

Effect of metal spiking on different chemical pools and chemically extractable fractions of heavy metals in sewage sludge

Geeta Kandpal^a, Bali Ram^a, P.C. Srivastava^{b,*}, S.K. Singh^b

^a Department of Chemistry, G.B. Pant University of Agriculture and Technology, Pantnagar 263 145, India

^b Department of Soil Science, G.B. Pant University of Agriculture and Technology, Pantnagar 263 145, India

Received 25 February 2003; received in revised form 28 October 2003; accepted 31 October 2003

Abstract

A laboratory experiment was conducted to study the effect of metal spiking and incubation on some properties and sequentially extractable chemical pools of some heavy metals (F₁, two extractions with 0.1 M Sr(NO₃)₂; F₂, one extraction with 1 M NaOAc (pH 5.0); F₃, three extractions with 5% NaOCl (pH 8.5) at 90–95 °C; F₄, three extractions with 0.2 M oxalic acid + 0.2 M ammonium oxalate + 0.1 M ascorbic acid (pH 3.0); and F₅, dissolution of sample residue in HF–HClO₄ (residual fraction,) and also 1 M CaCl₂ and 0.005 M DTPA extractable heavy metals in sewage sludge. Metal spiking and incubation decreased pH and easily oxidizable organic C content of sludge but increased electrical conductivity. Metal spiking and incubation increased F₁ fraction of all heavy metals, F₂ fraction of Ni, Pb, Cu, and Cd, F₃ fraction of Pb, Cu, and Cd, F₄ or reducible fraction of Ni, Cu, and Cd and residual fraction of Zn and Pb, but decreased F₂ fraction of Zn, F₃ of Zn and Ni, F₄ fraction of Zn and F₅ fraction of Ni, Cu, and Cd. Metal spiking and incubation increased 1 M CaCl₂ and 0.005 M DTPA extractable amounts of all heavy metals in sludge except for 0.005 M DTPA extractable Zn, which registered only very marginal decrease.

© 2003 Published by Elsevier B.V.

Keywords: Extractable heavy metals; Metal spiking; Sequential extractions; Sewage; Sludge

1. Introduction

Sewage sludge is a heterogeneous mixture of inorganic and organic components, which contains plant nutrients as well as elements not essential for plant growth. Some of the elements (Pb, Cd, Cr, Cu, and Ni) are potentially toxic to plants and animals and can find their way into human and animal food chain [1]. The principal metal forms in sludge are soluble, precipitated or co-precipitated with other metal oxides, adsorbed and complexed by biological residues [2]. The distribution of metals among the different chemicals pools varies widely according to the properties of the individual metal and the characteristics of the sludge, which are in turn governed by the specific sludge treatment process. The parameters such as pH, temperature, oxidation–reduction potential, the presence of complexing agents, and the concentration of precipitant ligands play important roles [3].

The spiking of sludge with heavy metals is a widely used technique for experimental purposes [4] to increase the rate of buildup of metals in soils treated with sludge without having to apply excessive amounts of sludge to the soil, or to distinguish the effects of the spiked metals from that of other metals and various other contaminants present in the sludge. Since, bioavailability of metals added to soil as metal salts may differ from the bioavailability of metals added through non-spiked sewage sludge [5], sludge spiked with additional quantity of metals is commonly incubated for a period of time, to allow the metals to react with and become incorporated into the sludge matrix [6,7].

Sequential extraction procedures have been developed predominantly to determine the amounts and proportions of metals present in soil or sediment sample [8], sewage sludge [9], enriched sludge [10], and sludge treated soils [11,12]. These procedures extract operationally defined “chemical pools” of metals that are presumed to be associated with particular solid phases.

The objective of this study was to investigate the changes in different chemical pools of these heavy metals in sewage sludge upon metal spiking and incubation.

* Corresponding author.

E-mail address: pcsriv@yahoo.com (P.C. Srivastava).

2. Experimental

2.1. Sludge

Bulk sample of sewage sludge was collected in plastic bags from Karula drain of Moradabad, UP, India, a city having brass plating and policing industrial units. The sample was processed to remove the non-recyclable materials and passed through a sieve having openings of diameter 2 mm.

One kilogram of sludge (on dry weight basis) was spiked with 100 ml of a solution containing 1000 mg Zn, Ni, and Pb, 500 mg Cd and 2000 mg Cu/l in the form of zinc sulfate, nickel chloride, lead acetate, cadmium chloride, and copper sulfate. Moist slurry was thoroughly stirred and incubated at 30% moisture content at 27–29 °C for 1 month. After incubation, the treated sludge was again thoroughly stirred. Triplicate samples of both unspiked and metal spiked sludge were drawn for chemical analysis.

2.2. Chemical analysis

Both metal spiked and unspiked samples of sludge were analyzed for pH, electrical conductivity in 1:2 sludge:water suspension and easily oxidizable (wet oxidation by chromic acid) organic C content [13].

Total contents of heavy metals in both unspiked and metal spiked samples of sludge were determined in HF–HClO₄ digest by atomic absorption spectrophotometry [14]. The total content of these metals in both unspiked and metal spiked samples of sludge are given in Table 1.

Sludge samples were subjected to sequential extraction in triplicate as per the scheme given by [15] to obtain the following five operationally defined chemical pools.

Two extractions with 0.1 M Sr(NO₃)₂ (soluble + exchangeable form, F₁), one extraction with 1 M NaOAc (pH 5.0) (specifically sorbed and carbonate bound form, F₂), three extractions with 5% NaOCl (pH 8.5) at 90–95 °C (organically bound or oxidizable fraction, F₃), three extractions with 0.2 M oxalic acid + 0.2 M ammonium oxalate + 0.1 M ascorbic acid (pH 3.0) extractable (reducible form, F₄) and dissolution of remaining amount of metals in sample through HF–HClO₄ digestion (residual fraction, F₅). All extracts separated through centrifugation from F₁ to F₃ were acidified to 0.16 M HNO₃. A drop of toluene was

added to F₄ fraction to prevent bacterial growth in extract. These sequential extraction procedures extract some operationally defined ‘chemical pools’ of heavy metals which could be presumed to be associated with particular solid phase.

The sludge and spiked sludge samples were also analyzed in triplicate for 0.005 M DTPA- [16] and 1 M CaCl₂-extractable heavy metals [17]. All the extracts were analyzed for heavy metals by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Properties of sludge

Metal spiking and incubation of sludge led to decrease the pH of sludge by about one unit and increased electrical conductivity more than two-fold (Table 1). Easily oxidizable content of organic C in metal-spiked sludge after 1-month incubation was also significantly lower than that of unspiked sludge. This indicated microbial oxidation of organic C present in sewage sludge during incubation. Metal-spiking markedly increased the total content of Ni, Cd, and Pb in the sludge but spiking had relatively little effect on total Cu and Zn which could be ascribed to the fact that the unspiked sludge had initially much higher concentration of Zn and Cu, and therefore, spiking brought in only little relative change in the total concentrations of these metals in sludge.

3.2. Chemical pools of heavy metals

Among various chemical pools, major portion of metals in unspiked sludge occurred in the residual fraction (F₅) followed by F₃, F₂, F₄, and least being observed in soil solution (exchangeable, F₁) fraction, which is considered to be an immediately bioavailable form (Table 2). However, in case of Cu and Pb, the second most dominant fraction next to F₅ fraction was F₂, possibly indicating the tendency of these metals to enter in carbonates in the sludge materials. A similar sequence was reported earlier also [18]. Higher content of the F₃ and F₅ fractions of heavy metals could explain the lower concentration of heavy metals in F₂ and F₁ fractions [19]. This might be ascribed to the presence of unoxidized organic matter and the higher pH value of unspiked sludge.

Table 1
Some properties and total content of heavy metals in unspiked and spiked samples of sludge

	Contents (mg kg ⁻¹)					Other properties		
	Ni	Zn	Pb	Cu	Cd	pH	EC	% OC
E. sludge	257.62**	2225.75**	407.62**	1517.37**	53.75**	5.22**	1.14**	4.80**
Sludge	168.00	2164.00	340.50	1434.50	16.00	6.29	0.44	5.46

** Significant at $P = 0.01$ for paired t -test.

Table 2

The contents of heavy metals in different chemical pools, DTPA And 1 M CaCl₂ extracts in sewage sludge (SS) and heavy metal spiked, incubated sewage sludge (HMSS) samples

	Contents (mg kg ⁻¹)									
	Ni		Zn		Pb		Cu		Cd	
	SS	HMSS	SS	HMSS	SS	HMSS	SS	HMSS	SS	HMSS
Water soluble + exchangeable (F ₁)	17.1**	114.5	49.8**	54.1	0.6**	2.6	4.3**	120	0.6**	35.4
Carbonate bound (F ₂)	25.9**	50.5	51.8**	46.5	67.6**	93.2	102.9**	534.3	1.4**	9.7
Organically bound (F ₃)	39.2**	21.5	125.6**	115.9	17.1**	32.4	83.0**	174.1	1.5**	4.1
Reducible (F ₄)	11.7**	16.3	181.0**	171.1	2.8NS	2.0	63.9**	396.4	0.2*	0.3
Residual (F ₅)	74.1**	54.8	1755.8**	1838.1	252.4**	276.9	1180.4**	292.6	12.3**	4.3
DTPA	36.4**	93.4	59.7**	57.3	2.2**	11.7	119.1**	416.3	2.0**	22.8
1 M CaCl ₂	32.6**	52.6	51.3**	53.5	2.9**	10.9	29.7**	197.2	1.9**	15.5

** , * and NS indicate significance at $P = 0.01$, 0.05 and non-significant difference between pairs, respectively.

3.3. Effect of metal spiking and incubation on chemical pools

Heavy metal spiking and incubation significantly increased the F₁ fraction of all metals in sludge, however, the effect was very small in case of Zn (Table 2). The F₂ fraction of Ni, Cd, Pb, and Cu in sludge also significantly increased but that of Zn was about the same with metal spiking and incubation probably because Zn spiking had little effect on total Zn.

The F₃ fraction of Pb, Cu, and Cd significantly increased in sludge with metal spiking and incubation, but that of Ni and Zn suffered a decrease. Metal fraction of Ni, Cu, and Cd in F₄ fraction, i.e. largely Fe–Al oxides bound fraction significantly increased while that of Zn significantly decreased with metal spiking and incubation. The F₅ (residual) fraction of Zn and Pb significantly increased with metal spiking and incubation while that of Ni, Cu, and Cd registered a significant decrease. Based upon the changes in different chemical pools of heavy metals in sludge due to metal spiking and incubation, it appeared that bio-oxidation of organic carbon and consequent acidification effected release of Ni, Cu, and Cd from F₅ (residual fraction), of Ni and Zn from F₃ fraction, of Zn from F₄ and F₂ fractions from sludge. The released and added metals were incorporated into F₅ (residual) fraction in case of Zn and Pb, into F₄ (reducible or Fe–Al oxide bound) fraction in case of Ni, Cu, and Cd, into F₄ fraction in case of Pb, Cu, and Cd, into F₂ fraction in case of Ni, Cd, Pb, and Cu and invariably increased the F₁ fraction (water soluble and exchangeable form) of all the tested heavy metals.

Heavy metal spiking and incubation significantly increased 1 M CaCl₂ extractable content (water soluble and exchangeable) of all heavy metals in sludge except Zn which registered only a minor increase. The 0.005 M DTPA (pH 7.3) extractable content of all heavy metals in sludge also significantly increased with metal spiking and incubation. This chelating agent is supposed to partly extract metals from most chemical pools [20] except the F₅ (residual) fraction.

The percent distribution of different chemical pools of heavy metals in sludge and metal-spiked incubated sludge is depicted in Fig. 1.

Spiking and incubation appeared to increase the proportions of Cd and Ni in F₁ and F₂ fractions at the expense of F₅ and F₄ fractions which might be due to oxidative breakdown of organic components during incubation as well as dissolution of Fe–Mn oxides. This result suggests that there might be higher mobility of Cd and Ni when added through enriched sludge to the soil.

A high proportion of Zn occurred in the F₅ (residual pool) and could be related to the preferential binding of Zn for high energy sites on clay minerals present in the sludge or conversion to insoluble solid phase like ZnS. In the case of Pb, a small increase in the percentage of F₂ and F₁ fractions might be due to a decreased residual Pb proportion in the spiked sludge.

Spiking and incubation also appeared to increase the Cu percentage in all the chemical pools (fractions) except F₅ (residual fraction). The greatest increase was observed for the F₄ fraction which might be due to the high affinity of Cu for Fe–Mn oxides [21,22]. The increase in F₃ fraction was observed for Cu and Pb in spiked sludge. This result is consistent with the known affinity of copper and lead for organic ligands [23].

The changes in per cent fractions of heavy metals extracted in 1 M CaCl₂ and 0.005 M DTPA (pH 7.3) upon metal spiking and incubation are depicted in Fig. 2. The increase in percentage of 1 M CaCl₂ extractable heavy metal upon metal-spiking and incubation was most pronounced for Cu followed by Cd and Pb, but least marked for Ni and Zn. The increase in percentage of 0.005 M DTPA extractable heavy metal upon metal-spiking and incubation was most pronounced for Cd followed by Cu, Pb, and Ni. The percentage of 0.005 M DTPA (pH 7.3) extractable Zn underwent a little decrease which could be anticipated in view of a small difference in Zn content spiked and unspiked sludge.

The observed difference in metal distribution among operationally defined chemical pools in unspiked and spiked sludge could well have implications on the mobility and/or

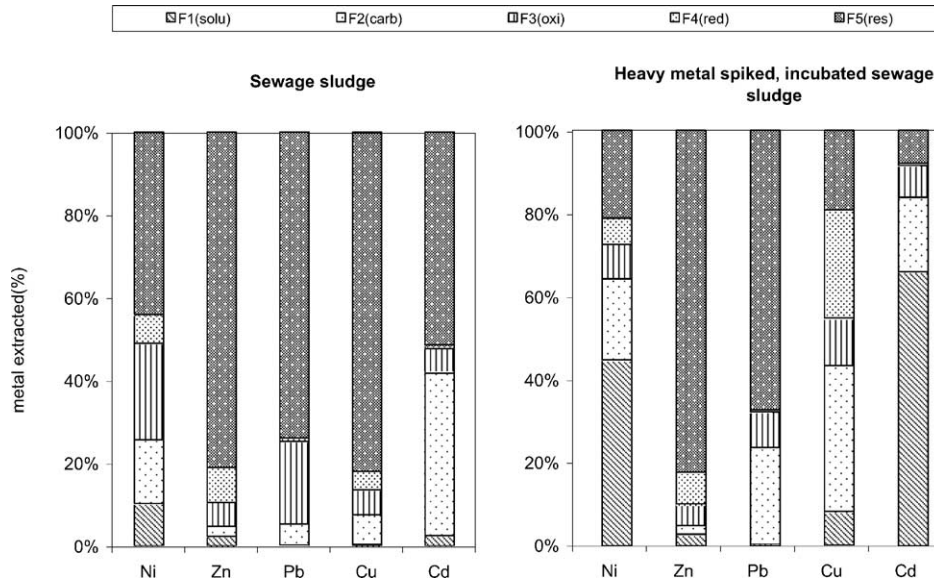


Fig. 1. Mean percentage of different chemical pools of heavy metals in sewage sludge and metal spiked, incubated sewage sludge samples (all pairs of respective pools between sewage sludge and metal spiked, incubated sewage sludge samples were significantly different as per paired *t*-test at $P = 0.05$ except for F_4 pool of Pb).

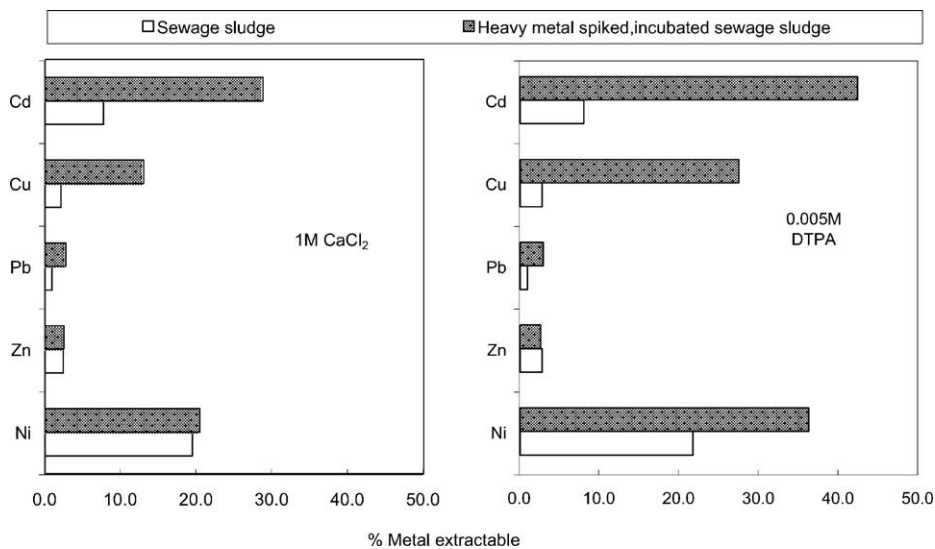


Fig. 2. Mean percentage of total metals extracted in 1M CaCl₂ and 0.005M DTPA from sewage sludge and heavy metal enriched, incubated sewage sludge samples (all pairs between sewage sludge and heavy metal spiked, incubated sewage sludge were significantly different as per paired *t*-test).

bioavailability of these metals when the sludges are applied to soil.

However, application of sludge to the soil is also likely to result in changes in the distribution of metals among chemical pools.

4. Conclusion

The results obtained from this study demonstrated that when sewage sludge is spiked with additional metals added

as simple salts and incubated, some physico-chemical properties like pH, EC, and also easily oxidizable organic C content change and substantial proportions of the metals become incorporated into the sludge matrix. In case of Zn, the fractional distribution of Zn between spiked and non-spiked sludge remains more or less similar principally due to the minor difference in their total Zn content but in the case of other heavy metals such as Ni, Cu, Pb, and Cd the intensities of different chemical pools are altered to influence the bioavailability of these metals in metal spiked and incubated sludge.

References

- [1] M.B. McBride, Toxic metal accumulation from agriculture use of sludge. Are USEPA regulations protective, *J. Environ. Qual.* 24 (1995) 5–18.
- [2] J.N. Lester, R.M. Sterritt, P.W.W. Kirk, Significance and behaviour of heavy metals in wastewater treatment processes. II. Sludge treatment and disposal, *Sci. Total Environ.* 30 (1983) 45–83.
- [3] M.S. Gould, E.J. Genetelli, Heavy metal complexation behaviour in anaerobically digested sludges, *Water Res.* 12 (1978a) 505–512.
- [4] J.J. Street, W.L. Lindsay, B.R. Sabey, Solubility and plant uptake of cadmium in soils amended with cadmium and sewage sludge, *J. Environ. Qual.* 6 (1977) 72–77.
- [5] P.F. Bell, B.R. James, R.L. Chaney, Heavy metal extractability in long term sewage sludge and metal amended soils, *J. Environ. Qual.* 2 (1991) 481–486.
- [6] R.D. Davis, C.H. Carlton-Smith, The preparation of sewage sludges of controlled metal content for experimental purposes, *Environ. Pollut.* 2 (1981) 167–177.
- [7] S. Coppola, S. Dumontet, M. Pontonio, G. Basile, P. Marino, Effect of cadmium bearing sewage sludge on crop plants and microorganisms in two different soils, *Agric. Ecosyst. Environ.* 20 (1988) 181–194.
- [8] L.M. Shuman, Fractionation methods for soil microelements, *Soil Sci.* 140 (1985) 11–12.
- [9] R.C. Stover, L.E. Sommers, D.J. Silveira, Evaluation of metals in wastewater sludge, *J. Water Pollut. Control Fed.* 48 (1976) 2165–2175.
- [10] R.G. McLaren, L.M. Clucas, Fractionation of copper, nickel and zinc in metal spiked sewage sludge, *J. Environ. Qual.* 30 (2001) 1968–1975.
- [11] D.L. Lake, P.W.W. Kirk, J.N. Lester, Fractionation, characterization and speciation of heavy metals in sewage and sludge amended soils. A review, *J. Environ. Qual.* 13 (2) (1984) 175–183.
- [12] S. Dudka, A. Chlopecka, Effect of solid-phase speciation on metal mobility and phytoavailability in sludge amended soil, *Water, Air Soil Pollut.* 51 (1990) 153–160.
- [13] M.L. Jackson, *Soil Chemical Analysis*, Prentice Hall, New Jersey, USA, 1958, pp. 38–226.
- [14] A.L. Page, R.H. Miller, D.R. Keeney, Chemical and microbiological properties, in: *Methods of Soil Analysis*, second ed., ASA, SSSA, Madison, WI, 1982, p. 1159.
- [15] Z.S. Ahnstrom, D.R. Parker, Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium, *Soil Sci. Soc. Am. J.* 63 (1999) 1650–1658.
- [16] W.L. Lindsay, W.A. Norvell, Development of a DTPA soil test for zinc, iron, manganese and copper, *Soil Sci. Soc. Am. J.* 42 (1978) 421–428.
- [17] S.D. Young, A. Tye, A. Carstensen, L. Resende, N. Crout, Methods for determining labile cadmium and zinc in soil, *Eur. J. Soil Sci.* 51 (2000) 129–136.
- [18] T. Chitdeswari, P. Savithri, S. Mahimairaja, Fractionation and characterization of sewage sludge, *J. Ecotoxicol. Environ. Monit.* 12 (2) (2002) 161–165.
- [19] G. Brummer, K.G. Jiller, U. Herms, P.N. Clayton, Adsorption–desorption and/or precipitation–dissolution processes of zinc in soils, *Geoderma* 31 (1983) 337–354.
- [20] W.F. Pickering, Metal ion speciation—soils and sediments. A review, *Ore Geol. Rev.* 1 (1986) 83–146.
- [21] D.G. Kinniburgh, M.L. Jackson, J.K. Syers, Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminum, *Soil Sci. Soc. Am. J.* 40 (1976) 796–799.
- [22] J.W. Murray, The interaction of metal ions at the manganese dioxide solution interface, *Geochim. Cosmochim. Acta* 39 (1975) 505–519.
- [23] R.W. Taylor, H. Xiu, A.A. Mehadi, J.W. Shuford, W. Tadesse, Fractionation of residual cadmium, copper, nickel, lead and zinc in previously sludge amended soil, *Commun. Soil Sci. Plant Anal.* 26 (13–14) (1995) 2193–2204.