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Contaminant Source as Factor of Soil Heavy Metal Toxicity and Bioavailabilty to Plants

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Abstract: Mine waste and sewage sludge treated soil were used as contaminants in a greenhouse pot experiment and the effect of the contaminants on ryegrass growth, soil metal levels and plant metal uptake was evaluated over a period of 16 weeks. Soils were amended with bone meal, compost, peat, coir or lime phosphate and amendments led to immobilization of Pb, Cu and Zn. Biomass yield was significantly reduced in contaminated soil, with greater reduction in mine waste contaminated soil. EDTA extractable soil metal and metal uptake by ryegrass was significantly higher in mine waste contaminated soil than in sewage sludge treated soil.

Key words: Heavy metal, source, mine waste, sewage sludge, bioavailability

INTRODUCTION

Soil physicochemical properties are adversely affected by high concentrations of heavy metals, rendering contaminated soils unsuitable for crop production (Hernandez-Allica *et al*., 2007; Udom *et al*., 2004). It has been documented that soils polluted by industrial effluents or wastes tend to exhibit a reduced porosity, have poor hydraulic conductivity and increased acidity (Hernandez-Allica *et al*., 2007). The source of metals in soil may be due to the parent material or may be anthropogenic. Metals can also be transported from the soil into the groundwater and crops growing on contaminated soil (Sharma a *et al*., 2008).

Two devastating sources of heavy metal contamination in modern times is from industrial activities linked to mining (ADB, 2001) from the long-term use of sewage sludge for agricultural purposes (Fuentes *et al*., 2006). Metals in the soil environment may exist as free metal ions and soluble metal complexes in the soil solution, occupy exchange sites, precipitated as insoluble compounds, be bound to inorganic or organic soil fractions, or occur as metals in the structure of silicate minerals (Basta *et al*., 2005; Roberts, 2003). The bioavailable fraction is composed of free ions and those bound on exchangeable sites, while those bound to organic matter can also be rendered available on decomposition (Yin *et al*., 2002). The mobility of trace metals, their bioavailability and related ecotoxicity to plants, depend strongly on their specific chemical forms or ways of binding (Basta *et al*., 2005) and also on the nature of soil or material which serves as carrier of the contaminant material (Voutsa *et al*., 1996).

Sewage sludge has been used successfully as a source of adding nutrients in the soil (Poykio *et al*., 2007), at the same time it increases organic matter content; raises soil pH and thus, render the metals less soluble/bioavailable. However, depending on their characteristics the long-term use of sludge can cause heavy metal accumulation in soils (Alvarenga *et al*., 2008; Fuentes *et al*., 2006). Remediation of contaminated soil is possible by amending such soils with agricultural materials, as soil metals are adsorbed onto the amendment materials, immobilising such metals and thus, reducing their soil and plant availability (Abbaspour *et al*., 2008; Nwachukwu and Pulford, 2008). The objective of the study was to evaluate the effect of contaminant source on soil and plant metal concentrations.

MATERIALS AND METHODS

Mine waste from Tyndrum and sewage sludge treated soil from Stoke Bardolph, both in Scotland, were used as contaminants in a greenhouse pot experiment in 2004. The effects of the contaminants on ryegrass growth and uptake of Pb, Cu and Zn was evaluated over a period of 16 weeks. Three sets of pot experiments were set up concurrently, using sharp sand as the major component of the growth medium. Mine waste and sewage sludge treated soil were manually added at the rates of 2.5 and 25%, respectively, while amendments bone meal, general purpose compost, peat, coir and lime phosphate were applied as 10% of soil weight. Each experiment was set up as a 5×2×4 CRD. Total metal analysis in contaminants and amendments was by aqua regia digestion, extractable soil metal was determined using EDTA, while leaf metal was

Table 1: Chemical properties of contaminants and amendments before crop growth (Nwachukwu, 2007; Nwachukwu and Pulford, 2008)

Material	pH	OM (%)	CEC cmol K kg^{-1}	Pb (ug g^{-1})	Cu (ug g^{-1})	Zn (ug g^{-1})
Bone meal	6.9	32	19	61	23	188
Compost	6.4	77	62	30	23	49
Peat	3.6	95	197	23	12	22
Coir	5.6	93	120	28	33	56
Phosphate	2.8	9	33	43	33	252
Mine waste	5.9	18	8	65593	2947	25083
Sewage	6.9	29	60	1024	895	2302

OM = Organic Matter; pH and metal values (n = 10); CEC and OM% (n=5)

determined by hot nitric acid digestion. Initial metal concentrations in contaminated soils were above normal levels as stated by Ross and Kaye (1994). All metals were read on the AAS.

Experiment I: Sand was amended with the 5 materials and left to incubate for 5 days, following which each pot was sown with approximately 1 g of ryegrass seed (*Lolium perenne*) and harvested twice, first after 8 weeks of growth and again after a further 8 weeks of growth.

Experiment II: Sand was first manually contaminated with mine waste or sewage, amended with bone meal, compost, peat, coir and lime phosphate and incubated for 16 weeks.

Experiment III: Sand was manually contaminated with mine waste or sewage, amended with bone meal, compost, peat, coir and lime phosphate and incubated for 5 days before planting with ryegrass.

Total Pb, Cu and Zn concentrations were much higher in mine waste than the sewage sludge, while metal concentrations in the amendments were negligible (Table 1).

All statistical analyses were carried out with the programme MINITAB version for windows, analysed using a general linear model of ANOVA. Where, F-test was significant, Tukey's test at ($p<0.05$) was used to determine LSD for the comparison of means.

RESULTS AND DISCUSSION

Buffering capacity of contaminants: The response of the different agricultural materials to pH changes was evaluated by subjecting them to increasing amounts of HCl or NaOH. Mine waste was readily subject to changes in pH at the slightest increase in amounts of acid or alkali added, but the sewage treated soil was resistant to pH changes in the presence of either acid or alkali (Fig. 1). This showed that the inorganic mine waste had a very low buffering capacity, while sewage treated soil (organic) on the other hand, had a high buffering capacity, typical of organic materials (Fig. 1).

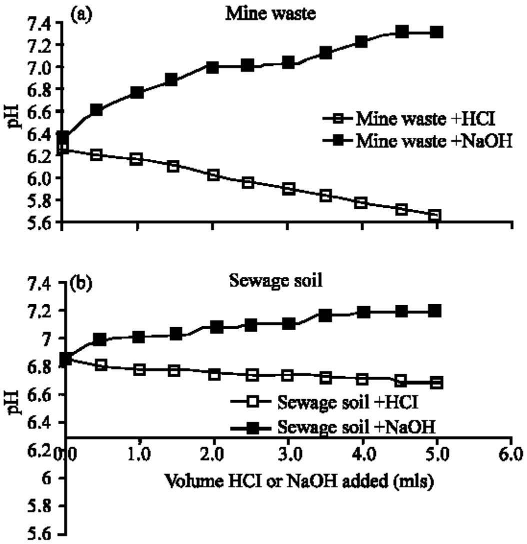

Fig. 1: Buffering capacity of mine waste and sewage soil contaminants ryegrass biomass in contaminated soil

Ryegrass biomass was significantly higher in the sewage sludge treated soil had better yield when compared to mine waste contaminated soil (Fig. 2), which may be explained by the fact that sewage would be nutrients to the soil. Metal induced leaf chlorosis was observed in plants growing in both contaminated soils, but significantly greater in mine waste contaminated soil (Fig. 2). Addition of amendments led to a significant increase in biomass yield in both the mine waste and sewage spiked soil when compared to that of the non amended soil.

Metal uptake of ryegrass from amendments and contaminants only (experiment I): In comparing, the relative effect of metal present in amendments (experiment I) and that in the contaminants to the total metal taken up into ryegrass leaves, it was observed that the contribution of metals from the amendments to overall metal uptake from contaminants was negligible (Fig. 3). The very tow concentrations of Pb, Cu and Zn in the amendments was however, available to the ryegrass plants, confirming that it is impossible to completely exclude metal uptake by plants, even when such plants are growing in non contaminated soil (Friesl *et al*., 2006).

Metal uptake by ryegrass in contaminated soil: After 8 weeks of plant growth, metal uptake in mine waste spiked soil was significantly higher than in the sewage contaminated one (Fig. 4), taking initial metal concentrations into consideration.

Fig. 2: Ryegrass in non-amended metal 'spiked' soil after 4 weeks of growth (G-0 = mine waste contaminated soil + no amendment added; SB-0 = sewage treated soil + no amendment added)

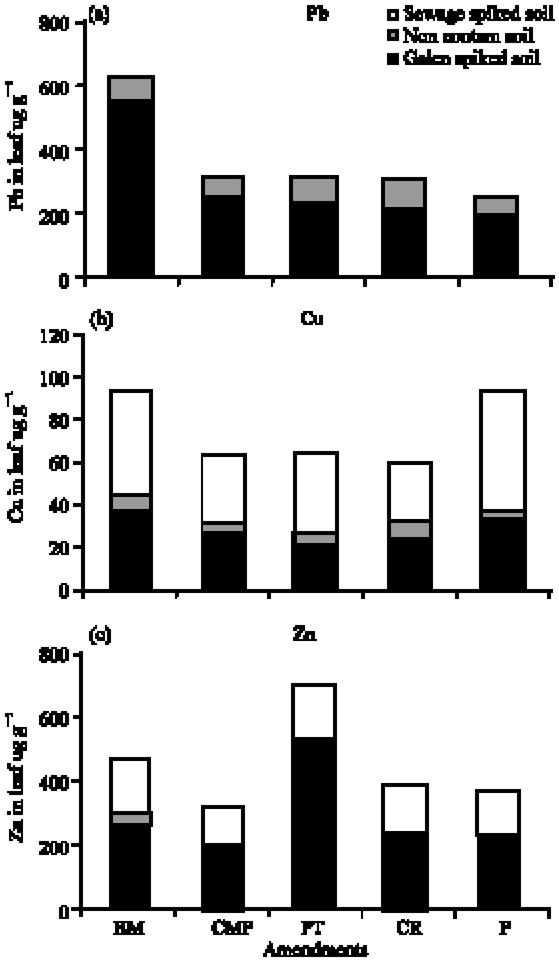

Fig. 3: Comparative contributions of amendments and contaminants to the uptake of Pb, Cu and Zn by ryegrass after 8 weeks of growth

For instance, Zn concentrations in both the mine waste treated and sewage sludge treated 'made soils' was approximately the same (25000 µg g^{-1}) having used mine waste at 1% and sewage soil at 10%, yet plant uptake of Zn was much higher in the mine waste treated soil (Fig. 4). Zn uptake from mine waste ranged from 200-550 µg g^{-1}, but only from 120-180 µg g^{-1} from sewage sludge. This indicates that Zn was more readily available from the inorganic mine waste and less from the organic sewage treated soil within the first 8 weeks. Amendments in the mine waste spiked soil led generally to a decrease in uptake of Pb and Zn when compared to non amended soil, while in the sewage treated soil, the impact of amendments was significant on Pb and Cu uptake (Fig. 4).

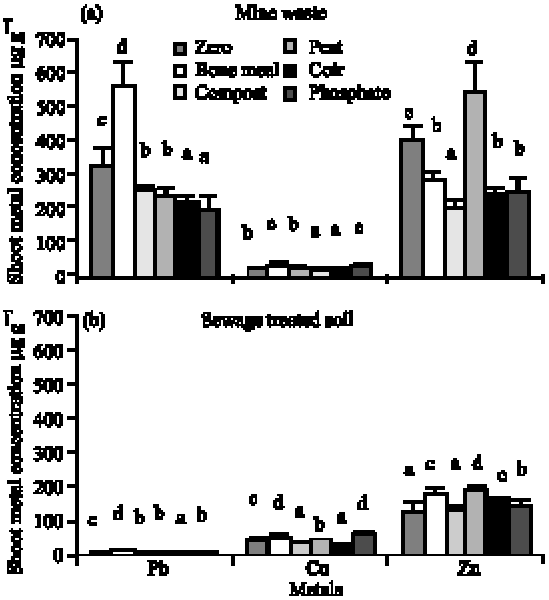

Fig. 4: Total Pb, Cu and Zn in ryegrass leaves after 8 weeks of growth in contaminated soil (error bars represent±standard deviation of 4 replications)

At 16 weeks, metal uptake from mine waste remained significantly higher than that from sewage sludge however, metal uptake from both contaminants had increased above that observed at 8 weeks, indicating greater solubility of the metals over time (Fig. 5).

This confirms the findings of Karaca (2004) and Clemente *et al*. (2006) and it is thought that this may be due to the re-release of metals which complexed with organic matter during the earlier phase of an experiment (Madrid *et al*., 2006).

Bioavailability of metals from mine waste and sewage sludge: Using a bioavailability index or factor which was essentially a ratio of plant metal concentration to soil metal, Pb and Zn from mine waste contamination was consistently more bioavailable than that from the sewage contamination in non amended soils. There was no

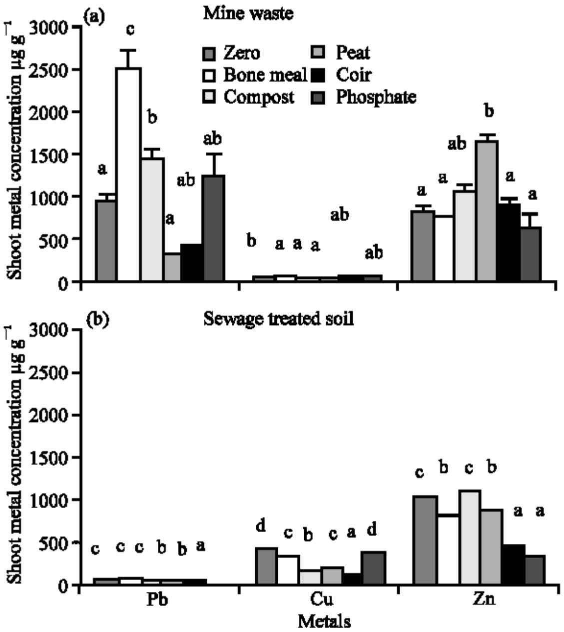

Fig. 5: Total Pb, Cu and Zn in ryegrass leaves after 16 weeks of growth in contaminated soil (error bars represent±standard deviation of 4 replications)

Table 2: Effect of contaminant source on Pb, Cu and Zn bioavailability

	Bioavailability factor (BF)		
Contaminant	Pb	Cu	Zn
Mine waste	19.0±3.3b	34.1±5.2ab	56.7±5.5b
Sewage sludge	6.7±0.8a	27.6±2.2a	29.4±5.5a
LSD	2.6	9.7	7.9

Means±S.D. (n = 4); Values within a column followed by the same letter are not significantly different at p<0.05

significant difference in Cu bioavailability from either contaminant (Table 2). The trend was the same in soils amended with agricultural materials (Kidd *et al*., 2007; An *et al*., 2004).

$$BF = \frac{\text{mg HM (kg plant leaves)}^{-1} \times 00}{\text{Total content HM (mg kg soil}^{-1}\text{)}}$$

where:

BF = Bioavailability Factor.
HM = Heavy Metal.

Sewage sludge has been known to present greater assimilation of the metals when compared to inert material like sand, probably due to the presence of anionic groups, which favors adsorption and complexation processes (Barros *et al*., 2007; Srivastava *et al*., 2005). Thus, there is slower metal release from soils treated with sewage (Pampura *et al*., 2007; Jamali *et al*., 2006). Metals from mine waste on the other hand is readily available in soil (Kiikkila, 2002).

CONCLUSION

The origin or source of contamination influences soil metal availability and plant uptake, as metals due to mine waste contamination (inorganic) was more readily extractable and available for plant uptake than that from the sewage treated soil (organic). Conversely, metal immobilisation by addition of amendments is greater in soils contaminated by an organic source. For instance, Zn immobilisation was greater in the organic sewage treated soil whereas the same metal was more easily taken up by plants growing in soil contaminated by the inorganic mine waste. Soils subjected to the 2 contaminant sources varied in terms of metal availability, concentration or immobilisation, regardless of similar initial contaminant pH values of 6.4 and 6.9. This suggests that contaminant source may take precedence over pH as dominant factor influencing metal availability in soils where pH values are similar.

Amendments were effective in immobilizing lead, copper and zinc to a certain extent in the contaminated soils, even though the initial metal concentrations in both contaminated soils were at toxic levels. Finally, the findings of the study confirm that where negligible concentrations of metals occur in soils or agricultural materials, plants will take up such metals whenever present, even in non contaminated soil. The evaluation of sewage sludge toxicity by chemical characterisation and biological testing is therefore, extremely important for screening the suitability of sludge for land application.

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