MOBILIZATION OF Cu AND Zn IN CONTAMINATED SOIL BY NITRILOTRIACETIC ACID

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Abstract. Batch and upflow column leaching experiments were used to evaluate the nature and extent of Cu and Zn solubilization from contaminated soil by nitrilotriacetic acid (NTA) in 0.025 M $NaClO_4$. In batch soil suspensions, NTA levels of 10^{-5} to 10^{-3} M substantially promoted Cu and Zn release from the metal-enriched soil. The ability of NTA to enhance Cu and Zn solubility decreased with increasing solution acidity probably due to competitive binding of NTA by protons and Fe released by hydrous oxide dissolution. However, in the pH range typically encountered in northeastern U.S. soils, soluble metal levels were nearly constant for a given NTA concentration. Leaching soil columns with NTA solutions enhanced Cu release more than Zn, as the enrichment ratio (cumulative metal leached by NTA compared to the 0.025 M $NaClO_4$ control leachate) after 85 pore volumes displacements was 23.6 and 4.3 for Cu and Zn, respectively. While Cu release by 0.01 M $CaCl_2$ differed little from the control, 0.01 M $CaCl_2$ was substantially more effective than 10^{-5} M NTA in displacing bound Zn. The data reflect different retention mechanisms for Cu and Zn in this soil.

1. Introduction

Increasing emphasis on water quality has led to close scrutiny of the environmental effects of compounds used widely in our society. In the 1970's, when sodium tripolyphosphates (STPP) were suspected as contributors to accelerated eutrophication of natural aquatic systems, substitutes for STPP in detergent formulations were sought. Nitrilotriacetic acid (NTA) appeared to be the most promising alternative. Nitrilotriacetic acid is used in some European countries, and in 1981 comprised 15% by weight of detergents in Canada (Perry *et al.*, 1984).

Widespread use of NTA was viewed with concern for several reasons. Since NTA would inevitably be introduced into domestic sewage, its biodegradability and effect on wastewater treatment processes were investigated. Studies indicated NTA will be degraded in conventional wastewater treatment operations once microbial populations become acclimated to it (Stephenson *et al.*, 1983). However, because NTA is a strong, nonspecific metal complexing agent, it can inhibit precipitative removal of heavy metals from wastewaters (Snoeyink and Jenkins, 1980). The toxicological properties of NTA have also been of concern since the National Institute of Environmental Health in 1970 indicated that some metal-NTA complexes could produce mutagenic and teratogenic responses in mice (Hammond, 1971). Despite the potential adverse effects, in 1980 the Office of Toxic Substances decided to allow use of NTA if certain restrictions were followed (Perry *et al.*, 1984). An understanding of the fate of NTA in natural and

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man-made aquatic systems continues to be an area of investigation (Garnett *et al.*, 1986; Nieuwstad and van 't Hof, 1986).

The NTA-induced mobilization of metals from reservoir and riverine sediments has been widely explored (Chau and Shiomi, 1972; Banat *et al.*, 1974; Hrubec and van Delft, 1981). Kirk and coworkers (Kirk *et al.*, 1983; Garnett *et al.*, 1985) have studied the fate and effects of NTA in soil environments. In batch experiments, NTA was found to increase the solubility of Mn, Ni, Pb, and Zn in sludge/soil mixtures, although an opposite effect was noted for Cu (Garnett *et al.*, 1985). The influence of NTA on metal mobility in soils is not fully understood (Garnett *et al.*, 1985).

The growing preference for land-based waste disposal systems, calls for a thorough understanding of the impact of NTA on metal bioavailability and leaching in soils. In a recent study, Garnett *et al.* (1986) used soil columns to study the impact of NTA on metal leaching. The present investigation amplifies previous research by utilizing both batch and column studies and exploring a wide range of pH conditions. Solution data have also been correlated with the various modes of metal retention in the soil. Mechanisms based on solution and surface chemistry principles have been proposed to interpret the data.

2. Materials and Methods

The soil used in this study was a Mardin silt loam (coarse-loamy, mixed, mesic Typic Fragiochrept) that had elevated heavy metal levels from excessively high application rates of municipal sludge. Soil metal analysis was performed by atomic absorption spectrophotometry (AAS) following HNO_3–HCl digestion using a modified version of the USEPA (1983) method. Selected soil properties are given in Table I: additional information can be found in Johnson and Chu (1983). The soil was air dried and sieved to pass a 2 mm sieve.

Stock NTA solutions were prepared such that the leaching solutions had concentrations ranging from 10^{-5} to 10^{-3} M. Levels in this range are expected in wastewaters

TABLE I

Selected soil and NTA metal-binding properties

Exchangeable bases, cmol(+) kg^{-1}		Metal	Soil levels (mg kg^{-1})	NTA formation constant (log*K*)[a]
Ca	4.6	Cd	8.6	6.4
Mg	1.0	Cr	94.5	–
K	0.42	Cu	98.0	12.9
CEC, cmol(+) kg^{-1}	2.1	Ni	51.0	11.5
pH (1 : 1 water)	5.3	Pb	52.7	11.3
		Zn	225	10.7
		Fe	1.1%	15.9
		Ca	–	6.4

[a] Values for 25 °C and $I = 0.1$ from Martell and Smith (1976).

from communities using NTA-based detergents (Stoveland *et al.*, 1980). Batch experiments were performed by combining appropriate amounts of NTA and $NaClO_4$ electrolyte solutions in 125 mL polyethylene bottles and diluting with distilled water to 100 mL total volume. The background electrolyte was 0.025 M $NaClO_4$. One gram of soil was added prior to pH adjustment with 0.1 or 1.0 M $HClO_4$ and NaOH. Samples were agitated at room temperature (near 25 °C) for 24 hr. The final equilibrium pH was recorded and a portion of the sample centrifuged for 15 min at 1500 rpm to remove the soil prior to metal analysis using AAS.

Soil leaching experiments were performed using Plexiglas columns (15 cm x 5 cm ID) designed and packed following the methods of Fuller (1982). A peristaltic pump was used to convey solutions from the bottom to the top of the column against gravity and into a fraction collector. Column flow rate was initially adjusted to $0.011\ \mathrm{kg\,m^{-2}\,s^{-1}}$. The leaching solutions were 10^{-5} or 10^{-4} M NTA with a 0.025 M $NaClO_4$ background electrolyte at pH 5.6. The fractions collected were analyzed for pH and then acidified with 3 M HNO_3 prior to metal analysis.

3. Results and Discussion

The influence of 10^{-5} to 10^{-3} M NTA on the solubilization of Cu and Zn in batch adsorption experiments is shown in Figures 1 and 2, respectively, for a range of pH conditions. The NTA caused a substantial increase in solution levels of both metals.

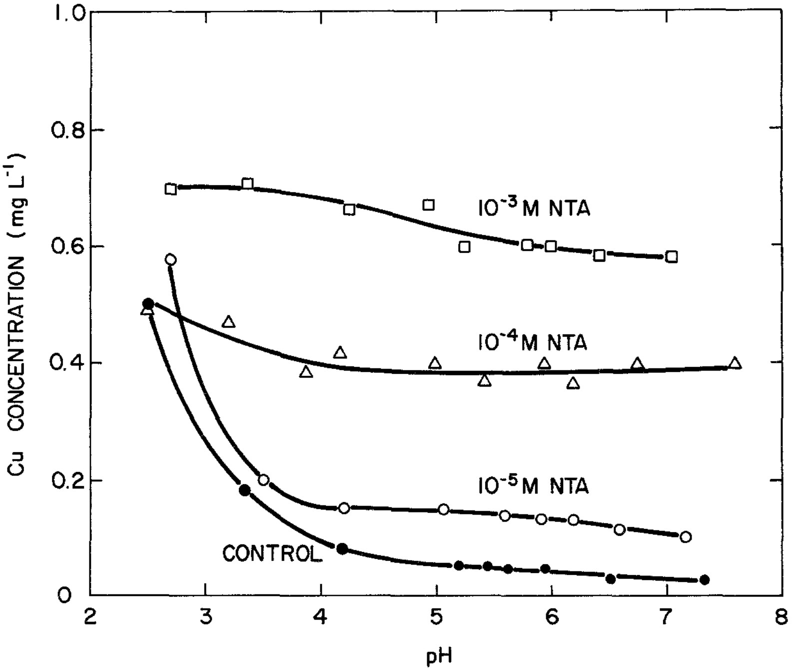

Fig. 1. Effect of pH and solution NTA levels on Cu extracted from the contaminated soil using batch equilibration experiments.

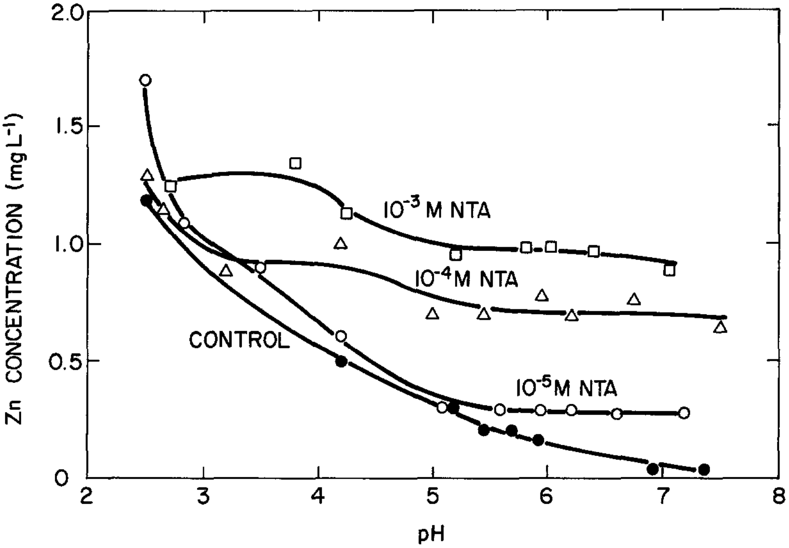

Fig. 2. Effect of pH and solution NTA levels on Zn extracted from the contaminated soil using batch equilibration experiments.

This ability to promote metal release is not surprising since chelating agents like NTA, ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA) form stable, water soluble metal complexes and have been used as extractants to estimate the biological and physicochemical availability of elements (Lindsay and Norvell, 1978).

The effect of solution pH was similar for both Cu and Zn (Figures 1 and 2). In the pH range typically encountered for soils in the northeastern U.S., levels of Cu and Zn in solution were nearly invariant for a given NTA concentration. For the more acid conditions (Figures 1 and 2), metal levels increased with decreasing pH. When the pH was substantially reduced, the data tended to converge, indicating a progressively smaller impact of NTA on solubility. Since protons compete with metal ions for NTA coordination, lowering the system pH reduced the metal extracting efficiency of NTA. Similar reasoning was given for the decreasing ability of NTA to inhibit Cd adsorption on soils as the solution pH was lowered (Elliott and Denneny, 1982).

To investigate metal leaching from soils in contact with NTA solutions, soil column experiments were performed. Figures 3 and 4 show the cumulative amounts of Cu and Zn leached by 10^{-4} and 10^{-5} M NTA solutions. As expected from the batch data in Figures 1 and 2, the quantity of metal leached increased with increasing NTA concentration. The extent to which NTA enhanced solubilization differed for Cu and Zn. For comparison, the enrichment ratio (R_e) has been defined as the ratio of the cumulative concentration leached by the extracting solution to that of the control solution (0.025 M $NaClO_4$ at pH 5.6). The NTA stimulated greater relative increase in Cu release compared to Zn, as indicated by R_e values of 23.6 and 4.3, respectively, for the

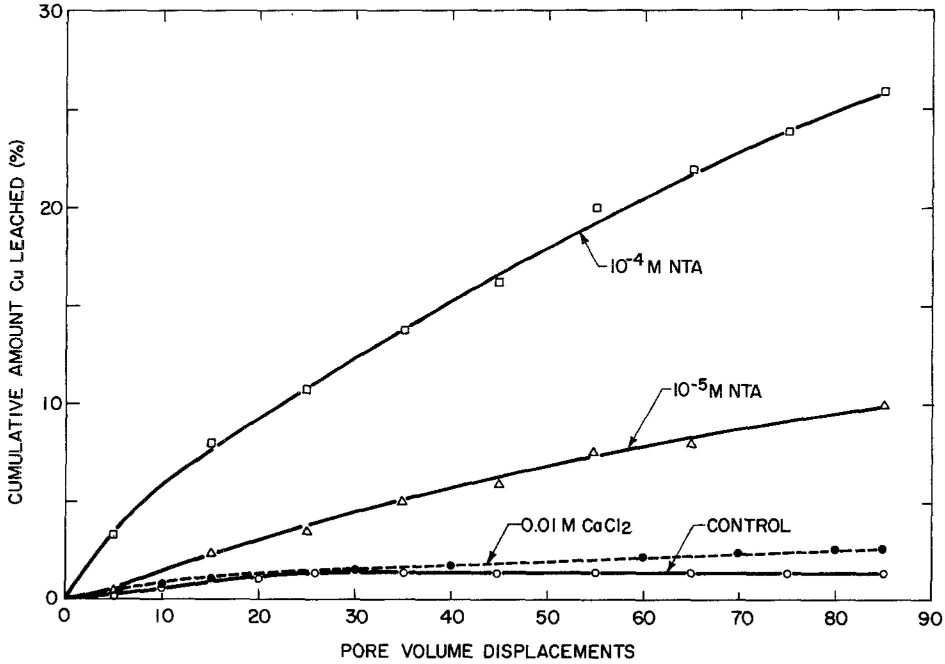

Fig. 3. Effect of NTA and $CaCl_2$ solutions on cumulative Cu efflux from soil columns. Metal release is reported as percent of total sorbed metal levels (Table I).

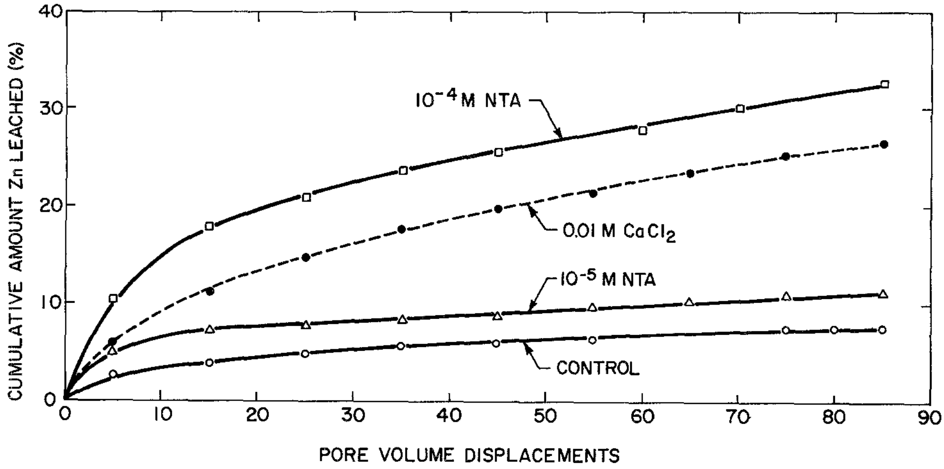

Fig. 4. Effect of NTA and $CaCl_2$ solutions on cumulative Zn efflux from soil columns. Metal release is reported as percent of total sorbed metal levels (Table I).

10^{-4} M NTA systems at 85 pore volume displacements. The NTA should bind Cu in preference to Zn (Table I), thus causing a proportionally greater increase in Cu release.

Solution chemistry principles alone, however, are insufficient to fully describe the differences in Cu and Zn extractability. Techniques developed to extract metals from minerals, sediments, and soils have confirmed the existence of different binding forms of metals (Pickering, 1986). Because metals exist in a variety of retention modes, the extent and rate at which they are released differs.

Sequential extraction schemes can be employed to obtain an overall picture of the partitioning of metals among various fractions. Such procedures solubilize different metal fractions by extraction with the least aggressive reagents (e.g., water) and proceeding through several steps to total HF-digestion of silicates. Because the objective in each step is to selectively displace a given elemental form while minimizing solubilization other fractions, reagent ordering is critical (Miller *et al.*, 1986). Although close correlation to environmentally-relevant processes (bioavailability, leaching) may not always be achieved, these sequential extraction procedures should help interpret these data.

The sequential extraction method of Miller *et al.* (1986) was used to characterize Cu and Zn in this polluted soil. The operationally-defined fractions of Cu and Zn identified by this nine-step procedure are shown in Table II. Although sequential extraction procedures vary in the number of fractions evaluated, it is conceptually convenient to consider two broad categories, distinguished by whether solid phase dissolution is required to effect metal release. Metals that are displaceable without substrate dissolution are termed 'adsorbed' (Miller *et al.*, 1986) or 'non-detrital' (Gad and LeRiche, 1966). This fraction seems to include water soluble, exchangeable, specifically and physically sorbed and, arguably, organically bound metals.

TABLE II

Distribution of metals in the soil[a]

Fraction	Percent of total metal	
	Cu	Zn
Soluble	0.8	1.7
Exchangeable (neutral salt)	8.3	16.4
Pb-displaceable	14.3	7.6
Acid soluble	18.2	7.7
Organically bound	3.3	1.3
Mn-oxide occluded	9.1	6.3
Amorphous Fe oxide occluded	5.4	6.9
Crystalline Fe oxide occluded	9.4	22.5
Residual	31.3	29.5

[a] Using the sequential extraction methodology of Miller *et al.* (1986). Note that the procedure is ordered to solubilize Mn-oxide occluded metals before determining organically-bound metals.

The release of non-detrital metals can be viewed simply in terms of a solution coordination reaction. Consider an exchangeable divalent metal ion (Me^{2+}) partitioned at equilibrium between the soil solution and reactive soil surface (S) sites:

$$S - \mathrm{Me} + \mathrm{A}^{2+} \rightleftharpoons S - \mathrm{A} + \mathrm{Me}^{2+} . \qquad (1)$$

When NTA, existing predominantly as the HNTA^{2-} species in the pH 3 to 9 range, is added to the system, the activity of Me^{2+} in solution is reduced through complexation

$$\mathrm{Me}^{2+} + \mathrm{HNTA}^{2-} \rightleftharpoons \mathrm{MeNTA}^{-}(\mathrm{aq}) + \mathrm{H}^{+} \tag{2}$$

causing further displacement of metal ions into solution. The overall reaction should be moderately fast and limited by the surficial exchange rate (Equation (1)). Ostensibly, plant available trace elements are largely non-detrital, and tests to evaluate soil micronutrient status have relatively short extraction periods, typically 2 hr (Lindsay and Norvell, 1978).

Metals requiring solid phase dissolution for release into solution are called 'detrital' (Gad and LeRiche, 1966) or 'structural' metals (Miller *et al.*, 1986). The detrital fraction seems to include metals present as precipitated compounds (e.g., hydroxides, carbonates, sulfides) and bounds to Fe/Mn oxides through occlusion, chemisorption, or coprecipitation. There is considerable evidence to suggest that a substantial portion of the total soil metals is associated with the hydrous oxide fraction of a soil (LeRiche and Weir, 1963). Oxides or Fe and Mn can 'scavenge' trace metals from solution thereby serving as an effective sink for fixation by soils and sediments (Jenne, 1968). Indeed, in this soil more than half of the total Cu and Zn was present in nonlabile fractions (Table II).

While a reaction scheme similar to Equations (1) and (2) can be visualized for release of detrital metals from the soil by NTA, a surface coordination reaction is also possible. Conceptually, the NTA enters into a surface complexation reaction which is then followed by detachment of the metal-NTA complex into solution:

$$\begin{array}{rcl} S - \mathrm{MeOH} + \mathrm{HNTA}^{2-} & \rightleftharpoons & S - \mathrm{MeNTA}^{2-} + \mathrm{H_2O} \\ & & \Big| \\ & & \mathrm{MeNTA}^{-}(\mathrm{aq})\,. \end{array} \tag{3}$$

According to Chang and Matijevic (1983), dissolution of hematite by NTA follows a reaction mechanism of this type. Detachment of the surface complex and release into solution require sufficient energy to break lattice bonds. The overall reaction should, therefore, be temperature sensitive, as indicated by the dramatic enhancement of Fe leaching from hematite by 0.1 M NTA when the temperature was raised from 25 to 100 °C (Chang and Matijevic, 1983).

The above mechanistic description assumes that Cu and Zn are mobilized as 1 : 1 metal-NTA complexes. The recent work of Garnett *et al.* (1986), however, suggests the leaching process may be more complex. The substantial retention of NTA by soils (Kirk *et al.*, 1983) resulted in molar concentrations of NTA in the leachate significantly below stoichiometric amounts (Garnett *et al.*, 1986). Metal transport via complexation by intermediate products resulting from NTA biodegradation (e.g., iminodiacetic acid) has been offered as an explanation for this behavior (Garnett *et al.*, 1986). Since NTA biodegradation requires an acclimation period ranging from a few days to several weeks

(Hrubec and van Delft, 1981; Nieuwstad and van 't Hof, 1986) it may play a subordinate role in the short-term experiments reported in this study.

Certain features of the data in Figures 3 and 4 suggest fundamentally different retention modes for the easily mobile fractions of Cu and Zn. The release of Cu by 0.01 M $CaCl_2$ deviated only slightly from that by 0.025 M $NaClO_4$. In contrast, the $CaCl_2$ was significantly more effective than 10^{-5} M NTA in releasing soil Zn. A relatively low Cu release by chloride salts has been previously documented. McLaren and Crawford (1973) found the 0.05 M $CaCl_2$ extracted only about 1% of the total soil Cu. Magnesium, Ca, and Na chloride solutions released little of the Cu pre-adsorbed on Fe(III) hydrous oxide suspensions (Slavek and Pickering, 1986).

Differences in metal displacement by chloride salts are often attributed to chloro-complex formation. Sauerbeck and Rietz (1983) state that Ca and Mg chloride solutions much more effectively extract Cd than Zn because of the formation of Cd chloro-complexes. This explanation is appropriate when one metal forms stable chloro-complexes (e.g., Hg, Cd, Pb), however, this condition is not fulfilled in the present study. The stability constants (adjusted to $I = 0.025$) for the formation of $CuCl^+$ ($\log K = -0.27$) and $ZnCl^+$ ($\log K = 0.13$) are essentially equal. Thus, chloride binding is of minor consequence in the differential partitioning of Cd and Zn between the soil and solution phases.

The different leaching behaviors of Cu and Zn can be more readily accounted for by variations in their mode of occurrence in the contaminated soil. As Table II shows, on a percentage basis twice as much Zn compared to Cu exists in the soluble and neutral salt exchangeable fractions. Metals in these forms tend to be rapidly released when contacted with solutions. Note the much steeper initial slopes in the Zn release data (Figure 4) compared to the Cu behavior (Figure 3). Biddappa *et al.* (1981) also noted that more Zn was readily exchangeable or water soluble whereas Cu was present largely in nonextractable forms.

The observed increase in soluble metal levels with NTA concentration are consistent with Ni, Pb, and Zn release from soil/sludge mixtures reported by Garnett *et al.* (1985). However, Garnett *et al.* (1985) found that increasing the NTA concentration from 0 to 0.212 mmol L^{-1} had little effect on Cu solubilization in one soil/sludge system and caused a sharp drop in soluble Cu for another system. These findings are at variance with the data reported herein (Figures 1 and 3) and predictions based on the high stability of the Cu-NTA complex (Table I). While it has been reported previously (Elliott and Huang, 1979) that increasing NTA levels can enhance adsorption of Cu, the adsorbent was Al_2O_3 which carries a net positive surface charge below pH 9. Since most soils are negatively charged over a wide pH range (Elliott and Denneny, 1982), and at a given pH the magnitude of the negative surface charge varies directly with soil organic matter content (van Raij and Peech, 1972) one would expect most sludge-amended soils to be negatively charged. Thus, electrostatic adsorption of $CuNTA^-$ onto an electropositive surface would be an unlikely explanation for the Cu data of Garnett *et al.* (1985). Intuitively, a reduction in soluble Cu with addition of NTA would not be expected for most soils.

While a reduction in soluble Cu with NTA addition would seem improbable for most soils, it demonstrates the complexity of such systems and the inability to make predictions which are universally applicable. Competitive binding of NTA by other cations is one complicating factor. It has been suggested that a high Ca content in calcareous soils might result in sufficient Ca-NTA formation to reduce complexation of trace metals (Garnett *et al.*, 1985). Substantial complexation by Ca would presumably result from its high concentration relative to the heavy metals, inasmuch as Ca forms weaker NTA complexes (Table I). Perhaps of greater importance is the competitive effect of dissolved Fe on the mobilization of heavy metals. The soil used in this study contains about 1.1% Fe, far in excess of the Cu and Zn levels. Furthermore, Fe(III) forms more stable NTA complexes than most trace metals (Table I). Since complexing agents like NTA are capable of solubilizing both amorphous (Borggaard, 1979) and crystalline (Chang and Matijevic, 1983) Fe oxides, released Fe^{3+} could conceivably outcompete heavy metals for NTA binding. There is, however, some evidence to suggest the NTA-induced dissolution of Fe oxides may be kinetically limited at low (25 °C) temperatures (Chang and Matijevic, 1983). Similarly, Borggaard (1979) reported Fe oxide dissolution by dilute EDTA solutions required 3 mo for complete reaction. The importance of soluble Fe in influencing short-term leaching experiments has not been clarified and is currently a topic of study.

4. Conclusions

Since NTA is a strong, rather nonspecific complexing agent, it is capable of significantly modifying the partitioning of trace metals between the soil surface and solution phases. Levels that might exist in wastewaters where NTA-based detergents are widely used would be expected to enhance desorption of trace metals from polluted soil. Land disposal of wastes containing NTA would likely increase bioavailability and leaching potential of trace metals. Once formed, metal NTA complexes will be quite resistant to biodegradation (Chau and Shiomi, 1972). Although metal solubilization was progressively enhanced with increasing NTA concentrations, it was insensitive to solution pH for slightly acid to circumneutral conditions.

Differences in the desorption behaviors of Cu and Zn arise from alternate metal retention modes within contaminated soils. In the soil studied, a larger proportion of Zn was present in a readily exchangeable form so that leaching with 0.01 M $CaCl_2$ substantially enhanced Zn release. In contrast, NTA had a greater effect on Cu than Zn release, probably because of the more stable Cu-NTA complex. The results underscore the need to understand both the metal solution chemistries and the metal distribution among various modes of fixation within the soil in evaluating the impact of NTA on metal solubilization in soils.

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