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Influence of Dissolved Organic Matter on the Solubility of Heavy Metals in Sewage-Sludge-Amended Soils

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Abstract: Sewage-sludge-amended soils generally contain elevated levels of organic matter and heavy metals compared to control soils. Because organic matter is known to complex with heavy metals, the solubility behavior of the organic matter in such soils may exert a significant influence on the solubility of the metals. Little is known about such a process. Using batch experiments in which the solubility of organic matter in a heavily sludge-amended soil was artificially manipulated, we show that the solubilities of the heavy metals copper (Cu), nickel (Ni), and lead (Pb) show a strong positive relationship to the solubility of organic matter, particularly at high pH. The results suggest that under field conditions, spatiotemporal variations in the solid–solution partitioning of organic matter may have a bearing on the environmental significance (mobility and bioavailability) of these heavy metals.

Keywords: DOC, DOM, organo-metals, solid–solution partitioning, sorption

INTRODUCTION

Sewage-sludge-amended soils generally contain elevated levels of organic matter and heavy metals [e.g., cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)] compared to control soils, particularly when very

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heavy sludge additions are made (Lund, Page, and Nelson 1976; Antoniadis and Alloway 2003a). The solid–solution partitioning of heavy metals in sewage-sludge-amended soils has been extensively investigated and is known to be related to a number of factors but primarily pH, soil organic matter, clay contents, and total metal loading (Alloway 1995). However, the influence of the solid–solution partitioning of sewage-sludge-derived organic matter on the sorption behavior of these heavy metals may also be significant, as stressed in reviews of this topic by Ross (1994) and Smith (1996), but has not been studied in much detail. Dissolved organic-matter (DOM) molecules contain functional groups (e.g., COOH and phenolic-OH) capable of complexing metals (Saar and Weber 1982). This process has been implicated in decreasing the sorption and increasing the mobility of heavy metals in soils (Zhou and Wong 2001; Antoniadis and Alloway 2002, 2003b; Kaschl, Romheld, and Chen 2002; Ashworth and Alloway 2004). This is thought to occur because of the formation of soluble, organic complexes of heavy metals, which tend to resist dissociation and hence (re)adsorption by the soil solid phase (Buffle 1988; McCarthy and Zachara 1989; Neal and Sposito 1986). In sewage-sludge-amended soils, this may be a particularly important process because of the potential for increased DOM quantity and molecular diversity (Dudley, McNeal, and Baham, 1986; Dudley et al. 1987; McBride et al. 1997; Cornu et al. 1999; Han and Thompson 1999a, 1999b).

There are essentially three, probably interrelated, processes by which the partitioning behavior of organic matter may influence the behavior of heavy metals. The three processes are (a) organic matter released into the soil solution results in the corelease of heavy metals already associated with that organic matter; (b) organic matter released into the soil solution serves to subsequently extract, or mobilize, heavy metals from the solid phase; and (c) organic matter and heavy metals released independently into the soil solution subsequently become associated with one another. Clearly, the first two of these processes would lead to an increase in the concentration of heavy metals in the soil solution. In addition, all three processes would lead to an increase in the concentration of organically complexed heavy metals in the soil solution.

Assessing the significance of the relationship between organic-matter partitioning and the sorption behavior of heavy metals is therefore an important component in quantifying the risk associated with sewage-sludge treatment of soils. The aim of the work described in this article was therefore to artificially manipulate the solid–solution partitioning of organic matter in a heavily sewage-sludge-amended soil and study the consequences on the partitioning of heavy metals.

MATERIALS AND METHODS

A clay loam soil that had been subject to extensive sewage-sludge application over several decades was collected from a UK urban sewage works site. The

top 20 cm of soil was collected from a number of randomly selected points across the site and placed into clean plastic buckets. The soil was mixed thoroughly. Upon return to the laboratory, the soil was sieved through a 2-mm mesh and then stored at field moisture content under aerobic conditions and at 4°C.

Prior to the main experiments, the solid and soluble phases of the soil were characterized. Air-dried samples were used for the determination of the solid-phase components. The methods used and data obtained are summarized in Table 1. Field-moist samples were used for the determination of soluble-phase components. These samples were allowed to equilibrate with purified water (18.2 MΩ) at a soil–solution ratio of 1:5. The equilibration was carried out on a slow end-over-end-shaker (14 rpm) for 24 h and at 20°C. After 24 h, the samples were centrifuged at 3600 rpm for 20 min before filtration of the resulting supernatant through a 0.45-μm cellulose nitrate filter. Methods used for analysis of the filtered solution, and the data obtained, are shown in Table 2.

For the main experiments, batch equilibration experiments based on the methods of Romkens, Bril, and Salomons (1996) were carried out. Two separate methods were used to manipulate DOM kinetics of the soil: manipulation of soil pH and manipulation of soil calcium (Ca) levels. Consequential effects upon the solubilization of heavy metals from the soil were studied.

Table 1. Solid-phase analysis of soil, methods used and mean values obtained

Variable	Method	Value
pH	1:2.5 soil–purified water ratio (Rowell 1994)	5.7
Sand	Dispersal and sedimentation (Rowell 1994)	16%
Silt	Dispersal and sedimentation (Rowell 1994)	51%
Clay	Dispersal and sedimentation (Rowell 1994)	32%
CEC	Leaching with ammonium acetate at pH 7 (Rowell 1994)	62 cmol _c kg ⁻¹
C _{org}	Digestion with potassium dichromate (Rowell 1994)	13.7%
N _{tot}	Mass spectrometry	1.9%
S _{tot}	Oxidation at 1400°C	0.5%
Cd _{tot}	Digestion in hot <i>aqua regia</i>	49 mg kg ⁻¹
Cu _{tot}	Digestion in hot <i>aqua regia</i>	527 mg kg ⁻¹
Ni _{tot}	Digestion in hot <i>aqua regia</i>	85 mg kg ⁻¹
Pb _{tot}	Digestion in hot <i>aqua regia</i>	680 mg kg ⁻¹
Zn _{tot}	Digestion in hot <i>aqua regia</i>	1430 mg kg ⁻¹

Notes: All values except pH expressed on an oven-dried soil basis.

N_{tot} analysis was carried out using a Europa scientific mass spectrometer. S_{tot} was carried out using a Leco C/S analyzer. Metal analysis was carried out by ICP-OES using a Perkin-Elmer Optima 3000.

Table 2. Soluble-phase analysis of soil, mean (with standard deviation) values

Variable	Value
C _{org}	283 (5) mg kg ⁻¹
N _{org}	40 (8) mg kg ⁻¹
Cd	19 (1) μg kg ⁻¹
Cu	989 (14) μg kg ⁻¹
Ni	374 (2) μg kg ⁻¹
Pb	23 (1) μg kg ⁻¹
Zn	3788 (221) μg kg ⁻¹

Notes: All values expressed on an oven-dried soil basis.

C_{org} analysis was carried out using a Shimadzu TOC-5000. N_{org} analysis was carried out by Kjeldahl digestion, steam distillation, and titration ([Rowell, 1994]). Metal analysis was carried out by ICP-OES using a Perkin-Elmer Optima 3000.

Manipulation of Soil pH

Samples of field-moist soil were allowed to equilibrate with purified water (18.2 MΩ) at a soil–solution ratio of 1:5. The equilibration was carried out on a slow end-over-end-shaker (14 rpm) for 24 h and at 20°C. The pH of the samples was adjusted to predetermined values to give a pH gradient between 3 and 9 for the set of samples. To achieve this, a few drops of either hydrochloric acid (HCl) or sodium hydroxide (NaOH) (each 0.5 M) were added at 1, 3, 6, 9, and 12 h of the equilibration. Each pH treatment was carried out in triplicate. After 24 h, the samples were centrifuged at 3600 rpm for 20 min before filtration of the resulting supernatant through a 0.45-μm cellulose nitrate filter. The filtered solution was analyzed for pH, DOC, and dissolved Cd, Cu, Ni, Pb, and Zn.

Manipulation of Soil Calcium Concentration

Samples of field-moist soil were equilibrated with a range of solutions containing 0 (purified water) to 430 mg Ca L⁻¹ (as calcium nitrate). The soil–solution ratio was 1:5, and samples were equilibrated for 24 h at 14 rpm and 20°C. The pH of the samples was adjusted to that of the 0 mg L⁻¹ Ca treatment (pH 5.7) after 1, 3, 6, 9, and 12 h using a few drops of 0.5 M NaOH. Each Ca treatment was carried out in triplicate. Following equilibration, samples were centrifuged, filtered, and analyzed as described for the pH experiment.

Effects of Added Sodium

Because NaOH was used in both of these experiments, it was deemed important to study the effect of added Na in terms of its potential for affecting the solubility of heavy metals and organic matter. Therefore, a further equilibration experiment was carried out with the same soil and with a range of solutions containing 50 to 750 mg Na L⁻¹ (as sodium nitrate). The equilibration was carried out as for the Ca equilibration experiment, but with the pH of all Na addition treatments adjusted to the natural soil pH (5.7) with a few drops of 0.5 M NaOH. Thus the Na concentration of the system was increased without an increase in pH. Again, centrifugation, filtration, and analysis were carried out as described for the pH experiment.

RESULTS AND DISCUSSION

The results of the equilibration experiments are expressed in terms of percentage solubility of each component (i.e., the percentage of the total concentration that was found in the soluble phase).

It should be noted initially that the effect of Na on the solubility behavior of organic matter and heavy metals in the soil was only slight (Table 3). This was important because it meant that Na-induced effects in the pH and Ca experiments were mitigated. Thus, organic matter and heavy-metal solubility behavior in these experiments could be attributed to the intended treatments.

Effects of pH Manipulation

Organic-matter solubility was relatively low between around pH 4.6 and 6.4 but increased markedly beyond this range to a maximum for this

Table 3. Effect of added sodium on the solubility (percentage of total component measured in the soluble phase) of metals and organic carbon

Equilibrium Na concentration (mg L ⁻¹)	Cd	Cu	Ni	Pb	Zn	C _{org}
69	0.08	0.23	0.60	0.003	0.34	0.25
71	0.07	0.23	0.56	0.003	0.38	0.25
89	0.07	0.22	0.57	0.003	0.32	0.25
146	0.08	0.23	0.57	0.004	0.34	0.25
264	0.09	0.22	0.58	0.003	0.33	0.25
502	0.10	0.22	0.59	0.003	0.37	0.26

experiment at the highest pH (7.7) (Figure 1a). Linear regression analysis showed that pH was positively correlated with DOC concentrations over the entire pH range used ($r^2 = 0.64$). Thus, a pH-induced gradient of organic-matter solubility, against which to compare heavy-metal solubility, was effectively achieved. The linear regression also showed that pH was more strongly correlated with DOC concentration when only pH values of 6.4 and greater were considered in the analysis ($r^2 = 0.94$). The pH influences organic-matter solubility via its effect on the pH-dependent charge of soil solids (e.g., organic matter and certain clay

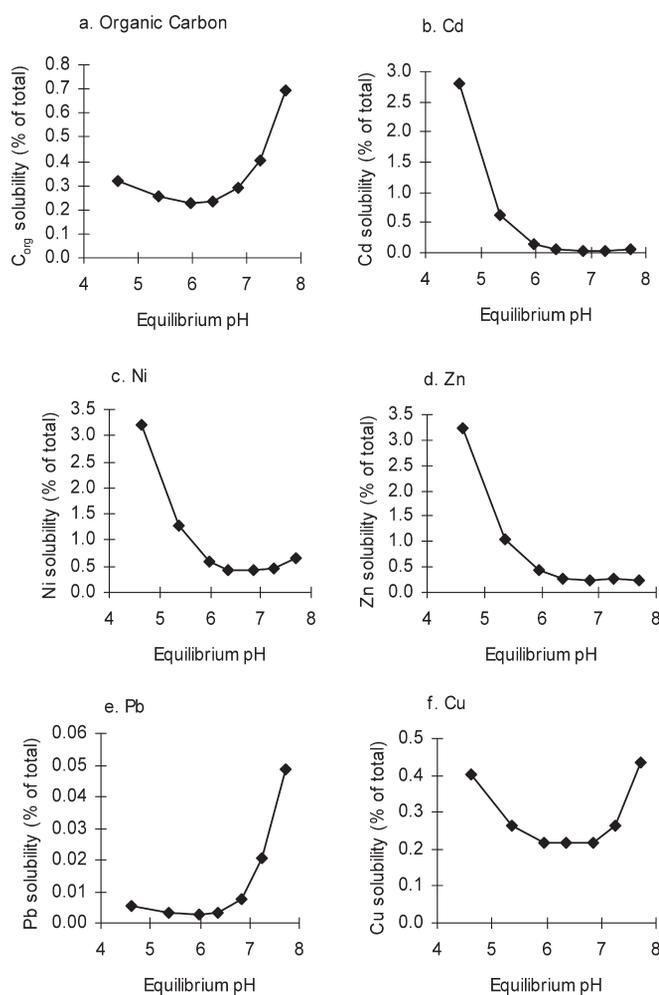


Figure 1. Effect of pH on the solubility of (a) organic carbon, (b) Cd, (c) Ni, (d) Zn, (e) Pb, and (f) Cu.

minerals). As pH increases, the negative charge on such surfaces is increased and repels negatively charged molecules (e.g., molecules of organic matter) into the soil solution, thereby increasing DOM concentration (Jardine, Weber, and McCarthy 1989).

The solubility of heavy metals fell into three categories: those that appeared to show greatest solubility at low pH with relatively low solubility at pH levels greater than 6.4 (Cd, Ni, Zn; Figures 1b–d, respectively), those that showed greatest solubility at high pH with relatively low solubility at pH levels less than 6.4 (Pb; Figure 1e), and those that produced a U-shaped curve with minimum solubility at intermediate pH and increasing solubility both greater than and less than this value (Cu; Figure 1f). Although this classification seems generally acceptable, upon closer inspection it is noticeable that the relatively high solubility of Ni at low pH (Figure 1c) obscures an increase in Ni solubility at high pH. Therefore, in Figure 2, the solubility of Ni at high pH only is shown, along with the solubility of Cu as a comparison. This figure clearly shows similarity in the solubility behavior of Ni and Cu at high pH. Thus for both elements, a U-shaped solubility curve was found, although for Ni a low pH had a much greater effect on solubility than a high pH. For Cu solubility, the low-pH and high-pH effects were similar in their extent.

For this experiment, linear regression analysis between pH and soluble heavy-metal concentrations and between DOC and soluble heavy-metal concentrations produced the correlation coefficients shown in Table 4. These indicate that pH showed a stronger relationship (negative) with Cd and Zn concentrations than DOC concentration did. Conversely, DOC concentration, particularly at high pH, showed a stronger relationship (positive) with concentrations of Pb, Ni, and Cu than pH did.

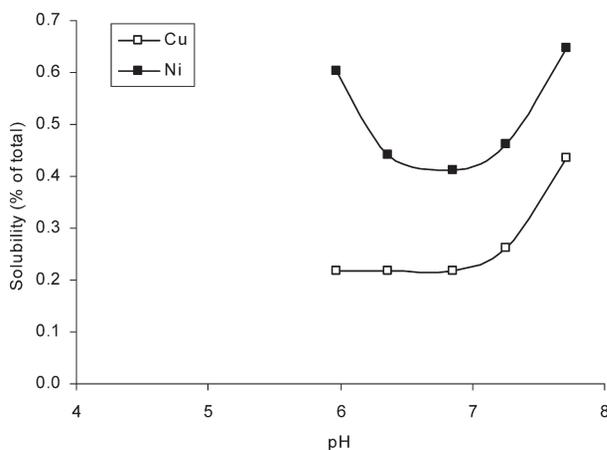


Figure 2. Comparison of the solubility of Cu and Ni at high (>6) pH.

Table 4. pH adjustment experiment: Correlation coefficients of linear regression between metal concentrations and pH and organic carbon concentration in the equilibrium solution

Element	pH	DOC	DOC (pH > 5.97)
Cd	-0.78 ^b	-0.13 n.s.	0.63 n.s.
Cr	0.66 n.s.	1.00 ^d	1.00 ^d
Cu	0.00 n.s.	0.76 ^b	0.99 ^c
Ni	-0.79 ^b	-0.10 n.s.	0.95 ^a
Pb	0.72 ^a	0.99 ^d	1.00 ^d
Zn	-0.81 ^c	-0.16 n.s.	-0.57 n.s.

Note: n.s.: Not significant.

^aSignificant (p < 0.05).

^bSignificant (p < 0.02).

^cSignificant (p < 0.01).

^dSignificant (p < 0.001).

Increased metal solubility at low pH is to be expected because of cation exchange processes involving hydrogen, decreases in negative (pH-dependent) charge on oxides and organic matter, and dissolution of precipitates (Alloway 1995). These processes would appear to have been important in controlling the solubility of Cd, Zn, and Ni, as relatively high solubility (3–3.5%) was observed for these elements at low pH (4–5). As pH was increased to 6–7, the solubility of these metals was much reduced. Indeed, Cd and Zn solubility remained low up to the maximum pH (7.7). The increasing solubility of Pb, Cu, and Ni as pH was increased was less expected. Because the effect of added Na can be discounted, the enhanced solubility of these metals can be attributed to the increased solubility of organic matter at high pH. This suggests that the solubilized organic matter was either acting as an extractant of the Pb, Cu, and Ni from the soil solid phase or that the metals were already bound to this organic matter on the solid phase prior to it entering the solution. In the case of Cu, this agrees with the work of Romkens, Bril, and Salomons (1996) and Salam and Helmke (1998), who also found Cu solubility to be increased in non-sludge-amended soils at both low and high pH (i.e., it had a U-shaped solubility curve). The apparent association of both Cu and Pb with DOM at high pH is consistent with previous work reporting a strong affinity of these metals for soil organic matter (i.e., they have high stability constants). However, in the case of Ni, the effect was less expected because it is not often regarded as an element that forms strong associations with organic matter in soils. Nevertheless, in sewage-sludge-amended soils, Ashworth and Alloway (2004) found that Ni mobility was more strongly related to DOM mobility than Cu was, suggesting that in such soils, the formation of organo-Ni complexes may be a particularly important factor

in the speciation of Ni. Furthermore, McBride (1998) found that high Ni solubility in an alkaline sludge product was governed by complexation with N-ligands in dissolved amines.

Effects of Calcium Concentration Manipulation

The pH of the system was effectively maintained at natural soil pH throughout the Ca addition experiments by the addition of NaOH. The largest difference in pH was between the 0 and 430 mg Ca L⁻¹ treatments and was 0.2 pH units. Thus, pH effects on metal and organic matter solubility were effectively

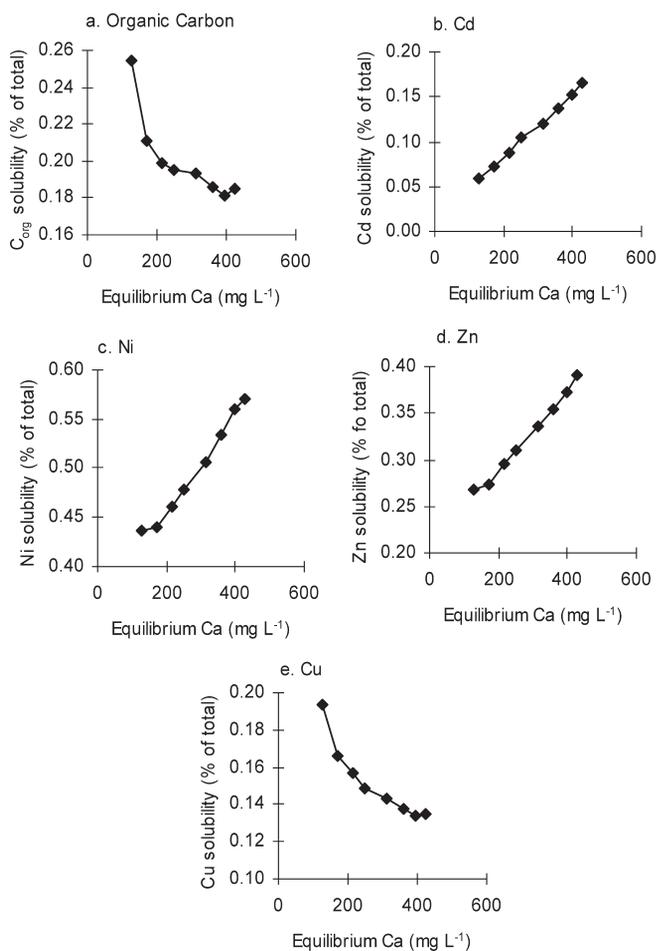


Figure 3. Effect of Ca concentration on the solubility of (a) organic matter, (b) Cd, (c) Ni, (d) Zn, and (e) Cu.

mitigated in this experiment. Effects on their solubility can therefore be attributed to the Ca additions to the system.

Calcium addition was found to reduce the solubility of organic matter (Figure 3a). Romkens, Bril, and Salomons (1996) attributed the removal of DOM from solution as Ca concentration of the solution was increased to cation bridging. In this scenario, negatively charged DOM molecules in the soil solution become adsorbed onto negatively charged solid-phase surfaces via the excess of positively charged Ca ions, which act as a bridge between the two phases. A Ca-induced gradient of organic-matter solubility, against which heavy-metal solubility could be compared, was thus created.

The effect of increasing Ca concentration was to increase the solubility of Cd, Ni, and Zn (Figures 3b–d, respectively) and to decrease the solubility of Cu (Figure 3e). The Pb concentrations in this experiment were at, or less than, the detection limit of the ICP-OES ($2 \mu\text{g L}^{-1}$), and so no relationship was observed. These data are therefore not presented.

Correlation coefficients for linear regressions between Ca concentration and soluble heavy-metal concentrations and between DOC concentration and soluble heavy-metal concentrations are shown in Table 5. Highly significant positive relationships were observed for all comparisons, although it would appear that Ca had the stronger influence on concentrations of Cd, Ni, and Zn and that DOC had the stronger influence on Cu concentration.

The addition of Ca to the soil system would be expected to lead to increasing solubility of heavy metals because of cation exchange reactions (i.e., the excess of Ca ions displacing heavy-metal ions from exchange sites). This would adequately explain the observed behavior of Cd, Ni, and Zn because increasing the equilibrium Ca concentration from 150 to 400 mg L^{-1} increased the solubility of these elements by factors of around 2, 1.3, and

Table 5. Ca adjustment experiment. Correlation coefficients of linear regression between metal and Ca and organic carbon concentrations in the equilibrium solution

Element	Ca	DOC
Cd	1.00 ^b	-0.83 ^a
Cr	-0.89 ^b	0.98 ^b
Cu	-0.92 ^b	0.98 ^b
Ni	0.99 ^b	-0.76 ^a
Pb	n.d.	n.d.
Zn	0.99 ^b	-0.78 ^a

Note: n.d.: Not determined.

^aSignificant ($p < 0.01$).

^bSignificant ($p < 0.001$).

1.5, respectively. However, the addition of Ca also led to a reduction in Cu solubility. Marked similarities between the trends observed in the solubility graphs of Cu and organic matter were found. Increasing the equilibrium Ca concentration from 150 to 400 mg L⁻¹ reduced the solubility of both organic matter and Cu by approximately the same factor (around 1.4). As was seen in the pH manipulation experiment, this again suggests that the solubility of organic matter controlled the solubility of Cu.

CONCLUSIONS

These experiments have shown that the solubility of organic matter in a sewage-sludge-amended soil has the potential to exert an influence on the solubilities of Cu, Ni, and Pb. All three of these elements have been shown previously to have a relatively high affinity for organic complexation either in soils generally (Cu and Pb) or specifically in sewage-sludge-amended soils (Ni). Thus, when organic-matter solubility increases, it is likely to result in (a) increased concentrations of these heavy metals in the soil solution and (b) increased concentrations of organically complexed forms of these metals in the soil solution. Although organic-matter solubility was manipulated artificially in these experiments, organic-matter solubility is known to fluctuate, both temporally and spatially, in the field. This is controlled by a number of factors. In the broadest sense, these factors can be considered as either soil-specific (e.g., native organic-matter content, clay mineralogy, abundance of certain cations and anions) or environmental (e.g., temperature, soil moisture content, rainfall, land use, and timing of inputs of organic material). Of these, the environmental variables are likely to be the most dynamic, and changes in these may potentially lead to significant, perhaps short-term, effects on DOM concentrations of the soil solution. In contrast, changes in the soil-specific variables are likely to occur over the longer term, resulting in slow, and perhaps less significant, changes in DOM concentrations. In either case, a cosolubilization of heavy metals such as Cu, Ni, and Pb, and the likely formation of organo-metal complexes, may lead to an enhanced potential for their migration and bioavailability.

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