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Forms of Heavy Metals in Sewage Sludge and Soil Amended with Sludge

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Abstract: A number of extractions were carried out on soils, in order to assess both the relative concentrations of metals available to plants and also the major forms in which these metals existed in soils. The objective of this study was to assess the quantity and forms of metals in different soils, sludge and soils amended with sludge. It seemed that initially each metal will respond differently after incorporation into the soil system. There was a greater fraction of soluble metals in the sludge amended soils than the controls. Micro-organisms might, by using organic and inorganic matter as source of carbon and energy, bring about oxidation and reduction sufficient to change the state of metals.

Key words: Heavy metals, soil, sewage sludge, chemical forms, extraction.

Introduction

In general, concentrations of heavy metals are consistently greater in the extracts obtained from sludges than those obtained from soils (Bradford *et al.*, 1975; Alloway, 1995). McLaren and Crawford (1973) developed an extraction procedure for separating copper in soils, into soluble, exchangeable, weakly adsorbed, organically bounds, occluded, and residual fractions. This type of fractionation procedure could also be useful for evaluating the forms of metals in sewage sludge. Chelating agents vary enormously in their ability to extractions, depending on the stability constant of the chelate and the cation (Martell and Calvin, 1952; Alloway and Jackson, 1991). Several workers, including Lindsay and Norvell (1969 a,b), have shown that the concentrations of some metals, including cadmium, extracted with 0.005 M DTPA, are correlated with the concentrations in several types of crop plants growing in the soil. Bloomfield and Pruden (1975) showed that the chelating agent EDTA is capable of extracting a greater proportion of total cadmium, lead, copper and zinc from waste water sludge than 2.5 % acetic acid. Page (1974) cited several studies concerning the water and acetic acid soluble metals in sludge. Berrow and Webber (1972) have studied the solubilities of nickel, copper and zinc in 42 sludges by extraction with 0.5 M acetic acid or using water leachates. Alloway *et al.* (1979) used partial extractants to determine the forms of heavy metals in polluted soils and sewage sludge. The objective of present study is to assess the quantity and forms of metals in different soils, sludge and soils amended with sludge.

Materials and Methods

The soils amended with sludge and the sewage sludge were collected and chemically prepared .

a) Soils amended with sludge
1 Bordeaux
2 Barningham
3 Elveden
4 Galley Hill
5 Trent Valley

b) Sewage sludge
Deephams digested sludge: The "total" concentrations of metal were determined using nitric acid and aqua regia ("total" based on concentrated nitric acid or aqua regia digestion). The major sites of metal sorption in the soils and sludge were assessed by extracting samples with a range of selective extractants and soil test reagents. Their modes of action are shown in Fig. 1. The extractions were carried out on replicates as described in Table 1.
The compounds in the chelating agents were as follows:

DTPA solution: DTPA acid- 0.005 M (diethylentriamine pentaacetic acid)
TEA buffer- 0.1 M (triethanolamine)
$CaCl_2$- 0.01 M
HCl to adjust pH to exactly 7.30

EDTA Solution: $(NH_4)_2$ EDTA- Ethylenediamine tetraacetic acid

Table 1: Methodological details using partial extractants

Extractant	Molarity	pH	Soil-Extract ratio	Shaking time (hr)	Reference
Deionized water		6.1	2:20	2	
Calcium chloride *	0.05	6.5	20:200	16	McLaren and Crawford, (1973)
Ammonium acetate	1.0	7.0	2:20	2	Andersson and Nilsson, (1974)
Acetic acid	0.5	2.4	5:50	16	Chumbley, (1971)
Hydrochloric acid	0.1	1.0	1:5	1	Sorensen *et al.* (1971)
Hydrochloric acid	1.0	0.5	10:25	1	Lagerwerff *et al.* (1973)
Potassium pyrophosphate*	0.1	9.5	2:200	8	McLaren and Crawford, (1973)
DTPA	0.005	7.3	10:20	2	Lindsay and Norvell, (1969a,b)
Diammonium EDTA	0.05	4.0	10:50	1	Chumbly, (1971)
Ammonium oxalate *	0.2	3.25	1:50		McLaren and Crawford, (1973)
Concentrated nitric acid or aqua regia			2:20	**	Warren and Delavault, (1960)

* Used sequentially ** Sample digested with hot concentrated acid

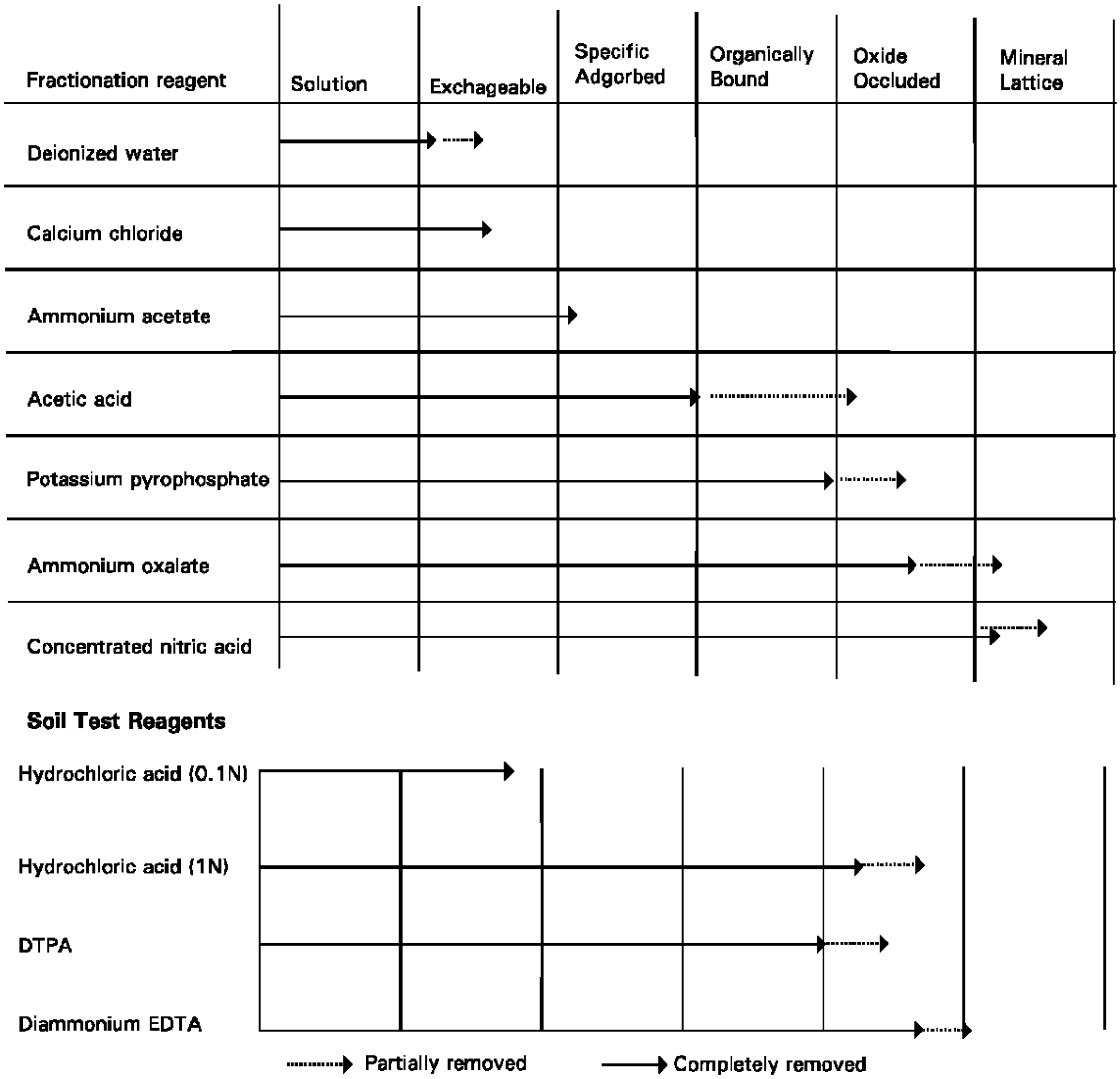

Fig. 1: Fractionation of metal by various extractants from different soil/ sludge sites (McLaren and Crawford, 1973)

Table 2: pH and organic matter contents of soils amended with sludge. (values represent the mean and range of the n replicates)

Soil group	pH ($CaCl_2$)	Organic matter (%)
Galley Hill	5.5	18.0
(n = 4)	(5.2-6.2)	(8.0-25.0)
Bordeaux	5.5	6.0
(n = 6)	(5.4-5.7)	(3.0-8.0)
Barningham	7.5	3.8
(n = 7)	(7.3-7.8)	(2.5-4.8)
Elveden	7.4	3.0
(n = 9)	(6.0-7.8)	(1.7-4.1)
Trent Valley	6.5	10.0
(n = 10)	(5.7-6.9)	(8.0-13.0)

diammonium salt 0.05 M, pH 4.0.

A sequential extraction procedure adapted from McLaren and Crawford (1973) was used for Deephams sludge and Galley Hill soils amended with sludge.

Preliminary individual (non- sequential) extraction studies were conducted to evaluate the capacity and selectivity of different reagents. However, the suitability of the reagents used as empirical extractants varied according to the element of interest and the soil or sludge type.

Results

Using partial extractants, the forms of cadmium, lead, nickel, zinc and copper were assessed in the sludge and soils amended with sludge. From Table 2, it can be seen that the sludge-amended soils have lower pH values and higher organic matter content than the untreated ones. The most marked feature of the data for extractions presented in Tables 3 to 10 is the markedly higher proportions of total cadmium, lead, zinc and copper which were removed by all the extractants from the Bordeaux soils. In some cases up to eight times more of the total nickel was extracted with DTPA compared with the next highest groups of samples, those from the Trent Valley (Tables 7 and 8). This was probably due both to differences in texture between the groups of samples, and also the concentrations of metals involved. The Bordeaux soils had a loamy sand texture and the highest concentrations of metals. This implied that, with the exception of organic matter (which was mainly of sludge origin) there was a relatively small potential sorptive capacity in these soils. With regard to the adsorption maxima implied by the sorption of metals according to Freundlich or langmuir equations, it is expected that in soils with high metal concentrations these metals will be less strongly adsorbed.

Levels of both extractable and total heavy metals in soils amended with different sludges typically showed large variations (Tables 3 to 9). The Barningham and Elveden soils, which had received light applications of low- metal sewage sludge, had a low organic matter content and relatively high pH values (Table 2). These high pH values would be expected to render the metals relatively immobile. Indeed, the total metal concentrations in these soils were relatively low and no phytotoxic effects would be expected. The total metal results showed that the highest concentrations occurred in the Galley Hill soil (Table 8) and the lowest in the Elveden soils amended with sludge.

The pattern of total metal concentration was: Galley Hill〉 Bordeaux〉 Trent Valley〉 Barningham〉 Elveden (except for Cd which was higher in the Bordeaux than Galley Hill). This indicated that the Bordeaux soils appeared to be noteworthy samples particularly with regard to cadmium. The greatest proportion of cadmium, lead, copper and zinc in the Trent Valley soils were extracted with a strong chelating agent EDTA, which seemed to be a superior reagent for a complete extraction of these metals in this soil (Tables 3 to 7). However, DTPA extracted a higher proportion of lead in Bordeaux soils and since DTPA extraction has frequently been found to correlate with amounts taken up by plants, this implied that a greater proportion of lead in Bordeaux soils may be available to plants. In Barningham and Elveden soils, DTPA was the only chelating agent used and removed 64.7% of cadmium in Barningham and 54.3 % in Elveden soils (Table 10). The proportions of cadmium extracted were higher than those for other metals but the actual concentrations involved were relatively low (0.33 μg g $^{-1}$ for Barningham and 0.25 μg g $^{-1}$ for Elveden) (Table 10).

The sequential fractionation of the Galley Hill soil (Table 9) showed that higher proportions of cadmium, nickel and lead were organically bound in the control soil (8 % L.O.I.) than amended soil (25 % L.O.I.). Indeed, in the latter soil, concentrations of cadmium, nickel and lead shown to be organically bound did not seem to be correlated with the amount of organic matter present. This illustrated the greater tendency of these metals to form stable organic complexes in this soil. However, exchangeable, specifically adsorbed and oxide occluded forms of these elements were proportionally greater in the amended soils.

A similar sequential fractionation was carried out on the metal-rich sewage sludge from the Deephams treatment plant (Table 10), which was where the sludge applied to the Galley Hill sites came from. Although it has been shown that the forms of metal in the sludge at any treatment plant can vary over time (Stover *et al.*, 1976), a fractionation of the type

Table 3: Extractability of cadmium in various soils amended with sludge* (percentage of total cadmium values represent the mean and range of the n replicates)

Techniques	Soils			
	Bordeaux (n = 6)	Trent Valley (n = 10)	Barningham (n = 7)	Elveden (n = 9)
Selective extractants				
water	8.5 (5.1-10.5)	5.6 (3.8-8.6)		
Ammonium acetate	25.6 (10.6-30.4)	21.0 (17.2-26.8)	19.6 (15.8-24.4)	15.2 (13.0-19.6)
Acetic acid	63.6 (30.8-70.2)	48.0 (30.2-57.9)		
Soils test reagents				
Hydrochloric acid (0.1 N)	58.1 (27.6-68.2)	47.0 (29.0-60.2)		
Hydrochloric acid (1 N)	78.5 (50.2-81.5)			
DTPA	62.0 (33.7-72.5)	53.3 (41.5-66.9)	64.7 (50.6-78.4)	54.3 (43.5-60.9)
EDTA	76.7 (64.1-80.2)	70.2 (54.5-78.9)		
"Total" concentration ** (μg g $^{-1}$)	137.5	4.13	0.51	0.46

* Non- sequential extractions ** "Total" based on concentrated nitric acid digestion

Table 4: Extractability of lead in various soils amended with sludge* (percentage of total lead values represent the mean and range of the n replicates)

Techniques	Soils			
	Bordeaux (n = 6)	Trent Valley (n = 10)	Barningham (n = 7)	Elveden (n = 9)
Selective extractants				
water	4.9 (3.8-5.4)	2.2 (1.0-2.6)		
Ammonium acetate	24.1 (18.5-30.7)	18.4 (11.1-22.2)	3.4 (2.4-5.4)q	2.9 (2.2-4.1)
Acetic acid	48.6 (42.0-55.2)	26.2 (20.5-29.1)		
Soil test reagents				
Hydrochloric acid (0.1N)	32.3 (22.8-42.3)	17.3 (12.1-24.4)		
Hydrochloric acid (1N)	78.1 (56.5-89.2)			
DTPA	77.1 (72.8-80.5)	31.9 (17.5-38.8)	26.8 (153-31.4)	26.7 (17.2-30.2)
EDTA	75.4 (71.3-78.6)	59.4 (43.9-63.4)		
"Total" concentration** (μg g $^{-1}$)	114	160	29.6	24.6

* Non- sequential extractions ** "Total" based on concentrated nitric acid digestion

Table 5: Extractability of zinc in various soils amended with sludge* (percentage of total zinc values represent the mean and range of the n replicates)

Techniques	Soils			
	Bordeaux (n = 6)	Trent Valley (n = 10)	Barningham (n = 7)	Elveden (n = 9)
Selective Extractants				
Water	10.4 (7.2-19.6)	2.9 (1.6-3.5)		
Ammonium acetate	30.0 (20.7-37.7)	12.3 (5.4-15.9)	1.2 (0.7-2.0)	1.6 (0.9-2.7)
Acetic acid	56.1 (39.8-60.9)	22.9 (16.0-26.5)		
Soil test reagents				
Hydrochloric acid (0.1N)	42.9 (36.9-54.6)	16.7 (12.3-23.0)		
DTPA	65.6 (58.9-70.2)	27.1 (18.2-31.7)	36.3 (21.4-44.8)	44.6 (30.7-53.4)
EDTA	75.7 (68.9-81.7)	33.7 (23.7-36.4)		
"Total" concentration** ($\mu g\ g^{-1}$)	279	195	44.5	35.7

* Non- sequential extractions ** "Total" based on concentrated nitric acid digestion

Table 6: Extractability of copper in various soils amended with sludge * (percentage of total copper values represent the mean and range of the n replicates)

Techniques	Soils			
	Bordeaux (n = 6)	Trent Valley (n = 10)	Barningham (n = 7)	Elveden (n = 9)
Selective extractants				
Water	5.0 (3.9-9.8)	1.2 (0.9-1.8)		
Ammonium acetate	25.4 (21.4-36.9)	2.8 (1.9-4.5)	2.9 (1.7-3.8)	3.3 (2.0-5.7)
Acetic acid	49.1 (38.2-52.0)	5.5 (3.7-6.6)		
Soils test reagents				
Hydrochloric acid (0.1 N)	37.2 (32.5-46.0)	6.5 (4.2-10.6)		
DTPA	63.1 (55.2-66.0)	45.5 (37.1-52.6)	28.0 (25.0-36.6)	25.7 (18.6-35.0)
EDTA	74.3 (63.0-80.2)	56.4 (39.2-68.3)		
"Total" concentration** ($\mu g\ g^{-1}$)	128	110	28.5	23.8

* Non- sequential extractions ** "Total" based on concentrated nitric acid digestion

Table 7: Extractability of nickel in various soils amended with sludge* (percentage of total nickel values represent the mean and range of the n replicates)

Techniques	Soils		
	Bordeaux (n = 6)	Barningham (n = 7)	Elveden (n = 9)
Selective extractants			
Ammonium acetate	2.5 (2.2-3.6)	3.0 (2.5-5.3)	
Soils test reagents			
Hydrochloric acid (1 N)	46.5 (39.3-50.5)		
DTPA	84.5 (40.0-94.5)	10.8 (4.5-11.6)	16.4 (13.3-32.0)
"Total" concentration** ($\mu g\ g^{-1}$)	254	20.2	17.3

* Non- sequential extractions ** "Total" based on concentrated nitric acid digestion

Table 8: Major forms of metals in various soils amended with sludge (percentage of total metal concentrations)

Soils	Techniques	Cd	Pb	Zn	Cu	Ni
Galley Hill	Exchangeable *	5.87	3.73	-	-	5.8
	Specific adsorbed **	14.2	0.97	-	-	15.7
	Water soluble	8.5	4.9	10.4	5.0	-
Bordeaux	Exchangeable	17.1	19.2	19.6	20.4	-
	Specific adsorbed	38.0	24.5	26.1	23.7	-
	Water soluble	5.6	2.2	2.9	1.2	-
Trent Valley	Exchangeable	15.4	16.2	9.4	1.6	-
	Specific adsorbed	27.0	7.8	10.6	2.7	-
Barningham	Exchangeable	19.6	3.4	1.2	2.9	2.5
Elveden	Exchangeable	15.2	2.9	1.6	3.3	3.0
Sewage sludge	Exchangeable	4.8	1.4	-	-	2.9
	Specific adsorbed	9.8	1.1	-	-	4.7

* Exchangeable = Ammonium acetate or Calcium chloride ** Specific adsorbed = Acetic acid – Ammonium acetate

Table 9: Major forms of metal in Galley Hill amended with sludge (% of total metal concentrations)

Forms	Cadmium		Nickel		Lead	
	control	amended	control	amended	control	amended
Exchangeable	2.5	5.87	3.3	5.8	2.9	3.73
Specific adsorbed	9.7	14.2	5.29	15.7	1.95	0.97
Organically bound	31.8	30.3	40.6	23.3	51.7	33.0
Oxide occluded	25.2	13.4	20.2	28.0	22.5	19.4
Mineral lattice	33.0	37.7	34.6	27.2	20.5	42.5
Sum	102.2	101.47	103.99	100.0	99.55	99.6
"Total" concentration * ($\mu g\ g^{-1}$)	1.3	132.0	39.5	686.0	97.3	440.0

* "Total" based on concentrated Aqua regia, 1 volume HNO_3 and 3 volume HCl digestion.

Table 10: Sequential extractability of heavy metals in Deephams sewage sludge. (values in $\mu g\ g^{-1}$ d. wt.)

Extractant	Cadmium	nickel	lead
Calcium chloride	2.5 (4.8) *	25.6 (2.9)	6.0 (1.4)
Acetic acid	5.1 (9.8)	40.6 (4.7)	4.7 (1.1)`
Potassium pyrophosphate	13.7(26.3)	228.0 (26.5)	103.8 (24.1)
Oxalic acid and ammonium oxalate	5.5 (10.6)	139.0 (16.2)	53.6 (12.5)
Aqua regia	27.5 (52.9)	421.0 (48.9)	257.0 (59.8)
Sum	54.3 (104.4)	854.2 (99.2)	425.1 (98.9)
"Total" concentration ** ($\mu g\ g^{-1}$)	52.0	860.0	430.0

* Numbers in parentheses expressed as percentage of "Total" concentration.
** "Total" based on concentrated Aqua regia, 1 volume HNO_3 and 3 volume HCl digestion.

described here provided an indication of the proportion of metals sorbed in various forms within the sludge. The higher proportion of metal associated with the exchangeable, specific adsorption sites in the amended soil, compared with the sludge, indicate that a certain degree of decomposition had occurred as a result of mixing with soil.

Discussion

Most of the routine soil test reagents in general use remove amounts of heavy metals which can be correlated with plant response (Nouri, 1980). As heavy metal toxicities became a matter of increasing concern, many of the existing extraction procedures for trace elements were used for heavy metals, including cadmium, nickel and lead. The selective extractants used in this project extracted metals from specific pools within the soil or soil/sludge system (Essington and Mattigod, 1991). This approach was particularly used for the sequential fractionation of cadmium, nickel and lead in sludge amended soils from Galley Hill and the Deephams digested sewage sludge. The proportion of the total metal concentrations present in a given fraction varied in various soils amended with sludge, due to different sources of metals applied in the sludges. The predominant forms of cadmium, lead and nickel are not the same in each sludge amended soil (Stover *et al.*, 1976), it may be expected that each metal will respond differently after incorporation into the soil system, at least initially. Even though the exact forms of metals in sludge are not apparent the results obtained for the adsorbed and exchangeable fractions may indicate which metals will be most readily available to plants growing in soils amended with sewage sludge. There was a greater fraction of water soluble metals in sludge amended soils than controls. This can be explained by the relatively high proportion of water soluble metals in sludge itself (the sludge used in this experiment had been stored in an air- dry state for some time and would have undergone some microbial decomposition). Relative to other soils, Bordeaux and Galley Hill soils may pose a greater hazard to groundwater and crop quality due to the high concentrations of extractable metals. This may be due to much lower pH of these soils (Brallier and Harrison, 1996). Total concentrations are often referred to as "total" in quotation marks because the concentrated acid digestion procedure used does not remove all the mineral bound metal, for this HF is required to destroy all silicates. Nevertheless, the concentrated acid- extractable proportion provides an adequate assessment of the total amount which is likely to be of potential biological importance. The Bordeaux samples also differed from other soils in having relatively large amount of exchangeable, specifically adsorbed, as well as organically bound for cadmium, lead, zinc and copper, and may be explained by the much lower organic matter content of this soil. In contrast to exchangeable metals, the mechanisms responsible for less readily available specifically adsorbed fraction appeared to exert a greater effect in some of the amended soils and the sludge itself. The proportions of total cadmium specifically adsorbed in the Bordeaux, Trent valley and Galley Hill samples were 38, 27 and 14 % respectively, whereas for Deephams sewage sludge this was only 9.8 %.
The Galley Hill amended soils, with low proportions of exchangeable cadmium, nickel and lead had the highest specifically adsorbed fractions of cadmium and nickel. The specifically adsorbed fraction of nickel was higher, but cadmium gave greater values than for any other metal in the other sludge amended soils used. The high cadmium concentrations in Bordeaux soils were largely due to the use of sewage sludges which received the effluent from an accumulator factory, the sludge contained about 2450 $\mu g\ g^{-1}$ cadmium (Juste and Solda, 1977). Ammonium EDTA and DTPA are frequently used in soil tests for several metals and the results show that in most cases EDTA removes more metals than DTPA. However, the metals extracted by latter have been found to correlate with plant uptake in some cases (Silviera and Sommers, 1977). Taking this into account, the Bordeaux soils are likely to give rise to the highest cadmium concentrations of 85 $\mu g\ g^{-1}$ in crops.
From the present results it can be seen that most of the metals in amended soils are organically bound even though some soil containing organically bound metal (Keefer and Singh, 1986), such as the Bordeaux, have relatively low organic matter contents. However, the opposite was found in the Galley Hill sludge amended soil. The proportion of nickel bound by organic matter was highest in Bordeaux soils (85 %) and this was much higher than for any of the other metals.
Silviera and Sommers (1977) used DTPA as a solvent to identify metals which showed increased solubility, or decreased their solubility over time. They also showed that it was possible for a metal to have an increased solubility in one sludge and a decreased solubility in another sludge over the same period. Hence it is evident that several forms of the same metal may exist in different sludges. The organically bound fractions (potassium pyrophosphate acetic acid) of nickel and lead, expressed as a percentage of the total metal was found to be larger in the Galley Hill control soil than the sludge amended soil. This was unexpected since it seemed likely that organic sorption would have been greatest in the sludge amended soils. The same trend was shown by EDTA extractions. This finding could possibly be explained by a higher proportion of the metals being present in the form of insoluble precipitates, such as phosphates and sulfides. It would be expected that, in time, these would have altered to more soluble forms within the soil system and then would probably be sorbed to a greater extent by the organic matter. The levels of precipitated cadmium, nickel and lead in some of the samples, particularly in Deephams sewage sludge and Galley Hill and Bordeaux sludge amended soils, were found to be relatively low. In considering the fate of precipitated metals, one must pay due regard to the fact that soil microbial activity may render soluble some of the solid forms of heavy metals (Pavoni, 1970). Microorganisms may, by using organic

and inorganic matter as sources of carbon and energy, bring about oxidation and reduction sufficient to change the state of metals.

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