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# Monometal and competitive adsorption of heavy metals by sewage sludge-amended soil

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## Abstract

Sewage sludge-amended soils may alter their ability to adsorb heavy metals over time, due to the decomposition of sludge-borne organic matter. Thus, we studied Cd, Ni, and Zn adsorption by a sewage sludge-amended soil (Typic Xerofluvent) before and after one-year incubation in both monometal and competitive systems. In the monometal system, the order of decreasing sorption was Zn > Cd > Ni. Competition significantly reduced metal $K_d$, especially that of Cd which decreased by nearly 50%. Over the course of the incubation there was a 31% reduction of soil organic matter content. At the same time, in competitive systems Cd $K_d$ significantly decreased, while Zn $K_d$ significantly increased, and Ni $K_d$ remained unaffected. This study shows that sewage sludge-amended soils may change in their ability to sorb heavy metals over time at high metal concentrations. The data suggest that Cd is likely to be of most environmental significance in such soils, since it exhibited decreased sorption under competitive conditions and as the organic matter content of the soil was reduced. The potential for long-term release of metals should be considered in the risk assessment associated with sewage sludge addition to soils, particularly in climates where degradation of organic matter is likely to be enhanced.

*Keywords:* Cadmium; Nickel; Zinc; Organic matter degradation

## 1. Introduction

Sewage sludge has been used in agricultural soils for many years, because it contains appreciable amounts of macronutrients and organic matter. However, it also contains heavy metals, which may have adverse effects on crops and the environment (Bhogal et al., 2003; Granato et al., 2004). The most important chemical process that affects heavy metal availability is sorption onto soil solid phases. Metal sorption, among many factors, depends on the nature of organic and inorganic soil constituents, as well as soil pH. Inorganic phases do not usually change over the time-scale of a few decades, but soil organic C and dissolved organic C (DOC) tend to decrease due to decomposition of sludge-borne organic matter. Thus, many have supported the hypothesis that the ability of soils to bind heavy metals and to keep their availability to a minimum, months or years after sewage sludge application, may decrease over time (Chang et al., 1997). These concerns are greater in areas where relatively fast organic matter decomposition patterns are expected due to relatively high temperatures, such as in soils of the Mediterranean basin. There is a void in the literature concerning the behaviour of metals in sludge-amended soils before and after some decomposition of organic matter has taken place, particularly research that deals with soil processes relevant to semi-arid Mediterranean areas. Some workers have attempted to study the difference in metal adsorption by soils before and after organic matter content has been removed artificially (Li et al., 2001). However, these results do not show the fate of heavy metals over time, because in

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such studies soil organic constituents are likely to change in a dramatic and un-natural manner. Moreover, artificial treatments remove both native and sludge-derived organic matter, while decomposition in sludge-amended soils primarily affects sludge-borne organic constituents, which are generally less recalcitrant than the native, humidified organic matter in soil. One way of satisfactorily inducing decomposition of organic matter in a sludged soil is incubation. With incubation, measurable differences in soil organic C and DOC can be obtained over a relatively short time (Sleutel et al., 2005), without departing significantly from natural conditions.

Heavy metal adsorption, and hence availability, does not only depend on soil constituents (inorganic and organic), but also on the nature of metals involved, and on their competition for soil sorption sites. Usually, when competitive sorption of metals is compared with their monometal behaviour, it is found that their adsorption is lower in the competitive systems (Harter, 1992). More strongly sorbed metals, such as Pb and Cu, are less affected by competition than mobile metals, such as Cd and Zn (Basta and Tabatai, 1992; Zhu and Alva, 1993). However, the effect of competition among poorly sorbed metals, such as Cd, Ni, and Zn, especially in sludged soils, has not been documented. Moreover, it is not clear how the competitive adsorption of poorly sorbed heavy metals affects their behaviour and availability over time, i.e., after a significant proportion of the sludge-borne organic matter has decomposed.

The aim of this study was to test the hypothesis that soils decrease in their ability to bind heavy metals over time due to a reduction in the number of sorption sites as decomposition of sludge-borne organic matter takes place, especially when metals are in competition for these adsorption sites. Therefore, Cd, Ni, and Zn adsorption experiments in monometal and competitive systems were conducted both immediately following sewage sludge addition to soil, and after an incubation period of 310 d from the sludge addition. Changes in the physical and chemical nature of the sludge soil mix during the incubation period were also quantified.

## 2. Materials and methods

### 2.1. Soils and analyses

The studied soil was obtained from a farm in Larissa, Central Greece. A typical uncontaminated agricultural soil of the area, it was a light sandy loam Typic Xerofluvent, with 20% clay, 20% silt, and 60% sand. Soil was sampled from the 0 to 20 cm layer, air-dried and passed through a 2-mm sieve. Sewage sludge was obtained from the Larissa municipal sewage treatment works where it had been anaerobically digested, and contained 2.02 mg kg$^{-1}$ Cd, 61.56 mg kg$^{-1}$ Ni, 1377.74 mg kg$^{-1}$ Zn, had a pH of 5.72, and an organic C content of 318.2 g kg$^{-1}$. Sludge was air-dried and sieved through a 1-mm sieve. Soil and sludge were thoroughly mixed at a rate equivalent to 100 t sewage sludge ha$^{-1}$ (1:18 sludge:soil on a gravimetric basis). Soil–sludge mixtures were placed in plastic bags (three replicates), wetted to 65–70% of their water holding capacity, and were then incubated for 310 d in a temperature-controlled chamber at 28 °C. During that period, soil–sludge mixtures were weighted and rewetted so that the soil moisture content remained constant, as appropriate. Soils were aerated and oxic conditions were maintained throughout the duration of incubation. Soil pH (1:2.5 $H_2O$), electrical conductivity (1:5 $H_2O$) [both according to Rowell (1994)], DOC [extracted according to Antoniadis and Alloway (2002), and measured on a isotope ratio mass spectrometer, 20–20 ANCA-SL, PDZ Europa, Crewe, UK], and total organic C [by wet oxidation, according to Nelson and Sommers (1982)] were measured in the soil and in sludge–soil subsamples before and after incubation (Table 1). Total soil concentrations of Cd, Ni, and Zn were not expected to change over time and so were only determined before incubation (Table 1). To do this, the metals were digested for 3 h with *aqua regia* (hot concentrated HCl and $NHO_3$ at 3:1 ratio, Ure, 1995), and were then analysed by atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia).

### 2.2. Batch adsorption tests

Samples of the sludge–soil mix were obtained at the beginning (referred to as T1 samples hereafter) and end (referred to as T2 samples hereafter) of the incubation. These samples were air-dried, and passed through a 2-mm sieve. On these two samples adsorption experiments (both monometal and competitive) were conducted. Monometal adsorption isotherms of Cd, Ni, and Zn were obtained by weighing 2 g of soil into acid-washed polyethylene bottles prior to addition of 20 ml of either Cd, Ni, or Zn chloride solutions. Competitive adsorption isotherms were performed in the same way but by adding Cd, Ni, and Zn at a 1:1:1 concentration ratio. The added metal

Table 1
Selected physical and chemical characteristics of the sludged soil and its unsludged control before (T1) and after (T2) their 310-d incubation

| | Sludged soil | | | Unsludged soil | | |
|---|---|---|---|---|---|---|
| | T1 | T2 | | T1 | T2 | |
| Organic C (g kg$^{-1}$) | 19.86 | 13.62 | * | 8.03 | 8.26 | NS[a] |
| DOC[b] (mg l$^{-1}$) | 61.7 | 39.9 | * | 30.4 | 46.5 | NS |
| Cd[c] (mg kg$^{-1}$) | 0.13 | ND[d] | | 0.05 | ND | |
| Ni[c] (mg kg$^{-1}$) | 271.42 | ND | | 271.04 | ND | |
| Zn[c] (mg kg$^{-1}$) | 145.31 | ND | | 72.46 | ND | |
| pH (1:2.5 soil:$H_2O$) | 7.22 | 7.02 | NS | 7.55 | 7.50 | NS |
| EC[e] (μS cm$^{-1}$) | 624 | 730 | NS | 390 | 440 | NS |

[a] Differences between values at T1 and T2 not significant ($p > 0.05$).
[b] Dissolved organic C.
[c] *Aqua regia*-digested.
[d] Not determined.
[e] Electrical conductivity.
[*] Significant at the 0.05 level.

concentrations were 0, 1, 2.5, 5, 10, 25, 50, and 100 mg $l^{-1}$. Thus the highest added metal concentration was 1000 mg $kg^{-1}$, because the soil:solution ratio used was 1:10. Both experiments were carried out in a background electrolyte of 0.01 M $CaCl_2$ and were replicated three times. Samples were equilibrated for 24 h (sufficient time for the system to reach equilibrium, as determined by a preliminary kinetics experiment) on a reciprocating shaker at constant room temperature (20 ± 2 °C), and then centrifuged at 2500 rpm for 15 min. The supernatant was then filtered through slow filter paper (Whatman No. 42). Cadmium, Ni, and Zn concentrations in the supernatant were measured by atomic adsorption spectrometry (Varian, SpectrAA-400 Plus, Australia). Total metal retained was calculated from the difference between that added (including the sludge-borne metals added to the systems with sludge application before the beginning of incubation) and that measured in the equilibrium solution. The pH values of the equilibrium solution in all tests were monitored, but they did not change significantly compared to the initial soil pH. The adsorption isotherms were described by the Freundlich model. Distribution coefficients, $K_d$ (l $kg^{-1}$) were also calculated for each metal isotherm for the equilibrium concentration value corresponding to half of the maximum added metal concentration, i.e., 50 mg $l^{-1}$, as suggested by Gomes et al. (2001).

### 2.3. Statistical analysis and quality control

All results were analysed statistically using ANOVA (SPSS 10 for Windows, Release 10.0.1), and the multiple range test was employed to determine the significance of differences between treatments (monometal and competitive systems) and different times. When significant differences are mentioned in the text, they are at the 0.05 level. Data quality control was addressed with the systematic use of in-house reference materials and blanks for each batch of extraction and analysis.

## 3. Results and discussion

### 3.1. Incubation

Incubation over the 310-d period significantly decreased organic C by 31%. Table 1 indicates that most of the organic matter degraded was sewage sludge-borne, since organic C of the unsludged control did not change. Likewise, DOC decreased significantly over time, mainly due to the reduction in sludge-borne DOC. This was indicated by the fact that DOC in the unsludged control did not change significantly over time, although it had an increasing trend. On the other hand, pH did not change significantly over time, and neither did electrical conductivity (Table 1), indicating that any differences in metal sorption behaviour can not be attributed to changes in these variables. This is particularly significant for pH which is known to strongly affect metal sorption in soil. Thus, the primary soil change during incubation, and hence the process most likely to influence metal sorption, was organic matter degradation.

### 3.2. Adsorption isotherms and $K_d$ values

Experimental data from the batch adsorption tests for all metals and all treatments (monometal and competitive systems, T1 and T2 samples) gave a satisfactory fit to the Freundlich model ($R^2 > 0.900$, except for the Zn competitive isotherms, Table 2). The adsorption isotherms of Cd (Fig. 1a), Ni (Fig. 1b), and Zn (Fig. 1c) were of the L-curve type, which is characterized by an initial slope that does not increase with the concentration of the added metal in the soil solution. This type of isotherm indicates a relatively high affinity of the soil particles for the studied metals at low added metal concentrations (Sposito, 1989). The shape of the isotherms at this low concentration range (0–10 mg $l^{-1}$) did not change markedly between times T1 and T2 even after the significant reduction of organic matter and DOC during incubation. This was in disagreement with Neal and Sposito (1986) who, in their study on Cd adsorption, found that with the removal of soil organic matter the formation of preferential soluble organo-metallic associations was reduced and thus Cd sorption on the solid surfaces increased at low added metal concentrations. They explained that this happened because at low metal concentrations associations with soluble organic ligands can reduce metal affinity for the solid phases, while at higher metal concentrations soluble organo-metallic species become less important. A possible reason for the disagreement between Neal and Sposito (1986) and the current study may be that in the former the whole soil organic

Table 2
Summary of the monometal and competitive Freundlich parameters of the adsorption of Cd, Ni, and Zn by sludge-amended soil before (T1) and after (T2) its 310-d incubation

| | T1 | | | T2 | | |
|---|---|---|---|---|---|---|
| | $K$ (l $kg^{-1}$) | $N$ | $R^2$ | $K$ (l $kg^{-1}$) | $N$ | $R^2$ |
| Cd-monometal | 91.92 | 0.67 | 0.999 | 47.87 | 0.78 | 0.985 |
| Cd-competitive | 48.20 | 0.68 | 0.657 | 36.26 | 0.56 | 0.956 |
| Ni-monometal | 61.70 | 0.67 | 0.978 | 76.37 | 0.58 | 0.973 |
| Ni-competitive | 59.84 | 0.54 | 0.922 | 64.65 | 0.52 | 0.904 |
| Zn-monometal | 150.45 | 0.54 | 0.928 | 189.75 | 0.55 | 0.908 |
| Zn-competitive | 118.95 | 0.54 | 0.768 | 145.47 | 0.55 | 0.837 |

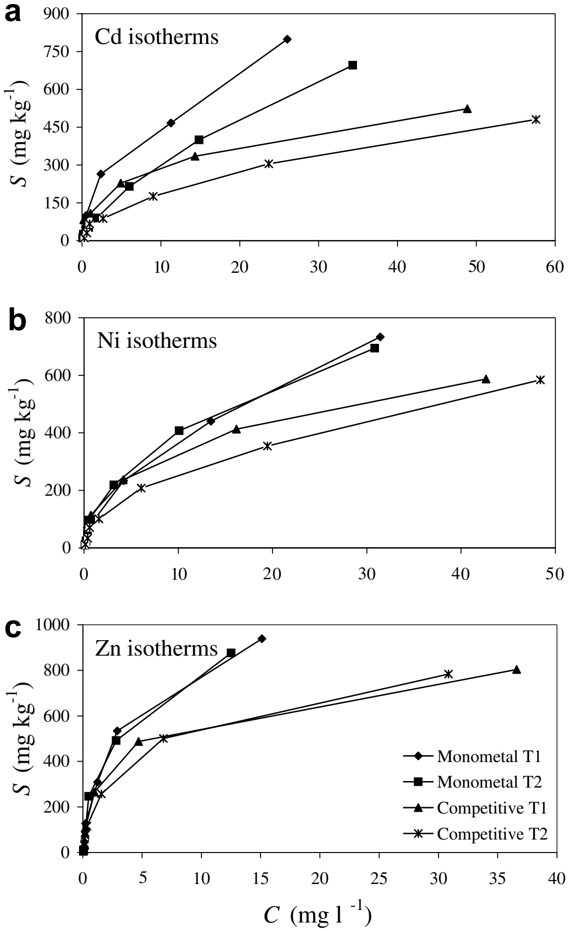

Fig. 1. Monometal and competitive Cd, Ni, and Zn isotherms in samples obtained before (T1) and after (T2) the 310-d incubation of sludge-amended soil. On the *y*-axis *S* represents the metal concentration sorbed onto solid phases, and on the *x*-axis *C* represents metal equilibrium concentration in solution.

fraction was removed artificially. In our study organic matter decreased naturally with incubation, resulting in the decomposition of the sludge-borne organic matter and, subsequently in DOC reduction (Table 1). Thus, if, as would be expected, DOC is an important factor in determining metal sorption at low concentrations, this may indicate that the fraction of DOC added with sludge application was less effective than native soil DOC in creating stable soluble complexes with the studied metals. Thus the reduction of sludge-derived DOC did not significantly affect metal sorption. Additional evidence that this may be plausible derives from Gigliotti et al. (1997), who found that soil DOC has higher percentage of olefinic groups (which are highly reactive) than municipal waste compost-amended soil.

Distribution coefficient, $K_d$, is an index of a metal's potential mobility. The higher the $K_d$ of a metal the stronger its sorption onto the soil surfaces, and thus the lower its solubility. Distribution coefficients have been used extensively in studies where heavy metal mobility is evaluated using adsorption experiments (e.g., Cruz-Guzman et al., 2006). The $K_d$ values of all metals indicated that the order of reduced metal sorption was Zn > Cd > Ni in most of the cases. If metal adsorption was entirely electrostatic, metal ions of lower ionic radii would be more strongly adsorbed, and that would predict a different sequence, as follows: Ni (0.069) > Zn (0.074) > Cd (0.097), with values in parentheses being the ionic radii in nm. Metal adsorption in this study was not entirely covalent either, because covalent bonds would predict the following affinity sequence: Cd > Ni > Zn (Gomes et al., 2001). Those discrepancies indicate that metal sorption can not solely be predicted by any given affinity sequence model. This may be particularly acute for sludge-amended soils, where sludge-derived organic phases are likely to modify significantly metal sorption characteristics (as they add chelating agents that form stable complexes with metals, as well as new solid adsorption sites). Also sludge-borne organic phases change in nature and composition very rapidly and continuously due to decomposition of freshly applied sludge organic matter. The observed metal adsorption sequence may also be related to the soil pH value, since Zn is often reported with lower solubility than the other two metals in soils with circum-neutral pH values (e.g., Elliot et al., 1986; Saha et al., 2002). In concurrence, Ashworth and Alloway (2004) observed very low Zn solubility and mobility, and relatively high Ni solubility and mobility, in sewage sludge-amended soil columns of neutral pH. Other workers have also observed high Ni solubility in sludge-amended soils (Karapanagiotis et al., 1991).

### 3.3. Effect of competition on metal adsorption

Competition among the three metals reduced their $K_d$ values significantly both in T1 and T2 samples (Table 3). This suggests that the metals were competing for the same binding sites as one another, though the total amount of added metals was not so high as to occupy a large part of the available surface adsorption sites. Significant suppressive effects of competitive metals on the adsorption of a particular metal have also been reported by Basta and Tabatai (1992). Although $K_d$ values indicated a reduction in metal adsorption due to competition over the whole range of added metal concentrations (0–100 mg kg$^{-1}$), metal isotherms (Fig. 1) show that the differences in metal

Table 3
Distribution coefficients, $K_d$ (l kg$^{-1}$) for the monometal and competitive adsorption of Cd, Ni, and Zn by sludge-amended soil before (T1) and after (T2) its 310-d incubation

| | Monometal | | | Competitive | | |
|---|---|---|---|---|---|---|
| | Cd | Ni | Zn | Cd | Ni | Zn |
| T1 | 25.28 | 16.97 | 26.88 | 13.78 | 9.90 | 19.67 |
| T2 | 20.08 | 14.77 | 30.20 | 6.48 | 9.89 | 25.02 |
| | * | NS[a] | NS | * | NS | * |

[a] Differences between values at T1 and T2 not significant ($p > 0.05$).
[*] Significant at the 0.05 level.

sorption were evident mostly at the higher end of equilibrium concentrations (especially at 25, 50, and 100 mg kg$^{-1}$). Thus at low metal concentrations, effects of competition were not strong. This seems to concur with the work of Saha et al. (2002), who found no evidence of metal (Cd, Zn, and Pb) competition at low concentrations ($5 \times 10^3$ times lower than the highest added concentration in the present study). Saha et al. (2002) explained that at low added metal concentrations metals are mainly adsorbed onto specific adsorption sites, while at higher metal inputs soils lose some of their ability to bind heavy metals as adsorption sites overlap, becoming thus less specific for a particular metal. This in turn induces a reduction in metal sorption.

Although competition reduced sorption of all three metals, the magnitude of these effects was different for each metal. Cadmium $K_d$ decreased by nearly 45% at T1 due to competition, and by 68% at T2. This compares to competition-induced reductions of around 42% and 33% for Ni at T1 and T2, respectively, and 27% and 17% for Zn at T1 and T2, respectively. Thus the effect of competition in reducing the sorption of metals followed the order Cd > Ni > Zn. This suggests that upon co-addition of the three metals to the soil, Zn, and to a lesser extent Ni, became preferentially adsorbed at the expense of Cd. This is likely to have been the result of differences in the nature of the dominant sorbing surfaces for each metal. Cadmium sorption appeared to be strongly controlled by organic matter dynamics, as evidenced by the reduction in Cd $K_d$ between times T1 and T2 (discussed below). Zinc and Ni sorption was not controlled in this way and is therefore likely to be associated with the potential for adsorption onto specific mineral phases. Alloway (1995) explained that specific adsorption is related to the hydrolysis of heavy metal ions. The metals most able to form hydroxy complexes are specifically adsorbed to the greatest extent. Therefore, the pK values of metal hydrolysis product determine the adsorption behaviour of the studied metals, with specific adsorption decreasing with increasing pK. Thus, the order of increasing pK values: Zn (9.0) > Ni (9.9) > Cd (10.1) offers an explanation for the preferential sorption of Zn and Ni at the expense of Cd. These results indicate that competition decreased metal sorption when metals were in sufficiently high concentration and suggest that the magnitude of any sorption that did take place depended on the affinity of the soil surfaces for the metals, coupled with chemical properties of the metals themselves.

### 3.4. Effect of reduced organic matter on metal sorption

In monometal systems, Cd $K_d$ at T1 was significantly higher than at T2 and in competitive systems, this difference was even greater (Table 3). This behaviour of Cd was not unexpected, since organic matter contributes solid adsorption sites that bind sewage sludge-borne heavy metals (Hooda and Alloway, 1993). Thus the degradation of soil organic matter during incubation is likely to have resulted in the significant decrease in Cd adsorption, a finding, and more specifically the breakdown of chemical bonds between the organic matter and the metal, is likely to have resulted in the significant decrease in Cd adsorption. This finding concurs with that of Yuan and Lavkulich (1997). In contrast, the reduction in organic matter did not reduce Ni and Zn sorption to the soil solid phase. In fact, in Zn $K_d$ increased between T1 and T2 (although this difference was significant only in the competitive system). This again suggests that Ni and Zn had stronger association with the inorganic soil phase than with organic matter in this particular system. As mentioned previously, these two metals can become easily diffused into mineral phases, due to their favorable ionic radii, while Zn is known to become specifically bound onto certain inorganic soil constituents over time (Alloway, 1995).

The metal isotherms showed that the effect of the sludge-borne organic matter degradation on metal sorption was mostly evident at the higher end of added metals concentrations (50 and 100 mg l$^{-1}$) even in the case of Cd, whose $K_d$ decreased over time. This indicates that even sludge-amended soils with low sludge-borne organic matter content (e.g., years after sewage sludge application), can still retain their ability to sorb heavy metals as strongly as before organic matter decomposition, provided that added metals are at relatively low concentrations. Soil constituents responsible for preserving the sorptive capacity of soils under such conditions are mineral surfaces, as well as resistant, non-readily decomposable native soil organic matter (Oliver et al., 2005).

## 4. Conclusions

In this work the sorption of three poorly sorbed elements, Cd, Ni, and Zn, was studied in sewage sludge amended soils. Metal $K_d$ values in monometal systems followed the order Zn > Cd > Ni. When the studied metals were in competition, this order did not change, although the $K_d$ values of all metals decreased significantly. During incubation for around 1 year, Cd and Zn sorption behaviour changed significantly, while Ni did not. Cadmium $K_d$ was significantly higher at T1 than at T2 as a result of soil organic matter decomposition, both in monometal and competitive systems, while Zn $K_d$ was significantly lower at T1 than at T2 in competitive systems. This study showed that although sewage sludge-amended soils can decrease their ability to sorb heavy metals (e.g., Cd) over time at high added metal concentrations, soil affinity seems to be unaffected at low metal concentrations. It also showed that co-presence of metals (as would be observed in sewage sludge-amended soils in the field), led to a decrease in the sorption of all three metals due to competition for adsorption sites. The effects of competition and potential for organic matter degradation (e.g., at relatively high ambient temperatures) should therefore be considered in assessing the risk associated with applying sewage sludge to agricultural soils.

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