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Speciation of Phosphate, Fe, Zn, Mn, Cu and their Availability in Soils Amended with Sewage Sludge

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ABSTRACT

Urban sludge was applied in both Ap and Bt horizons of a red soil and in Ap horizon of a calcareous soil; the corresponding pH values of these soils were 4.82, 7.34 and 8.38. The rates of sludge applied were 0, 1.8, 3.6, and 5.4 g of air dried sludge per 100 g of soil. The samples were maintained in a temperature of 28 °C for 9 weeks at 2/3 of water holding capacity. At the end of the incubation period an extraction procedure was applied, with 0,1N NaOH in order to extract P bound to Fe and to Al, and with HCl 1N in order to remove P bound to Ca. In addition, to approach the partition of Fe, Zn, Mn and Cu into the soil fractions, a sequential fractionation was applied, so metals were extracted with KNO₃ (exchangeable forms), NaOH 0.5N (organic forms), Na₂EDTA 0.05M (precipitated forms), and with 4.0 M (residual forms).

The liming effect of the used sludge was mostly effective on the pH of the acid horizon, and available-P (Olsen) increases with increasing rates of sludge. In acid Ap horizon a large amount of P was found in forms bound to Fe and Al minerals, but in the neutral Bt horizon and in the calcareous soil the important amounts of P were found bound to Ca for all soil treatments. Most Fe and Mn were included in the residual forms, as far as the samples with the high rate of sludge are concerned. Sludge applied caused significant reduction in Fe and Mn extracted by DTPA in Ap horizon of the red soil; no significant effects have been observed in Bt horizon, and the same was observed in the calcareous soil for Mn; on the contrary, sludge affected positively Fe extracted by DTPA in the calcareous soil. Appreciable portions of Cu were in organic forms and in the high rate of sludge, a large fraction of Zn was in Zn-EDTA. Sludge affected positively Zn and Cu extracted by DTPA in all tested soils.

key words: sewage sludge, phosphate partition, metal partition

INTRODUCTION

The use of wastes, induces both the additions of plant nutrient elements (especially P and metals), and the modification of soil conditions; therefore recycling waste materials through agricultural systems, it requires

an evaluation of the agronomic benefits and environmental consequences, in a largest possible soil sample; otherwise the bioavailability of phosphates (Sommelier et al., 1996) and of metals (Morel, 1997) in soil, depend on the composition of the waste used, and on soil properties.

The rate of replenishment of soil solution with PO_4^{3-} during plant growth, is more important than its concentration, then the available-P is due to different forms of phosphate. Phosphate may adsorb to iron and aluminium hydroxides, to clay minerals, to calcium carbonate, and may also form precipitates with calcium, iron and aluminium. Calcareous soils favour the formation of Ca-phosphates, and acid soils promote the formation of (Al, Fe, Mn)-phosphates; Fe and Al salts eliminates P availability (De Haan, 1981) and these metallic cations are present at sufficiently low pH; the calcareous soils retain also inorganic P forms, but organic P forms are more mobile (James et al., 1996). According also to Stevenson (1982), the formation of complexes between P and humates may decrease P fixation and precipitation in soils, but other authors support adverse effects (Vo Dinh Quang et al. 1996). As far as pH is concerned, studies have variously found no effect, an increase or a decrease in solution phase phosphate with decreasing pH, depending on the soil and pH range investigated (Stauntont and Leprince, 1996).

The elements Fe, Mn, Zn and Cu in soils are found in a number of chemical forms including exchangeable, adsorptive, organic bound, precipitated, and within minerals. The solubility and therefore bio-availability of heavy metals ions is variable because many factors affect their concentration in the soil solution; among these factors soil pH is more important but clay content, oxides, ion interaction, redox potential, and organic matter content are also of significance (Lorenz et al., 1994; Moraghan et Mascagni, 1991). The redox conditions have a strong influence on metal solubility, and at the same time the redox conditions are depending on the decomposition of the organic matter (Amreich et al., 1994); then the solution concentration of trace elements in soils, is controlled by the relative rates of adsorption, desorption, organic matter decomposition, dissolution and precipitation of solid phases (Ros Sheila, 1994).

With the present work, the act of sewage has been studied to the bioavailability of P, Fe, Mn, Zn and Cu into soil, in comparison with their partition into different fractions.

MATERIALS AND METHODS

In a red Mediterranean soil (Typic Rhodoxeralf, Table 1) selected from Almiros region of Magnesia, and in a calcareous soil (Typic Xerofluvent) selected from Pirgetos region (Greece), urban sludge (biological cleaning of Larissa) was applied in both Ap and Bt horizons of a red soil and in Ap horizon of a calcareous soil; the sewage sludge used is a result of secondary treatment (Table 2), and before its use was passed through a 2 mm sieve.

Table-1: Characteristics of soil.

Soil	Depth cm	Horizon	Texture	Org. Matter (%)	CaCO ₃ %	pH (H ₂ O) 1:5	C.E.C. cmol/kg	(S/T) *
Red	0-25	Ap	SCL	1,5	0	4,82	7	43
	25-50	Bt	C	0,8	0	7,34	20	sat
Calcareous	0-25	Ap	SiL	1,7	2,7	8,38	22,5	sat

SCL: Sandy Clay Loam, C: Clay, SiL: Silty Loam, T=C.E.C. S=Exchangeable bases

Table 2. Chemical composition of the sewage sludge used

Organic matter	%	19
pH (H₂O)	(1:5)	6.78
Total N	%	2.8
Total P	%	0.4
Total Na	%	0.1
CaCO₃	%	4.5
Total Fe	µg/g	21400
Total Zn	µg/g	1450
Total Mn	µg/g	370
Total Cu	µg/g	240

The pH values of the Ap and Bt horizons of the red soil were 4.82 and 7.34, and the corresponding value of the Ap horizon of the calcareous soil was 8.38.

The rates of sludge applied were 0, 1.8, 3.6, and 5.4 g of air dried sludge per 100 g soil. The treatments were prepared in triplicate and the samples were maintained in a temperature of 28^o for 9 weeks. All samples were saturated at 2/3 of water holding capacity, during the first 3 and the last 3 weeks, while they were

maintained dry for the rest of the time.

At the end of the incubation period, soil samples were analysed for pH, organic matter, inorganic-P, organic-P, P-Olsen, and for available forms of Fe, Zn, Mn and Cu, extractable by DTPA.

To point out the partition of P into soil fractions, especially of P bound to Fe, to Al, and to Ca, an extraction procedure was applied; it involved the sequential extraction with 0,1N NaOH, in order to extract P bound to Fe and to Al, with citrate - bicarbonate to remove P sorbed by carbonate during the preceding NaOH extraction, with citrate - dithionite - bicarbonate to remove P occluded within Fe oxides, and with HCl 1N to remove P bound to Ca. All these procedures are referred by Page et al., 1982.

In addition, to approach the partition of Fe, Zn, Mn and Cu into the soil fractions, metals were extracted with KNO₃ (exchangeable forms), NaOH 0.5N (organic forms), Na₂EDTA 0.05M (carbonate or generally precipitated forms), and HNO₃, 4.0 M (residual forms), according to the sequential extraction procedure, referred by Emmerich et al., 1982.

The same procedures were also performed on sludge.

RESULTS AND DISCUSSION

In soil samples of the Ap horizon treated with the higher rates of sludge (red soil), pH was raised from 4,82 in the control sample, to 6,90 (liming effect of sludge, Hue 1992); in the Bt horizon pH was also increased to a lower extent by the sludge applied; sludge however supplied Ca, which is the dominate cation of the sludge phosphates (O' Connor et al., 1986). In the calcareous soil there was n' t found out any significant effect of the sludge on the pH. As far as the organic matter content concerned, it was significantly increased by sludge application, for all treatments (Table 3).

Table 3. Effect of the sewage sludge on soil properties.

	Red Soil								Calcareous Soil			
	Ap horizon				Bt horizon				Ap horizon			
	E0	E1	E2	E3	E0	E1	E2	E3	E0	E1	E2	E3
pH(1:5)	4.82a*	5.49b	5.91b	6.90c	7.34cd	7.94e	7.92e	7.87de	8.38e	8.33e	8.19e	8.15e
OM %⁺	1.5bc	1.9cd	2.1de	2.5ef	0.8a	1.3ab	1.7bcd	1.9cd	1.7bcd	2de	2.5ef	2.7f

E0, E1, E2, E3: sludge rates, ⁺Organic Matter, * Values in the same line followed by different letters differ significantly at the probability level 0.05 according to the Tukey's multiple range test

Phosphorus

Our results showed that available P, inorganic P and organic P were positively and strongly affected by sludge application in all treated samples, and the same was observed for P fractions bound to Fe, Al and Ca in red soils, and also for P bound to Ca in calcareous soil (Table 4); inorganic P in soil samples is always more than 70% of the total-P (inorganic + organic), for all sludge rates (Fine and Mingelgrin, 1996); that percentage in the sludge was 74%. According to Frossard et al., 1994, a complex mixture of P species is present in sludge, comprising a mixture of octacalcium phosphates and apatites.

Table 4. P fractionation in sludge and sludge effect on P forms in soil ($\mu\text{g/g}$)

	Sludge	Red Soil								Calcareous Soil			
		Ap horizon				Bt horizon				Ap horizon			
		E0	E1	E2	E3	E0	E1	E2	E3	E0	E1	E2	E3
P-av	213	39*cd	54de	62e	69ef	7a	16ab	23abc	37bcd	22abc	57de	90f	168g
P-in	2562	278a	409b	514cd	591d e	200a	286a	449bc	543d	427bc	548d	670e	798f
P-or	936	158cd	85abc	130bcd	181c d	30a	49ab	48ab	106abcd	157cd	87abc	199d e	282e
Ps	477	166d	203ef	213f	192e	26a	52b	65bc	64bc	67c	68c	69c	70c
Pca	1084	41a	73ab	77bc	111c	42a	90bc	105bc	153d	194e	213ef	237fg	265g

E0, E1, E2, E3: sludge rates, P_{av}: P_{Olsen}, P_{in}: Inorganic-P, P_{or}: Organic-P, P_s: to Fe and to Al bound P, P_{ca}: to Ca bound P. * Values in the same line followed by different letters differ significantly at the probability level 0.05 according to the Tukey's multiple range test

The sequential fractionation showed that in the Ap horizon of the red soil (acid pH), most P was found in P forms bound to Fe and Al for all sludge rates; in Bt horizon of the red soil (neutral pH) and in the calcareous soil,

the higher rate of sludge induced mostly the increase of P forms bound to Ca (table 4).

The percentage of available P in comparison with total P(organic + inorganic), it was 6% for sludge, and ranged from 9% to 11% respectively for the control and for all sludge rates added in the Ap horizon of the red soil; it was 3% in the case of control for Bt horizon and 10% for the higher rate of sludge; they also ranged from 4% for the control, to 16% for the higher rate of sludge in the calcareous soil; then the sludge improved stronger the portion of P availability in the neutral and calcareous soil (O' Connor et al., 1986).

Metallic elements

The percentages of metals in DTPA forms in comparison with the amounts extractable by the sequential procedure (table 5), were in the order $Fe < (Mn, Zn) < Cu$ for the sludge; into soil samples with added sludge, these percentages, were in the order $Fe < (Mn, Cu) < Zn$ (Lena Q. Ma and Rao, 1997). The added sludge increased those percentages in the case of Zn and Cu for all soils, and in the case of Fe and Mn into the calcareous soil, but that decreased for Fe and Mn into acid and neutral soil; according to Morel (1997), the availability of metals in soil is first governed by the chemical state of the element in the contaminating material, but in the long time it is governed by physicochemical reactions and by biological activity.

As far as the partition of the metals into the different fractions obtained by the sequential extraction concerned, it has been found that most Fe (>85%) and Mn (>65%) are included in the residual forms extracted by HNO_3 , for the samples with the high rate of sludge; in the case of sludge, this percentage was 92% for Fe, and 62% for Mn respectively; in the controls this relative distribution of Fe among these forms was >83% and >34% for Mn; Mn-EDTA relative fractions are important; in the contrary relative Mn-NaOH (organic forms) for all samples, and Mn- KNO_3 (exchangeable forms) for calcareous soil, were unimportant (table 5).

Appreciable portions of Cu were extracted by NaOH; in the samples with the high rate of sludge, these percentages in comparison to the total extractable Cu were >29% and for the controls > 23%; the same percentage in the case of sludge was 25%. Then it is confirmed that Cu has a high affinity for organic matter (McLaren and Crawford, 1973); Cu- HNO_3 and Cu-EDTA fractions were also significant.

In the high rate of sludge, an important amount of Zn is extracted by EDTA, with a relative distribution >39%; for the controls these values were >23%, and for sludge 25%. Residual-Zn fraction was also important; the most labile forms (exchangeable Zn) are at more important portions in the acid horizon and according to Guadalix and Padro (1995) the Zn labile forms must be negatively affected by pH.

The study of the sludge by using the same sequential extraction, showed that Fe- HNO_3 fraction was the most appreciable among the Fe extractable

in this way; for the other metals those residual forms were also the more concentrated but in less important portions.

Sludge applied, caused significant reduction in Fe and Mn extracted by DTPA in Ap horizon of the red soil; no significant effects have been observed in Bt horizon as well as in the calcareous soil for Mn; on the contrary sludge affected positively Fe extracted by DTPA in the calcareous soil.

Sludge also affected positively Zn and Cu extracted by DTPA in all tested soils, (Table 5). These results agree also with those of van der Watt et al., 1994 who showed that the increase of soil pH, has the greatest negative effect on Mn bioavailability in comparison to Zn and Cu.

CONCLUSIONS

Available-P (Olsen) increases with increasing rates of sludge. In Ap horizon of the red soil, a large amount of P was found in forms bound to Fe and Al minerals, but in the neutral Bt horizon and in the calcareous soil the important amounts of P were found bound to Ca for all soil treatments. The sludge also improved stronger the portion (%) of P-availability in comparison to the total-P, into the neutral and the calcareous soil.

Sludge applied caused significant reduction in Fe and Mn extracted by DTPA in Ap horizon of the red soil; no significant effects have been observed in Bt horizon of the calcareous soil for Mn; on the contrary sludge affected positively Fe extracted by DTPA in the calcareous soil and Zn and Cu in all tested soils.

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(Table 5). Metal fractionation in sludge and sludge effect on Fe, Zn, Mn and Cu forms in soil ($\mu\text{g/g}$).

	Red Soil									Calcareous Soil			
	Sludge	Ap horizon				Bt horizon				Ap horizon			
		E0	E1	E2	E3	E0	E1	E2	E3	E0	E1	E2	E3
FeDTPA	20	10,7ef*	8,8cdef	7,6c	8,3cd	5,0ab	3,6a	4,1a	4,8ab	6,5a	8,6cde	11f	10cde
FeKNO ₃	13	11,9c	11,9c	10,4c	12,4c	13,5c	11,4c	11,4c	14,0c	0,5a	0,8a	4,4ab	5b
FeNaOH	350	13,8b	12,5b	15,0b	20,9c	6,3a	11,3b	4,2a	2,5a	3,8a	4,3a	4,7a	4,8a
FeEDTA	286	137,5ab	150abc	229,2de	262,5e	155,0abc	116,3a	153,8abc	131,3ab	124a	119a	194bcd	216cde
FeHNO ₃	7174	770a	935a	1467a	1650a	2237a	2970a	3080a	3410a	19549b	22462c	25542d	25564d
ZnDTPA	28	1,4a	7,2bc	10,1d	10,4d	0,9a	6,8b	9,2d	9,9d	1,1a	5,4b	9,3cd	14,7e
ZnKNO ₃	5.5	4,2e	4,4e	4,1de	2,8cd	2,6bc	2,6bc	2,6bc	2,6bc	1,6abc	1,4ab	1,1a	0,6a
ZnNaOH	294	1,7ab	4,4de	7,9f	11,9g	2,4bc	2,5bc	4,0cd	5,9e	0,5a	2,1ab	4,1cde	5,7de
ZnEDTA	524	4,8a	13,2cd	22,1de	32,6f	4,1a	12,4bc	19,4cde	26,7ef	2,4a	6,9ab	18cd	24,8de
ZnHNO ₃	611	9,2a	11,0a	14,7a	20,0abc	7,0a	11,8a	15,7a	18,2ab	51e	34cd	41de	33bcd
MnDTPA	5.7	299,2d	123,3c	98,3c	82,6c	41,7b	35,9b	43,5b	57,9b	6,1a	5,9a	6,7a	7,2a
MnKNO ₃	5.7	302,5f	115,6e	58,3d	24,5bc	16,6ab	23,7b	42,5cd	54,9d	1,3a	1,3a	1,3a	1,3a
MnNaOH	16	2,6bc	2,8c	2,6bc	3,1c	2,0b	2,0b	2,6bc	2,8c	0,4a	0,3a	0,4a	0,5a
MnEDTA	94.7	251,5cd	307bcd	265,8d	265,8d	115,8a	99,2a	122,1ab	105,4a	131abc	103a	110a	106a
MnHNO ₃	190	286,0a	469 abc	616cde	689e	524abcde	579cde	653de	671de	542bcde	433abcde	493bcde	325ab
CuDTPA	40	2,1a	2,7abc	3,1bcd	3,2bcde	2,6ab	3,3cdef	3,4def	4,3g	2,8bcd	3,2abcde	3,6ef	3,8fg
CuKNO ₃	9.8	2,9c	2,9c	2,9c	2,9c	2,9c	1,6a	1,6a	2,9c	1,9b	1,8ab	1,6a	3,4d
CuNaOH	55.5	12,9d	12,9d	15,4e	15,8e	15,4e	16,6e	18,7f	19,1f	8,5a	8,2ab	9,8bc	10,5c
CuEDTA	32	5,0a	7,5ab	8,7bc	10,8cde	11,6de	12,5ef	12,9ef	15,0f	6,9ab	6,8ab	8,4bc	9,4bcd
CuHNO ₃	132	6,9a	8,6ab	7,6a	8,4ab	10abc	11,7bcd	12,4cd	12,4cd	13,3d	12,7cd	13cd	12,3cd

E0, E1, E2, E3: rates of sludge, * Values in the same line followed by different letters differ significantly at the probability level 0.05 according to the Tukey's multiple range test.