**EXTRACTION OF HEAVY METALS IN A SEWAGE SLUDGE-TREATED
LATOSOL**

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ABSTRACT: *The presence of heavy metals is one of the main hazards against the use of sewage sludge in agronomy. In a field experiment applications of sewage sludge in medium textured Dark Red Latisol (DRL) were evaluated by the extraction of essential or non-essential metals with a DTPA extractor. Experimental design consisted of randomized blocks subdivided in sections of 6 treatments of sewage sludge (0, 6, 20, 40, 60 and 80 t ha⁻¹) during the first year and (0, 6, 20, 40, 60 and 80 t ha⁻¹) during the second year. The experiment had 4 replications and 5 soil collection periods (0, 30, 60, 90 and 120 days of sludge incorporation). Sewage sludge was applied at a mean depth of 0–20 cm. Soil sampling was undertaken during the periods of sludge incorporation so that the elements available in the soil in different doses could be evaluated. Soil samples were analyzed as to fertility level. Concentrations of the metals Cu, Zn, Cd, Ni, Co, Pb and Cr were determined by atomic absorption in DTPA extractor solution. Concentrations of Cd, Ni, Co, Pb and Cr were not detected since values were lower than the detection limit of each. Application of sewage sludge increased Cation Exchange Capacity (CEC) and there was an initial pH variation, albeit the latter returned concentration to its original level. Owing to the repetition of applied sludge, Cu and Zn rates in soil samples gradually increased during the two agricultural years caused by an increase in the doses of applied sewage sludge.*

Key words: heavy metals; biosolid; DTPA; availability of nutrients.

RESUMO: *Um dos principais motivos da insegurança na utilização agrônômica do lodo de esgoto é a presença de metais pesados. Desta forma, em experimento em campo, foram avaliados os efeitos de aplicações deste lodo num Latossolo Vermelho distrófico (LVd) de textura média mediante a extração de metais (essenciais e não) pelo extrator DTPA. O delineamento experimental foi o de blocos casualizados, em parcelas subdivididas no tempo constituídas por seis tratamentos de lodo de esgoto (0, 6, 20, 40, 60 e 80 t ha⁻¹) no 1^o ano agrícola e (0, 20, 40, 60 e 80 t ha⁻¹) no 2^o. O experimento teve 4 repetições e cinco épocas de coleta de solo (0, 30, 60, 90 e 120 dias da incorporação do lodo). O lodo de esgoto foi aplicado numa profundidade média de 0 - 20 cm. Nos períodos (dias) previstos foi feita a amostragem de solo para fins de avaliação dos elementos disponíveis. As amostras de terra foram analisadas com relação ao nível de fertilidade. As concentrações dos elementos Cu, Zn, Cd, Ni, Co, Pb e Cr foram determinadas pelo método da absorção atômica na solução obtida com o extrator DTPA. As concentrações dos metais Cd, Ni, Co, Pb e Cr não foram detectadas por se encontrarem abaixo do respectivo limite de detecção do método. A aplicação de lodo de*

esgoto causou aumento na CTC, e uma variação inicial do pH que após manteve-se próximo ao inicial. Foi possível concluir que, com a repetição da aplicação lodo, os teores de Cu e Zn nas amostras de solos aumentaram gradativamente nos dois anos agrícolas, com o aumento das doses do lodo aplicado.

INTRODUCTION

Society is increasingly aware of preserving and protecting the environment, especially the water body, the basis of life on the planet. Although sewage treatment should come prior to its disposal, this rule is rarely accomplished¹.

Sewage treatment produces sewage sludge made up of organic matter and mineral components including heavy metals. Disposal of sludge is a matter of great importance due to the possibility of the presence of heavy metals and pathogens that may pollute the environment if not properly treated. The agricultural recycling of sewage sludge is currently one of the best alternatives for its disposal when the necessary requirements related to concentrations of pollutants and pathogens are attended to. Since high fluctuations in the composition of these concentrations exist and there are several difficulties to foresee the behavior of some metals in certain types and qualities of soil, some criteria should be adopted with regard to these restricting factors, including the application of high doses of residues².

Organic matter added to the soil improves its physical, chemical and biological qualities. In proper conditions (for example, in aerobic conditions) it undergoes mineralization and releases mineral components in their highest oxidation states, such as, CO_2 , H_2O , NO_3^- , SO_4^{2-} , PO_4^{3-} and metals coupled to them. Organic matter disappears after a certain period of time and more is needed to improve soil conditions. There is, however, great concern with regard to the environmental safety needed for the feasibility of the practice when successive applications of sewage sludge are made. Depending on their rates, heavy metals accumulated by applications and soil conditions may be available to plants at phytotoxic levels. They will negatively affect the plant development, possibly transfer them to the food chain, with damaging results to the consumer's health³ and contaminate surface and sub-surface water through erosion and percolation.

As a rule, home-originated biosolids have less metal concentration than those from industrial discharges. Actually, the origin and the treatment process affect the characteristics of these discharges.

The behavior of heavy metals in the soil after the end of the application of biosolids is unknown. Heavy metals may be adsorbed in the soil through specific or non-specific adsorption reactions. Iron oxides and organic matter are among the components that most retain heavy metals. pH, CEC and cations affect adsorption and the type of ions of heavy metals in the soil. Metals may be found as free ions in solutions or they may constitute compounds with organic and inorganic links. The free types are more important in environmental pollutant studies since they are immediately bioavailable^{4,5}.

Heavy metal contamination in soil treated with town residues is frequently assessed by their total concentration in the soil. Total metal content in the soil is not a

good criterion to foresee phytoavailability⁶. Nevertheless, total concentrations aim at furnishing data on the accumulation of these elements through a certain period of time.

Laws that monitor levels of heavy metals in biosolids and maximum concentration in soils fail to give clear indications. However, phytoavailable concentrations should be known when effects on plants and on food chain are involved⁶.

Most methods that determine the availability of metals in the soil are based on the extraction of the specific element by a solution that imitates the plant's course of action. Quelant agent DTPA-TEA has also been used in certain studies of the extraction of heavy metals, others besides Cu, Mn and Zn, according to original suggestion by Lindsay & Norwell (1974)⁷, in several types of biosolid-treated soils^{8,9,10}. There are certain difficulties to define an extractor that would simultaneously process several heavy metals and be efficient enough to diagnose their availability in different vegetation species cultivated in several types of soils. In the case of sludge interruption doubts still exist with regard to the availability of these elements when the residue's organic change degenerates and the soil's acidity increases. The need for more research is urgently felt, especially when conditions peculiar to Brazil are taken into consideration.

Keeping in mind the verification of parameters for the application of sewage sludge in soils, the present research aims evaluating results of successive applications of sewage sludge on pH and CEC variations and the availability of these heavy metals in the soil.

MATERIALS AND METHODS

General characteristics of site, soil and sludge

The experiment was undertaken on the Experimental Farm of the State University of Maringá, in the Iguatemi district, municipality of Maringá PR Brazil, 23° 25'00" S and 51° 25'00" W, 555 m above sea level, with slightly hilly relief, during the agricultural years 2000-2001 (agricultural first year) and 2001-2002 (second year). Soil belongs to the dystrophic Dark Red Latisol group with average clayey texture. Rates of fine and thick sand, silt and clay were 570, 280, 20 and 130 g kg⁻¹, respectively.

Sewage sludge was obtained from the Sewage Treatment Station, STS-01, of the Paraná Water Works (SANEPAR), in Maringá. Sewage sludge, matured and stocked in the open air, naturally humid and limeless, was solid at the time of collection. A sample to determine its humidity and chemical characteristics was taken. Three aliquots of the sample were removed to determine their humidity. They were dried in a buffer at 65 °C till the formation of a constant mass. Humidity was determined by difference of mass¹¹. Thus the amounts of humid sewage sludge necessary for distribution in each experimental unit were calculated and doses for the different treatments to be applied in soil were obtained.

Aliquots of 10 g of recently collected *in natura* sewage sludge were obtained to determine their pH, according to technique developed by Andreoli & Bonnet¹¹.

For the chemical characterization of sewage sludge, the dried aliquots were mixed, ground, homogenized, sieved and the resulting sample treated to a constant mass. For the determination of nutrient and non-nutrient metals, 0.5000 g of aliquots

from sample were then decomposed, by a wet method, with a nitro-perchloride mixture, in a digester block. Metal concentrations were determined by the atomic absorption flame-type method¹². Kjeldahl method was used for nitrogen (N) determination and the gravimetric method of thermal decomposition was used to determine organic matter (OM)¹³. Whereas Table 1 shows results, Table 2 gives results for heavy metals used in the current analysis.

Table 1. Mean rates of chemical parameters of sewage sludge used in experiment, associated to soil fertility (†).

Sewage sludge	N	C	OM	C:N	Mn	Cu	Zn	Fe	pH(‡)
	$\leftarrow \text{g kg}^{-1} \rightarrow$				$\leftarrow \text{mg kg}^{-1} \rightarrow$				
1st application	37.0	264.0	405.0	7:1	274.1	480.0	1320.0	42800.0	4.68
2nd application	32.2	235.8	406.5	8:1	298.0	450.00	1540.0	48600.0	4.72

(†) – Analyses were undertaken in the Agro-Chemical and Environment Lab of UEM. (‡) – pH rates were measured in the original material and the others in dry material at 65°C. OM – Organic Matter.

System of Experiment

Field experiment was designed in randomized blocks with four repetitions each. Sewage sludge doses consisted of 0, 6, 20, 40, 60 and 80 t ha⁻¹. Sampling periods were 0 (blank), 30, 60, 90 and 120 days of sludge incorporation to soil, respectively. Each block consisted of 6 experimental units. Experimental unit referring to each sludge dose was made up of five 23 m-long rows (with maize plants), space 1.0 m and 0.20 m between plants, with total area 5 m x 23 m = 115 m². Real unit area was 3 m x 20 m = 60 m².

Sewage sludge was applied on the surface of the area; spreading was made with spades and hoes; incorporation occurred by harrowing at approximately 0–20 cm depth, equally in both applications.

Table 2. Concentration of heavy metals without any essential trait for plants in the sewage sludge used in soil treatments (†).

Sewage sludge	Cd	Ni	Cr	Co	Pb
	$\leftarrow (\mu\text{g g}^{-1}) \rightarrow$				
1st application	2.8	88.0	72.5	72.5	492.0
2nd application	2.1	142.0	125.0	125.0	380.0

(†) – Analyses were undertaken at the Agro-Chemical and Environment Lab of UEM.

Collection, preparation and analysis of soil samples

Collection of soil samples of each experimental unit, corresponding to 5 treatments and control, of each randomized block, at 0–20 cm deep, was undertaken at 0, 30, 60, 90 and 120 days of sewage sludge incorporation, for each agricultural year. A

sample composed of 4 simple samples resulted from each experimental unit. Collected compound samples were identified, air dried, sieved in 2 mm-mesh polypropylene sieves, homogenized and stored as ADFE (Air-Dried Fine Earth).

Analysis for Soil Characterization

ADFE samples were routinely analyzed to determine traditional parameters: pH, potential acidity, concentrations of C, N, P, K, Ca, Mg and S, according to IAPAR techniques¹⁴. Table 3 shows results for treatment-less soil samples for 0 days of incorporation.

Table 3. Chemical characterization of soil used in experiment.

Soil (0-20 cm)	pH CaCl ₂	P	S	N	C	Ca	Mg	K	H ⁺ +Al ³⁺	CEC	SB	C:N	V%
		←mg dm ⁻³ →		←g kg ⁻¹ →		←cmol _c kg ⁻¹ →							
DDRL	5.0	1.8	6.6	0.6	7.6	3.58	0.88	0.08	3.42	7.96	4.54	12:1	57.0

DDRL – Dystrophic Dark Red Latisol; [H⁺ + Al³⁺] – potential acidity; CEC – Cation Exchange Capacity. Results are mean of analyses with two repetitions.

Analysis of total metal rates in soil

Total rates of metals in soil were determined by interpreting respective concentrations and by atomic absorption technique in the solution from the decomposition of samples obtained by wet method, using a mixture of HNO₃ and HClO₄¹³.

Analysis of metal rates available in soil

Soluble rates of metals, or rather, the rates available for plants in the soil solution, were determined by the respective metal concentrations of the atomic absorption technique in the solution obtained from the extraction of 20.0000 g of ADFE with 40 mL of the extracting mixture formed by DTPA (Diethylenetriaminepentaacetic acid) 0.005 mol L⁻¹ + TEA (triethanolamine) 0.1 mol L⁻¹ + CaCl₂ 0.01 mol L⁻¹, corrected at pH 7.3¹⁵. Table 4 shows mean rates of three analytic repetitions for the elements under analysis.

Statistic analysis

The conventional method was used to analyze parts subdivided by periods. The surface response methodology was adopted for regression analysis as from the quadratic polynomial model with two independent variables, according to equation [02]¹⁶.

$$Y_i = B_0 + B_1N_i + B_2T_i + B_3N_i^2 + B_4N_iT_i^2 + B_5N_iT_i + E_i \quad [2]$$

where Y_i = variable responses; N_i = biosolid levels; T_i = time levels; E_i = randomized error; B_i with i = 0,1,2,...,5 = parameters to be assessed.

From the complete model above, the equation that best adjusted itself to data was based on the coefficient of determination (CD), represented by r^2 , and on the regression coefficient by Student's t test (up to 10% probability) and by the analysis of residues. Since only three evaluations were done during the second agricultural year, the result was equation [03]

$$Y_i = B_0 + B_1N_i + B_2T_i + B_3N_i^2 + B_4N_iT_i^2 + E_i \quad [03]$$

RESULTS AND DISCUSSION

Cation Exchange Capacity (CEC) and pH

Regression analysis showed that the applied sewage sludge dose is significantly related to the soil's CEC (Figure 1 (a) $r^2 = 0.9283$; (b) $r^2 = 0.8822$; (c) $r^2 = 0.9651$). Variance analysis indicated that during the two agricultural years significant results occurred only in sewage sludge doses. There was an increase in CEC as a result of residue doses during these years (Figure 1). The variable CEC increased linearly in the first agricultural year (2000-2001), Harvest 1 and 2, and during the second year (2001-2002), Harvest 3. However, during the second year (2002), Harvest 4 failed to show any significant treatment results: mean was $7.16 \text{ cmol}_c \text{ dm}^{-3}$.

Figure 1. Cation Exchange Capacity (CEC) of soil during agricultural years 2000-2001 and 2001-2002, Harvests 1 (a), 2 (b), 3 (c) and 4 (d), as a result of increasing dose of sewage sludge.

CEC increase, as a result of residue doses, showed a linear behavior within the samples (Figure 1). There was a rising linear trend in the variable under analysis: 0.0272

$\text{cmol}_c \text{ dm}^{-3}$ were added to the soil for each dose of 80 t ha^{-1} of applied residue. Research showed CEC increase when sewage sludge was applied^{17, 18}. In fact, the above authors have reported increasing CEC when sewage sludge was applied in doses ranging between 0 and 240 t ha^{-1} (dry base).

Increase of soil's CEC, resulting from a rise in sludge dose, is normal. Organic matter has active sites with a capacity for linking and exchanging ions according to pH. Carboxylic, phenolic, carbonylic, alcoholic, amminic groups are among the active sites directly proportional to the amount of organic matter that has been stabilized by mineralization.

Figure 2 shows the behavior of pH as a result of increasing doses of sewage sludge applied to soil. There was a pH increase up to 6 t ha^{-1} ; pH stabilized for other doses in Harvest 1. During the same year, in Harvest 2 there was a decrease in pH when residue doses increased. There was a decreasing trend in the effect of residue on the soil's pH, which stabilized during harvest and maintained itself close to the initial value.

Mineralization of sewage sludge in an aerobic environment oxidizes C, N, and S to the higher oxidation state. Carbonic acid, H_2CO_3 , nitric acid, HNO_3 , and sulfuric acid, H_2SO_4 are formed. However, in a water solution, they dissociate and form protons which cause a decrease in pH. Logan et al. (1997)¹⁹ reported a decrease in pH rate for the smallest sewage doses 7.5 and 15 t ha^{-1} in soil from calcareous rocks during the first year of limeless sludge application. The authors accounted acidification to reactions of nitrification of the residue's ammoniacal nitrogen.

Oliveira (2000)²⁰ and Bertoni & Mattiazzi (1999)²¹ reported an increase in pH rates when increasing doses of biosolid were added. According to these author, pH increased due to alkalinity of material used. Discrepancy in results must be linked to the different characteristics of sewage sludge in different experiments.

During the second year (Harvests 3 and 4, Figure 2) no significant effect on pH occurred as a result of levels of applied sludge and culture period. Mean pH was 4.40 and 4.35 respectively.

Mean pH = 4.40

(c) Harvest 3

Mean pH = 4.35

(d) Harvest 4

Figure 2. Mean pH rates in soil during agricultural years 2000-2001 and 2001-2002, in Harvests 1(a), 2 (b), and mean pH in Harvests 3 (c) and 4 (d), as a result of increasing doses of sewage sludge.

Heavy metals (non-essential elements): Cd, Cr, Ni, Co and Pb

According to Table 2, atomic absorption method, flame-mode, revealed heavy metals Cd, Cr, Ni, Co and Pb in sewage sludge when total decomposition of sample occurred with nitric-perchloric mixture. However, when soil with doses 0, 6, 20, 40, 60, 80 t ha⁻¹ of sewage sludge (corresponding to the different treatments) was extracted by DTPA-TEA, these elements failed to be detected since their concentration was below the method's detection limit.

Oliveira (1995)⁹ and Bertoncini (1997)¹⁰ did not report removal of Cr by DTPA extracting solution. Anjos (1999)²² analyzed Dark Red Latisol and Red Latisol treated with different sludge doses, totaling 388 t ha⁻¹ (dry base), and found that Cd and Pb concentrations, assessed by extractor DTPA-TEA, were lower than the method's detection limit. In field work Oliveira (2000)²⁰ evaluated the phytoavailability of heavy metals in a Red Latisol treated with 33, 66 and 99 t ha⁻¹ of sewage sludge (dry base) during the first year, and with 37, 74 and 110 t ha⁻¹ (dry base) during the second year. The above mentioned researcher reported that Cd, Cr and Pb rates, evaluated by three extractors, including DTPA-TEA, were below the detection limit of the analytic method. Simonete (2001)²³ found that in a Red Agrisol treated with 0, 10, 20, 30, 40 and 50 t ha⁻¹ of sewage sludge (dry base), in a hot house, rates of Cd, Ni, Pb and Cr, extracted by DTPA-TEA, were below the method's detection limit for all treatments.

Evaluation of available rates of Cu and Zn in soil

Cu and Zn amounts removed from soil samples by extractor solution increased according to sewage sludge doses which were applied, or rather, Zn²⁺ > Cu²⁺. The above shows current rates in sewage sludge (1320.0; 480.0 and 1540.0; 450.0 mg kg⁻¹, respectively) and respective doses incorporated to soil (Table 4).

Table 4. Mean rates of Cu and Zn extracted by DTPA-TEA, obtained by analytic results of 5 samples composed of soil collected in 0, 30, 60, 90 and 120 days of biosolid incorporation, according to increasing doses of sewage sludge.

Agricultural Year	0	6(12)	Sewage sludge doses (t ha ⁻¹)*			80(160)	CDD (r ²)
			20(40)	40(80)	60(120)		
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Copper (mg kg ⁻¹)							
2000-IE	0.82	1.23	1.89	2.21	2.77	3.12	0.92
2001-RE	0.86	1.49	2.31	2.87	3.63	4.01	0.92
2001-IE	0.91	1.75	3.27	4.91	5.95	6.78	0.88
2002-RE	1.05	2.68	4.76	6.74	7.94	8.93	0.90
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Zinc (mg kg ⁻¹)							
2000-IE	0.74	1.13	3.78	5.62	7.12	8.19	0.95
2001-RE	0.83	1.82	4.58	6.50	8.36	9.56	0.96
2001-IE	0.81	2.55	6.41	8.97	11.04	13.74	0.92
2002-RE	0.86	3.57	8.45	11.35	14.95	17.35	0.94

* Doses between brackets are for 2001 and 2002; IE: Immediate Effect (1st - 3rd Harvest: conventional); RE: Residual Effect (2nd - 4th Harvest: winter harvest). CD - Coefficient of Determination, r².

This fact may be explained by the concentration of the metals in the residue. Mean rate increases of available elements were reported when compared to that of control. They varied from the lowest to the highest dose applied in the harvests, or rather, from 53 to 1007%; 119 to 1052%; 215 to 1596%; 315 to 1917%, respectively, for Zn (Table 4). The above was corroborated by Simonete (2001)²³ who applied sewage sludge in soil cultivated with maize, in a hothouse, and discovered higher rates for iron and zinc. Oliveira (2000)²⁰ applied sewage sludge to soil with sugarcane and found higher zinc rates when compared to other metals. The high amount of metal in the residue accounted for the increase. However, in this context, copper also contributed towards such increase and varied from 50 to 280%; 73 to 366%; 92 to 645%; 155 to 750%, respectively. The increase was due to high amount of the metal in the sewage sludge.

When amounts of these metals in the soil during the first agricultural year (Harvests 1 and 2) have been taken into account, mean extraction of Cu and Zn were respectively 24% and 20% in treatments with sewage sludge doses by DTPA. During the second agricultural year (Harvests 3 and 4) values were respectively 31% and 21% (Table 4). Cu and Zn rates removed from soil by extractor were, as a rule, significantly affected by doses and periods with an increase in these metals (Figures 3 and 4).

Several authors^{20, 22, 24} found results satisfactory for DTPA-TEA and Mehlich-3 for foreseeing availability of Cu and Zn in plants cultivated in soils with sewage sludge. Nevertheless, variations in extractors may exist according to plants under analysis²⁵.

Copper

Variance analysis showed that the availability of copper in the soil was significantly related to sewage sludge doses and sampling periods, although no interaction between these factors has been detected. (Figures 3 a, b). Besides the fact that rate increase due to residue doses and to sampling period had a linear behavior, in the second agricultural year (2001-2002), Harvests 3 and 4, the variables period and doses showed an increasing linear trend of the applied residue (Figures 3 c, d).

The main link of copper with organic matter lies in humic and fulvic acids, probably forming stable compounds with copper. In some soils copper is associated with insoluble organic material⁴ with only a slight mobility. The interaction of copper with humic acids decreases according to the increase of the amount of copper applied²⁵, it increases according to humification rates⁵ and to pH²⁶. However, not all organic copper in the soil is insoluble⁵. According to McLaren and Crawford (1973)²⁷ the copper in soil solution available to plants is replaced by modes weakly associated to organic matter. In field conditions, after 15 years of sludge application²⁸, it was demonstrated that part of the soluble copper returned in a complex organic mode. Copper availability was affected by the soil's pH and tended to decrease with the latter's rise. Redente and Richards (1997)²⁹ verified that liming decreases the availability of the element in copper-rich soils.

Zinc

Variance analysis revealed a rising linear trend in zinc between the period and sewage sludge doses applied to the soil for the agricultural year 2000-2001 (Figure 4 a, b).

Figure 3. Variation of mean rates of Cu (a) Harvest 1, (b) Harvest 2, (c) Harvest 3 and (d) Harvest 4, removed by DTPA pH 7.3 as a result of sewage sludge applications in the four harvests.

In the second year, 2001-2002, zinc showed a significant rising linear trend according to the period and sewage sludge doses applied to the soil (Figure 4 c, d).

In the second agricultural year availability of zinc was higher in the two harvests due to the cumulative effect of two sewage sludge applications to soil with a high concentration of the element in the residue and a decrease in pH. However, availability of the element decreases when a rise in pH occurs³⁰. Machado and Pavan (1987)³¹ evaluated zinc adsorption in the soils of the state of Paraná with different pH rates. They concluded that maximum capacity of soil's adsorption and the link energy between the

soil and zinc ion increased in proportion to pH rise. Further, adsorption was significantly correlated to pH and CEC.

Figure 4. Variation in mean rates of Zn (a) Harvest 1, (b) Harvest 2, (c) Harvest 3 and (d) Harvest 4, removed by DTPA pH 7.3, owing to sewage sludge applications in four harvests.

Cunha et al. (1994)³² concluded that, in soils of the state of São Paulo, pH and CEC of soil were the factors that best explained maximum adsorption of zinc adsorbed to the organic part, by means of an increase in CEC and especially the residual part. Addition of biosolid produced significant increase in Zn (in the three years evaluated). This fact has been detected by all extraction methods, including DTPA at pH 7.3²⁵.

CONCLUSION

Application of sewage sludge in soil produced simultaneously an increase of CEC in soil and a decrease in pH; later on the latter maintained itself close to start rate.

Heavy metals, non-essential to plants, showed concentrations lower than the detection limit of the analytic method.

Rates of metal in soil gradually increased, in proportion to the increase of doses of sewage sludge applied.

Results of sewage sludge application may be considered as metal sources.

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