 08/97	2.44	19.1	8:1	3.26	32.3	10:1	3.35	24.8	7:1
(2) 11/97	3.64	27.7	8:1	2.40	22.6	10:1	3.08	22.7	7:1
(3) 03/98	3.11	25.0	8:1	2.91	21.0	8:1	3.50	23.5	7:1
(4) 05/98	3.40	26.2	8:1	3.11	21.2	7:1	3.39	29.6	9:1
(5) 06/98	3.73	26.8	7:1	3.79	26.6	7:1	5.09	24.5	5:1
(6) 08/98	3.38	26.4	8:1	3.75	16.3	5:1	3.09	21.4	7:1
(7) 10/99	3.10	24.8	8:1	2.70	26.4	10:1	2.90	22.9	8:1
(8) 01/00	3.39	25.7	8:1	2.39	21.9	9:1	3.10	24.0	8:1
(9) 03/00	3.50	26.0	7:1	3.10	25.0	8:1	2.80	27.0	10:1
Mean:	3.30	25.3		3.05	23.7		3.37	24.5	
SD \pm s(r):	± 0.38	± 2.49		± 0.51	± 4.5		± 0.69	± 2.5	
Total rates:									
			% de N			% de C			
Mean:			3.24			24.5			
Interval:			2.39 – 5.09			16.3 – 32.3			

% of OM* = 1.72.%C: total mean = 42.1%; interval of rates: 28.0% - 55.6% of OM

* By multiplying % of C by factor 1.72 the % of Organic Matter (OM) is obtained; (r) DP \pm s – Standard Deviation; analyses are done in triple.

Table 7 also shows the ratio C:N, with intervals from 5:1 to 10:1. This means that, due to its nitrogen rate, sludge is good for agricultural use. Besides its good organic matter for the soil, its mineralization will not consume nutrient N in the environment and plants will not be impaired²¹.

Concentrations of copper and other heavy metals in the biosolid are lower than maximum rates in the current Norms for the use of Sewage Sludge in Agriculture^{57, 58, 59}. Consequently biosolids from STSs of Maringá may be used for agricultural purposes in so far as other conditions (restriction of place, soil capacity, recommended culture, maximum rate of application which depends on each element, and others) are observed.

CONCLUSIONS

From the experimental data above, we may conclude that:

- a) there was no significant difference, at 5% level, in STSs' input sewage, with regard to copper;
- b) in the case of copper and other heavy metals analyzed, RALF sewage system undertakes output without further need of any other treatment;
- c) there was no significant difference, at 5% level, in sludge from the three STSs throughout the collection period;
- d) total mean copper concentration in biosolid, 0.74 mg g^{-1} , is higher than the world average, although it is lower than the maximum limit, and thus proper for agricultural use;
- e) there was no significant difference, at 5% level, in organic matter rate and in ratio C:N of sludge from the three STSs, and is thus recommended for agricultural use.

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