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CONTRIBUTION TO CO(III) NITROCOMPLEXES CHEMISTRY. NEW ANALOGUES OF $NH_4[CO(NO_2)_4(NH_3)_2]$ COMPLEX WITH HEXAMETHYLENETETRAMINE

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ABSTRACT

The work presents experimental data about new analogues of ammonium tetranitro-diamine Co(III) complex (Erdmann complex) with hexamethyleneteramine (hta). The base complex obtained, $NH_4[Co(NO_2)_4(hta)_2]$, as well as the Erdmann complex, present practical importance for agriculture. They contain nitrogen under cationic, anionic and molecular form and Co(III) as micronutrient and can serve as source of other micronutrients through replacement of NH_4^+ with other complexes cations. Some of these complexes are soluble in water, others are hardly soluble and nonhygroscopic. Their efficiency in fertilizing was demonstrated by us experimentally.

KEYWORDS : Co(III) Nitrocomplexes, Hexamethylenetetramine, Micronutrients

RESUMO

O presente artigo apresenta dados originais obtidos para análogos novos do complexo de amônio e Co(III) com tetranitrodiamina (Complexo de Erdmann) com hexametilenotetramina (hta). O complexo obtido, $NH_4[Co(NO_2)_4(hta)_2]$, bem como o complexo de Erdmann tem importância prática na agricultura. Eles contêm nitrogênio nas formas catiônica, aniônica e molecular e Co(III) como micronutrientes e podem servir como fontes de outros micronutrientes através da troca de NH_4^+ com complexos de outros cátions. Alguns destes complexos são solúveis em água, outros são pouco solúveis e nonigroscópicos. A sua eficiência como fertilizantes foi demonstrada experimentalmente.

INTRODUCTION

There exists a wide range of complexes of nitroamine [1,2,3] as tetranitro-diamine ammonium Co(lll) complex, a compound which was obtained for the first time by Erdmann [2]. This complex can serre as a fertilizer because it contains nitrogen and an element that can be a micronutrient. It has, however some disadvantages, we have extended the Co(lll) nitrocomplexes series with fertilizing action to new nitrocomplexes with the general formula $(NH_4)_{n-3}[Co(NO_2)_{6-n}(N_4C_6H_{12})_n]$, where $N_4C_6H_{12}$ is hexamethylenetetramine noted *hta* [2,3] and n has the values of 2 or 3. These complexes are macrocrystalline substances, partially soluble in water, with red or yellow-orange colour. They decompose only at temperature between 138-175°C.

Starting from the base complex with two molecules of *hta* we have obtained a range of other ligands with or without nitrogen and also be replacing NH_4^+ ion with other simple complex ions.

EXPERIMENTAL PROCEDDURE

The procedure of preparing nitrocomplexes that have the general formula mentioned above consisted in treating $CoCl_2 \cdot 6H_2O$ dissolved in distilled water with a solution which contains NH_4Cl, $NaNO_2$ and $N_4C_6H_{12}$ taken in stoichiometrical ratios. The reaction took place in excess NH_4Cl and the oxidation of the reactions mixture is done by bubbling air 1.5 to 2 hours at room temperature. The product is obtained by crystallization for 12-24 hours.

The $NH_4[Co(NO_2)_4(hta)_2]$preparation

The Erdmann analogue preparation was done as follows: A sample of 91.5g $CoCl_2 \cdot 6H_2O$ (0.4mols) was dissolved in 200 mL distilled water which is the first solution and 100 g NH_4Cl (1.8 mols), 110.4 g $NaNO_2$ (1.6 mols) and 112 g $N_4C_6H_{12}$ (0.8 mols) in 1050 mL distilled water which is the second solution. The two solutions were mixed and a clear red with purple blue solution was obtained. The oxidation of the reactions mixture was done by bubbling air for 1.5-2 hours at room temperature. The solution was then allowed to crystallize for 12-24 hours. The reaction is as follows:

$$4CoCl_2 + 8NH_4Cl + 16NaNO_2 + 8N_4C_6H_{12} + O_2 \rightarrow 4NH_3 + 16NaCl + 4NH_4[Co(NO_2)_4(hta)_2] + 2H_2O \quad (1)$$

The nitrocomplex was dissolved in warm water in order to recrystallize it and there was no danger of hydrolyzing. In the case of Erdmann's salt recrystallization was done from a 1M CH_3COOH solution with an efficiency of 91%. The complex obtained has macrocrystals under the form of red bright lamellae of different sizes within regular outlines. It is partially soluble in water (0.23g/100g water at 22°C) and it decomposes at 175°C.

The pentanitro- and trinitrocomplexes preparation with $N_4C_6H_{12}$

Modifying the stoichiometrical ratio between components (increasing $NaNO_2$ quantity and reducing the $N_4C_6H_{12}$ quantity) we obtained the pentanitrocomplex with

the formula $(NH_4)_2[Co(NO_2)_5(hta)]$. It presented macrocrystals as bright lamellae with yellow- reddish colour a little different from the one of tetranitrocomplex.

As in the case of Erdmann's salt preparation, excess of $N_4C_6H_{12}$ leads to the formation of the nonelectrolyte form with the formula $[Co(NO_2)_3(hta)_3]$ during the bubbling of air. This is a precipitate with yellow – orange colour, with microcrystals and it is hardly soluble in water.

The three nitrocomplexes, which were obtained with hexamethylenetetramine (hta), were studied using many chemical and physical – chemical methods in order to establish their composition and structure.

The chemical analysis of the complexes

Cobalt was determined by complexonometrical titration using 0.01M complexon III with murexide [4]. For the calculation the following relation was used:

$$Co\% = \frac{0.5894n}{a} x100$$

where n is ml complexon used for titration, a is grams substance analyzed and 0.5894 is mg cobalt which corresponds to 1 ml complexon.

The measurement of NH_4^+ ion was done spectrometrically (λ=410 nm) using Nessler reagent. The total nitrogen was determined using the micro-Kjeldahl method. The difference between the total nitrogen and the ammnoniacal nitrogen represents the nitrogen, which is in the complex ion. This make possible to establish the number of NO_2^- groups and complexed *hta* molecules. In the Table 1 are presented the data obtained through chemical analysis for the three-synthetized complexes.

Table 1. The results of the chemical analyses.

Formulae	M_{calc}	η%	Content %					
			Co		NH_4^+		N_{total}	
			Found	Calc.	Found	Calc.	Found.	Calc.
$(NH_4)_2[Co(NO_2)_5(hta)]$	464.93	76.3	12.52	12.67	7.90	7.74	33.01	33.12
$NH_4[Co(NO_2)_4(hta)_2]$	536.93	91.0	10.87	10.97	3.52	3.35	33.70	33.89
$[Co(NO_2)_3(hta)_3]$	616.93	42.5	9.68	9.55	-	-	34.22	34.04

The thermal analysis

Using a Dr. Erdey derivatograph important data were obtained about the composition and the structure of the complexes synthesized. In Figures 1, 2 and 3 the penta-, tetra- and trinitrocomplexes thermograms are presented and in Figure 4 the thermogram of Erdmann's salt is presented.

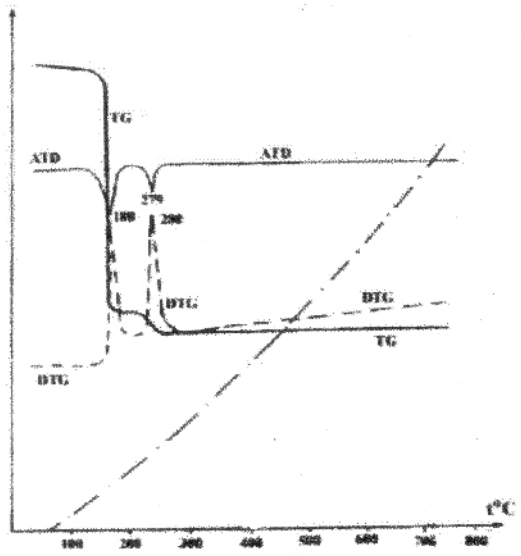


Figure 1. The thermogram of $(NH_4)_2[Co(NO_2)_5(hta)]$

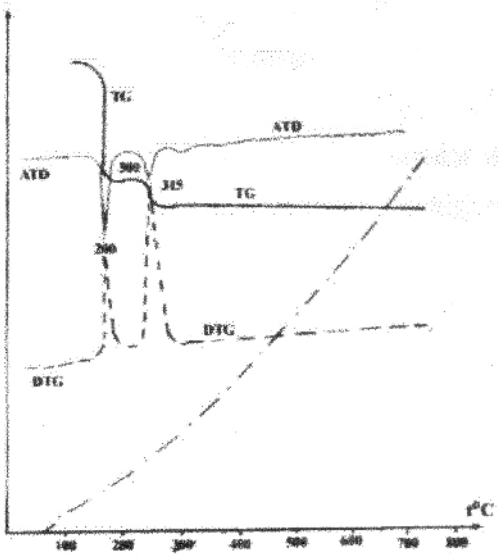


Figure 2. The thermogram of $NH_4[Co(NO_2)_4(hta)_2]$

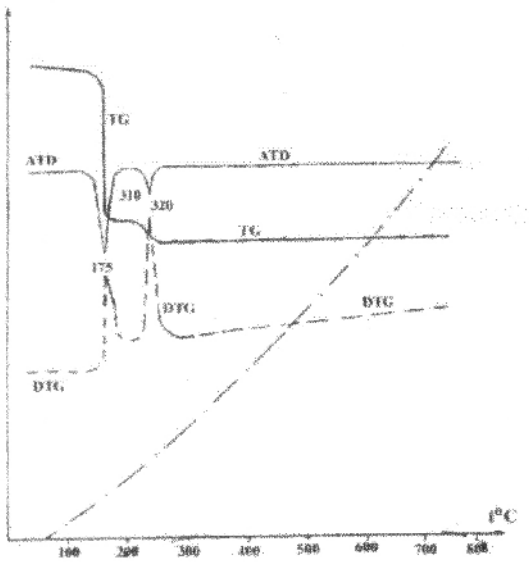


Figure 3. The thermogram of $[Co(NO_2)_3(hta)_3]$

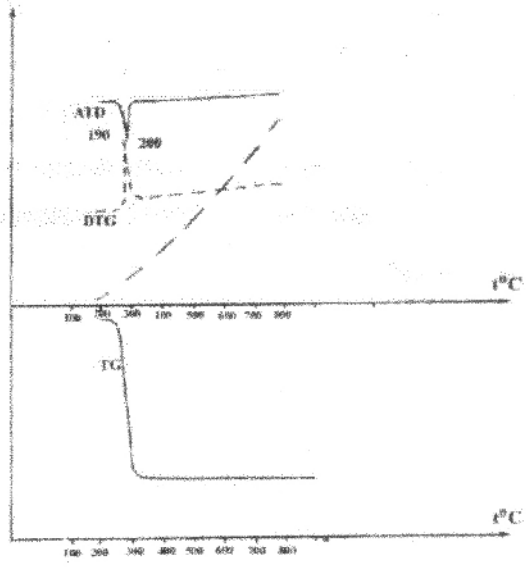


Figure 4. The thermogram of $NH_4[Co(NO_2)_4(NH_3)_2]$

Comparing these thermograms (Figures 1-3) with the thermogram of Erdmann's salt (Figure 4) we notice that:

- the endothermic effect which appears at 175-200°C, for Erdmann's salt, is due to NH_4^+, NH_3 and NO_2^- groups which leave the complex;
- the effect which appears at 275-320°C (Figures 1-3), which is not presented with Erdmann's salt, is due to *hta* which having a higher bond energy, needs a higher temperature in order to leave the complex.

The analysis of the first three thermograms demonstrates that the endothermic effect, which is present because of the chemical bond break between the central ion and *hta*, is bigger than the one produced by of Co-NO_2 bond break. This can be explained both by the strength of bond and by the ligand nature and mass. The ligand with a larger mass and stronger band requires a larger quantity of heat in order to leave the complex. The sharp maximum of DTG curve proves that the effect is produced at a precise temperature (320°C) corresponding to the chemical bond break.

Analyzing the DTG curves of the three new combinations we can show that:
- the first maximum attributed to NO_2^- groups (175-200°C) decreases at the same time with the diminishing number of NO_2^- groups;
- the second maximum from 275 to 320°C, attributed to *hta* groups, increases in temperature and intensity simultaneously with the increase of number of the *hta* molecules.

This is the result of internal interactions, which are bigger when the complex contains more ionic ligands (NO_2^-) than neutral ligands *(hta)*. That is why the Co-NO_2 bond break occurs in the case of pentanitrocomplex at 175°C and the Co-hta bond break takes place at 275°C. In the case of tetranitrocomplex the temperature are higher: 200°C for the Co-NO_2 bond break and 315°C for the Co-hta bond break.

The higher stability of the tetranitrocomplex can also be explained by its octahedral configuration. There are two possible arrangements:
- the two bulky molecules of *hta* at the two tops of the octahedral:
- two NO_2^- ions at the two tops of the octahedral and the other two at the opposite diametrical corners if the base in order to assure a repulsion as small as possible among the NO_2^- ions.

The lamellar structure of pentanitro- and tetranitrocomplex suggests that the second variant is correct. In the case of trinitrocomplex it is not possible to find three bulky groups of *hta* in the base plane. One of the groups is found in one of the octahedral tops. For this reason:
- the macrocrystal lamellar structure disappears and a microcrystal structure appears;
- the solubility decreases;
- the colour is modified from red to yellow as compared to the other two complexes.

The TG curves, which show mass loss varying with temperature, confirm the conclusions drawn from the diagrams ATD and DTG analysis.

The IR spectral analysis

The absorption spectrum in IR of the complexes prepared was recorded with a UR 10 Jenna spectrometer. The tested sample was included into a KBr pellet at a pressure of 80 atm in dilution of 2-10 mg substance / 0.5g KBr. There frequencies were recorded in the range of 400-3600 cm^{-1} (Table 2).

Table 2. The IR spectra of the complexes

Band	$(NH_4)_2[Co(NO_2)_5(hta)]$	$NH_4[Co(NO_2)_4(hta)_2]$	$[Co(NO_2)_3(hta)_3]$
$\delta(NO_2)$	830 s, sh	830 s, sh	830 s, sh
$\nu_{sym.}(NO_2)$	1270 w	1250 w	1230 w
$\nu_{asym.}(NO_2)$	1465 w	1440 w	1420 m
$\gamma(CH_2)$	710 w	710 w	710 w
ν(C-N)	1065 s, sh	1065 s,sh	1065 s,sh
ν(Co-N)(l)	570 w	570 w	570 w
ν(Co-N)(ll)	510 w	510 w	510 w
$\nu(NH_4^+)$	3080-3300 w, br	3080-3300 w, br	-

s- strong; w- weak; sh- sharp; m- medium, br- broad
l: Co-N(NO_2); ll: Co-N(hta)

From Table 2 it can be noticed that generally with all three complexes there are the same absorption bands but they are shightly shifted and have different intensities. This is because of the resonance state of the atoms, which are fixed in a total correlation with the whole molecular structure, which is different from one substance to anoher.

This explain why the bands at 1270 and 1465 cm^{-1}, which were assigned to the symmetrical and unsymmetrical stretching vibrations of NO_2^- groups [4-6], from the pentanitrocomplex, are shifted ~ 40 cm^{-1} with tetra- and trinitrocomplexes. It can be noticed that the $\delta(NO_2)$ and $\gamma(CH_2)$ vibrations at 830 and 710 cm^{-1} are constant respectively in all three complexes. The C-N stretching vibration characteristic of the C-N bond of *hta* appears at 1065 cm^{-1} and decreases in intensity from pentanitro- to trinitrocomplex.

The Co-N(l) and Co-N(ll) stretching vibrations appear in all three complexes at 570 and 510 cm^{-1} respectively. The vibrations at 3080-3300 cm^{-1}, characteristic of NH_4^+ ion, do not appear for the trinitrocomplex, which demonstrates that it is a nonelectrolyte.

The UV spectra

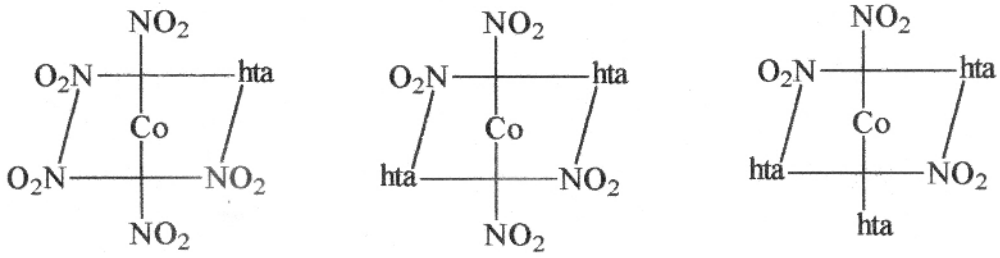
A UNICAM SP 8000 spectrometer was used for recording the absorption spectra in UV. Depending on the number of the NO_2^- and *hta* groups two maxima of absorption were obtained in UV domain.

Analysing these spectra one can notice that the three complexes present the first maximum at 253 nm (with Erdmann's salt λ_1=254 nm) and the second at 350 nm (with Erdmann's salt λ_1=348 nm). From the absorption maxima there were determined the maxim absorbance:

- in the case of pentanitro- and tetranitrocomplexes they are very close (0.30 and 0.33 respectively 0.12 and 0.12);
- in the case of the nonelectrolyte they are very different (0.12 and 50 respectively for the second maximum of absorption);

From the chemical analyses and the other physical-chemical methods which were used we proposed the following structure and the composition of the three nitrocomplexes synthezised:

$(NH_4)_2[Co(NO_2)_5(hta)]$ $NH_4[Co(NO_2)_4(hta)_2]$ $[Co(NO_2)_3(hta)_3]$



NEW DERIVATIVES OF $NH_4[Co(NO_2)_4(hta)_2]$

The $NH_4[Co(NO_2)_4(hta)_2]$ complex is an Erdmann analogue as well as all the derivatives resulting from partial or total substitution of *hta* groups. Starting from this base combination we synthetized numerous Erdmann analogues. They contain a useful element for the plant, within the complex ion or they contain instead of the NH_4^+ cation another complexed microelement of the type $[Me(NH_3)_6]^{n+}[Co(NO_2)_4(hta)_2]_n^-$.

Thus, the $NH_4[Co(NO_2)_4(NH_3)(hta)_2]$ complex was studied. It was obtained by introducing into the mixture of reaction both *hta* (according to the stoichiometrical reaction) and NH_3, in small excess. The favourable efficiency was obtained by mixing two solutions as follows:

- the first solution was obtained by dissolving $CoCl_2 \cdot 6H_2O$ (0.4 mols) in 200 mL distilled water:
- the second solution by dissolving NH_4Cl (1.8 mols), *hta* (0.4 mols), $NaNO_2$ (2 mols) and NH_3 25% (2 mL) in 950 mL distilled water;

Air was bubbled in the two solutions for 2 hours after mixing. The purple colour of the solution becomes red and it is turbid because the nonelectrolyte $[Co(NO_2)_3(hta)_3]$ is formed in a small quantity. It need 2-3 days for crystallizing after filtering. Crystals with bright red lamellae are obtained. The chemical and physical-chemical studies confirm the $NH_4[Co(NO_2)_4(NH_3)(hta)]$ complex composition and structure. The fact that the Erdmann salt does not appear even in traces (it can be seen with naked eye), because it has dark-brown prismatic crystals, proves that *hta* as a ligand a higher affinity for cobalt than for NH_3. The IR spectrum of this complex confirms the presence of the NH_3 groups by the presence of the weak band at 1620 cm^{-1} (δ_{asym} NH_3 vibrations) [7-9] and the band at 1310 cm^{-1} (δ_{sym} NH_3 vibrations).

In the same way we obtained new derivatives, which contain, another ligand ion or molecule in the complex ion besides the four NO_2^- groups and one *hta* molecule. The formula of the new complex ion is $[Co(NO_2)_4(hta)X]^-$ where W is the new ligand which is introduced by synthesis [10-13].

Table 3 presents examples of such derivatives, which are considered Erdmann's analogues. In the same table are presented analogues, which are obtained by replacing the NH_4^+ cation with metallic cations such as Ag^+, Hg_2^{2+} and Tl^+. They are obtained by a simple precipitation of $[Co(NO_2)_4(hta)X]^-$ ion with the metal salts or with ammonia complex cations or derivatives [14-16].

Table 3. New analogues of $NH_4[Co(NO_2)_4(hta)]$

Complex combination	M (calculated)	η%	Aspect	Co(III)%	
				Calculated	Found
$NH_4[Co(NO_2)_4(hta)(SCN)]$	476.93	68.20	irregular plates, microcrystals, pink-lilas coloured	12.35	12.5
$NH_4[Co(NO_2)_4(hta)(py)]$	480.03	71.10	rhombic plates macrocrystals, pink coloured	12.27	12.38
$Ag[Co(NO_2)_4(hta)(NH_3)]$	507.83	*	plates microcrystals, dark-yellow coloured	11.60	11.32
$Hg_2[Co(NO_2)_4(hta)(NH_3)]_2$	1201.04	*	plates microcrystals, reddish coloured	4.91	5.18
$Tl[Co(NO_2)_4(hta)(NH_3)]$	604.3	*	plates microcrystals, dark-yellow coloured	9.75	9.60
$(NH_4)_2[Co(NO_2)_4(hta)(CN)]$	444.93	64.50	irregular plates microcrystals, red-brick coloured	13.24	13.11
$[Cu(NH_3)_4]A_2$	931.41	*	plates microcrystals, greenish coloured	6.33	5.98
$[Zn(NH_3)_4]A_2$	933.23	*	plates microcrystals, yellow-golden coloured	6.31	6.14
$[Co^{III}(NH_3)_4(CO_3)]A$	586.86	*	plates macrocrystals, brown coloured	10.04	10.41
$[Co^{III}(NH_3)_4(C_2O_4)]A$	702.86	*	plates macrocrystals, chocolate coloured	8.38	8.02

*- total precipitating; $A=[Co(NO_2)_4(hta)(NH_3)]$

The latter compounds are hardly soluble and they have different colours due to the presence of the second complexed metal which could be used as a microelement for fertilizing plants.

CONCLUSIONS

The Erdmann complex presents properties of fertilizing plants because it contains both nitrogen under different forms and Co(III) as a microelement. But this combination has many disadvantages for use. Among them we mention: decomposing under action of light and unstable character in water solution.

The analogue obtained by us, $NH_4[Co(NO_2)_4(hta)_2]$, eliminates these disadvantages because *hta* is tied more strongly to Co(III) and has a higher stability. The paper presents the way for obtaining and studying the composition and structure of the above mentioned analogue and a number of other derivatives. The general formula of

the complex ion is $[Co(NO_2)_4(hta)X]^-$ and its charge is neutralized by monovalent metallic cations or complex ions.

REFERENCES

1. S.M.Jörgensen, *Z.Anorg.Allgen.Chem.*, *5*, 169 (1893).
2. I.Cernaev and I.Ganiev, *Zhur.Neorg.Khim.*, *2*, 460 (1893).
3. R.Ripan, Cs.Varhely and V.Simon, *Studia Univ.Babeş-Bolyai Chem.*, 123 (1963).
4. J.Erdmann, *Prakt.Chem.*, *1*, 97, 385 (1866).
5. L.Burnea, *Doctoral Thesis*, Polytechnic Institute Iaşi, Department of Chemistry, România, 72 (1981).
6. N.Calu, L.Burnea and S.Burnea, *Certificate of Inventor*, nr. 84952, România (1984).
7. H.Flaschka, *Microchem.*, *39*, 38 (1952).
8. K.Nakamoto, J.Fujita and H.Murata, *J.Amer.Chem.Soc.*, *80*, 4817 (1958).
9. Y.Puget and C.Duval, *Comptes Rendus*, *250*, 4141 (1960).
10. I. Nakagawa and S.Mizushima, *Bull.Chem.Soc.Japan*, *28*, 589 (1955).
11. S.Mizushima and I.Nakagawa, *J.Chem.Phys.*, 33, 1367 (1955).
12. M.Kobayashi and J.Fuita, *J.Chem.Phys.*, *23*, 1354 (1955).
13. D.B.Powel and N.Shepard, J.Chem.Soc., 3108 (1956).
14. I. Gănescu, A.Popescu and I.Papa, *Anal.Univ.Buc.*, *XLVII*, 33 (1998).
15. I. Gănescu, I.Papa, A. Gănescu, L.Chirigiu and V.Popescu, *Rev.Chim.*,*51(10)*, 278 (2000).
16. I. Gănescu, N. Mureşanu, A. Popescu, I. Papa and A. Gănescu, *Anal. Univ. ''Al.I.Cuza'' Iaşi, A.Chim.*, *VII(2)*, 271 (1999).

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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 μg 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 μg 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 life[3].

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 mortality[4].

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 metal[7], 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 world[8]. Copper may be found naturally (Cu) and as a mineral, cuprite [Cu_2O], malachite [$Cu_2(CO_3)(OH)_2$], chalcosite [Cu_2S], chalcopyrite [$CuFeS_2$], azurite [$Cu_3(CO_3)(OH)_2$], and others[9]. Mean rate of copper in rocks of the earth's crust is close to 55 $\mu g\ g^{-1}$ [10]. Since copper is relatively available and movable in the soil[11], it has variable concentrations in the latter, frequently at toxic rates for biota[12]. It is also a contaminating element carried through the air[13] and in water[14]. In the largest rivers it is found at interval rates of 0.830 - 152 $\mu g\ L^{-1}$ [15, 16, 17].

Several copper derivatives are toxic and even highly toxic[18]. Although used as a fungicide in vineyards and coffee plantations[19], it is one of the micronutrients necessary for animal and vegetative life[20]. Actually its presence in protein and enzymes makes it an essential element[21].

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 $\mu g\ L^{-1}$ (Class 1 and 2 water) and 50 $\mu g\ L^{-1}$ (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 agents[27].

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 plants[32], 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 international[26] and national[23] levels to establish usage criteria[23]. Even the state of Paraná has tackled the problem[24].

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 Biosolids[36]. In the wake of analyzing sludge application, current research is concerned with copper, which has been used for many years and in 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^{-1} [39]. 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 mode[40]. Method had a detection limit of $(c_L) = 0.027$ μg mL^{1-}, with 99% confidence level[41].

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 matter[42].

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 added[44], the mixture was shaken, and the pH of supernatant was measured by a pH-meter after decantation.

Sewage: collection and initial preparation of samples[45]

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 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 HCl 5 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 Sperling[40]. Although the method's detection limit (c_L) was 0.027 μg 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 μg 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 μg 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).

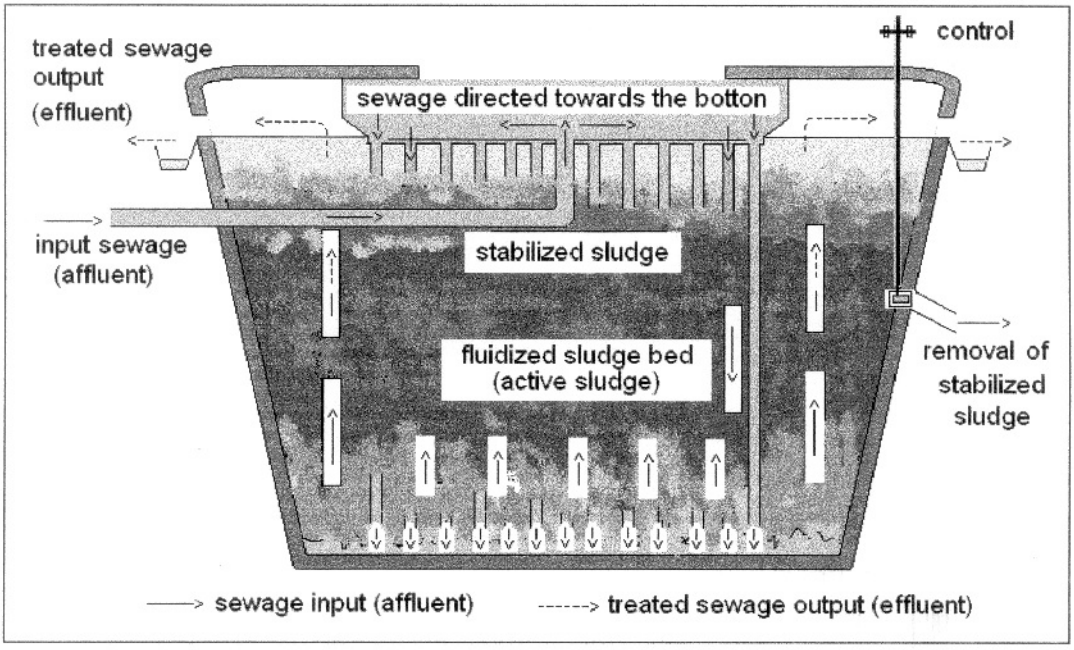

Figura 1. Cross-section and processing of an Anaerobic Reactor of Fluidized Bed (RALF)[52].

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 reaction[51] too.

$$2\,|\underset{\text{biomass}}{CH_2O}| \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{Methane}}{CH_4} + CO_2 + \text{Energy} \qquad [1]$$

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.

1st Stage

$$2.\,|\underset{\text{biomass}}{C^{(0)}H_2O}| + 2.H_2O \xrightarrow[\text{organisms}]{\text{anaerobic}} 2.C^{(4+)}O_{2(g)} + 8.H^+ + 8.\mathbf{e} \qquad [2]$$

2nd Stage

$$C^{(4+)}O_{2(g)} + 4.H^+ + 8.\mathbf{e} \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{methane}}{C^{(4-)}H_4} + 2.H_2O \qquad [3]$$

$$2.\,|\underset{\text{biomass}}{C^{(0)}H_2O}| \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{methane}}{C^{(4-)}H_4} + C^{(4+)}O_2 + \text{Energy} \qquad [1]$$

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 (C^o) to carbon with oxidation status 4+ (C^{4+}) of CO_2. Released electrons of the latter may also reduce other species, such as CO_2 to CH_4, in which C^{4+} of CO_2 becomes 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.

$$\underset{\text{Sulfate}}{SO_4^{2-}{}_{(aq)}} + 2\,|\underset{\text{biomass}}{C^{(0)}H_2O}| + 2\,H^- \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{Hydrogen sulfide}}{H_2S_{(g)}} + 2\,CO_2 + 2\,H_2O \qquad [4]$$

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 $\mu g\ mL^{-1}$, 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 $(0.40\text{-}56.4)10^{-2}$, 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 ($\mu g\ mL^{-1}$)	Output ($\mu g\ mL^{-1}$)	Input ($\mu g\ mL^{-1}$)	Output ($\mu g\ mL^{-1}$)	Input ($\mu g\ mL^{-1}$)	Output ($\mu g\ mL^{-1}$)
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:	$(0.40\text{-}45.8)\times10^{-2}$	$(0.40\text{-}56.4)\times10^{-2}$
Mean ±s:	$(7.73\pm10.1)\times10^{-2}$	$(5.76\pm11.5)\times10^{-2}$
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 $\mu g.mL^{-1}$) 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 = $7.73.10^{-2}$
Variation Coefficient = 115.215 %

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

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.

Metal	Total Metal Concentration of Metals from STS-1, STS-2 and STS-3				
	Sewage				Sewage
	Affluent Sewage from STSs		Effluent Sewage from STSs		
	Mean (μg mL^{-1})	Interval (μg mL^{-1})	Mean (μg mL^{-1})	Interval (μg mL^{-1})	sludge (μg g^{-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 ±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 ±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-2[53] and in STS-2 and STS-3[54].

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) x 1.72[55] (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.

	STS-1			STS-2			STS-3		
(Sample) Month/Year	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 ± 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 ±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 impaired [21].

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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REFERENCES

1. L.M. Lima, *Tratamento do Lixo* [Treatment of Refuse], HEMUS Editora Ltda., São Paulo (1985), pp.09-15.
2. IPT (Institute for Technological Research) *Lixo Municipal – Manual de Gerenciamento Integrado* [Municipal Refuse – Integrated Administration Handbook]. São Paulo: Instituto de Pesquisas Tecnológicas de São Paulo (1995), pp. 1-278.
3. L.C.B. Przybysz, & E.F. Guidi, *Sanare*, 7(7), 20-23 (1997).
4. C. V. Andreoli, F. Fernandes, and S. C. Domaszak, *Reciclagem Agrícola do Lodo de Esgoto* [Agricultural Recycling of Sewage Sludge], SANEPAR, Curitiba, PR (1997), pp. 1-81.
5. EPA, *Biosolids Generation, Use and Disposal in the United States* (EPA530-R-99-009), Office of Solid Waste, U.S. Environmental Protection Agency, Washington (1999), pp. 1-74.
6. A.B.S. De Deus, *Avaliação sanitária e ambiental de lodos de ETEs* [Health and Environmental Evaluation of STSs Sludge]. Master's Thesis, Engenharia de Recursos Hídricos e Saneamento Ambiental, UFRS, Porto Alegre, RS (1992).
7. D. Kemp, *The Environment Dictionary*, Routledge, London (1998), pp. 1-464.
8. KIRK-OTHMER, *Encyclopedia of Chemical Technology*. 3. ed., John Wiley Sons, New York (1981), vol. 6, pp. 819-869.

9. A. Betejtin, *Curso de Mineralogia* [Course in Minerology], 3. ed., translated by L. Vládov, Editorial MIR, Moscú (1977), pp. 1-739.
10. S.R. Taylor, *Geochim. Cosmochim. Acta*, *28*, 1273-1285 (1965).
11. D.C. Adriano, *Trace Elements in the Terrestrial Environment,* Springer-Verlag, Berlin (1986), pp. 1-533.
12. A. Kabata-Pendias, and H. Pendias, *Trace Elements in Soils and Plants*, 2. ed., CRC Press, London (1992), pp. 1-365.
13. D. Purves, *Trace - Element Contamination of the Environment,* rev. ed., Elsevier Science Publishing Company Inc., Amsterdam (1985). pp. 57 – 61 and 48-61.
14. J.W. Moore, *Inorganic Contaminants of Surface Water*, Springer-Verlag, Berlin (1991), pp. 1-334.
15. M. Ajmal, R. Uddin and U. Khan, *Hydrobiologia, 148*, 151-157 (1987).
16. M. Ajmal, R. Uddin and U. Khan, *Environ. Int.*, *14*, 515-523 (1988).
17. C. Polprasert, *Water Research*, *16*, 775-784 (1982).
18. R.J. Lewis, *Sax's Dangerous Properties of Industrial Materials,* 9. ed., Van Nostrand Reinhold, New York (1996), vol. II, pp. 913-921 and vol. III, pp. 2032-2033.
19. F.R. Benn, and C.A. McAuliffe, Pesticidas e Poluição [Pesticides and Pollution]. In: *Química e Poluição*, translated by L.R.M. Pitombo and S. Massaro, Livros Técnicos e Científicos Editora S.A. and Editora da Universidade de São Paulo, São Paulo (1985), pp. 41-66.
20. H.J. Sanders, *Chem. & Eng. News*, *57*, 27-40 (1970).
21. E. Malavolta, *Manual de Química Agrícola Adubos e Adubações* [Handbook of Agricultural Chemistry: Fertilizers and Manuring], 3. ed., Editora Agronômica CERES Ltda., São Paulo (1981), pp. 1-59.
22. Coletânea de Legislação Ambiental. [Collection of Laws on Environmental Legislation]. Organized and edited by the State Secretariat for the Environment and of Water Resources – SEMA and Deutsche Gesellschaft für Technische Zuzammenarbeit/GTZ (GmBH). Curitiba (PR): Instituto Ambiental do Paraná, IAP (1996).
23. W. Bettiol, O.A. Camargo, Ed., *Impacto Ambiental do Uso Agrícola do Lodo de Esgoto* [Environmental Impact of the Agricultural Use of Sewage Sludge], Embrapa Meio Ambiente, Jaguariúna, SP (2000), pp. 1-312.
24. C.V. Andreoli, A.I. Lara, and F. Fernandes, *Reciclagem de Biossólidos: Transformando Problemas em Soluções* [Recycling Biosolids: Transforming Problems into Solutions], SANEPAR – Companhia de Saneamento do Paraná, Curitiba (1999), pp. 1-300.
25. N. Favaretto, C. Deschamps, E. Daros, and A. Pissaia, *Braz. Arch. Biol. Tecnol.*, *40*(4), 837-848 (1997).
26. M.B. McBride, Issues. *J. Qual.*, *24*, 5–18 (1995).
27. C. V. Andreoli and F. Fernandes, *Sanare*, *7*(7), 68-72 (1997).
28. D.V. Ladonin, and S.E. Margolina, *Euras. Soil Sci.*, *30*, 710-1715 (1997)
29. P.S. Hooda, and B.J. Alloway, *J. Agric. Sci.*, *127*, 289-294 (1996).
30. S.R. Smith, *Environ. Pollut.*, *85*, 321-327 (1994).
31. N. Cavallaro, N. Padilla, and J. Villarrubia, *156*(2), 62-70 (1993).
32. M.P.W. Farina, M.E. Summer, C.O. Plank, and W.S. Letzch, *Comm. Soil Sci. Plant Anal. 11*(10), 981-992 (1980).

33. T. Hernandez, C. Garcia, F. Costa, J.A. Valero, M. Ayuso, *Suelo y Planta*, Madrid, v.2, n.3, p.373-83, 1992.
34. K. Sarkis, *Biocycle*, *28*(1), 7-28 (1987).
35. Epstein, E. *Nutrição Mineral das Plantas: Princípios e Perspectivas* [Mineral Nutrition of Plants – Principles and Perspectives]. São Paulo: EDUSP, 1975. 341 p.
36. Anais do I Seminário sobre Gerenciamento de Biossólidos do Mercosul. Seminário realizado no período de 01 a 04 de dezembro de 1998, em Curitiba, Paraná, Brasil. Realização: SANEPAR e ABES-PR, pp. 1-326. [Annals of the I Seminar on Biosolid Administration of the Mercosur. Organized from 1-4 December 1998 in Curitiba PR Brazil, by Sanepar & Abes PR].
37. W. Wilcke, S. Kretzscmar, M. Bundt, G. Saborio, and W. Zech, *Soil Sci.*, *136*(6), 463-471 (1998).
38. F. Galli and P.C. Carvalho, Ferrugem do cafeeiro: medidas gerais de controle [Oxidation in the Coffee Plant: Control Measures]. *In*: Seminário sobre Ferrugem do Cafeeiro, 1971, Londrina., GERCA. *Resumos*, pp.47-48 (1971).
39. B. Griepink, H. Muntau, and E. Colinet, *Fresenius Z. Anal. Chem.*, *318*, 490-494 (1984).
40. B. Welz, and M. Sperling, *Atomic Absorption Spectrometry*, 3. rev. ed., VCH Verlagsgesellschaft mbH, Weinheim (Germany) (1999), pp. 1-941.
41. Analytical Methods Committee. *Analyst*, *112*, 199-204 (1987).
42. F.C. Silva, Organizador, *Manual de Análises Químicas de Solos, Plantas e Fertilizantes* [Handbook of Chemical Analyses in Soil, Plants and Fertilizers], Embrapa Comunicação para a Transferência de Tecnologia, Brasília (1999), pp.1-370.
43. W. Horwitz, Ed., *Official Methods of the Analysis of the Association of Official Analytical Chemists*, 13. ed., Association of Official Analytical Chemists – AOAC, Washington (1980), pp. 1-1018.
44. R. M. Handa and A. Nogueira, Determinação do pH de amostras de Lodo de Esgoto [Calculation of pH in Sewage Sludge Samples] In: C. V. Andreoli e B. R. P. Bonnet, Manual de Métodos para Análises Microbiológicas e Parasitológicas em Reciclagem Agrícola de Lodo de Esgoto [Handbook in Methods for Microbiological and Parasitological Analyses in the Agricultural Recycling of Sewage Sludge], SANEPAR, Curitiba, PR (1998), pp.75-76.
45. M.O.S.A. Silva, *Análise Físico-Química para Controle das Estações de Tratamento de Esgotos* [Physical and Chemical Analysis for the Control of STS], CETESB, São Paulo, SP (1977), pp. 1-225.
46. J.R. Moody, and R.M. Lindstrom, *Anal. Chem.*, *49*(14) 2264-2267 (1977).
47. R.W. Karin, J.A. Buono, and J.L. Faching, *Anal. Chem.*, 47(13) 2296-2299 (1975).
48. L.H. Keith, Ed., *Principles of Environmental Sampling*, 2. ed. Americam Chemical Society, Washington (1996a), pp. 1-648.
49. L.H. Keith, Ed., *Compilation of EPA's Sampling and Analysis Methods*, 2. ed. Lewis Publishers, New York (1996b), pp. 1-1691.
50. SANEPAR (Companhia de Saneamento do Paraná), Regional de Maringá, *Plano Anual de Operação e Manutenção de Esgotamento Sanitário* [Annual Plan for the Maintenance of Sanitary Sewage]. SANEPAR-Maringá, Maringá (1997), pp.1-16.
51. S.E. Manahan, *Environmental Chemistry*, 6. ed., Lewis Publishers, Chelsea, USA (1994), pp. 1-612.

52. E. Lenzi, D. Galli, S. A. R. Melo and E. V. Silva, *Acta Scientiarum*, *23*(6), 1325-1334 (2001).
53. V. C. Almeida, E. Lenzi, L. O. B. Favero, E. B. Luchese, Avaliação de metais pesados no lodo da Estação de Tratamento de Esgoto (ETE-2) de Maringá, Paraná. [Evaluation of heavy metals in sludge from STS of Maringá, Paraná]. *In*: *Anais do I Seminário sobre Gerenciamento de Biossólidos do Mercosul*. Curitiba (PR), pp. 175-182, (1998).
54. V. C. Almeida, E. Lenzi, L. O. B. Fávero and E. B. Luchese, *Acta Scientiarum*, *20*(04), 419-425 (1998b).
55. J.B. Costa, *Caracterização e Constituição do Solo* [Characterization and Constitution of Soils], 3. ed., Fundação Calouste Gulbenkian, Lisboa (1973), pp. 1-527.
56. M.B. McBride, *Environmental Chemistry of Soils*, Oxford University Press, Oxford (1994), pp. 1-406.
57. C. V. Andreoli, B. R. P. Bonnet, A. I. Lara, and F. R. Wolter, *Sanare*, 7(07), 76-84, 1997.
58. E.L. Straus, Normas da utilização de lodos de esgoto na agricultura [Norms for the use of sewage sludge in agriculture]. In: W. Bettiol, and O.A. Camargo, Ed., *Impacto Ambiental do Uso Agrícola do Lodo de Esgoto* [Environmental Impacto in the Agricultural Use of Sewage Sludge], Embrapa Meio Ambiente, Jaguariúna, SP (2000), pp. 1-312.
59. F. Fernandes, A.I. Lara, C.V. Andreoli, and E.S. Pegorini, Normatização para reciclagem agrícola do lodo de esgoto [Norms for the agricultural recycling of sewage sludge]. *In*: C.V. Andreoli, A.I. Lara, and F. Fernandes, *Reciclagem de Biossólidos: Transformando Problemas em Soluções* [Recycling Biosolids – Transforming Problems into Solutions], SANEPAR – Companhia de Saneamento do Paraná, Curitiba (1999), pp. 1-300.