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Zinc and Cadmium Solubility Controls in Arid-Zone Soils

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Title

ZINC AND CADMIUM SOLUBILITY CONTROLS IN ARID-ZONE SOILS

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C. EXTENDED ABSTRACT

Zinc and Cd are heavy metals that are increasingly employed in industry. Although Zn is essential for life processes, both elements are recognized as soil pollutants, especially cadmium whose half-life in humans ranges from 10 to 30 years. Even small amounts are harmful to humans. This project examined the solid-phase controls of these two metals in soils.

Chelation methods were used to measure Zn^{2+} activity in both normal and polluted soils. These methods avoid errors in measuring metal activities caused by natural organic-metal complexes. Measured Zn^{2+} activities showed a strong pH dependency described by the reaction: $\log (\text{Zn}^{2+}) = 5.8 - 2\text{pH}$, which is near the solubility of ZnFe_2O_4 (franklinite) in equilibrium with soil-Fe. Synthetic franklinite was prepared in the laboratory and its solubility was measured along with that of a natural franklinite. Solubility studies strongly support the hypothesis that franklinite may indeed control the solubility of Zn in normal arid-zone soils. The chelation method was also used to measure the activity of Fe^{3+} because both Fe and Zn are components in franklinite. In contaminated soils Zn solubility was much higher and appeared to be controlled by Zn_2SiO_4 and/or ZnCO_3 .

Two methods of measuring Cd^{2+} activity in soils were examined in this study. These included the competitive chelation method and the addition method utilizing the Cd^{2+} ion-selective

electrode (Cd-ISE). Analyses of 36 non-polluted soils from Israel using the Cd-ISE showed that Cd^{2+} activity was in the range of $<10^{-9}$ to $10^{-7.2}$ M and was independent of pH in the range of 6.8 to 8.4. It appears that adsorption reactions control the solution activity of Cd^{2+} in this group of soils. An adsorption model predicting cation binding to charged surfaces was coupled with a sub-routine for solution complexation and was used to predict Cd adsorption to montmorillonite in the presence of various anions. Agreement was found in the case of Cl^- and ClO_4^- , but CdHCO_3^+ was adsorbed more tightly possibly due to the surface precipitation of CdCO_3 .

A chelation method involving the chelating agent DTPA and Pb^{2+} as the counter ion was used to measure Cd^{2+} activity in several Colorado soils. Eight soils ranging in pH from 7.15 to 8.25 showed Cd^{2+} activities ranging from $10^{-6.6}$ to $10^{-9.4}$ and could be predicted from the equation: $(\text{Cd}^{2+}) = 10^{7.61}(\text{H}^+)^2$, which we designate soil-Cd solubility. This solubility of Cd^{2+} is approximately 100-fold less than that in equilibrium with CdCO_3 and atmospheric CO_2 . An addition 7 soils showed very similar Cd^{2+} solubility relationships. For 10 polluted soils that were examined, the Cd^{2+} activities were above the soil-Cd solubility, and a few soils showed equilibrium with CdCO_3 .

A method for partitioning trace metals among solid-phase components of soils has been optimized. The transformations of Cd among solid-phase components of two soils from Israel amended

with soluble Cd to 0.1, 1.0, and 10.0 mg/kg were followed with time after addition. The soils tended to return to the "equilibrium" distribution of the non-amended soil. The rate of attainment of equilibrium depended on the moisture content of the soils. Equilibrium was attained within a few days (8-26) when the soils were saturated, and more than a year when the soils were incubated at field capacity. The availability of Cd to plants may be affected by these slow transformations of added Cd.

D. OBJECTIVES

The overall objectives of this project were to identify and characterize the solid-phase controls of Zn^{2+} and Cd^{2+} in arid-zone soils. Both native and polluted soils were included in this study. Knowledge of these solubility relationships can be used to predict Zn and Cd availabilities to plants and toxicities of these metals in the human food chain.

E. BODY OF THE REPORT

The body of this report consists of 13 separate scientific reports. Four of these reports have been published in refereed journals and reprints of these papers are included. The other nine reports are in various stages of publication and are scheduled to be published within the next two years.

The first five reports deal with the solubility measurement of Zn in normal and in contaminated soils using chelation methods. Franklinite was prepared, characterized, and reacted with soils to clarify its role in controlling Zn^{2+} in soils. Since Fe is a component in this mineral, its solubility was also examined in both mineral systems and in soils.

The next six reports deal with the solubility measurements of Cd in soils. Included are studies on Cd speciation in soil solution, adsorption Cd on to montmorillonite, and the measurement of Cd^{2+} activities in a number of soils from Israel and from Colorado. Two methods were used: the first was the addition method which utilized a Cd ion selective electrode to measure Cd^{2+} activity, and the second was the chelation method which utilized DTPA and Pb^{2+} as the counter ion.

The final two reports deal with a sequential dissolution, differential IR and XRD spectroscopy procedure for determining the solid phases in which various metals are held in soils. This method was used on two soils to which Cd additions had been made. The 13 separate scientific reports follow.

2. MEASUREMENTS OF FREE Zn^{2+} ACTIVITIES IN NORMAL AND CONTAMINATED SOILS USING CHELATION

Qiyang Ma and W. L. Lindsay

ABSTRACT

Measurement of free Zn^{2+} activities is important for understanding the mechanisms controlling Zn^{2+} solubility in soils. The free Zn^{2+} activities were measured in 12 normal soils and 8 contaminated soils using the chelation method. The measured Zn^{2+} activities ranged from $10^{-9.97}$ to $10^{-6.49}$ M for the normal soils, and $10^{-8.11}$ to $10^{-2.26}$ M for the contaminated soils. They are inversely related to soil pH, with a correlation coefficient of 0.96 for the normal soils and 0.89 for the contaminated soils. The measured Zn^{2+} activities and pH for the normal soils can be expressed as follows: $\log (\text{Zn}^{2+}) = (5.9 \pm 0.24) - 2 \text{ pH}$. The solid phases that govern Zn activities in the normal soils is not clear, but the measured Zn^{2+} activities are very near that of soil-Zn reported previously and near the solubility of ZnFe_2O_4 (franklinite). The precipitation and dissolution of Zn_2SiO_4 or ZnCO_3 appears to control Zn solubility in the contaminated soils. Different solid phases may control Zn solubility in different soils depending on the sources of contamination.

INTRODUCTION

The determination of free Zn^{2+} activities in soils is of importance in examining the mechanisms controlling Zn^{2+} solubilities in soils. Zinc has received considerable attention for its role both as an essential micronutrient and as a pollutant (Lindsay, 1972).

Numerous studies have been carried out to study Zn from the perspective of adsorption-desorption. These studies were conducted in different types of soils including acid soils (Kuo and Baker, 1980; and McBride and Blasiak, 1979), calcareous soils (Patil and Deshpande, 1981; and Udo et al., 1970), and alkaline soils (Singh and Sekhon, 1977; and Kuo and Mikkelsen, 1979). Zinc adsorption is known to be pH-dependent (Xie and MacKenzie, 1988; Sanders, 1983; Bar-Yosef, 1979; and Bar-Tal et al., 1988) and is related to the CEC of soils (Shukla et al., 1980). Soil properties including organic matter, CaCO_3 and clay content (Bar-Tal et al., 1988; Raikhy and Takkar, 1983; and Tillier et al., 1984), solution composition (Elrashidi and O'Connor, 1982) and P fertilization (Xie and MacKenzie, 1990; and Rayar, 1981) also play an important role in influencing Zn adsorption-desorption reactions. Clay minerals (Puls and Bohn, 1988; Tillier et al., 1984; and Cavallaro and McBride, 1984), sesquioxides (Forbes et al., 1976; Kalabasi and Racz, 1978; Kalbasi et al., 1978; and Zasoski and Burau, 1988), carbonates (Udo et al., 1970), and soil organic matter (Bar-Tal et al., 1988) have been suggested as constituents involved in the adsorption or precipitation of

applied Zn in soils. Barrow and Ellis (1986a,b) and Barrow (1986 a,b, and c) used a mechanistic model to describe Zn retention by soils under different pH and temperature conditions. Both physisorption (ion exchange) (Shuman, 1975) and chemisorption (covalently bonded) (McBride and Blasiak, 1979) were suggested as adsorption mechanisms. To date, the Zn species in solution which are adsorbed by soils are still not clearly understood despite intensive studies of the mechanisms and constituents involved in Zn adsorption.

Understanding the various chemical fractions of Zn is important to determine which fractions regulate Zn solubility in soils. There are many studies conducted to determine Zn fraction distributions (Neilsen et al., 1986; Ghanem and Mikkelsen, 1987; Nasseem and Roszyk, 1978; Mukhopadhyay and Gupta, 1980; and Mandal and Mandal, 1986). Zinc was usually partitioned into five operationally defined fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual (Hickey and Kittrick, 1984). According to Liang et al. (1990), Zn in residual mineral fraction is the most important form (86%), and only 2% Zn present as exchangeable form. In soils contaminated with heavy metals, the majority of Zn was associated with Fe-Mn oxides (39%), which agrees with the observations of Gupta and Chen (1975), Elsokkary and Lag (1978), White (1957), and Tessler et al. (1980). The carbonate fraction was the next important Zn fraction (28%) (Hickey and Kittrick, 1984). While in soils treated with sewage sludge, carbonate and organically bound Zn (58% and 28%) are important fractions.

These studies suggest that different Zn minerals may be important solid phases controlling Zn solubility in different soils.

The Zn^{2+} solubility in soils is determined by the simultaneous equilibria of several competing reactions such as chemical bonding, solid phase precipitation, and solid and solution phase chelation of Zn^{2+} . Precipitation mechanisms have been dismissed as the Zn minerals are too soluble to exist in the normal soil pH range ($\text{pH} < 8$). Recently, several studies showed that precipitation can play an important role in regulating Zn concentration in soils, especially in soils with high pH and high Zn concentrations (Ma and Lindsay, 1990; and Singh, 1982).

When Zn activity in soil solution exceeds the equilibrium concentration of a Zn mineral, that mineral can precipitate. Conversely, whenever Zn in soil solution drops below the equilibrium solubility of a Zn solid phase, that solid phase can dissolve (Lindsay, 1972). In case of soils with high pH, exchangeable Zn^{2+} fraction is extremely small compared to that of exchangeable Ca^{2+} and Mg^{2+} , though it can be important in acid soils. This suggests that the adsorption-desorption mechanism may not be important in soils of high pH. Unfortunately, many of the Zn minerals in soils have not been widely examined or well characterized. Direct Zn^{2+} activity measurements were carried out by only a few authors (Ma and Lindsay, 1990; Singh, 1982; Norvell and Lindsay, 1969; and Norvell et al., 1987), and there has been no such measurements in contaminated soils.

This study was undertaken to: 1) determine Zn^{2+} activities in both normal and contaminated soils using chelation; 2) compare the measured Zn^{2+} solubilities to those of known Zn minerals; and 3) discuss the mechanisms controlling Zn activities in these soils.

MATERIALS AND METHODS

Twelve normal soils and eight contaminated soils were collected from Colorado. Some of the characteristics of these soil samples are summarized in Tables 2.1 and 2.2. The soil samples were air-dried, passed through a 1-mm stainless steel sieve, and stored in polyethylene-lined containers. The contaminated soils were collected from three different places, and a description of each place is given below:

Aspen Soil: The site is located near Aspen, Colorado. The soil was contaminated through silver mining. Silver was mined both as argentite (Ag_2S) and elemental silver. Other ores associated with the mineral deposits include galena (PbS), pyrite (FeS_2), sphalerite (ZnS), smithsonite (ZnCO_3), cerussite (PbCO_3), siderite (FeCO_3), and barite (BaSO_4) (Volin and Hild, 1950). The soil, thus contained high levels of Pb, Zn, and possibly Fe (Volin and Hild, 1950).

Leadville Soils: This site is near Leadville, Colorado. The soils were contaminated through acid mine drainage and tailings. The ores in the geologic deposits beneath Leadville are rich in As, Pb, and Fe sulfides. The soils contained high levels of Al, Cu, Zn, Cd, and Pb (Williams, 1975).

Table 2.1 Properties of the uncontaminated soils used in this study

Soil series	Texture	pH*	AB-DTPA		lime content
			Zn	Fe	
			----- μ M-----		
Amherst	Clay loam	6.48	0.49	5.19	1 [#]
Willard	Sandy loam	6.59	0.28	5.54	l
Punkin Center	Sandy loam	6.55	0.29	11.4	l
Eads	Clay loam	7.83	0.28	4.03	vh
Lamar	Silt loam	7.94	0.32	3.42	vh
Sheridan Lake	Clay loam	7.61	0.28	5.54	l
Walsh	Clay loam	7.92	0.45	4.34	h
Genoa	Clay loam	6.79	0.51	8.06	m
New Ramyer	Clay loam	6.95	0.29	4.41	l
Burlington	Silt loam	6.70	0.78	5.99	l
Bennett	Silt loam	7.03	0.59	9.36	h
Castle	Silt loam	7.90	1.90	----	m

* Measured in 1:2 soil:water suspension after 24 h.

l-low, m-medium, h-high, and vh-very high.

Table 2.2 Properties of the contaminated soils used in this study

Soil series	Classification	pH [*]	CaCO ₃
Aspen	NA [#]	8.15	<0.1
Leadville-1	Histic cryaquolls	6.95	<0.1
Leadville-2	Histic cryaquolls	6.85	<0.1
Leadville-3	Typic cryaquolls	6.75	<0.1
Globeville-1	NA	6.65	0.3
Globeville-2	NA	8.15	4.2
Globeville-3	NA	7.75	0.2
Globeville-4	NA	7.30	<0.1
5 NA		6.35	<0.1

* Measured in 1:2 soil:water suspension after 24 h.

Not available for they were disturbed soils.

Globeville Soils: This site is in Denver, Colorado. The soils were contaminated through mining of Ag, Au, Cd, and Pb. Many contaminants were discharged through the refinery smokestacks. The soils contained high levels of Pb, Cd, Zn, and As (Booth, 1989; and Gottlieb, 1989).

In the present study, DTPA was chosen as the chelate and Pb²⁺ as the competing cation. Reagent-grade DTPA was used to prepare metal DTPA solutions. Zn- or Pb-DTPA solutions were prepared by adding 400 μM ZnCl₂, or Pb(NO₃)₂ to 400 μM DTPA solutions. When all the Zn or Pb in solution had reacted with DTPA, the solution pH was near 3.1. The pH of solutions were

then adjusted to pH 7 after 12 h reaction. The solutions were stirred for another 12 h to make certain that all the Zn or Pb was chelated with DTPA, then adjusted pH to 7 using dilute $\text{Ca}(\text{OH})_2$.

The suspensions consisting of 15 ml of deionized water and 10 g of soil were first shaken for 1 d. For the uncontaminated soils, 0.02 g PbCO_3 was added to maintain a controlled Pb^{2+} activity. For the contaminated soils, 0.12 g PbCO_3 was added since these soils contained high levels of heavy metals which could interact with PbCO_3 . Sufficient PbCO_3 was added to ensure that enough PbCO_3 was present to control Pb^{2+} activity. Although it is possible for PbSO_4 to form in soils of pH below than 7, there was sufficient PbCO_3 present to precipitate all the SO_4^{2-} and still have some left to control the Pb^{2+} activity in these soils.

After 1 d shaking, 5 ml of DTPA solutions of different Zn mole fraction (MF) ($[\text{ZnL}^{3-}]/([\text{ZnL}^{3-}] + [\text{PbL}^3])$) were added and the solutions were then shaken for another 4 d. Preliminary experiments showed these reaction periods to be adequate to obtain measurable changes in chelated metal concentrations. All soil suspensions contained 10 g of soil and a final volume of 20 ml chelate solution. The soil suspensions were aerated and shaken continuously on a rotational shaker at room temperature of 24-26°C. The initial DTPA concentration was 100 μM for all soils. In addition, deionized distilled water with soil was used as the blank treatment.

The suspensions were centrifuged at 15,000 g for 30 min at the end of each reaction period, and the clear supernatants were filtered through Whatman No. 42 paper. When necessary, a 0.2 μm membrane filter was used to ensure clear filtrates. The filtrates were then analyzed for cations by inductively-coupled plasma atomic emission spectrometry. The pH of filtrates was measured with a combination glass electrode and electrical conductivity was measured using a Yellow Springs Model 35 conductivity meter.

Preliminary experiments were performed to determine the initial Zn MF range for each soil. Generally speaking, small initial Zn MF ranges (0-0.05) were used for uncontaminated soils and larger initial Zn MF ranges (0-1) were used for contaminated soils.

The following reactions describe the competition between Zn^{2+} and Pb^{2+} for the DTPA ligand, "L".

Rearranging combined Eq. 4 and specifying $\text{CO}_2(\text{g})$ as 0.003 atm. gives:

$$(\text{Zn}^{2+}) = \frac{(\text{ZnL}^{3-})}{(\text{PbL}^{3-})} \cdot 10^{(8.54 - 2 \text{ pH})} \quad (5)$$

Since the activity coefficient of ZnL^{3-} and PbL^{3-} are equal, the above equation can be written as follows:

$$(\text{Zn}^{2+}) = \frac{[\text{ZnL}^{3-}]}{[\text{PbL}^{3-}]} \cdot 10^{(8.54 - 2 \text{ pH})} \quad (6)$$

The ratio of $[\text{ZnL}^{3-}]/[\text{PbL}^{3-}]$ needed to solve Eq. 6 was calculated from the measured equilibrium value of $[\text{ZnL}^{3-}]/([\text{ZnL}^{3-}] + [\text{PbL}^{3-}])$, which is defined as the Zn MF. This value was obtained from the graphs relating the initial and final Zn MF of each soil. A typical example for the Leadville-3 soil is given in Figure 2.1. Similar graphs were obtained for other soils. The equilibrium Zn MF's were smaller for the uncontaminated soils than for the contaminated soils. A detailed description of the method is given by Ma and Lindsay (1990).

Water extractable Zn was obtained by shaking soil suspensions of 1:2 soil to water ratio for 3 d. Zinc concentrations in 0.25 M DTPA extracts were obtained by shaking soil suspensions for 1 d. Zinc concentrations in the extracts were determined by ICP. Different soil to water ratios were used in 0.25 M DTPA extracts, they were 1:20 for Globeville-1, -2 and -3, and Leadville-3 soils, 1:10 for Aspen and Leadville-1 and -2 soils, and 1:5 for Globeville-4 and -5 soils (Table 3.1). The procedure for obtaining Zn concentration in HClO_4 digests was described by Workman et al. (1991).

Fig. 2.1 Equilibrium Zn MF in the Globeville-3 soil

RESULTS AND DISCUSSION

The Zn concentrations in 2:1 water, AB-DTPA, 0.25 M DTPA extracts, and HClO₄ digests are presented in Table 2.3. The Zn concentrations in 2:1 water extract were relatively low, except in Leadville-3 and Globeville-1 soils. They ranged from 0.006 to 4.58 µg/g, suggesting that Zn in these soils was not water soluble. The AB-DTPA extractable Zn concentrations in these soils ranged from 10.5 to 627 µg/g. The Zn concentrations

Table 2.3 Zinc concentration in 2:1 water, 0.25 M DTPA, AB-DTPA extracts and HClO₄ digests

Soil	2:1 water	AB-DTPA	0.25 M DTPA	HClO ₄ digest
	-----µg/g-----			
Aspen	0.92	627	5300	
Leadville-1	0.42	532	1090	1660
Leadville-2	0.51	333	504	1250
Leadville-3	4.58	529	5060	8990
Globeville-1	3.83	425	212	2640
Globeville-2	0.006	10.5	25.0	94.5
Globeville-3	0.061	128	952	421
Globeville-4	0.625	34.6	64.0	166

in 0.25 M DTPA extracts ranged from 25 to 5300 µg/g, which were between those in AB-DTPA extracts and HClO₄ digests. The Zn concentrations in HClO₄ digests were high, ranging from 94.5 to 8995 µg/g. In the Leadville-1 soil, Zn solubility in water was 0.92 µg/g, while it was 532, 1092, and 1659 µg/g in AB-DTPA, 0.25

M DTPA extract, and HClO_4 digests, respectively. On other hand, the Golbeville-1 soil showed $3.83 \mu\text{g/g}$ of water soluble Zn, while Zn in AB-DTPA, 0.25 M DTPA extract, and HClO_4 digests were only 425, 212, $2642 \mu\text{g/g}$. The results suggest that water soluble Zn and Zn in AB-DTPA, 0.25 M DTPA extracts and HClO_4 digests were not related.

Measured pH and EC values, initial Zn MF range, equilibrium Zn MF, and measured Zn^{2+} activities in uncontaminated and contaminated soils are summarized in Table 2.4 and Table 2.5, respectively.

Table 2.4 Measured pH, equilibrium Zn MF and Zn^{2+} activities (M) in 12 uncontaminated soils

Soil	pH	EC	Initial Zn MF range	Equilibrium Zn MF	$\log(\text{Zn}^{2+})$
Amherst	6.02	0.40	0-0.014	0.0017	-6.56
Burlington	6.33	0.62	0-0.011	0.0062	-6.49
P Center	6.48	0.34	0-0.014	0.0023	-7.19
Willard	6.65	0.37	0-0.014	0.0018	-7.59
N Ramyer	6.74	0.45	0-0.011	0.0020	-7.71
Genoa	6.86	0.43	0-0.011	0.0017	-8.01
Bennett	7.01	0.36	0-0.011	0.0029	-8.06
Lamar	7.73	0.50	0-0.011	0.0035	-9.38
Eads	7.81	0.60	0-0.011	0.0013	-9.97
Castle	7.87	0.28	0-0.5	0.0280	-8.68
S Lake	7.9	0.50	0-0.011	0.0034	-9.73
Walsh	8.07	0.60	0-0.011	0.0048	-9.92

The measured Zn^{2+} activities were highly pH-dependent, decreasing with increased pH. The coefficient of correlation between the $\log (\text{Zn}^{2+})$ and pH values in the uncontaminated soils was 0.96 and in the contaminated soils was 0.89. The measured $\log (\text{Zn}^{2+})$ and pH, in uncontaminated soils can also be expressed as $\log (\text{Zn}^{2+}) = (5.9 \pm 0.24) - 2 \text{ pH}$, which is close to the results of Ma and Lindsay (1990) and Norvell and Lindsay (1969). A slightly lower $\log K^{\circ}$ were obtained by Dayanand and Sinha (1984). According to their results, $\log (\text{Zn}^{2+}) = (5.52 \pm 0.32) - 2 \text{ pH}$, can be calculated. Calcareous soils in the pH range of 8.16 - 8.56 were used in their study.

Table 2.5 Measured pH, equilibrium Zn MF and Zn^{2+} activities (M) in 8 contaminated soils

Soils	pH	EC	Initial Zn MF range	Equilibrium Zn MF	$\log(\text{Zn}^{2+})$
Leadville-3	6.06	0.65	0-1.0	0.973	-2.26
Leadville-2	6.54	0.74	0-1.0	0.949	-3.37
Golbeville-1	6.54	0.64	0-1.0	0.872	-3.80
Globeville-4	6.74	0.20	0-0.8	0.601	-4.75
Leadville-1	7.07	0.96	0-1.0	0.956	-4.31
Globeville-3	7.94	0.60	0-1.0	0.713	-6.93
Aspen	7.99	0.70	0-0.8	0.989	-5.48
Globeville-2	8.14	0.54	0-0.5	0.286	-8.11

Tables 2.6 and 2.7 show the concentrations of the initial and final chelated Zn and Pb, and the initial and final Zn MF in

Genoa and Walsh soils, respectively. The concentrations of both Pb-DTPA and Zn-DTPA in the filtrates after reaction were pH-dependent, decreasing with decrease of soil pH. For example, the Pb-DTPA concentration in Walsh soil near pH 7.8 was between 62.5-63.4 μM , and the Pb-DTPA concentration in Genoa soil was 43.2-45.3 μM at pH 2.7. This is a typical example, similar results were obtained for other soils. The Zn-DTPA concentrations in these two soils were about the same, though slightly lower Zn-DTPA concentrations were obtained in low pH soils. The Zn or Pb on the DTPA chelates were either adsorbed by soil or displaced by other cations. Forbes et al. (1976) and Abd-Elfattah and Wada (1981) found that the affinities of the metal ions for oxides and clay minerals increase in the order, $\text{Cd} < \text{Zn} < \text{Pb}$. Abd-Elfattah and Wada (1981) indicated that Pb adsorption on clay minerals increased with decrease of pH. It is not possible to distinguish adsorption from displacement reactions in this experiment. Thus it difficult to determine if there is a differential adsorption between Zn and Pb by soils. In low pH soils, Fe^{3+} may be the dominant cation and Ca^{2+} is important in soils with high pH soils to displace Zn or Pb on the DTPA chelate (Lindsay, 1979). There is only limited information available in the literature about differential adsorption behavior of various metal chelates, which affects the measurement of metal solubility in soils (Norvell and Lindsay, 1982). It seems important to study further the differential adsorption behaviors of these metal chelates.

Table 2.6 Initial and final concentrations of chelated Zn and Pb, and initial and final Zn MF in Walsh soil

pH	Initial			Final		
	Zn MF	Zn-DTPA	Pb-DTPA	Zn MF	Zn-DTPA	Pb-DTPA
	----- μ M-----			----- μ M-----		
6.65	0	0.0	100	0.006	0.26	43.2
6.85	0.002	0.1	99.9	0.007	0.32	44.2
6.64	0.007	0.3	99.7	0.007	0.31	44.1
6.53	0.013	0.6	99.4	0.008	0.34	45.3
6.72	0.038	1.1	98.9	0.009	0.38	45.3

Table 2.7 Initial and final concentrations of chelated Zn and Pb, and initial and final Zn MF in Walsh soil

pH	Initial			Final		
	Zn MF	Zn-DTPA	Pb-DTPA	Zn MF	Zn-DTPA	Pb-DTPA
	----- μ M-----			----- μ M-----		
7.82	0.000	0.0	100	0.003	0.24	62.5
7.77	0.001	0.2	99.8	0.005	0.34	63.0
7.65	0.003	0.7	99.3	0.005	0.34	63.4
7.94	0.006	1.3	98.7	0.005	0.34	63.4
7.69	0.011	3.8	96.2	0.007	0.47	63.0

In view of the pH dependence of Zn^{2+} activities, the solubility data are plotted as a function of pH together with known Zn minerals in Figure 2.2. The measured Zn^{2+} activities

Fig. 2.2 Measured Zn^{2+} activities in soils compared with Zn minerals

for the uncontaminated soils lay close to the soil-Zn line (Norvell and Lindsay, 1969), and to the solubility ranges of franklinite-Soil-Fe and franklinite-maghemite. For the contaminated soils, the measured Zn^{2+} activities were much more soluble than those of the uncontaminated soils. These activities were between the these expected for Zn_2SiO_4 and ZnCO_3 . The activities also fall in franklinite-maghemite and franklinite-geothite solubility lines.

In the uncontaminated soils, franklinite seems like a possible mineral controlling Zn^{2+} solubility, but the actual franklinite identification was not included in this experiment. The possibility of franklinite controlling Zn^{2+} activities in soils is examined further in Chapters 4 and 5. In the contaminated soils, the Zn solubilities vary depending on the sources of the samples. In general, the Zn solubilities in these soils were in the order of Globeville site < Leadville site < Aspen site. The Zn solubilities in Globeville soils were close to that of Zn_2SiO_4 , which suggests that this mineral may be controlling Zn solubility. The Zn solubilities of Leadville soils were between Zn_2SiO_4 and ZnCO_3 at CO_2 levels lower than 0.003 atm.

The Zn solubility in the Aspen soil was highest of all soils, it was near the ZnCO_3 line when CO_2 is 0.003 atm., which is a reasonable CO_2 level in soils. According to Volin and Hild (1950), ZnS and ZnCO_3 were the Zn minerals associated with the Ag

minerals deposit in Aspen. It is possible that ZnCO_3 is the mineral that governs the Zn solubility in this soil.

There is only limited research conducted to determine Zn solubility in contaminated soils. Garcia-Miragaya and Castro (1981) concluded that Zn solubilities in contaminated roadside soils were controlled by $\text{Zn}(\text{OH})_2$ when soil pH was higher than 8, while ion exchange or sorption mechanisms controlled Zn solubility when soil pH was below 8.

To date, it is still not clear what is the mechanisms controlling Zn solubility in soils, whether adsorption-desorption or precipitation-dissolution process or both. The results of this experiment support the precipitation-dissolution mechanism. Hopefully this research will stimulate new development that can help resolve the controversial issue of what control Zn solubility in soils.

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3. DETERMINATION OF Fe^{3+} ACTIVITIES IN NORMAL AND CONTAMINATED SOILS BY CHELATION

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ABSTRACT

The chelation method was used to determine Fe^{3+} activities in 12 normal soils and 8 contaminated soils. The measured Fe^{3+} activities were pH dependent with a correlation coefficient of 0.97 in the normal soils and 0.96 in the contaminated soils. The Fe^{3+} activities could be predicted using the equation: $\log (\text{Fe}^{3+}) = (3.43 \pm 0.6) - 3 \text{ pH}$ in the normal soils, and $\log (\text{Fe}^{3+}) = (4.65 \pm 0.5) - 3 \text{ pH}$ in the contaminated soils. The Fe^{3+} activities in the contaminated soils were higher than those of the normal soils. The results indicate that amorphous Fe hydroxide may be the solid phase controlling Fe solubility in contaminated soil, and soil-Fe or amorphous Fe hydroxide are the solid phases governing Fe solubility in the normal soils. Due to the complexity of Fe solution chemistry, high centrifuge speeds and fine filters are needed to remove suspended solid phases.

INTRODUCTION

Iron solubility in soils is of interest to both plant and soil scientists. Iron deficiencies are frequently encountered in calcareous soils. Although the conditions are known to exist in acid soils as well, they are very rare (Murphy and Walsh, 1972). Recently, several solid phases containing Fe were suggested as potential minerals that control associated metal ion activities

such as ZnFe_2O_4 (franklinite) controlling Zn^{2+} (Ma and Lindsay, 1990; Bruemmer, 1983; and Pulford, 1986), NiFe_2O_4 (trevorite) controlling Ni^{2+} (Aboulroos et al., 1991), CuFe_2O_4 (cupric ferrite) controlling Cu^{2+} (Tawfic, 1990), and CdFe_2O_4 controlling Cd^{2+} activities in soils (El-Falaky et al., 1991). Thus, it is important to be able to determine free Fe^{3+} activities to test the validity of these double oxide minerals as solid phases controlling the accompanying metal ion activities.

Norvell and Lindsay (1982a) used the chelation method to determine free Fe^{3+} activities in neutral soils. They also applied this method to determine the effect of FeCl_3 additions on Fe^{3+} activities in near-neutral soils (Norvell and Lindsay, 1982b). This method was employed by Vlek et al. (1974) to measure the solubility product of various Fe hydroxides and jarosite. Thus, the method has been successfully used by many researchers to study Fe solubility. The equation used to calculate Fe^{3+} activities is as follows:

$$(\text{Fe}^{3+}) = [\text{Ca}^{2+}] \cdot \frac{[\text{FeL}]}{[\text{CaL}]} \cdot \frac{K^{\text{m}}_{\text{CaL}}}{K^{\text{m}}_{\text{FeL}} + K^{\text{m}}_{\text{FeOHL}}} \cdot \gamma_{\text{Fe}^{3+}} \quad (1)$$

where $\gamma_{\text{Fe}^{3+}}$ is the activity coefficient of Fe^{3+} , and K^{m} for the indicated species is the mixed equilibrium constant expressed in terms of concentrations except for H^+ , OH^- , and e^- , which are expressed as activities. The concentration of CaL was obtained as follows:

$$[\text{CaL}] = \text{EDTA}_t - \Sigma[\text{ML}] \quad (2)$$

where EDTA_t is the total EDTA concentration after reaction and usually ranges between 75 to 82% (Norvell and Lindsay, 1982a; and Hill-Cottingham and Lloyd-Jones, 1957) while $\Sigma[\text{ML}]$ is the total concentration of all significant metal chelates present.

The solubility relationships of Fe, Mn, Cu and Zn in alkaline and calcareous soils were studied using similar methods by Sinha et al. (1978) and Dayanand and Sinha (1984). Sinha et al. (1978) essentially used the same method as Norvell and Lindsay (1982a). There are two points which deserve to be mentioned regarding their studies: 1) They obtained Ca^{2+} concentration by subtracting CaL^{2-} from total Ca, which included CaL^{2-} , inorganic and natural organic Ca^{2+} complexes. Even though free Ca^{2+} is the dominant species, this would overestimate Ca^{2+} activities, and in turn overestimate Fe^{3+} activity measurements (Eq. 1); 2) The measurement of total EDTA concentration was not mentioned in their experiment. It is assumed that they used the initial total EDTA concentration. This would give a higher CaL^{2-} concentration, which would underestimate Fe^{3+} activity (Eq. 1). Similar problems present in the study of Dayanand and Sinha (1984), who used DTPA as the chelating agent. The modified chelation method was used in this study (Workman and Lindsay, 1990). The DTPA was used chelate agent, and Pb^{2+} as the competing cation, whose solubility was controlled by PbCO_3 added to soils.

Iron oxides play an important role in regulating Fe^{3+} activities in soils. Most of the iron released through weathering is precipitated as ferric oxides or hydroxides due to the extreme low solubilities of these minerals in the normal pH ranges of soils (Schwertmann, 1988). Chukhrov et al. (1973), and Schwertmann and Fischer (1973) suggested that ferrihydrate may control Fe^{3+} activities in soils. Lindsay (1988) concluded that Fe^{3+} solubility in soils was controlled by Fe(III) oxides near the measured $\text{Fe}(\text{OH})_3$ (soil) level. Amorphous Fe hydroxide was suggested as the possible solid phase that governs Fe^{3+} activities under some conditions (Lindsay, 1988). This amorphous Fe hydroxide is less structurally ordered than the crystalline Fe(III) minerals. According to Schwertmann (1970), freshly precipitated ferrihydrate reacts very strongly with both organic and inorganic compounds, which prevents it from further crystallization. The slow decomposition of associated organic compounds may later allow the formation of more crystalline Fe oxide. Thus, it appears that the transformation of amorphous to crystallized Fe oxides is slow.

Many investigators have become aware of the problems caused by acid drainage, which results from the oxidation of pyrite (FeS_2). Pyrite is a waste product of mining and coal cleaning (Smith et al., 1974). Under natural aerobic conditions, pyrite slowly oxidizes and produces acidity. The lowering of soil-pH increases Fe solubility, which may even reach toxic level for

plants. To date, there is little research conducted to directly measure free Fe^{3+} activities in contaminated soils.

The present research was conducted to 1) measure Fe^{3+} activities in both normal and contaminated soils, 2) compare the measured Fe^{3+} activities to known Fe minerals, and 3) define possible solid phases that may control Fe solubility in soils.

MATERIALS AND METHODS

Twelve normal soils and eight contaminated soils were used. Some of the characteristics of these soil samples are given in Table 2.1 and 2.2 of Chapter 2. Preliminary experiments were conducted to determine the most appropriate initial Fe mole fraction (MF) ($[\text{FeL}^{2-}]/[\text{FeL}^{2-}] + [\text{PbL}^{3-}]$) range for each soil. In general, smaller initial Fe MF ranges (0-0.05) were found appropriate for the normal soils and larger initial Fe MF ranges (0-1) were found for the contaminated soils.

Reagent-grade DTPA was used to prepare metal DTPA solutions. Fe-DTPA solution was prepared by adding 400 μM FeCl_3 to 400 μM DTPA solution. When all the Fe in solution was chelated with DTPA, the solution pH dropped to 2.92. The pH was then raised to 6.5 with dilute $\text{Ca}(\text{OH})_2$. After 12 h, the solution pH was again adjusted to 6.5. A similar procedure to that used for Zn^{2+} activity measurements was used for Fe^{3+} . After 1 d shaking, 5 ml of DTPA solutions of different Fe MF were added. The suspensions were centrifuged at 17,000 g for 40 min, and the supernatants were filtered through 0.2 μm membrane filter.

The following reactions describe the competition between Fe^{3+} and Pb^{2+} for DTPA ligand, where "L" stands for the DTPA ligand:

Equilibrium reaction (4) can be rearranged, assuming a CO_2 level of 0.003 atm, to give:

$$(\text{Fe}^{3+}) = \frac{[\text{FeL}^{2-}]}{[\text{PbL}^{3-}]} \cdot 10^{0.91-2\text{pH}} \cdot \tau_{\text{Fe}^{3+}} \quad (5)$$

The example is given for ionic strength of 0.01, and the $\log K^m$ value can be adjusted to correspond to any measured ionic strength. The ratio of $[\text{FeL}^{2-}]/[\text{PbL}^{3-}]$ was obtained from the measured equilibrium Fe MF defined as $[\text{FeL}^{2-}]/([\text{FeL}^{2-}] + [\text{PbL}^{3-}])$. A typical example of the equilibrium Fe MF for the Globeville-3 soil is given in Fig. 3.1. For detailed description of the method, see Chapter 2.

Iron concentrations in the filtrates of 0.2 μm membrane and Whatman #42 paper filters in the Globeville-4 soil were determined. An experiment was conducted to compare the effects of different Fe salts, different initial Fe concentrations, and different initial pH's on final Fe concentrations after the

Fig. 3.1. Equilibrium Fe MF in the Globeville-3 soil

solution pH's were raised to 5 and filtered through 0.2 μm membrane filters.

The salts used were FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, and the initial Fe concentrations were 200, 500, and 600 μM , respectively. The solution pH was initially adjusted to 2, 3, 4, and 5 with dilute HCl. Dilute KOH was then slowly added to raise pH to 5, except for the solutions initially at pH 5. After 2 h of settling, the suspensions were filtered through 0.2 μm membrane filters. The Fe concentrations in filtrates of 0.2 μm membrane filters were determined by inductively-coupled plasma at the Colorado State University Soil Testing Laboratory.

The procedures for water extractable Fe and Fe in 0.25 M DTPA extracts were the same as described in Chapter 2 for Zn.

RESULTS AND DISCUSSION

The Fe present in 2:1 water extract and 0.25 M DTPA extracts of the contaminated soils are presented in Table 3.1. The Fe concentration in 2:1 water extracts ranged from 0.06 to 24.9 $\mu\text{g/g}$, and those in 0.25 M DTPA extract ranged from 174 to 5260 $\mu\text{g/g}$. The Fe concentration in the 2:1 water extract of the Globeville-4 soil of pH 7.3 was very high (24.9 $\mu\text{g/g}$). According to Lindsay (1979), inorganic Fe usually can not be detected in soil solutions of pH higher than 7. Some organic soluble forms of Fe may be present in this soil.

Table 3.1 Fe concentration in 2:1 water and 0.25 M DTPA extracts

Soils	2:1 water extract	0.25 M extract
	-----μg/g-----	
Aspen	0.06	937
Leadville-1	0.53	2244
Leadville-2	3.44	2056
Leadville-3	5.34	5260
Globeville-1	0.18	378
Globeville-2	0.22	278
Globeville-3	0.81	550
Globeville-4	24.9	174

Table 3.2 shows the measured pH and EC values, the initial Fe MF range, the equilibrium Fe MF, and the measured Fe^{3+} activities of the 12 normal soils, and Table 3.3 for the eight contaminated soils. It is apparent that the measured Fe^{3+} activities were pH-dependent, with a correlation coefficient of 0.97 for the normal soils and 0.96 for the contaminated soils. The relationship between $\log (\text{Fe}^{3+})$ and pH can be expressed as follows:

In the normal soils,

$$\log (\text{Fe}^{3+}) = (3.43 \pm 0.6) - 3 \text{ pH} \quad (6)$$

and in the contaminated soils,

$$\log (\text{Fe}^{3+}) = (4.65 \pm 0.5) - 3 \text{ pH} \quad (7)$$

Results obtained by Dayanand and Sinha (1984) were:

$$\log (\text{Fe}^{3+}) = (3.90 \pm 0.2) - 3\text{pH} \quad (8)$$

which is about 0.5 log unit higher than those in the present experiment. Sinha et al. (1984) reported the following results:

$$\log (\text{Fe}^{3+}) = (2.95 \pm 0.23) - 3\text{pH} \quad (9)$$

which is very close to the solubility of soil-Fe.

Table 3.2 Measured pH, equilibrium Fe MF, and Fe^{3+} activities in 12 normal soils

Soil	pH	EC	Initial Fe MF Range	Equilibrium	
				Fe MF	$\log(\text{Fe}^{3+}) \text{ M}$
Amherst	6.02	0.40	0-0.045	0.0128	-15.36
Burlington	6.21	0.62	0-0.038	0.0122	-15.64
New Ramyer	6.32	0.45	0-0.038	0.0025	-16.58
P Center	6.48	0.37	0-0.045	0.0410	-16.74
Willard	6.65	0.42	0-0.045	0.0110	-17.25
Genoa	6.72	0.43	0-0.038	0.0380	-16.20
Bennett	6.99	0.36	0-0.038	0.0119	-17.27
Walsh	7.70	0.60	0-0.021	0.0015	-19.56
Eads	7.76	0.60	0-0.021	0.0023	-19.49
S Lake	7.81	0.50	0-0.021	0.0039	-19.38
Lamar	7.84	0.50	0-0.021	0.0028	-19.58
Castle	7.87	0.28	0-0.2	0.0110	-18.86

Compared to the calculated $\log K^0$ of Zn, the standard deviation of $\log K^0$ for Fe is two times larger. This is caused partially by the complicity of Fe solubility measurements. According to Lindsay (1972), soluble Fe may include small amount

Table 3.3 Measured pH, equilibrium Fe MF, and Fe^{3+} activities in 8 contaminated soils

Soil	pH	EC	Initial Fe MF Range	Equilibrium	
				Fe MF	$\log(\text{Fe}^{3+})\text{M}$
Leadville-1	6.06	0.65	0-1	0.66	-13.08
Globeville-1	6.22	0.64	0-0.5	0.08	-14.76
Leadville-3	6.54	0.74	0-0.8	0.04	-15.76
Leadville-2	6.85	0.96	0-0.8	0.15	-15.80
Globeville-4	6.94	0.20	0-0.8	0.056	-16.23
Aspen	7.73	0.64	0-0.8	0.2	-17.34
Globeville-3	7.9	0.60	0-0.5	0.009	-19.10
Globeville-2	8.12	0.54	0-0.2	0.051	-19.78

of colloidal $\text{Fe}(\text{OH})_3$ and soluble natural Fe chelates in addition to soluble inorganic Fe species. These forms of Fe increase the total Fe concentration in solution. They are difficult to remove even with a $0.2\ \mu\text{m}$ membrane filter. Table 3.4 compares the effect of different types of filters on Fe concentrations in the filtrates. Theoretically, the Fe concentration of a water blank, which consists of water and soil only, should be lower than those in filtrates where a chelate was added. Although the Fe concentrations in $0.2\ \mu\text{m}$ membrane filter were lower than those of Whatman #42 paper filter, the Fe concentration in the blank was still higher than those with chelate addition (Exp. 1). This indicates that $0.2\ \mu\text{m}$ membrane filter could reduce the colloidal

Fe in solution, but could not completely filter out all the colloidal Fe from the solution once they were formed.

Table 3.4 Comparison of Fe concentration in the filtrates of 0.2 μm membrane and Whatman #42 paper filter in the Globeville-4 soil

Added Fe MF	0.2 μm membrane		Whatman #42 paper
	Exp. 1	Exp. 2	Exp. 1
----- μM -----			
Blank	49.1	13.4	53.7
0.00	31.3	17.5	33.9
0.01	28.3	17.5	29.9
0.05	32.2	20.8	34.6
0.20	34.7	15.1	37.6
0.50	45.3	18.0	49.1

The experiment was repeated (Exp. 2) and the results are shown in Table 3.4. Though both solutions in Exp. 1 and Exp. 2 were filtered through 0.2 μm membrane filters, very low and reasonable values were obtained in Exp. 2. The Fe concentration in the blank was lower than those treated with chelate in Exp. 2. For example, in the filtrates of 0.2 μm membrane filters, the Fe concentration of blank was 49.1 and those in soils treated with chelate was less than 45 μM in Exp. 1. In Exp. 2 the Fe concentration in the blank was 13.9 μM , and those treated with chelate were above 15 μM . The difference between Exp. 1 and 2 was how the samples were handled. It is important to separate the supernatant as soon as the centrifuging process is through.

Once the colloidal Fe is formed, it is difficult to eliminate. The samples in Exp. 1 were left in the centrifuge for 20 min. before they were filtered. The Fe concentrations of different treatments in Table 3.4 did not follow regular patterns. It is expected that the Fe concentration would increase with increase in Fe MF. This again reflects the difficulty in filtering out colloid Fe. Either higher centrifuge speed or finer membrane filters should be used to obtain clean filtrates.

Tables 3.5 and 3.6 show the effects of the initial Fe concentration, initial solution pH, and the types of Fe salts on the Fe concentrations in filtrates where the suspension pH was adjusted to 5. With initial Fe concentration of 200 μM , Fe concentration in the filtrate was 0.2 μM when the initial pH was 2, and 0.79 when the initial pH was 4. The highest concentration was obtained in the filtrate with an initial pH of 5 (5.93 μM). Thus we can conclude that the lower the initial pH, the lower the Fe concentration in the filtrate after the solution pH's were raised to 5.

Table 3.5 The effects of initial Fe concentration and initial solution pH on Fe concentrations in filtrate at pH 5

Initial Fe concentration	Initial pH			
	2	3	4	5
	----- μM -----			
200	0.20	0.43	0.79	5.93
500	0.05	0.11	0.27	0.34
1000	0.00	0.07	0.00	0.00

At initial pH 3, the Fe concentration in the filtrate was 0.43 μM when the initial Fe concentration was 200 μM , and 0.07 μM when the initial Fe concentration was 1,000 μM . Thus the higher the initial Fe concentration, the lower was the Fe concentration in the filtrate. This indicates that higher OH^- and Fe concentrations enhanced Fe precipitation leaving less colloidal Fe.

From Table 3.6, we find that the Fe concentrations in the filtrate prepared from FeCl_3 solutions were much higher

Table 3.6 The effects of different Fe salts on Fe concentration in filtrates of pH 5 whose pH was initially at 3

Initial Fe concentration	FeCl_3	$\text{Fe}_2(\text{SO}_4)_3$
	----- μM -----	
200	21	0.43
500	453	0.11
1000	119	0.07

than those prepared from $\text{Fe}_2(\text{SO}_4)_3$. For example, at initial Fe concentration of 500 μM , the Fe concentration of FeCl_3 solution was 453 μM , and for $\text{Fe}_2(\text{SO}_4)_3$ it was only 0.11 μM . Thus, it seems much easier for Fe to precipitate in the presence of SO_4^{2-} than Cl^- . The exact mechanism is not clear. The SO_4^{2-} anion actually forms stronger complexes than does Cl^- . The results indicate the complexity of Fe precipitation chemistry. Thus, special attention is needed when working with Fe such as higher

centrifuge speeds and finer filters. The addition of CaCl_2 is also expected to obtain cleaner filtrates. In this study, the maximum centrifuge speed (17,000 g) available in the laboratory and 0.2 μm membrane filters were used to ensure clean filtrates. If the filtrates were not clear, the experiment was repeated.

The measured $\log (\text{Fe}^{3+})$ vs. pH is plotted in Figure 3.2 together with solubility lines for soil-Fe and amorp-Fe hydroxides. The Fe solubilities for the uncontaminated soils were within Fe levels maintained by soil-Fe and amorp-Fe. The measured Fe activities of the contaminated soils were closer to those maintained by amorp-Fe hydroxide. On the average, Fe^{3+} activities were 1.22 log units higher than those in the uncontaminated soils. The Fe solubility of the Aspen soil was highest, and those in Leadville and Globeville soils were approximately the same. According to Lindsay (1988), in an oxidized environment, the concentration of Fe is controlled by the most soluble Fe oxide phase, which in this case, is amorp-Fe hydroxide. Norvell and Lindsay (1982b) showed that addition of FeCl_3 to soils only temporally increased Fe^{3+} levels, while over a period of 30 d, it returned to the initial soil-Fe level.

It is reasonable to conclude that amorp-Fe is the solid phase controlling activities in these contaminated soils. In the normal soils, the measured Fe activities obtained in this experiment are slightly higher than soil-Fe (Norvell and Lindsay, 1982a) but still in the solubility range of soil-Fe to amorp-Fe.

Fig. 3.2 Measured Fe^{3+} activities in soils compared with Fe minerals

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4. FRANKLINITE SYNTHESIS AND SOLUBILITY MEASUREMENTS

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ABSTRACT

Franklinite has been considered as one of the potential solid phases controlling Zn^{2+} activities in soils. This study was conducted to synthesize franklinite, verify it with x-ray diffraction, and determine its solubility chemically. Franklinite was synthesized at temperatures ranging from 900-1100°C and heating periods ranging from 24 to 96 h. Its solubility was determined by three different methods: speciation using MINTEQA2 program, chelation and competitive chelation methods. Total Zn and Fe concentrations were determined after franklinite reacted with acid solutions for 6 to 30 d, and MINTEQA2 program was used to speciate free Zn^{2+} and Fe^{3+} activities. In the chelation method, EDTA and Ca^{2+} were used, and in the competitive chelation method, DTPA and Pb^{2+} were used as the chelating agent and the competing cation, respectively. Higher temperatures and longer heating periods produced a darker and less soluble product. The synthesized franklinite had a range of solubilities that were between those of soil-Zn and franklinite-maghemite depending on temperature and period of heating. It is important to wash franklinite samples with acid to eliminate extraneous phases. Franklinite in solution reach equilibrium slowly, taking longer than 30 d. Natural franklinite from Sterling Hill, New Jersey was also verified by x-ray diffraction, and its solubility was determined by chelation and

competitive chelation methods. Its solubility also fell between soil-Zn and franklinite-maghemite, reflecting a higher solubility than the least soluble and a lower solubility than the most soluble synthetic franklinite.

INTRODUCTION

Considerable efforts have been devoted to study the mechanisms controlling Zn solubility in soils since it is both an essential micronutrient and a toxic pollutant. Precipitation-dissolution has been considered as an important mechanism controlling Zn solubility (Sigh, 1982; Singh and Abrol, 1985; Gilmour and Kittrick, 1979; Gupta et al., 1987; and Garcia-Miragaya and Castro, 1981). Soil-Zn was used to predict Zn solubility in soils (Norvell and Lindsay, 1969) and was confirmed by Ma and Lindsay (1990). The solubility of franklinite is close to that of soil-Zn and is among the Zn minerals considered as potential solid phases in regulating Zn^{2+} activities in soils (Lindsay, 1981; Reddy et al., 1988; Ma and Lindsay, 1990; and Bruemmer et al., 1983), although some workers dismissed franklinite as a possible mineral controlling Zn solubility (Pulford, 1986; and Emmerich et al., 1982 a,b).

Franklinite is a mineral of the spinel group of cubic oxides with the general formula AB_2O_4 . Several metallic elements can occupy the A and B positions. While the composition of franklinite varies greatly, Zn^{2+} and Fe^{3+} are the dominant cations as expressed by the formula $(\text{Zn}, \text{Mn}^{2+}, \text{Fe}^{2+}) (\text{Fe}^{3+} \text{Mn}^{3+})_2\text{O}_4$ (Fleischer, 1975). Franklinite is a normal spinel, with

divalent atoms on the tetrahedral and trivalent atoms on the octahedral sites.

The mineral franklinite is found in Franklin and Sterling Hill, New Jersey. It is a primary mineral and is classified as uncommon to scarce (Marshall, 1977). Franklinite has been synthesized by many workers (Tyson and Chang, 1981; Mason, 1947; Weatrum, Jr. and Grimes, 1957; and Marshall and Dollase, 1984). It can be formed by heating a mixture of Zn and Fe oxides at temperatures of 900-1300°C. High pressure was not required under laboratory conditions. Franklinite was studied mainly from mineralogical system of Fe_3O_4 - Mn_3O_4 - ZnMnO_4 - ZnFeO_4 . To date, there has been no research conducted to study franklinite in connection with soil systems.

The objectives of this research were to 1) synthesize franklinite in the laboratory under different heating periods and temperatures; 2) verify franklinite by x-ray diffraction; 3) determine and compare franklinite solubility of both natural and synthesized samples; and 4) discuss the possibility of franklinite as a solid phase controlling Zn^{2+} activities in soils.

MATERIALS AND METHODS

Natural Franklinite

Natural occurring franklinite was obtained from the Smithsonian Institution. The sample was collected from Sterling Hill, New Jersey, with catalog number of C1602-3. It consists of

compacted friable black masses of grains. This sample is referred as F-0 in this study.

Thermochemical data relevant to the stability of the major ore mineral deposits in Sterling Hill, described by Takahashi and Myers (1963), indicate that the temperature of formation of the deposits was likely between 557 to 827°C assuming lithostatic pressure in the range of 700-1,300 atm. In other words, the natural franklinite sample in our experiment was formed under relative high pressure and temperature.

The sample was then ground into a fine powder, washed with 0.05 N HCl, rinsed repeatedly with tap water, and then deionized water. The sample was finally dried using acetone. The washing and rinsing procedures were carried out on a suction funnel with Whatman #42 filter paper.

Synthetic Franklinite

Franklinite was synthesized in the laboratory from a mixture of equal molar ZnO and Fe₂O₃ under conditions of different temperatures and heating periods. The mixtures consisted of 16.274 g of ZnO and 31.938 g of Fe₂O₃. Reagent grade ZnO and Fe₂O₃ were used for samples 1 to 5, and puratranic grade (99.999%) was used for samples 6 to 7. The materials were mixed in a plastic bottle, first by hand, then on a shaker overnight. To speed up the formation of franklinite, some samples were compressed into thin discs using a hydraulic compressor, and contaminated surfaces were discarded before heating. The following treatments were used in this study.

- F-1 The mixture was treated with acetone, and heated at 900°C for 24 h.
- F-2 The mixture was heated at 900°C for 24 h.
- F-3 Sample F-1 was compressed into a disc and then heated at 1000°C for 48 h.
- F-4 Sample F-1 was compressed into a disc and then heated at 1100°C for 24 h.
- F-5 Sample F-4 was compressed into thin disc and heated at 1100°C for another 48 h.
- F-6 Mixture of ZnO and Fe₂O₃ (puratranic grade) was compressed into a thin disc, then heated at 1100°C for 48 h.
- F-7 Sample F-6 was heated at 1100°C for another 48 h.

The same washing and rinsing procedures were used for the synthetic franklinite samples as were used for the natural franklinite samples. The franklinite samples were then ground into a fine powder.

Identification with X-ray Diffraction

Franklinite samples were put on glass microscope slides using double stick tape. The tape was first put on the glass slide, and then the samples were put on the tape. The slides were tapped lightly to eliminate extra samples, so that only a thin layer of samples was left on the slides. The samples were examined with an XRD 700 unit. The operating conditions were: range-2.5 K, and time constant-2.5 K. The highest refractive index of mineral oil available in our laboratory was 1.78, and

the refractive index of franklinite is 2.3, thus verification using refractive index was not made.

Solubility Measurement

The franklinite samples used in this study were not acid washed. However, a slight amount of acid was added to increase the solubility of franklinite. There were two experiments carried out to measure Zn^{2+} and Fe^{3+} solubilities. In the first experiment, solutions with pH of 2, 3, and 4, respectively, were used. A 0.1 g sample of franklinite was added to solutions of pH 2, and 0.01 g to solutions with pH 3 and 4. Franklinite samples F-1, F-3, F-4 and F-5 were used in this experiment. In the second experiment, solutions of pH 2.5, 3, and 3.5 were used. Franklinite at 0.03 g was used for all solutions. Franklinite samples F-1, F-3, F-4, F-5, and F-6 were used in this experiment. In both experiments, the final volume for all solutions was 20 ml. The pH of the solutions was adjusted with dilute HCl and measured with a pH meter. Theoretically, the total concentration of H^+ should be equal to that of Cl^- . Thus, the Cl^- concentration was estimated through pH. The samples were covered with parafilm with small holes to permit aeration in 125-ml Erlenmeyer flasks, which required addition of approximately 1 ml water per 4 d. The samples were then shaken for 15, and 30 d, respectively. Two duplicates were used in these experiments. At the end of each shaking period, the solutions were filtered through 0.45 μ Whatman membrane filter. Both pH and EC values of the filtrates were then measured. Total Fe and Zn concentrations

were determined by ICP. MINTEQA2 speciation program was used to calculate free Zn^{2+} and Fe^{3+} activities with the inputs of total concentrations of Zn, Fe, and Cl, pH, and EC values.

Solubility Measurement using Chelation

EDTA was used as the chelating agent, and Ca^{2+} as the competing cation in this study. According to Lindsay (1979), the abilities of Zn^{2+} and Ca^{2+} to complex with EDTA are comparable in the pH range of 6.5 to 7.5 in soils. In the case of DTPA, ZnL^{3-} is the dominant species compared to CaL^{3-} throughout the pH range. Thus, DTPA was not an appropriate chelate for this study. Reagent-grade Na_2EDTA was used to prepare metal EDTA solutions. Zn- and Ca-EDTA solutions were prepared by adding 400 μM ZnCl_2 , or CaCl_2 to 400 μM EDTA solutions. When all the Zn^{2+} or Ca^{2+} in solution had reacted with EDTA, the solution pH was near 3.1. The pH's were then adjusted to 7 after 12 h reaction. The solutions were stirred for another 12 h to make certain that all the Zn^{2+} or Ca^{2+} was chelated by EDTA. The pH of the solutions was again adjusted to pH 7 using dilute $\text{Ca}(\text{OH})_2$.

A known amount of CaCl_2 was added to the suspension to supply Ca^{2+} activity in solution. Approximately 18.5 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (FW = 147.02 g) was dissolved in 1000 ml of deionized water, and the solution pH was adjusted to 7. All suspensions contained 0.01 g of franklinite and a final volume of 20 ml of solution, which consisted of 5 ml of 400 μM metal-EDTA solution with different Zn MF, and 15 ml of CaCl_2 solution. The soil

suspensions were aerated and shaken continuously on a rotational shaker for 5 d at room temperature (24-26°C). The initial EDTA concentration was 100 μM for all treatments. Six different franklinite samples were used: F-0, F-1, F-2, F-3, F-4, and F-5. The description of each sample is given in section 4.1. Franklinite plus 15 ml of CaCl_2 and 5 ml of water was used as the blank treatment.

At the end of the reaction period, the supernants were filtered through a 0.45 μm Whatman membrane filter. The filtrates were then analyzed for cations by inductively-coupled plasma atomic emission spectrometry. The pH in filtrates was measured with a combination glass electrode and electrical conductivity was measured using a Yellow Springs Model 35 conductivity meter. The Ca^{2+} activity was determined with a calcium-specific ion electrode.

The following reactions describe the competition between Zn^{2+} and Ca^{2+} for EDTA ligand, "L"

Rearranging Eq. 3 gives:

$$(\text{Zn}^{2+}) = 10^{-5.83} \cdot (\text{Ca}^{2+}) \cdot \frac{(\text{ZnL}^{2-})}{(\text{CaL}^{2-})} \quad (4)$$

Since the activity coefficients of ZnL^{2-} and CaL^{2-} are equal, Eq. 4 can be written:

$$(\text{Zn}^{2+}) = 10^{-5.83} \cdot (\text{Ca}^{2+}) \cdot \frac{[\text{ZnL}^{2-}]}{[\text{CaL}^{2-}]} \quad (5)$$

The ratio of $[\text{ZnL}^{2-}]/[\text{CaL}^{2-}]$ was obtained from the measured equilibrium Zn MF defined as $[\text{ZnL}^{2-}]/([\text{ZnL}^{2-}] + [\text{CaL}^{2-}])$. A typical example is given in Fig. 4.1. The equilibrium Zn MF was obtained by connecting two Zn MF points, one lower and one higher than the equilibrium Zn MF. The following describes how the equilibrium Zn MF was calculated. The initial Zn MF with the lower value was designated as A and the measured Zn MF of the lower point as C. Those with higher values were designated as B and D, respectively, as illustrated in Fig. 4.1. The equilibrium Zn MF was then calculated using Eq. 6:

$$\text{Equilibrium Zn MF} = \frac{A \cdot D - C \cdot B}{(A+D) - (C+B)} \quad (6)$$

The Ca^{2+} activities were determined by a calcium-specific electrode. The concentration of $[\text{ZnL}^{2-}]$ was taken as the total Zn determined by ICP after subtracting the Zn in the blank. The $[\text{CaL}^{2-}]$ concentration was obtained by subtracting ZnL^{2-} and FeL^- concentrations from the total chelate concentration, which was $100 \mu\text{M}$.

Fig. 4.1. Equilibrium Zn MF in sample F-2

Franklinite Solubility Measurement Using Competitive Chelation

The Zn^{2+} and Fe^{3+} activities of samples F-0, F-5, F-6, and F-7 were measured using the competitive chelation method. All suspensions contained 0.01 g of franklinite, 0.03 g of PbCO_3 , and a final volume of 20 ml solution, which consists of 5 ml of 400 μM metal-DTPA solutions of different Zn or Fe MF, and 15 ml of deionized water. The suspensions were shaken for 5 d. For a detailed description, see Chapters 2 and 3.

RESULTS AND DISCUSSION

Sample Preparation

Both natural and synthetic franklinite samples were used in this experiment. The natural franklinite sample is referred as F-0. There were 7 synthetic franklinite samples: F-1, F-2, F-3, F-4, F-5, F-6, and F-7, which were synthesized under different temperatures and different heating periods. Samples F-1 and F-2 were not compressed before heating, sample F-1 was treated with acetone. The remaining samples were compressed and not treated with acetone.

Sample F-0 had a gray-black color with shining faces under light. F-1 had a darker yellowish color than F-2, the only difference between these two samples was that F-1 was treated with acetone. It seems that acetone which was used to dry the samples affected the physical appearance of the samples. Samples F-3, F-4, and F-5 looked gray-brown, becoming darker in the order of $\text{F-3} > \text{F-4} > \text{F-5}$. This indicates that higher heating

temperature and longer heating period produce darker franklinite. The color of samples F-6 and F-7 was intermediate between F-2 and F-3, with F-7 being dark brown and were finer particles compared with samples F-3, F-4 and F-5. These samples were ground and compressed before heating.

Mineral Identification with X-ray Diffraction

All the franklinite samples were identified with x-ray diffraction. They were confirmed as franklinite. Two peaks were used to verify synthetic franklinite samples: 29.9° and 35.3° . An additional peak at 42.8° to identify the natural franklinite sample. The peaks for ZnO included 31.7° , 34.4° , and 36.2° , and those for Fe_2O_3 were 33.2° and 35.7° . Only qualitative analysis was carried out in this experiment.

Peak height is related sample thickness. Since sample thickness was not controlled in this study, peak height was not evaluated. Three variables were considered in the mineralogical study: peak broadness, peak area, and peak position. In general, broader peaks indicate more amorphous like materials, and the peak area is a reflection of mineral quantity. The peak position serves as a qualitative criteria for mineral identification.

Some typical x-ray diffractograms are showed in Fig. 4.2, 4.3, 4.4 and 4.5. Figure 4.2 represents the results of samples F-3, F-4, and F-5. There was not much difference among these three samples, though they were synthesized under different temperatures and for different periods of time. Diffractograms of franklinite samples obtained in this study showed no peaks for

Fig. 4.2. Diffractograms of samples F-3, F-4, and F-5

Fig. 4.3 Diffractograms of sample F-2 compared to ZnO

Fig. 4.4 Diffractograms of sample F-1 compared to Fe₂O₃

Fig. 4.5 Diffractograms of natural franklinite (F-0) compared to synthetic franklinite (F-6)

ZnO and Fe_2O_3 . An example is given for samples F-2 and F-1 in Fig. 4.3 and 4.4, respectively, which were heated at the lowest temperature (900°C) and for the shortest period (24 h). For example, the peaks for the Fe_2O_3 sample were detected at 33.2° and 35.7° , while those for sample F-1 were at 29.9° and 35.3° (Fig. 4.4). There were no peaks at 2θ of 33.2° and 35.7° (ZnO) in sample F-2 (Fig. 4.3). This either indicates that there was no ZnO or Fe_2O_3 left in the samples or x-ray diffraction was not sensitive enough to detect small amounts that may have remained.

Figure 4.5 shows the diffractogram of sample F-0 (natural franklinite) compared with synthetic franklinite sample F-6. It is obvious that sample F-0 is not pure franklinite as reflected in sample F-6. There are 3 additional peaks, which indicate that the samples contained minerals other than franklinite. No attempt was made to identify these additional minerals. The strongest peaks in both samples appeared at 2θ of 35.3° . The second strongest peak for sample F-6 was at 29.9° ; while for sample F-0, the second strongest peak was at 42.8° . The third strongest peak for sample F-6 was at 42.8° and for sample F-0, it was at 29.9° . One possible explanation is that the peak at 42.8° for sample F-0 was produced by franklinite alone with other minerals.

Franklinite Solubility in Aqueous Solution

From the x-ray diffractograms, it was reasonable to assume that there was no ZnO or Fe_2O_3 left in the franklinite samples.

Because of the purity of the samples as suggested by the diffractograms, the synthetic franklinite samples used in the initial experiment were not acid washed.

Table 4.1 compares the Zn and Fe concentrations in water extracts of washed and unwashed samples. The HCl used to wash franklinite samples was 0.05 N. The extracts were shaken for 5 d on the rotation shaker.

Table 4.1 Comparison of Zn and Fe concentrations in water extracts in washed and unwashed samples

Sample #	Zn		Fe	
	unwashed	washed	unwashed	washed
-----μg/g-----				
0	0.98	0.54	0.78	0.42
1	5.17	1.93	0.71	0.44
2	1.95	1.31	0.74	0.40
3	2.00	0.60	0.94	0.41
4	2.37	0.51	1.07	0.42
5	1.20	0.48	0.82	0.43

Both Zn and Fe concentrations were reduced significantly by washing with acid, indicating that the mineral samples contained trace amount of ZnO, Fe₂O₃, or other soluble phases which were not detected by x-ray diffraction. For example, the Zn concentration of sample F-3 was 2 μg/g and it reduced to 0.6 μg/g after washing. The Fe concentration of sample F-3 was 0.94 μg/g and reduced to 0.41 μg/g after washing. Thus, it is important to acid wash mineral samples before solubility studies are

undertaken. Because the samples used in this experiment were not acid washed, the measured Zn^{2+} and Fe^{3+} activities were overestimated for franklinite. Therefore solubility results obtained are not shown.

One observation is that the Zn concentration in both washed and unwashed samples decrease in the order of F-0, F-1, F-2 F-3, F-4 and F-5. Natural franklinite had the highest Zn concentration. In the synthetic samples, the higher the temperature and the longer the heating period produce, the less soluble was franklinite in terms of Zn. The solubility of Fe seems unaffected by different synthesis conditions. One explanation is that ZnO is very soluble compared to Fe_2O_3 . Thus, it requires higher temperature and longer period for ZnO to become insoluble. In other words, any ZnO left in the franklinite sample will increase Zn concentration, but Fe_2O_3 will not.

The results of this experiment (data not shown) indicate that the best pH range for determining Zn^{2+} and Fe^{2+} activities of franklinite is between 3 to 5. Franklinite consumes 8 moles H^+ for each mole dissolved. At $\text{pH} < 3$, Zn^{2+} and Fe^{3+} activities are underestimated. At such low pH, franklinite dissolves to give high ionic strengths (>0.1). At higher pH, Zn and Fe concentrations are not high enough to be easily determined by ICP. Thus, it is important to choose the correct pH range.

Table 4.2 shows the effect of shaking time on the final pH in solution, and Zn^{2+} and Fe^{3+} activities of sample F-3 initially

at pH 3. All the final pH's were higher than the initial pH, and slightly different for each shaking period. The Zn^{2+} activities seemed to increase slightly with shaking time, and Fe^{3+} activities were variable, but decreased with shaking time. The $\log (\text{Zn}^{2+})$ increased from -3.39 M at 6 d to -3.28 M at 30 d of shaking. The activities of Fe^{3+} decreased from $10^{-8.65}$ M at 15 d to $10^{-9.54}$ M at 30 d. The results indicate that long shaking periods are needed for franklinite to reach equilibrium.

Table 4.2 Effect of shaking time on Zn^{2+} and Fe^{3+} activities of sample F-3 at initial pH 3

Shaking time	pH	$\log (\text{Zn}^{2+})$	$\log (\text{Fe}^{3+})$
d		----- <u>M</u> -----	
6	4.04	-3.39	-8.59
11	4.59	-3.36	-10.08
15	3.94	-3.27	-8.65
30	4.20	-3.28	-9.54

Table 4.3 reports the effects of initial pH on Zn^{2+} and Fe^{3+} activities of sample F-5 after 30 d shaking. The final pH's were increased in all cases compared to the initial solution pH. For example, the final pH increased from 3 to 4.07. The measured Zn^{2+} activities decreased with increase of initial pH, while Fe^{3+} activities were affected vary little. The solutions of lower pH dissolved franklinite faster than solutions of high pH. The result suggests that franklinite did not reach equilibrium even

after 30 d of shaking. Similar conclusions were reported by Lindsay et al. (1959) when they studied the solubility of variscite. They used shaking periods up to 144 d to ensure the equilibrium conditions were obtained.

Table 4.3 Effect of initial pH on Zn^{2+} and Fe^{3+} activities of sample F-5 at 30 d shaking

Initial pH	Final pH	$\log(\text{Zn}^{2+})$	$\log(\text{Fe}^{3+})$
-----M-----			
2.5	4.26	-2.82	-9.60
3.0	4.07	-3.11	-9.31
3.5	4.24	-3.90	-9.64

Franklinite Solubility from Chelation

Franklinite solubilities were measured using the chelation method (Norvell and Lindsay, 1982; and Ma and Lindsay, 1990). The chelating agent EDTA with the competing cation Ca^{2+} were used in this study. Table 4.4 gives a typical example of the changes in Zn MF, ZnL and CaL concentrations after reacting the chelate solution with sample F-2. The pH of the solution did not change much from the initial pH 7. The initial and final Zn MF changes are plotted in Fig. 4.1. When the added Zn MF was low, the solution dissolved Zn from franklinite and increased the Zn MF. On the other hand, when the added Zn MF was high, the solution lost Zn and the Zn MF decreased. The unique equilibrium Zn MF for sample F-2 was 0.6.

Table 4.4. Changes in Zn MF, ZnL, and CaL concentrations after reacting chelate solutions with sample F-2

pH	Added			Measured		
	MF	ZnL	CaL	MF	ZnL	CaL
		-----M-----			-----M-----	
6.97	0.00	0.00	100	0.17	17.1	82.9
7.12	0.17	17.2	82.8	0.34	33.7	64.2
7.17	0.37	37.1	62.9	0.51	50.6	49.4
7.08	0.79	78.6	21.4	0.67	65.3	31.6
7.12	0.97	97.1	2.90	0.78	75.2	21.7

Table 4.5 summarizes the measured Zn MF's and equilibrium Zn MF's for the six franklinite samples. The natural franklinite (F-0) showed the highest equilibrium Zn MF, and samples F-4 and F-5 had the lowest Zn MF's. Higher Zn MF reflect higher Zn solubilities, though pH is an important factor as well. The Fe^{3+} activities were also measured in this experiment. Table 4.6 shows the measured Fe MF. It is obvious that all the solutions lost Fe MF except a few, which indicates that Fe^{3+} is not able to compete with Ca^{2+} or Zn^{2+} under these conditions. In case of sample F-3, its Zn MF's changed from 0.01, 0.19, 0.43, 0.82, and 0.98 to 0, 0.18, 0.33, 0.36, and 0.42, respectively. Some samples gained Fe MF, but the changes were not significant, and so the results could not be used to calculate Fe^{3+} activities. Thus, measured Fe^{3+} activities were not obtainable in this study.

Table 4.5 Summary of measured Zn MF and equilibrium Zn MF of various franklinite samples using EDTA

Added Zn MF	Measured Zn MF					
	F-0	F-1	F-2	F-3	F-4	F-5
0.00	0.24	0.18	0.17	0.22	0.08	0.04
0.17	0.61	0.32	0.34	0.29	0.20	0.21
0.37	0.69	0.49	0.51	0.52	0.39	0.44
0.79	0.86	0.64	0.67	0.70	0.59	0.61
0.97	0.91	0.74	0.78	0.86	0.82	0.77
Eq Zn MF	0.89	0.56	0.60	0.63	0.41	0.49

Table 4.6. Summary of measured Fe MF of various franklinite samples using EDTA.

Added Fe MF	Measured Fe MF					
	F-0	F-1	F-2	F-3	F-4	F-5
0.01	0.04	0.00	0.00	0.06	0.00	0.00
0.19	0.18	0.00	0.19	0.18	0.11	0.13
0.43	0.37	0.00	0.30	0.33	0.20	0.30
0.82	0.49	0.01	0.36	0.36	0.18	0.44
0.98	0.60	0.01	0.46	0.42	0.43	0.49

The measured Zn^{2+} activities of various franklinite samples vs. pH were plotted in Fig. 4.6. Samples F-2 and F-1 were most soluble, while sample F-5 was least soluble. Sample F-0 had the same solubility as F-3, which was between the solubility of F-2 and F-5. The results indicate that higher temperature and longer heating period make franklinite less soluble, which is consistent

Fig. 4.8. Measured franklinite solubility using chelation method

with the results reported in the previous section. Thus, the solubility of synthesized franklinite samples depends on the condition under which they were synthesized. The solubility of natural franklinite is slightly higher than soil-Zn and lower than franklinite-maghemite. It seems reasonable to conclude that franklinite in nature has a range of solubilities depending on how it was formed. It varies with the degree of crystallization and with variations in chemical composition.

Franklinite Solubility Using Competitive Chelation

Solubilities of some of the franklinite samples were also measured using competitive chelation. The chelate DTPA and competing cation Pb^{2+} were used for this purpose.

Table 4.7 shows the measured Zn MF, ZnL, FeL, and PbL concentrations and Table 4.8 shows the measured Fe MF, ZnL, FeL and PbL concentrations after reacting with sample F-6. "L" stands for the DTPA ligand. The Zn MF's of low values increased and those of high values decreased during reaction. It is consistent that the solution pH increases with increase in Zn MF or Fe MF. In Table 4.7, the solution pH was 4.95 with Zn MF of 0.01, and it increased to 6.48 as Zn MF increased to 0.798. One possible reason for this is that the solutions with low Zn or Fe MF had high Pb concentrations. Lead is expected to precipitate as PbCO_3 when its solubility product is exceeded, and this produces H^+ . Thus, the lower the initial Zn or Fe MF, the higher the Pb concentration, which, in turn, produced more H^+ and decreased the solution pH. This also indicates that

precipitation of PbCO_3 occurred within 5 d of reaction, which was used in this study.

Table 4.7 Changes in measured Zn MF, ZnL, FeL, PbL concentrations and pH in sample F-6 using competitive chelation

pH	Added			Measured				
	Zn MF	ZnL	PbL	Zn MF	ZnL	PbL	FeL	$\Sigma(\text{Zn}+\text{Pb}+\text{Fe})$
	---- μM ----			----- μM -----				
5.13	0.000	0.00	100	0.013	0.96	80.3	0.30	81.6
4.81	0.001	0.07	99.9	0.016	1.14	78.4	0.30	79.8
4.95	0.010	0.93	99.1	0.029	2.04	76.2	0.22	78.5
5.14	0.106	9.65	90.4	0.124	9.37	74.6	0.30	84.3
5.81	0.503	48.6	51.4	0.462	48.0	63.1	0.53	111.6
6.48	0.798	79.1	20.9	0.616	77.3	48.1	0.83	126.3

Table 4.8. Changes in measured Fe MF, ZnL, FeL, PbL concentrations and pH in sample F-6 using competitive chelation

pH	Added			Measured				
	Fe MF	FeL	PbL	Fe MF	FeL	PbL	ZnL	$\Sigma(\text{Fe}+\text{Pb}+\text{Zn})$
	---- μM ----			----- μM -----				
5.13	0.000	0.00	0.00	0.004	0.31	80.3	0.95	81.6
4.92	0.002	0.21	99.8	0.003	0.21	80.0	0.21	80.4
4.91	0.009	0.91	99.1	0.005	0.31	74.6	1.64	76.6
4.99	0.036	3.60	96.4	0.007	0.47	75.1	0.50	76.1
5.03	0.119	11.8	89.2	0.017	1.26	81.7	0.51	83.8
6.35	0.714	71.4	28.6	0.070	6.49	75.2	1.46	83.2

The concentrations of ZnL, PbL, or FeL in this experiment were obtained by subtracting the corresponding blank concentration from the total concentration measured by ICP. These procedures worked well for PbL and FeL, but there is a problem in case of ZnL. Table 4.7 shows that the sum of $\Sigma(\text{ZnL} + \text{PbL} + \text{FeL})$ was fairly constant at low Zn MF, but increased above $100 \mu\text{M}$ at the higher Zn MF, which was original EDTA added. The sum of ZnL + PbL + FeL at low Zn MF was around $80 \mu\text{M}$. At high Zn MF, the total Zn concentration was comprising of the sum of inorganic soluble Zn and ZnL; and inorganic soluble Zn increased with increase in Zn MF. At high Zn MF, Zn^{2+} on DTPA was replaced by Pb^{2+} and the Zn was supposed to precipitate from solution. This process was apparently slow, and by the end of 5 d, there was still a significant amount of inorganic soluble Zn in solution. Because of this, the method overestimates Zn^{2+} activities, which are reflected in Table 4.9. The measured Zn^{2+} activities were about one to two log units more soluble than soil-Zn. The calculated $\log K^0$ for sample F-0 was 8.42 and sample F-7 was 6.56. Thus a longer reaction period is required to reflect equilibrium Zn^{2+} activities.

In the case of Fe^{3+} activity measurements, there was no problem. The sum of FeL + PbL + ZnL was around 76.1 to $83.8 \mu\text{M}$ (Table 4.8). The process of Fe precipitation is relatively rapid compared to Zn. The other interesting point is that the chelate concentration decreased from $100 \mu\text{M}$ to the range of 76.1 to $83.8 \mu\text{M}$. Thus the added DTPA may be absorbed either by franklinite or

by PbCO_3 . The measured Fe^{3+} activities are presented in Table 4.10. The Fe solubility of sample F-0 was close to soil-Fe ($\log K^0 = 2.7$), while the other franklinite samples reflected Fe^{3+} solubilities closer to maghemite ($\log K^0 = 1.59$).

Table 4.9 Equilibrium pH, Zn MF, Zn^{2+} activities, and calculated $\log K^0$ of franklinite using competitive chelation

Franklinite Sample	pH	Equilibrium Zn MF	$\log (\text{Zn}^{2+}) \underline{M}$	Calculated $\log K^0$ ($\log (\text{Zn}^{2+}) + 2 \text{ pH}$)
F-0	6.28	0.549	-4.14	8.42
F-5	5.27	0.185	-3.35	7.19
F-6	5.48	0.215	-3.58	7.38
F-7	5.25	0.052	-3.94	6.56

Table 4.10 Equilibrium pH, Fe MF, Fe activities, and calculated $\log K^0$ of franklinite using competitive chelation

Franklinite Sample	pH	Equilibrium Fe MF	$\log (\text{Fe}^{2+}) \underline{M}$	Calculated $\log K^0$ ($\log (\text{Fe}^{3+}) + 3\text{pH}$)
F-0	6.16	0.009	-15.75	2.73
F-5	4.89	0.005	-13.15	1.52
F-6	4.92	0.003	-13.45	1.31
F-7	4.81	0.003	-13.18	1.25

The calculated $\log K^0$ values of some of the franklinite samples are summarized in Table 4.11. They ranged from 9.94 to 14.12. The competitive chelation method may slightly

overestimate the solubilities of franklinite as discussed above. The log K° of sample F-5 was 10.99 and that of sample -7 was 9.94. Thus sample F-7 was less soluble than that of sample F-5. Same heating period (96 h) for both samples, and lower heating temperature was used for F-5. This agrees with the results obtained in previous section. The solubility of synthetic franklinite depends on the conditions of synthesis. In the literature, many different log K° values have been reported from thermodynamic data (Lindsay, 1979; Woods and Garrels, 1987; and Wagman et al., 1982). It is important to critically examine the log K° and choose a reliable value. For more detailed information, see Sadiq and Lindsay (1981).

Table 4.11 Calculated log K° values of some franklinite samples using competitive chelation

Franklinite Sample	Average pH	Calculated log K°
F-0	6.22	14.12
F-5	5.08	10.99
F-6	5.20	11.12
F-7	5.03	9.94

CONCLUSIONS

1. Franklinite can be synthesized by heating a mixture of ZnO and Fe_2O_3 at temperatures higher than 900°C for 24 h.
2. Higher temperature and longer heating period produce darker colored and less soluble franklinite.

3. It is necessary to wash the sample with acid to eliminate any extraneous phases before making solubility measurements.
4. It is important to choose the right pH range for measuring franklinite solubility.
5. Longer shaking period (> 30 d) is needed for franklinite to reach equilibrium in acid solutions.
6. Both Zn^{2+} and Fe^{2+} activities can be measured using the chelation and with competitive chelation methods.
7. A longer reaction period (>5 d) is needed to reflect accurate Zn^{2+} activities using the competitive chelation method since the precipitation of Zn is slow compared to that of Fe^{3+} .
8. The $\log K^0$ values for synthetic franklinite samples ranged from 9.94 to 11.12, and the natural franklinite sample was 14.12 using the competitive chelation.

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5. FRANKLINITE EQUILIBRIUM STUDIES IN SOILS

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ABSTRACT

Zinc is important both as an essential micronutrient to plants and as a pollutant to plants and mammals. Free Zn^{2+} and Fe^{3+} activities were determined in two soils under different treatments with the competitive chelation method. These treatments included the addition of a soluble Zn salt (supersaturation) and addition of synthetic or natural franklinite to soils (undersaturation). Soil to water suspension (1:2) were shaken for 15, 30, 65, and 105 d. At the end of each shaking period, free Zn^{2+} and Fe^{3+} activities were determined in the soil suspensions. Measured Zn^{2+} activities fell in the solubility range of soil-Zn and Zn_2SiO_4 (willemite). They were pH dependent with correlation coefficients of $\log (\text{Zn}^{2+})$ with pH of 0.81, 0.90, 0.86 and 0.91 for 15, 30, 65, and 105 d of shaking, respectively. Addition of Zn minerals increased Zn^{2+} activities in the order: soluble Zn > natural franklinite > synthetic franklinite $\geq$ original soil at 15 d reaction. The Zn solubility maintained by natural franklinite was slightly higher than that of the original soil. Natural franklinite maintained the same Zn level as that in soils treated with ZnCl_2 , and the Zn^{2+} activities in soils treated with synthetic franklinite were very near to those of soil-Zn at 105 d reaction. This indicates the possible importance of franklinite as a mineral controlling

Zn^{2+} in soils. The added Zn was fixed by these soils during the first 15 d reaction; thereafter there was little change in Zn^{2+} activities. The measured Fe^{3+} activities were between the solubility of soil-Fe and amorp-Fe and were highly pH dependent having correlation coefficients of 0.99 for all shaking periods. Measured Fe^{3+} activities changed slightly with shaking period. The results reported here support the hypothesis that franklinite is an important mineral controlling Zn^{2+} activities in soils.

INTRODUCTION

Several studies have been conducted to directly determine free Zn^{2+} activities in soils (Ma and Lindsay, 1990; Sinha et al., 1978; Dayanand and Sinha, 1984; and Norvell et al., 1987), yet the mechanisms that control Zn^{2+} activities in soils are still poorly understood. Both adsorption-desorption and precipitation-dissolution have been reported as mechanisms controlling Zn activities in soils (Udo et al., 1970, Bruemmer et al., 1983, and Pulford, 1986). The measured Zn^{2+} activities are close to the solubility of franklinite, so this mineral is considered as possibly controlling Zn^{2+} activities in soils (Ma and Lindsay, 1990).

Numerous experiments have been conducted to study Zn adsorption upon the addition of soluble Zn to soils (Jahiruddin et al., 1989; Kuo and Mikkelsen, 1979; Kalbasi et al., 1978; Krishnasamy and Krishnamoorthy, 1989; Mehta et al., 1984; and Gupta et al., 1987). How Zn^{2+} activities following the addition

of soluble Zn was not included in these studies. There is little information on Zn solubility measurements following the addition of insoluble minerals.

In this study, both natural and synthetic franklinite were used. The objectives of this study were to: 1) measure Zn^{2+} activities with time following the addition of ZnCl_2 and natural or synthetic franklinite to soils; 2) compare Zn solubilities among different treatments; and 3) discuss the possibility that franklinite controls Zn^{2+} activity in soils.

MATERIALS AND METHODS

Two soils were selected in this study and their properties are listed in Table 2.1 of Chapter 2.

Natural ZnFe_2O_4 (franklinite) obtained from the Smithsonian Institution in Washington, D.C. and synthetic ZnFe_2O_4 samples made in our laboratory were used. The samples were characterized mineralogically, and their solubilities were measured. They were finely ground, acid washed, and stored in a decicator as described in Chapter 4.

Soil suspensions were prepared containing 50 g of soil and 100 ml of solution. There were ten treatments used in this study:

1. W+WT: Walsh Soil + Water
2. W+NF: Walsh Soil + Natural Franklinite
3. W+SF: Walsh Soil + Synthetic Franklinite
4. W+ZN: Walsh Soil + ZnCl_2

5. S+WT: S Lake Soil + Water
6. S+NF: S Lake Soil + Natural Franklinite
7. S+SF: S lake Soil + Synthetic Franklinite
8. S+ZN: S Lake Soil + ZnCl_2
9. NF+WT: Natural Franklinite + Water
10. SF+WT: Synthetic Franklinite + Water

Franklinite sample F-7 was used in this study. This franklinite sample was synthesized at 1100°C for 96 h, its physical property and solubility were described in Chapter 4. Its x-ray diffractogram is presented in Fig. 5.1. A 0.12 mg of ZnCl_2 and 0.3 g franklinite (natural or synthetic) were added to each soil. The soil suspensions were aerated and shaken continuously on a rotational shaker at room temperature ($24\text{--}26^\circ\text{C}$) for 15, 30, 65, and 105 d, respectively. Water lost during evaporation was replaced every 4 d. Duplicate treatments were included.

At the end of each shaking period, the activities of Zn^{2+} and Fe^{3+} were determined using the competitive chelation method. Each soil suspension was vigorously stirred with a magnetic stirring bar, and divided into eight equal sub-samples using a balance, each consisting of 15 g of soil suspension. For the chelation method of measuring Zn^{2+} activities, the initial Zn or Fe MF range presented in Tables 5.3 to 5.10 were used. The most suitable MF range was chosen for each treatment. A water blank was used for each treatment. The 0 MF which consisted of all Pb-DTPA was shared for both the Zn^{2+} and Fe^{3+} activity measurements.

Fig. 5.1 X-ray diffractogram of sample F-7

Thus, eight sub-samples (one blank, one 0 MF, three Zn MF's and three Fe MF's) were used to measure Zn^{2+} and Fe^{3+} activities.

A 5-ml aliquot of each chelate solution of 400 μM concentration with different Zn or Fe MF or water (blank) were added to each of the sub-samples. Thus, the sub-samples after chelate addition consisted of 15 g of soil suspension and 5 ml chelate solution. In 15 g of soil suspension, there was about 10 ml solution and 5 g of soil. Thus, the total chelate concentration used in this experiment was calculated as follows:

$$\text{Total DTPA concentration} = 400 \mu\text{M} \cdot \frac{5 \text{ ml}}{5 \text{ ml} + 10 \text{ ml}} = 133.3 \mu\text{M}$$

The new soil suspensions were then shaken for 5 d to determine Zn^{2+} and Fe^{3+} activities as described in Chapters 2 and 3.

RESULTS AND DISCUSSION

The measured Zn^{2+} solubilities in uncontaminated soils fell close to the soil-Zn line, which is close to franklinite solubility. The measured Fe^{3+} solubilities were close to the amorp-Fe and soil-Fe lines. Two typical soils were chosen for this study, they were Walsh soil which contained CaCO_3 , and S Lake soil which did not. Equilibrium was approached from both undersaturation by adding mineral franklinite and from oversaturation by adding soluble ZnCl_2 to soils.

The initial and final Zn MF, Zn-DTPA, and Pb-DTPA concentrations in the Walsh soil treated with synthetic

franklinite after 105 d of shaking are presented in Table 5.1, and similar information for Fe is presented in Table 5.2.

Table 5.1. The initial and final Zn MF, Zn-DTPA, and Pb-DTPA concentrations in Walsh soil treated with synthetic franklinite at 105 d of shaking

Final pH	Initial			Final		
	Zn MF	Zn-DTPA	Pb-DTPA	Zn MF	Zn-DTPA	Pb-DTPA
	----- μM -----			----- μM -----		
7.93	0.00	0.00	133.3	0.0056	0.74	132.2
7.93	0.002	0.27	132.7	0.006	0.81	134.7
7.49	0.01	1.33	131.7	0.0067	0.97	143.8
7.69	0.05	6.65	126.4	0.0142	2.04	141.9

The DTPA solutions gained metals when low metal concentrations were added, and lost metals when high metal concentrations were added. For example, when no Zn was added, Zn increased to 0.74 μM ; and when 6.65 μM Zn-DTPA was added, Zn decreased to 2.04 μM (Table 5.1). Similar trends were observed for Fe in Table 5.2.

Table 5.2. The initial and final Fe MF, Fe-DTPA, and Pb-DTPA concentrations in Walsh soil treated with synthetic franklinite at 105 d of shaking

Final pH	Initial			Final		
	Fe MF	Fe-DTPA	Pb-DTPA	Fe MF	Fe-DTPA	Pb-DTPA
	----- μM -----			----- μM -----		
7.93	0.00	0.00	133.3	0.0037	0.49	132.2
7.94	0.001	0.13	132.2	0.0046	0.60	130.8
7.89	0.005	0.67	132.6	0.0063	0.83	131.3
7.88	0.02	2.66	130.6	0.0055	0.73	132.2

Tables 5.3-5.6 show measured pH values, initial Zn MF range, equilibrium Zn MF, and measured Zn^{2+} activities after 15, 30, 65, and 105 d, respectively. Tables 5.7-5.10 show similar measurements for Fe. The initial Zn MF ranges that were used varied with treatments and were estimated from previous experiments. For example, the Zn MF ranges of 65-d experiment (Table 5.4) were adjusted based on result from the 30-d experiment (Table 5.5). The initial Zn MF range for treatments W+SF, W+NF, S+SF, S+NF, and NF-WT was changed from 0-0.5 in the 30-d experiment (Table 5.4) to 0-0.3 in the 65-d experiment (Table 5.5). In the 15-d experiment (Table 5.3), the initial Zn MF range was 0-0.01 for treatments of W+WT, and S+WT; 0-0.05 for

Table 5.3 Measured pH values, initial Zn MF range, equilibrium Zn MF, and measured Zn^{2+} activities (M) at 15 d shaking

Treatment	pH	EC	Initial Zn MF range	Equilibrium	
				Zn MF	log (Zn^{2+})
Walsh + WT	6.89	0.33	0-0.01	0.008	-7.38
Walsh + SF	7.79	0.33	0-0.05	0.011	-9.00
Walsh + NF	6.75	0.36	0-0.05	0.050	-6.32
Walsh + ZN	7.25	0.33	0-1	0.095	-6.97
S Lake + WT	6.89	0.31	0-0.01	0.007	-7.43
S Lake + SF	6.76	0.32	0-0.05	0.008	-7.16
S Lake + NF	7.18	0.31	0-0.05	0.094	-6.84
S Lake + ZN	7.42	0.30	0-0.05	0.097	-7.29
NF + WT	5.64	0.15	0-1	0.016	-5.04
SF + WT	4.56	0.16	0-0.05	0.015	-3.31

treatments of W+SF, W+NF, S+SF, S+NF, NF+WT, and SF+WT; and 0-1 for the W+ZN and S+ZN treatments.

Smaller Zn MF range was used for lower Zn concentrations and larger ranges were used for higher Zn concentration. In general, the Zn MF range increased with the addition of ZnCl_2 > natural franklinite > synthetic franklinite > no addition. The larger initial MF range was used to be on the safe side. If the

Table 5.4 Measured pH values, initial Zn MF range, equilibrium Zn MF, and measured Zn^{2+} activities (M) at 30 d shaking

Treatment	pH	EC	Initial Zn MF range	Equilibrium	
				Zn MF	$\log (\text{Zn}^{2+})$
Walsh + WT	7.86	0.45	0-0.05	0.005	-9.50
Walsh + SF	7.88	0.46	0-0.05	0.005	-9.55
Walsh + NF	7.94	0.43	0-0.5	0.067	-8.49
Walsh + ZN	7.91	0.38	0-0.5	0.426	-7.42
S Lake + WT	7.81	0.43	0-0.05	0.005	-9.37
S Lake + SF	7.78	0.44	0-0.05	0.008	-9.10
S Lake + NF	7.78	0.44	0-0.5	0.447	-8.08
S Lake + ZN	7.90	0.40	0-0.5	0.138	-7.36
NF + WT	5.96	0.12	0-0.5	0.013	-4.53
SF + WT	4.79	0.12	0-0.05	0.013	-3.84

Table 5.5 Measured pH values, initial Zn MF range, equilibrium Zn MF, and measured Zn^{2+} activities (M) at 65 d shaking

Treatment	pH	EC	Initial Zn MF range	Equilibrium	
				Zn MF	$\log (\text{Zn}^{2+})$
Walsh + WT	8.05	0.39	0-0.05	0.005	-9.85
Walsh + SF	7.74	0.52	0-0.05	0.012	-8.86
Walsh + NF	8.06	0.34	0-0.3	0.096	-8.56
Walsh + ZN	7.68	0.39	0-0.3	0.097	-7.80
S Lake + WT	7.92	0.44	0-0.05	0.009	-9.34
S Lake + SF	7.98	0.39	0-0.05	0.010	-9.44
S Lake + NF	8.04	0.39	0-0.3	0.090	-8.55
S Lake + ZN	7.99	0.43	0-0.3	0.105	-8.38
NF + WT	7.50	0.14	0-0.3	0.006	-8.70
SF + WT	5.64	0.11	0-0.05	0.002	-6.03

Table 5.6 Measured pH values, initial Zn MF range, equilibrium Zn MF, and measured Zn^{2+} activities (M) at 105 d shaking

Treatment	pH	EC	Initial Zn MF range	Equilibrium	
				Zn MF	$\log (\text{Zn}^{2+})$
Walsh + WT	7.92	0.59	0-0.05	0.004	-9.69
Walsh + SF	7.93	0.57	0-0.05	0.006	-9.52
Walsh + NF	7.76	0.58	0-0.5	0.117	-7.87
Walsh + ZN	7.93	0.61	0-0.5	0.079	-8.39
S Lake + WT	7.91	0.54	0-0.05	0.006	-9.54
S Lake + SF	7.91	0.50	0-0.05	0.006	-9.54
S Lake + NF	7.88	0.53	0-0.5	0.115	-8.11
S Lake + ZN	7.80	0.58	0-0.5	0.090	-8.07
NF + WT	6.67	0.13	0-0.5	0.094	-5.89
SF + WT	5.27	0.13	0-0.05	0.012	-4.62

Table 5.7 Measured pH values, initial Fe MF range, equilibrium Fe MF, and measured Fe^{3+} activities (M) at 15 d shaking

Treatment	pH	EC	Initial Fe MF range	Equilibrium	
				Fe MF	$\log (\text{Fe}^{3+})$
Walsh + WT	7.10	0.33	0-0.01	0.0028	-18.13
Walsh + SF	7.17	0.33	0-0.05	0.0032	-18.21
Walsh + NF	6.87	0.34	0-0.05	0.0036	-17.56
Walsh + ZN	7.21	0.33	0-0.01	0.0026	-18.38
S Lake + WT	6.71	0.31	0-0.01	0.0011	-17.16
S Lake + SF	6.83	0.32	0-0.05	0.0016	-17.83
S Lake + NF	6.82	0.31	0-0.05	0.0020	-17.72
S Lake + ZN	6.72	0.30	0-0.01	0.0031	-17.33
NF + WT	5.22	0.15	0-0.05	0.0021	-14.34
SF + WT	5.23	0.16	0-0.05	0.0019	-14.41

Table 5.8 Measured pH values, initial Fe MF range, equilibrium Fe MF, and measured Fe^{3+} activities (M) at 30 shaking

Treatment	pH	EC	Initial Fe MF range	Equilibrium	
				Fe MF	$\log (\text{Fe}^{3+})$
Walsh + WT	7.93	0.45	0-0.02	0.0069	-19.38
Walsh + SF	7.82	0.46	0-0.02	0.0072	-19.14
Walsh + NF	7.89	0.43	0-0.02	0.0066	-19.32
Walsh + ZN	7.84	0.38	0-0.02	0.0066	-19.23
S Lake + WT	7.59	0.43	0-0.02	0.0120	-18.46
S Lake + SF	7.80	0.44	0-0.02	0.0071	-19.11
S Lake + NF	7.78	0.44	0-0.02	0.0087	-18.98
S Lake + ZN	7.76	0.38	0-0.02	0.0099	-18.90
NF + WT	5.16	0.12	0-0.02	0.0083	-13.73
SF + WT	4.56	0.12	0-0.02	0.0042	-12.40

Table 5.9 Measured pH values, initial Fe MF range, equilibrium Fe MF, and measured Fe^{3+} activities (M) at 65 d shaking

Treatment	pH	EC	Initial Fe MF range	Equilibrium	
				Fe MF	$\log (\text{Fe}^{3+})$
Walsh + WT	8.01	0.39	0-0.01	0.0024	-20.01
Walsh + SF	7.16	0.52	0-0.05	0.0025	-18.27
Walsh + NF	7.97	0.34	0-0.05	0.0025	-19.92
Walsh + ZN	8.02	0.39	0-0.01	0.0038	-19.83
S Lake + WT	7.92	0.44	0-0.01	0.0026	-19.62
S Lake + SF	7.99	0.39	0-0.05	0.0053	-19.62
S Lake + NF	7.66	0.39	0-0.05	0.0036	-19.13
S Lake + ZN	7.97	0.43	0-0.01	0.0032	-19.80
NF + WT	7.44	0.14	0-0.05	0.0039	-18.72
SF + WT	5.36	0.11	0-0.05	0.0032	-14.52

Table 5.10 Measured pH values, initial Fe MF range, equilibrium Fe MF, and measured Fe^{3+} activities (M) at 105 d shaking

Treatment	pH	EC	Initial Fe MF range	Equilibrium	
				Fe MF	$\log (\text{Fe}^{3+})$
Walsh + WT	7.63	0.59	0-0.02	0.0033	-19.08
Walsh + SF	7.89	0.57	0-0.02	0.0062	-19.32
Walsh + NF	7.80	0.58	0-0.02	0.0043	-19.30
Walsh + ZN	7.83	0.61	0-0.02	0.0043	-19.36
S Lake + WT	7.84	0.54	0-0.02	0.0059	-19.25
S Lake + SF	7.82	0.50	0-0.02	0.0044	-19.35
S Lake + NF	7.75	0.53	0-0.02	0.0029	-19.38
S Lake + ZN	7.87	0.58	0-0.02	0.0067	-19.25
NF + WT	6.61	0.13	0-0.02	0.0082	-16.73
SF + WT	5.09	0.13	0-0.02	0.0060	-13.58

equilibrium MF was not in the initial MF range, the experiment had to be repeated at a more appropriate MF range. In contrast to the initial Zn MF ranges, the initial Fe MF range did not change much from one experiment to another. Similar initial Fe MF ranges were used throughout this study (Table 5.8-5.10)

The measured pH's in treatments of NF+WT and SF+WT were considerably lower than those of treatments containing soil (Table 5.3 to 5.10). The presence of soil buffer the pH, while treatments without soil were more acidic. Theoretically, pH should increase with the dissolution of franklinite. For each

mole of franklinite dissolved, eight moles of H^+ are consumed according to the reaction:

Apparently there was some residual acid remaining in the franklinite, which had been acid washed, even though it was rinsed with water and acetone.

The pH of treatments with synthetic franklinite were even lower than those with natural franklinite (Table 5.3 to 5.10). For example, the 15-d treatment (Table 5.3) had a pH of 5.64 for natural franklinite and 4.56 for synthetic franklinite.

The measured Zn^{2+} activities were pH dependent, decreasing with increase in pH, even for the same soil with different treatments. The correlation coefficients of $\log (Zn^{2+})$ with pH were 0.81, 0.90, 0.86, and 0.91 for the ten treatments listed in Table 5.3 to 5.6 for the shaking period of 15, 30, 65, and 105 d, respectively.

Surprisingly, the measured Fe^{3+} activities were significantly correlated with pH, the correlation coefficients for the ten treatments at all shaking period were 0.99. Thus, the correlation coefficients of $\log (Fe^{3+})$ vs pH are higher than those of Zn. This may be caused by the different kinetics of Zn and Fe in solid formation. It seems easier for Fe to precipitate in response to pH changes than for Zn due to the presence of Fe hydroxide in addition to franklinite.

The measured Zn^{2+} activities in the Walsh soil vs pH are plotted in Fig. 5.2 to 5.5 for shaking period of 15, 30, 65, and

Fig. 5.2 Measured Zn^{2+} activities in the Walsh soil after 15 d shaking

Fig. 5.3 Measured Zn^{2+} activities in the Walsh soil at 30 d shaking

Fig. 5.4 Measured Zn^{2+} activities in the Walsh soil at 65 d shaking

Fig. 5.5 Measured Zn^{2+} activities in the Walsh soil at 105 d shaking

105 d, respectively. Similar results were obtained in S Lake soil. The Zn solubility of natural franklinite was higher than that of synthetic franklinite in both pure water and soil treatments. The Zn^{2+} solubilities at 15 d of shaking decreased in the following order: $\text{W+ZN} > \text{W+NF} > \text{W+SF} > \text{W+WT}$.

After 30 d reaction, the Zn solubility in Walsh soil treated with ZnCl_2 was similar to that of natural franklinite, while the Zn solubility of synthetic franklinite was closer to that of the soil receiving no treatment. Addition of soluble Zn or the franklinite minerals increased the Zn^{2+} activities in these soils. The Zn^{2+} activities resulting from these four treatments fell between the solubilities of Zn_2SiO_4 -Soil-Si and Soil-Zn (Fig. 5.2 and 5.3). Similar results were obtained at 30 d of shaking. The Zn^{2+} activities in treatments of W+WT and W+SF at 15 or 30 d of shaking were about the same magnitude. At 62 d of shaking, the Zn^{2+} activities in treatments of W+ZN and W+NF were the same, at 105 d, the Zn^{2+} activities in W+ZN was lower than that of W+NF.

At 65 d of shaking, the Zn^{2+} activities for the various treatments were in the order: $\text{W+ZN and W+NF} > \text{W+SF and W+WT}$, and at 105 d of shaking: $\text{W+NF and W+ZN} > \text{W+SF and W+WT}$. The solubility of synthetic franklinite was close to that of soil itself. In other words, synthetic franklinite controls Zn^{2+} activities very near to soil-Zn.

The natural franklinite maintained a slightly higher Zn^{2+} activity at all shaking periods compared to soil itself. The Zn^{2+} activities maintained by natural franklinite and the reaction products from soluble Zn were similar but higher than those of synthetic franklinite and soil-Zn. The addition of soluble Zn to soil maintained higher Zn^{2+} activities even after 105 d reaction. Sufficient ZnCl_2 was added to furnish 6 ppm or $10^{-4.03}$ M Zn^{2+} concentration in soils. The measured Zn^{2+} activity after 105 d of shaking in the Walsh soil was $10^{-8.39}$ M and in S Lake $10^{-8.07}$ M (Table 5.6), showing that Zn^{2+} activities decreased considerably.

Changes in Zn solubility with shaking period for the S Lake soil are presented in Figure 5.6-5.9 for treatments of S+WT, S+SF, S+NF, and S+ZN, respectively. There were no significant difference in Zn solubility at the different shaking periods within each treatment. In S Lake soil with no addition (Fig. 5.6), the measured Zn^{2+} activities was near the soil-Zn line. A similar trend was observed with added synthetic franklinite. Treatment of the S Lake soil with either soluble Zn or natural franklinite raised the Zn^{2+} activity above the soil-Zn line and closer to the Zn_2SiO_4 -soil-Si line. The added soluble Zn was fixed by soil within the first 15 d of reaction, after which little change occurred.

When the soil suspensions were stirred with a magnetic stirring bar, some black magnetic Fe minerals adhered to the bar.

Fig. 5.6 Measured Zn^{2+} activities in water extracts of S Lake soil at different shaking periods

Fig. 5.7 Measured Zn^{2+} activities following the addition of synthetic frankinite to S Lake soil at different reaction periods

Fig. 5.8 Measured Zn^{2+} activities following the addition of natural franklinite to S Lake soil at different reaction periods

Fig. 5.9 Measured Zn^{2+} activities following the addition of soluble Zn to S Lake soil at different reaction periods

The mineral was manually put back into the soil suspensions. Maghemite is one of the magnetic Fe minerals present in these soils.

The measured Fe^{3+} activities in S Lake soil after 15, 30, 65 and 105 d of shaking are given in Fig. 5.10 to 5.13. Similar results were obtained with the Walsh soil. There was little difference in Fe solubility in treatments W+NF, W+ZN, and W+WT, and they were close to soil-Fe line at 15 d (Fig. 5.10). After 30 d of shaking, the measured Fe^{3+} activities were slightly above amorp-Fe (Fig. 5.11). The activity measurements of Fe^{3+} at 65 and 105 d of shaking showed very little change and raised slightly above the amorp-Fe line.

The measured Fe^{3+} activities in the Wlsh soil were very similar to the S Lake soil (Fig. 5.14 to 5.17). The measured Fe^{3+} activities did not change significantly with shaking periods or with addition of the various Zn minerals.

The conclusion is drawn that franklinite may vary slightly in composition and solubility depending upon the conditions of its synthesis. Carefully prepared franklinite supports Zn^{2+} activities very near that of the two soils studied here, and may indeed be an important mineral controlling the solubility of Zn^{2+} in soils.

Fig. 5.10 Measured Fe^{3+} activities in S Lake soil at 15 d shaking

Fig. 5.11 Measured Fe^{3+} activities in S Lake soil at 30 d shaking

Fig. 5.12 Measured Fe^{3+} activities in S Lake soil at 65 d shaking

Fig. 5.13 Measured Fe^{3+} activities in S Lake soil at 105 d shaking

Fig. 5.14 Measured Fe^{3+} activities in water extracts of Walsh soil at different shaking periods

Fig. 5.15 Measured Fe^{3+} activities following the addition of synthetic franklinite to Walsh soil at different reaction periods

Fig. 5.16 Measured Fe^{3+} activities following the addition of natural franklinite to Walsh soil at different reaction periods

Fig. 5.17 Measured Fe^{3+} activities following the addition of soluble Zn to Walsh soil at different reaction periods

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7. CADMIUM IONIC ACTIVITY IN NON-POLLUTED ARID-ZONE SOIL SOLUTIONS

by

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INTRODUCTION

The Cd ion selective electrode (Cd-ISE) was used to directly measure Cd^{2+} activity in water and in soil solutions in a number of studies in the past. The electrode is recommended for use in the range of 10^{-1} - 10^{-7} M cadmium and its response drops considerably below the theoretical 29.6 mV/10 fold change in concentration, between 10^{-6} M and 10^{-7} M.

In many cases, total cadmium concentration (Cd_t) in soil solutions is in the range of 10^{-9} - 10^{-7} M and Cd^{2+} constitutes only between 20-80% of this. Therefore the direct measurement of Cd^{2+} in extracted soil solutions did not yield meaningful data except for cases of high, non-realistic additions of Cd. In the present project, we have shown (Hirsch and Banin, 1990) that free Cd^{2+} fraction in extracted soil solutions can be accurately measured with Cd-ISE, using an addition method. Cd^{2+} activity in the non-treated solution can then be calculated from measurements of Cd_t , assuming excess complexing agents in solution. Cd_t in aqueous soil solutions can be precisely measured down to $5 \cdot 10^{-9}$ M (~0.5 ppb) using GFAA; thus, the "limit of detection" for Cd^{2+} activity in soil solutions by the addition method may be in the range of $1 \cdot 10^{-9}$ - $4 \cdot 10^{-9}$, assuming $\text{Cd}^{2+}/\text{Cd}_t$ of 0.2-0.8. This represents an improvement of about 2 orders of magnitude in our ability to measure directly Cd^{2+}

activity in water and in soil and sediment solutions. This enables the direct measurement of Cd^{2+} activity in non-polluted soil solutions and following the addition of realistic pollution loads of this metal, such as may be accumulated after prolonged irrigation with reclaimed sewage water.

EXPERIMENTAL

Cadmium speciation in the soil solution was determined in a group of 36 soils from Israel. The soils were sampled from the top 5 cm horizon of non-polluted, mostly non-cultivated lands representing the major soil types of Israel. Saturated soil pastes (SP) were prepared and extracted. Total Cd (Cd_t) was measured in the SP extract by GFAA and Cd^{2+} activity ("free Cd") was measured by the addition method using the Cd ion selective electrode (Cd-ISE). Both procedures are described in detail in Hirsch and Banin (1990; Chapter 6 in this report). The pH and the concentrations of the various ionic constituents in the extracted solutions were analyzed. The speciation model (Hirsch and Banin, 1990; Chapter 6 in this report) was used to calculate the fractions of the major soluble Cd species in the soil solutions.

RESULTS

Solution composition of the soils is presented in Table 1. The soil solutions varied widely in their total ionic strength, as

measured by their electrical conductivity, and in their ionic composition.

The speciation of cadmium is given in Table 2. The major species in most of the soil solutions was the "free Cd" (Cd^{2+}). It comprised from 40 to 80% of the Cd present in solution. In highly saline soils, the fraction of the Cd-Cl complexes increased considerably. In calcareous and alkaline soils, the Cd-carbonate species became important.

Agreement between Cd^{2+} fraction measured (m) by the Cd-ISE and calculated (c) by the speciation model is generally good, giving the following linear regression equation and coefficient of correlation:

$$C = 7.2 + 1.02m; \quad r = 0.81 \quad (n = 36)$$

This is significant at a probability $p = 0.01$.

To determine what mineral is controlling Cd^{2+} activity in these soils, a "solubility plot" ($\log \text{Cd}^{2+}$ vs pH) is given in Fig. 1. Free Cadmium (Cd^{2+}) activity did not show a negative dependence on pH, which was expected if the newly defined soil-Cd or otavite (CdCO_3) controlled it (Workman and Lindsay, 1990). It appears that Cd^{2+} activity in this group of non-polluted soils is controlled by sorption mechanisms rather than by a single solid-phase mineral. The difference between the behavior of the group of eight Colorado soils and the group of 36 Israeli soils may be related to differences in the mineralogical compositions of the soils and in the solid phase Cd-adsorption sites present. Further study is required to resolve this question.

Table 1. Total soluble concentrations and other properties of solutions extracted from saturated pastes of various soils of Israel.

Soil	Cd	Ca	Mg	Cl	NO ₃ meg/l	SO ₄	HCO ₃	pH	EC (dS/m)	pCO ₂ (atm.)
A1	20	4.3	25	1.3	0.00	1.1	52	7.40	0.71	0.0130
A2	13	3.2	3.9	1.0	0.00	0.8	27	7.65	0.46	0.0039
A4	8	5.5	12	2.8	0.01	2.2	3.5	7.90	0.86	0.0028
B1	18	4.9	0.7	0.7	0.12	2.0	4.8	7.40	0.63	0.0120
B2	6	3.2	0.5	0.4	0.09	0.8	3.0	7.15	0.39	0.0140
B5	12	5.6	0.9	1.5	0.12	1.9	1.6	7.30	0.82	0.0052
B8	26	8.0	1.3	1.8	0.15	7.4	5.4	7.90	1.21	0.0044
B9	13	9.8	0.9	1.2	0.01	8.4	5.1	8.05	1.17	0.0029
B10	17	2.3	0.5	1.4	0.01	1.5	2.3	7.80	0.48	0.0023
C5	7	4.6	1.0	0.8	0.21	1.9	3.8	7.50	0.64	0.0079
C10	15	5.9	1.6	1.3	0.14	2.5	5.9	7.25	0.87	0.0210
E1	19	2.7	0.6	0.7	0.34	0.9	3.9	7.50	0.50	0.0081
E4	13	3.5	0.1	1.4	0.17	0.9	3.7	7.10	0.57	0.0190
E5	33	6.4	1.8	6.5	2.40	9.2	1.3	7.20	1.82	0.0054
EB	11	1.3	0.4	0.6	0.25	0.7	0.6	6.05	0.22	0.0350
H1	15	3.1	0.7	2.0	0.01	2.4	3.3	8.20	0.73	0.0013
H4	14	4.4	0.7	1.3	0.00	2.0	4.3	8.15	0.67	0.0019
H6	20	5.1	2.2	28.3	0.26	10.7	2.2	8.30	4.32	0.0007
H11	63	6.9	2.5	16.6	0.26	4.0	2.5	7.90	2.31	0.0020
H13	42	5.8	2.2	1.6	0.05	3.9	4.9	8.45	0.86	0.0011
J1	22	7.4	4.0	6.2	9.86	3.0	2.0	7.80	2.24	0.0020
J2	25	11.3	3.0	6.3	0.14	6.6	6.2	8.50	1.63	0.0012
J3	20	4.8	1.8	1.2	0.02	0.9	5.6	8.30	0.70	0.0018
K1	21	192.0	164.0	485.0	3.47	8.6	1.7	6.95	37.70	0.0120
K2	23	23.9	18.0	23.8	0.59	20.2	13.8	8.30	4.80	0.0044
K3	21	16.0	16.3	18.1	1.17	8.3	3.6	7.80	7.97	0.0037
K4	27	66.4	87.5	320.0	16.60	46.8	2.6	7.45	30.00	0.0060
K5	10	5.6	3.1	9.3	0.32	2.0	4.5	7.90	1.56	0.0037
K6	8	6.7	3.2	16.1	0.24	4.3	4.1	7.90	2.44	0.0033
K7	33	3.9	2.4	3.2	0.07	2.7	4.9	8.00	0.96	0.0032
K8	35	9.2	16.4	50.0	0.50	13.3	3.7	7.55	5.93	0.0068
O1	101	5.4	2.0	2.6	0.03	3.2	3.5	8.10	0.86	0.0018
O4	49	10.0	3.8	40.0	0.79	2.3	2.2	7.70	4.82	0.0028
P1	37	35.8	2.4	1.0	0.14	37.4	1.6	6.90	2.59	0.0130
P2	50	24.8	10.9	13.6	1.02	66.7	1.0	7.35	6.12	0.0029
W1	47	4.3	1.7	7.8	0.22	5.8	2.2	8.25	1.48	0.0008

Table 2. Calculated cadmium speciation and measured free Cd percentages out of total Cd in the solutions of arid-zone soils.

Soil	Measured Cd ²⁺	Calc.	CdOH ⁺	CdCl ⁺	CdCl ₂ [°] (%)	CdSO ₄ [°]	CdHCO ₃ ⁺	CdCO ₃ [°]	CdNO ₃ [°]
A1	42	61.3	0.1	4.8	0.0	2.9	27.9	2.9	0.0
A2	61	71.5	0.2	4.6	0.0	2.8	17.5	3.3	0.0
A4	39	58.9	0.3	10.3	0.0	6.2	18.2	6.1	0.0
B1	37	61.3	0.1	2.7	0.0	6.2	26.7	2.8	0.0
B2	67	72.2	0.1	2.0	0.0	3.6	20.8	1.3	0.0
B5	67	74.0	0.1	7.1	0.0	6.9	10.8	0.9	0.0
B8	41	50.1	0.2	5.1	0.0	14.7	22.4	7.3	0.0
B9	37	49.9	0.3	3.3	0.0	16.2	20.7	9.5	0.0
B10	58	67.7	0.3	6.5	0.0	6.5	14.9	4.1	0.0
C5	50	64.8	0.1	3.3	0.0	6.3	22.5	3.0	0.0
C10	49	57.1	0.1	0.8	0.0	6.7	29.4	2.2	0.0
E1	37	65.9	0.1	2.3	0.0	3.8	24.5	3.3	0.0
E4	46	65.8	0.1	6.2	0.0	3.6	23.0	1.2	0.0
E5	58	54.2	0.0	19.5	0.5	19.6	5.7	0.4	0.2
E8	77	86.3	0.0	3.8	0.0	4.4	5.2	0.0	0.3
H1	38	56.0	0.5	7.3	0.0	7.8	16.9	11.4	0.0
H4	33	55.0	0.5	4.6	0.0	5.8	21.4	12.8	0.0
H6	25	31.4	0.3	44.2	0.0	11.2	5.1	4.0	0.0
H11	47	42.3	0.2	38.2	2.0	6.1	8.5	2.7	0.0
H13	24	45.7	0.7	4.4	0.0	7.9	19.0	22.3	0.0
J1	58	59.7	0.2	20.3	0.4	6.6	9.6	2.5	0.7
J2	34	37.5	0.6	12.6	0.3	8.0	18.0	23.0	0.0
J3	42	48.9	0.6	3.7	0.0	2.2	24.2	20.4	0.0
K1	10	3.5	0.0	46.4	49.8	0.1	0.3	0.0	0.0
K2	29	25.3	0.2	24.7	1.6	8.9	22.4	16.9	0.0
K3	31	40.6	0.1	35.4	2.0	8.5	10.7	2.7	0.0
K4	23	13.0	0.0	59.5	21.7	3.8	1.7	0.2	0.1
K5	43	46.9	0.2	24.9	0.7	3.9	17.5	5.7	0.0
K6	39	40.2	0.2	34.6	1.7	6.1	13.0	4.2	0.0
K7	53	51.5	0.3	10.1	0.1	6.8	22.0	9.2	0.0
K8	34	25.6	0.0	53.3	7.3	6.7	6.2	0.8	0.0
O1	41	56.3	0.4	8.9	0.0	8.3	17.0	9.0	0.0
O4	40	29.6	0.1	56.2	6.6	1.9	4.7	1.0	0.0
P1	42	53.6	0.0	2.3	0.0	38.1	5.8	0.2	0.0
P2	29	36.3	0.0	18.8	0.7	41.7	2.2	0.2	0.0
W1	48	48.7	0.5	22.1	0.6	12.6	8.9	6.6	0.0

Figure 1. Total Cd (Cd_t) measured by GFAA and Cd^{2+} activity calculated from it using a Cd speciation model (Hirsch and Banin, 1990), plotted vs pH. Measurements were done on saturated-paste extracts of 36 non-polluted arid-zone soils from Israel.

10. CADMIUM ACTIVITIES MEASURED IN CONTAMINATED SOILS USING COMPETITIVE CHELATION

S. M. Workman, R. Jump, and W. L. Lindsay

INTRODUCTION

Mining and mining-related industries have contaminated soils with Cd in areas of the western United States. Mechanisms controlling Cd solubility in these soils are not well understood. Measurement of free Cd^{2+} activities is useful for characterizing solubility controls in these soils. Direct measurement of this parameter is difficult for two reasons: 1) Contaminated soils usually contain high levels of other metals such as Cu, Pb, and Zn which interfere with the Cd ion selective electrode, 2) Calculation of free Cd^{2+} from total soluble Cd using equilibrium models cannot be accurately performed without knowing both organic and inorganic species in solution. These problems can be overcome by measuring Cd^{2+} activities using competitive chelation methods.

Review of Competitive Chelation Theory

Competitive chelation has been used to measure metal activities in soils by several researchers (Norvell and Lindsay, 1969; Lindsay and Norvell, 1969; Lindsay, 1979; Norvell and Lindsay, 1972; Norvell and Lindsay, 1980; and Ma and Lindsay, 1990). Workman and Lindsay (1990) described the general theory for competitive chelation methods and used competitive chelation to estimate Cd^{2+} activities supported by uncontaminated arid-zone soils.

Competitive chelation measurements were made by reacting a series of chelate solutions with a soil. The chelate solutions contained a constant total chelate concentration and varying initial mole fractions of chelated Cd and a competing metal. In this research, DTPA (diethylenetriaminepentaacetic acid) was chosen as the chelating agent along with Pb as the competing metal. When reacted with a soil, some of the solutions lost Cd and gained Pb, while other solutions gained Cd and lost Pb. From these results it was possible to determine the composition of a unique solution that would not change upon reaction with a given soil. The composition of the unique solution reflected the composition of a solution at equilibrium with the soil and was used to calculate Cd^{2+} activity.

MATERIALS AND METHODS

Soil samples were collected from three areas in Colorado. Table 10.1 lists the properties of the soils. The areas were known to have been contaminated with heavy metals. A brief description of each area is given below.

Table 10.1. Properties of the soils used in this study.

Sample	Site	pH (1:2)	----- % -----				
			CaCO ₃	Total Organic Carbon	Sand	Silt	Clay
G-1	Globeville	6.60	<0.1	0.6	68	19	13
G-2	Globeville	8.15	1.5	0.4	38	31	31
G-3	Globeville	6.30	<0.1	2.6	50	33	17
L-1	Leadville	6.50	<0.1	6.4	50	34	16
L-2	Leadville	6.85	<0.1	5.7	44	30	26
L-3	Leadville	7.20	<0.1	6.8	60	28	12
A-1	Aspen	8.00	5.5	1.4	66	19	15

Globeville site: This area is near a smelter on the northern edge of the city of Denver, Colorado. Smelting operations have been carried out at this site for over 100 years. Since 1926, the plant has smelted Cd. Three samples were collected and designated G-1, G-2, and G-3.

Leadville site: This area is located near Leadville, Colorado along the Arkansas River. Mining has been the principal industry in this region since the mid-1800's. The primary sources of heavy metal contamination are: irrigation water containing acid mine drainage; mining wastes which were washed into the valley by hydraulic mining activities; parent materials containing high levels of heavy metals. Three samples were collected and were designated L-1, L-2, and L-3.

Aspen site: This area is near Aspen, Colorado. Soils at this site have been contaminated by waste rock which was removed from silver mines. The waste rock contains high levels of heavy metal carbonate minerals. One soil was collected at this site and was designated A-1.

Preliminary experiments were performed to determine initial chelate loadings, i.e., $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fractions and total chelate concentrations, which would allow a unique $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fractions to be identified representing equilibrium conditions. The preliminary experiments consisted of reacting the soils with pure water, and solutions initially containing $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fractions of 0 and 1. Total chelate concentrations were also varied to accommodate the wide concentration ranges of potentially

chelatable metals in the soils. The following criteria were used to evaluate if a given combination of initial $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fractions and total chelate concentration could be successfully used.

First, a significant amount of Cd should be chelated by solutions which initially contained only chelated Pb (initial $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fraction = 0). Chelated Cd was determined by subtracting the Cd concentration measured in pure water extracts from the Cd concentration measured in the extracts containing DTPA. The chelated Cd concentration was considered significant if it was either at least 5 times higher than the instrument detection limit (if no Cd was detected in the pure water extract), or at least 2 times higher than the concentration of Cd measured in the pure water extract.

Second, a significant amount of Pb should be chelated by solutions which initially contained only chelated Cd (initial $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fraction = 1). Chelated Pb was determined by subtracting the Pb concentration measured in pure water extracts from the Pb concentration measured in extracts containing DTPA. The chelated Pb was considered significant if it was at least 5 times higher than the instrument detection limit (if no Pb was detected in the pure water extract) or at least 2 times higher than the concentration of Pb measured in the pure water extract. Following the preliminary experiments, a series of at least 6 solutions containing varying $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fractions were prepared for each soil. The

solutions were made by dissolving reagent grade DTPA, $\text{Cd}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ in deionized water. The pH of the solutions was adjusted to 7.0 using HCl or NaOH prior to reacting the solutions with the soils. Table 10.2 lists the compositions of the solutions used for each soil.

Table 10.2 Composition of the solutions reacted with soils in this study.

Sample	(moles/L) Total DTPA	Initial CdDTPA/(CdDTPA + PbDTPA) mole Fractions					
G-1	5×10^{-3}	0,	1.2,	0.4,	0.6,	0.8,	1.0
G-2	1×10^{-4}	0,	0.2,	0.4,	0.6,	0.8,	1.0
G-3	1×10^{-4}	0,	0.2,	0.4,	0.6,	0.8,	1.0
L-1	1×10^{-4}	0,	0.05,	0.1,	0.15,	0.5,	1.0
L-2	1.5×10^{-2}	0,	0.2,	0.3,	0.4,	0.5,	0.6, 0.8, 1.0
L-3	1×10^{-4}	0,	0.2,	0.4,	0.6,	0.8,	1.0
A-1	1×10^{-4}	0,	0.2,	0.4,	0.6,	0.8,	1.0

The soils were reacted with the chelate solutions and also with pure water by weighing 10 g subsamples into 125 ml Erlenmeyer flasks and adding 20 ml of solution. The flasks were covered with perforated parafilm and shaken at 180 rpm on a rotary shaker for 6 days. Either 10 mg of PbCO_3 or PbSO_4 was added to each suspension, prior to shaking, to maintain a constant Pb^{2+} activity. PbCO_3 was added to soils with pH values less than 7.0.

The pH of the suspensions were measured immediately at the end of the shaking period, using a combination glass electrode. The suspensions were centrifuged at 15,000 rpm for 20 minutes. The supernatant solutions were analyzed for: metals using a

Jarrell Ash model 975 inductively coupled plasma atomic emission spectrometer (ICP); electrical conductivity using a Yellow Springs Instruments Model 35 conductivity meter; SO_4^{2-} was measured using a Dionex model 2000i ion chromatograph.

Total heavy metal contents of the soils was evaluated by digesting 1 g of soil with 10 ml of 1:1 $\text{HNO}_3\text{-HClO}_4$ acid in 50 ml calibrated test tubes. The test tubes were heated in a block digester. The temperature was slowly increased from 100° to 200° C over a 2-hour period and was held at 200°C until dense, white fumes were produced and the soil appeared as grayish-white sand. When the digestion was completed, the volume was adjusted to 50 ml, the solution was mixed and allowed to settle; the clear solution was analyzed by ICP.

Calculations: The following reaction describes the competition between Pb^{2+} and Cd^{2+} for the DTPA ligand. An equilibrium constant for this reaction was measured by Workman and Lindsay (1990).

An expression for Cd^{2+} activity can be derived from this reaction:

$$(\text{Cd}^{2+}) = \frac{10^{0.644} (\text{Pb}^{2+}) (\text{CdDTPA})}{(\text{PbDTPA})} \quad [2]$$

from which (Cd^{2+}) can be calculated if equilibrium values for

(Pb^{2+}) and the (CdDTPA)/(PbDTPA) ratio can be determined. The Pb^{2+} activity was calculated from the following expressions. The equilibrium reactions used to derive these expressions are given by Lindsay (1979). When PbCO_3 was added to the suspensions:

$$(\text{Pb}^{2+}) = 10^{8.17 - 2\text{pH}} \quad [3]$$

When PbSO_4 was added to the suspension:

$$(\text{Pb}^{2+}) = 10^{-7.79 - \log(\text{SO}_4^{2-})} \quad [4]$$

The equilibrium (CdDTPA)/(PbDTPA) ratio was determined graphically as shown in Fig. 10.1 which shows changes in the composition of solutions of different initial $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fractions upon reaction with soil L-2. The unique $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA})$ mole fraction for soil L-2 was found to be 0.4. If $\text{CdDTPA}/(\text{CdDTPA} + \text{PbDTPA}) = 0.4$, then

$$\text{CdDTPA}/\text{PbDTPA} = \frac{0.4}{1 - 0.4} = 0.67$$

Equilibrium $\text{CdDTPA}/\text{PbDTPA}$ ratios for the other soils were determined similarly.

Fig. 10.1. Changes in CdDTPA/(CdDTPA + PbDTPA) mole fractions after reacting solutions with soil L-2 for 6 d. The intersection of the two lines gives the CdDTPA/(CdDTPA + PbDTPA) mole fraction that reflects equilibrium.

RESULTS AND DISCUSSION

Competitive chelation using DTPA with Pb^{2+} as the competing metal provides a good tool for measuring Cd^{2+} activities in contaminated soils. The solutions which were used for measuring Cd^{2+} activities in contaminated soils contained higher chelate concentrations than solutions which were used for determining Cd^{2+} activities supported by uncontaminated soils (Workman and Lindsay, 1990). The higher chelate concentrations were necessary to provide sufficient ligand to chelate the higher concentrations of heavy metals present in contaminated soils. Preliminary experiments showed that if insufficient chelate was used, the chelate became dominated by Zn and Cu, leaving little ligand available to chelate Cd and Pb.

The Cd^{2+} activities supported by the contaminated soils are plotted vs. pH in Fig. 10.2. Solubilities of CdCO_3 (in equilibrium with atmospheric CO_2) and CdSiO_3 (in equilibrium with soil-Si, Lindsay, 1979) are shown for reference. The Cd^{2+} activities measured by Workman and Lindsay (1990) in uncontaminated soils are also included. Contaminated soils with pH values greater than 7.0 (A-1, L-3, G-2) supported Cd^{2+} activities very near those in equilibrium with CdCO_3 . It seems likely that CdCO_3 controls Cd solubility in these soils. The Cd^{2+} activities in the alkaline contaminated soils were approximately 2 orders of magnitude more soluble than the Cd activities measured in uncontaminated soils.

Fig. 10.2 Plot of Cd²⁺ activity measured as a function of pH for the soils used in this study.

In acidic contaminated soils, Cd^{2+} was less soluble than CdCO_3 . The solubilities of Cd^{2+} in the acidic soils appeared to be independent of pH. Cation exchange reactions may be controlling Cd solubility in the acidic contaminated soils.

An interesting observation was made concerning the 0.25 M DTPA extracts which were used to determine the levels of potentially chelatable metals in these soils. The concentrations of Cd which were extracted using 0.25 M DTPA were very similar to concentrations found by digesting the soil with concentrated HNO_3 and HClO_4 acids (Table 10.3). This high chelate concentration provided sufficient ligand to chelate nearly all the Cd in these soils. This type of extraction could be used as a simple method for evaluating the extent of Cd contamination in soils without the use of strong acids.

Table 10.3 Total Cd and 0.25 M DTPA extractable Cd measured in contaminated soils.

Sample	Total	0.25 M DTPA Extractable
	- - - - - Cd (mg/kg) - - - - -	
G-1	131	138
G-2	21	19
G-3	31	26
L-1	40	30
L-2	72	62
L-3	20	18
A-1	107	76

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11. MEASUREMENT OF Cd^{2+} ACTIVITIES USING CHELATION

Qiyang Ma and W. L. Lindsay

ABSTRACT

Cadmium solubility in soils is of concern to many soil scientists due to its biological toxicity, including human health problems. Free Cd^{2+} activities in 7 normal and 3 contaminated soils were determined using the chelation method. The measured Cd^{2+} activities were highly pH dependent with a correlation coefficient of 0.98 and 0.99 in the normal and the contaminated soils, respectively. The measured Cd^{2+} activities in the contaminated soils were higher than those of the normal soils, and can be predicted using the equation: $\log (\text{Cd}^{2+}) = (7.33 \pm 0.09) - 2 \text{ pH}$. Those in the normal soils can be divided into two groups. The Cd solubility in soils of $\text{pH} > 7$ were close to soil-Cd, and can be predicted using the equation: $\log (\text{Cd}^{2+}) = (6.1 \pm 0.17) - 2 \text{ pH}$. Those in soils with $\text{pH} < 7$ were undersaturated with respect to soil-Cd. Adsorption-desorption may be important in regulating Cd^{2+} activities in the normal soils of low pH, while precipitation-dissolution process may operate in soils of high pH and high Cd levels. The formation of CdCO_3 seems unlikely in the soils reported herein.

INTRODUCTION

Recent concern over environmental contamination by Cd has generated interest in mechanisms governing Cd solubility in soils. The main sources of contamination include mining,

smelting, application of pesticides, phosphate fertilizers, sewage sludge and municipal compost (Tjell et al., 1981). Cadmium in soil solution is buffered by Cd in solid phases (Lindsay, 1972). The solid phases may involve either adsorption or exchange reactions or mineral precipitates. Understanding Cd levels and mechanisms controlling Cd solubility by various soil constituents is helpful for developing soil management practices to reduce plant uptake of Cd and to reduce groundwater contamination.

Despite extensive studies on Cd in soils, its solubility is poorly understood and difficult to predict. Cadmium solubility in soils may be controlled by different mechanisms depending on the chemical nature of soils. These include precipitation as sparingly soluble compounds such as CdCO_3 or $\text{Cd}_3(\text{PO}_4)_2$, co-precipitation and formation of solid solutions with other precipitates in soils such as CaCO_3 , adsorption onto charged surfaces of clays, organic matter, and free oxides, and complexation with organic ligands (Cavallaro and McBride, 1978; and Lindsay, 1972). According to Bruemmer et al. (1986), the adsorption-desorption process combined with the complexation process of organic and inorganic ligands determines Cd solubility in acid soils. Formation of sparingly soluble salts is possible under specific conditions where relatively high levels of Cd are present and sufficient anions and cations are present to form Cd compounds, and adsorption sites do not strongly bind Cd. Soil pH definitely plays an important role in precipitation process.

Precipitation of insoluble compounds are expected to control Cd^{2+} activities in soils in the neutral to alkaline pH range (Street et al., 1977; Neal and Sposito, 1986; and Soon, 1981).

Considerable effort has been devoted to estimating free Cd^{2+} activities in soils, which is critical for understanding the mechanisms controlling Cd^{2+} activities. The presence of unknown organic complexes complicated the use of speciation models such as GEOCHEM and MINTEQA2 to calculate activities from total concentrations of Cd in soil solutions. The organic complexes have often been neglected due to their uncertainty (O'Connor et al., 1984; Dudley et al., 1988; and Street et al., 1978).

With the advance of technology, Cd ion-selective electrode has been used by many researchers (Street et al., 1977; and McBride, 1980). The cadmium electrode is only useful when Cd^{2+} activity is above the detection limit of approximately $10^{-6.25}$ M (Street et al., 1977).

The solubility of Cd in soils is generally lower than the detection limit of Cd electrode except in acid soils or soils which are highly contaminated with Cd. Although the level of Cd in contaminated soils is high enough to be measured with the Cd electrode, there is often severe interference from other heavy metals. Workman and Lindsay (1990) successfully used the chelation method to measure free Cd^{2+} activities in arid zone soils. The method has two advantages: 1) it increases Cd detection limit, and 2) it avoids the problems of inorganic and organic complexes.

The purposes of this study were to 1) determine Cd^{2+} activities in 3 contaminated and 7 normal soils; 2) compare the measured Cd^{2+} activities to those of known Cd minerals; and 3) suggest possible mechanisms controlling Cd^{2+} activities in these soils.

MATERIALS AND METHODS

Seven normal and 3 contaminated soils were used in this study. Their properties are listed in Table 2.1 and 2.2 of Chapter 2. Preliminary experiments were performed to determine the most appropriate initial Cd MF range to use for each soil. The initial Cd MF ranges of 0 - 0.5 and 0 - 1 were selected for the normal and contaminated soils, respectively.

The Pb-DTPA solutions as described in Chapter 2 were also used in this study. A stock solution of Cd-DTPA was prepared by adding 400 μM CdCl_2 to 400 μM DTPA solution, and the pH was adjusted to 7. Solutions of 40 μM Cd-DTPA or Pb-DTPA were made by diluting the 400 μM Cd-DTPA or Pb-DTPA solutions 1:10, respectively. The remaining procedures are the same as described in Chapter 2.

The final equation used to calculate Cd^{2+} activities was the following:

$$(\text{Cd}^{2+}) = \frac{[\text{CdL}^{3-}]}{[\text{PbL}^{3-}]} \cdot 10^{7.83-2 \text{ pH}} \quad (1)$$

For detailed derivation of the equation, readers are referred to El-Falaky et al. (1991). The ratio of $[\text{CdL}^{3-}]/[\text{PbL}^{3-}]$ needed to

solve Eq. 1 was obtained from the measured equilibrium Cd MF ($\text{CdL}^{3-}/(\text{PbL}^{3-} + \text{CdL}^{3-})$). A typical example of equilibrium Cd MF for the Leadville-4 soil is shown in Fig. 11.1. The point of intersection of the initial Cd MF with the final Cd MF represents the equilibrium Cd MF. The procedures for water extractable Cd and Cd in 0.25 M DTPA extracts were the same as described in Chapter 2 for Zn.

RESULTS AND DISCUSSION

Cadmium extracted by 2:1 water, 0.25 M DTPA extracts and HClO_4 digests of the contaminated soils are given in Table 11.1. The Cd in these soils was highly insoluble in water, ranged from 0.02 to 0.04 $\mu\text{g/g}$. The Cd concentrations in 0.25 M DTPA extracts and HClO_4 digests were comparable. The Cd concentration in 0.25 M DTPA extracts ranged from 6.6 to 26 $\mu\text{g/g}$, and those in HClO_4 digests ranged 17 to 37 $\mu\text{g/g}$. These results indicate that these soils did not contain large amounts of Cd, and its water solubility was low.

Table 11.1 Cadmium concentration in 2:1 water, 0.25 M DTPA extracts, and HClO_4 digests

Soils	2:1 water	0.25 M DTPA	HClO_4 digest
	----- $\mu\text{g/g}$ -----		
Leadville-2	0.02	14	17
Globeville-4	0.04	6.6	30
Globeville-5	0.03	26	37

Fig. 11.1. Equilibrium Cd MF in the Leadville-4 soil

The initial concentration of metal DTPA used for the normal soils was 10 μM , and for the contaminated soils it was 100 μM . The advantage of using a lower initial DTPA concentration is the sensitivity to changes in the measured metal DTPA MF compared with a higher metal DTPA concentration. Under some situations, however, higher metal DTPA concentrations work better. In the case of Zn^{2+} and Fe^{3+} activity measurements, a higher initial metal-DTPA concentration was used because it permitted the use of a lower initial Zn or Fe MF. For example, the detection limit of Zn with ICP is about 0.04 μM . If the initial Zn MF is 0.004, in term of Zn-DTPA concentration, this corresponds to 0.04 μM for 10 μM and 0.4 μM for 100 μM total DTPA. Thus, the lowest Zn MF that could be used with 10 μM total DTPA concentration is 0.004, while for 100 μM total DTPA, the limit is 0.0004. Considering the competition of Fe^{3+} , Zn^{2+} , and Pb^{2+} for DTPA in the presence of PbCO_3 , Pb^{2+} predominates and only a small portion of the DTPA is occupied by Fe^{3+} or Zn^{2+} . Thus by using higher metal DTPA concentration, both Fe^{3+} and Zn^{2+} activities can be measured even though they are weak competitors with Pb^{2+} . Higher initial metal-DTPA was used when metal activities were measured in contaminated soils, since contaminated soils have higher concentrations of heavy metals. For example, although some of DTPA was occupied by these other heavy metals, there was still enough DTPA left for Cd^{2+} , and the competing metal ion Pb^{2+} in the contaminated soils of this study.

The measured pH, equilibrium Cd MF, and Cd^{2+} activities in the 7 normal and the 3 contaminated soils are given in Tables 11.2 and 11.3. The measured Cd^{2+} activities decreased with increase in pH. The correlation coefficient between $\log(\text{Cd}^{2+})$ and pH was 0.98 for the normal soils and 0.99 for the contaminated soils. The equilibrium Cd MF's for the contaminated soils were higher than those of the normal soils. The equilibrium Cd MF's for the contaminated soils ranged from 0.275 to 0.558 and for the normal soils from 0.003 to 0.042. Very little Cd was detected in most of the soils with pH values < 7 (Table 11.4). Similar results were obtained by El-Falaky et al. (1991). They reported that Cd adsorption increased with decreasing pH, and in some cases there was no detectable Cd.

Table 11.2 Measured pH, equilibrium Cd MF, and Cd^{2+} activities in the 7 uncontaminated soils

Soil	pH	EC	Initial Cd MF range	Equilibrium Cd MF	$\log(\text{Cd}^{2+}) \text{ M}$
Burlington	6.65	0.36	0-0.2	0.002	-8.29
Genoa	6.88	0.24	0-0.2	0.0025	-8.63
S Lake	7.87	0.25	0-0.1	0.026	-9.59
Castle	7.97	0.28	0-0.5	0.025	-9.80
Walsh	8.06	0.35	0-0.15	0.0197	-10.11
Eads	8.07	0.33	0-0.15	0.0139	-10.28
Lamar	8.19	0.26	0-0.15	0.042	-10.02

Table 11.3 Measured pH, equilibrium Cd MF and Cd^{2+} activities in the three contaminated soils

Soils	pH	Initial EC	Cd MF range	Equilibrium Cd MF	$\log(\text{Cd}^{2+})\text{M}$
Globeville-5	6.62	0.41	0-1	0.275	-5.95
Globeville-4	7.34	0.23	0-1	0.345	-7.23
Leadville-1	7.81	0.84	0-1	0.558	-7.87

Table 11.4 gives an example of the initial and final Cd-and Pb-DTPA concentrations in two low pH soils, that were not included for the Cd solubility measurements, for contrast Table 9.5 includes two high pH soils, which were included for the Cd solubility measurements. The highest Cd-DTPA detected in New Raymer soil (pH = 6.4 to 7.0) was $0.06 \mu\text{M}$ and no Cd was detected in Bennett soil, whose pH range was 6.5 to 6.9. One explanation is that all the Cd added in these low pH soils was adsorbed. This problem prevents the measurement of Cd^{2+} activities in soils of low pH using the chelation method. The complete removal of Cd from solution suggest that the adsorption mechanism may be important in these low pH soils. Recovery of Pb-DTPA in the Bennett soil was lower (46-64%) than in the New Raymer soil (71-79%). On the other hand, the concentrations of Cd-and Pb-DTPA in soils of high pH were much higher. For example, the highest Cd-DTPA concentration in the Walsh soil was $0.61 \mu\text{M}$ and the highest Pb-DTPA was $9.6 \mu\text{M}$. The results indicate that the adsorption of both Cd and Pb was pH dependent, and increased with decrease in pH.

Table 11.4 Initial and final Cd- and Pb-DTPA concentrations in two acid soils

Initial Concentration		Final concentration					
		Bennett soil			New Raymer soil		
Cd-DTPA	Pb-DTPA	Cd-DTPA	Pb-DTPA	pH	Cd-DTPA	Pb-DTPA	pH
----- μM -----		----- μM -----			----- μM -----		
0.0	10	0.0	5.2	6.4	0.0	7.9	6.8
0.05	10	0.0	6.4	6.5	0.0	7.7	6.9
0.1	9.9	0.0	4.6	6.0	0.0	7.1	6.5
0.5	9.5	0.0	5.1	6.6	0.0	7.1	6.7
2.0	8.0	0.0	5.5	7.0	0.1	7.3	6.8

Table 11.5 Initial and final Cd- and Pb-DTPA concentrations in two alkaline soils

Initial Concentration		Final concentration					
		Eads			Walsh		
Cd-DTPA	Pb-DTPA	Cd-DTPA	Pb-DTPA	pH	Cd-DTPA	Pb-DTPA	pH
----- μM -----		----- μM -----			----- μM -----		
0	10	0.09	8.6	7.8	0.13	9.6	8.1
0.1	9.9	0.11	8.5	8.1	0.15	9.5	8.1
0.4	9.6	0.19	8.5	8.1	0.25	9.6	8.1
0.7	9.3	0.34	7.9	8.1	0.37	9.2	7.9
1.4	8.6	0.47	7.7	7.9	0.61	9.1	8.0

Figure 11.2 summarizes the relationship between $\log (\text{Cd}^{2+})$ and pH. The soil-Cd line for El-Falaky et al. (1991) is also included in this figure. The measured Cd^{2+} activities of the contaminated soils can be expressed as:

$$\log (\text{Cd}^{2+}) = (7.33 \pm 0.09) - 2 \text{ pH} \quad (2)$$

and for the uncontaminated soils of $\text{pH} > 7$:

$$\log (\text{Cd}^{2+}) = (6.1 \pm 0.17) - 2 \text{ pH} \quad (3)$$

The solubility of Cd in the contaminated soils was slightly higher than that of soil-Cd reported by El-Falaky et al. (1991). The Cd^{2+} activities of the normal soils in Fig. 11.2 can be divided into two groups. The Cd^{2+} activities in soils of $\text{pH} > 7$ were close to soil-Cd (Eq. 3) (El-Falaky et al., 1991), while the Cd^{2+} activities in soils with $\text{pH} < 7$ were undersaturated with respect to soil-Cd. The result suggests the importance of adsorption-desorption process in regulating cd solubility in soils of low pH. These findings agree with the results by Soon (1981) and Bruemmer et al. (1986). However, the Cd^{2+} activities in soils of higher pH fell near the soil-Cd line, which may suggests the precipitation-dissolution mechanism may control Cd^{2+} activities.

In the contaminated soils, Cd^{2+} activities were higher than those of the normal soils. Regardless of pH, the Cd^{2+} activities fell between the solubility of CdCO_3 and soil-Cd. It seems that the soils studied here were not highly contaminated with Cd, although some of the soil samples from same locations were

Fig. 11.2. Measured Cd^{2+} activities in soils compared with Cd minerals

severely contaminated with Cd (Workman et al., 1991). Thus, it is reasonable to assume that CdCO_3 was not the mineral controlling Cd^{2+} activities in these contaminated soils even at a CO_2 level of 0.003 atm (Fig. 11.2).

When soils are loaded with soluble Cd, it is possible to form CdCO_3 . Sadiq and Zaidi (1981) suggested that formation of CdCO_3 controlled Cd concentration in calcareous soils receiving a spike of 100 ppm of Cd. They reported that adsorption may not significantly control soluble Cd, since CEC and organic matter were poorly correlated with Cd sorption. Soon (1981) also suggested that precipitation of CdCO_3 was likely in soils of $\text{pH} \geq 7$. Street et al. (1977) reported that addition of $\text{Cd}(\text{NO}_3)_2$ to soil may precipitate CdCO_3 or $\text{Cd}_3(\text{PO}_4)_2$.

Due to the uncertainty in the $\log K^0$ value of CdFe_2O_4 , no further discussion seems appropriate. There is uncertainty regarding the $\log K^0$ value for the following equation:

where "L" represents the DTPA ligand. Workman and Lindsay (1990) used a $\log K^0$ value of -0.644, which was experimentally determined using reactions of CdCO_3 and PbCO_3 with DTPA. The following equations were considered in the derivation of $\log K^0$ values:

El-Falaky et al. (1991) used a value of 0.34, which was taken from Lindsay (1979). This value was chosen in this experiment. There is a need to clarify the differences.

Thus, we suggest that adsorption-desorption process is important in soils of low pH or low Cd levels, while precipitation-dissolution reactions may occur in soils of high pH or high Cd pollution. The minerals controlling Cd^{2+} activities in soils are still not clear.

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12. STUDIES OF A COMBINED SEQUENTIAL SELECTIVE DISSOLUTION/DIFFERENTIAL IR AND XRD SPECTROSCOPY PROCEDURE FOR SOILS

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ABSTRACT

A procedure for sequential selective dissolution (SSD) of trace components in soils was tested using chemical and spectroscopical analyses. The procedure includes 5 sequential steps designed to selectively dissolve and extract the following phases: a. soluble and exchangeable ions, b. carbonates, c. easily-reducible oxides, d. organic matter and e. reducible oxides. Most of the extractants, and the adapted sequence, are based on already used techniques. The selectivity and specificity of each step was chemically and spectroscopically characterized. Spectral data included x-ray diffractometry (XRD) and infrared (IR) absorption measurements as well as differential XRD and differential IR spectra obtained by subtracting the soil spectra obtained at two consecutive steps. It was found that replacement of the exchangeable cations with 1M NH_4Cl (pH = 7) in the first step resulted in a mild attack of calcite and some NH_4^+ fixation. Sodium acetate (pH = 5) used in the second step failed to completely dissolve dolomite and calcite in a carbonate-rich soil. Reduction of Mn oxides with 0.04 M hydroxylamine hydrochloride (in 25% acetic acid at 25°C) in the third step is confirmed both from relatively high concentration of Mn in the extract solution and from direct identification of manganite (γMnOOH) in the difference spectra. Organic matter dissolution has also occurred in this step. Oxidation of organic

matter with H_2O_2 did not damage clay minerals or iron oxides. Reduction of iron oxides in the last step is done more efficiently and selectively with DCB than with hydroxylamine hydrochloride (in 25% acetic acid at $90^{\circ}C$), however the DCB treatment was less efficient in the extraction of trace metals. In both treatments, some dissolution of clay minerals was detected by both the chemical and spectroscopic analyses.

Additional Index Words: Elemental partitioning; exchangeable ions; carbonates; easily reducible oxides; organic matter; reducible oxides.

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Specific and selective dissolution methods are widely used in mineralogical research and in the investigation of the distribution of heavy metals among soil components (Mehara and Jackson, 1960; Forstner et al., 1981; Agemian and Chau, 1976; Tessier et al., 1979; Shuman, 1985; see reviews by Lake et al., 1984 and Becket, 1989). A common feature of these techniques is to extract sequentially various soil phases, a phase being defined, in this context, as including all the components which dissolve in a particular reagent. The elements dissolved in the extracting solution are then determined to define and quantify the major matrix components and/or the minor or trace components associated with the extracted phase. Although the methods used vary in detail, they commonly attempt to extract the soluble, the exchangeable, the carbonate, the organic, the various "reducible" phases, and a "residual" phase.

One of the major shortcomings of these methods is the lack of specificity of the extracting reagents. An optimal reagent should dissolve only the component for which it is intended and leave all others intact. The accomplishment of these two requirements is, for a complex system like the soil, almost impossible. Different minerals might have similar solubility in a given extraction solution. This is the reason why it is customary to associate the dissolved elements with the extraction solution itself rather than with the minerals purported to be dissolved in it. It is of great interest, however, to identify more accurately the actual mineralogical components that have been completely dissolved (or partly attacked) in a given step of a procedure.

One possible approach to do that is to use differential spectroscopy. In principle this approach entails the measurement of the characteristic spectrum of the soil, or a fraction of it, before and after a chemical

extraction step. The "spectral difference" is then obtained by a computerized spectra-subtraction procedure. This "spectral difference" is then correlated with the chemical composition of the extract. Small features in the original spectrum that may be related to the extraction of minor components, can be magnified and quantified by removal of the strong spectral background of the major soil components. These "difference spectra" are then used to identify the major matrix minerals which were attacked at this step and with which the extracted metals were associated, and if possible, to identify pure minerals of the extracted metals which were present in the soil. Such a procedure was used successfully to define iron-oxide minerals in soils by differential XRD (DXRD) (Schulze, 1981; Bryant et al., 1983), and to characterize chemical changes of organic molecules adsorbed on clays by differential FTIR (Margulies et al., 1985).

The objective of the present study was to experiment with a sequential selective dissolution (SSD) procedure, largely based on previously published protocols, and to test and define the selectivity and specificity of each step by differential infrared spectroscopy and differential x-ray diffractometry in order to identify the mineral components extracted from the soil at each step.

MATERIALS AND METHOD DEVELOPMENT

Soils

Samples were collected from the top 5 cm of two non-disturbed forested sites in the Judea Hills in Israel. The sampled soils were air-dried, lightly crushed and sieved through a 3 mm sieve. The general characterization of the soils (Table 1) was done by conventional methods.

Carbonate content was measured gasometrically after treatment of the soil with 5% HCl. Specific surface area (SSA) was measured by EGME adsorption (Ratner-Zohar et al., 1983) and cation exchange capacity (CEC) was determined by the ammonium acetate (pH = 7) method (Chapman, 1965). Soil 1 is a highly calcareous soil (Rendzina type; Xerathent), relatively poor in iron-oxides. Soil 2 is low in carbonates and relatively rich in iron oxides (Terra-rossa type; Xerachrept). Kaolinite and montmorillonite are the major clay minerals in soil 2 while illite and attapulgite are present in soil 1.

Sequential Extraction Procedures

Two aspects were considered in choosing a reagent for the dissolution of a phase. First, it should be as specific as can be. Second, the reagent employed should not contain indicative ions, i.e. ions that their presence in solution may be used to detect dissolution of a particular soil component. For example, Ca and Mg should be excluded because their presence in the extracted solution can indicate carbonates dissolution, and the kind of carbonate can be found from the Ca/Mg ratio.

There are 5 steps in the sequential extraction method, each presumed to selectively dissolve various components of the soils and extract the elements bound to them. The procedures for steps b and c are slight modifications of those used by Tessier et al. (1979) and steps d and e1 were adapted from Gupta and Chen (1975). Removal of iron oxides, step e2, was done by the procedure of Mehara and Jackson (1960). Kinetics of extraction were studied in preliminary experiments (unpublished data), and duration of extractions were optimized for minimum contact time of maximum extraction.

a. Soluble and exchangeable cations (EXCH). Twenty-five ml of 1N NH_4Cl solution (pH adjusted to 7 with NH_4OH) were added to 1 g of air-dry soil in a weighted 50 ml polycarbonate centrifuge tube and the mixture was agitated for 30 min at room temperature. Each soil was analyzed in triplicate. The soil was separated from the solution by centrifugation at 10,000 rcf for 15 min. The supernatant was decanted and kept for further analyses. The centrifuge tube with the residue was accurately weighed and the solution carry-over to the next step was calculated. A similar centrifugation-separation procedure was used in each of the following extraction steps described below.

b. Bound to carbonates (CARB). Twenty-five ml of 1N NaOAc solution adjusted to pH 5 with acetic acid was added to the soil residue from step (a) in the centrifuge tube, and the mixture was agitated for 16 h at room temperature. Excess of CO_2 gas was released by frequent opening of the tube covers in the first 6 h of contact. Then the soil was separated from the solution as described above.

c. Bound to easily-reducible oxides (ERO). Twenty-five ml of 0.04M hydroxylamine hydrochloride in 25% acetic acid solution were added to the residue from step b and agitated for 30 min. Then the sample was separated from the solution as described above.

d. Bound to organic matter (OM). The residue from step c was transferred to a pyrex glass test-tube using three ml of 0.01M nitric acid solution. Five ml of 30% H_2O_2 solution were added, and the contents were digested for 2 h at 80°C . Two ml of 30% H_2O_2 solution were added and the heating resumed for another hour. The mixture was allowed to cool to room temperature, 15 ml of 0.01M

nitric acid solution were added and, after agitation for 10 min, the supernatant was separated as described above.

e. Bound to reducible oxides (RO). Residues from replicate test tubes from step d were treated in parallel by two procedures to extract the metals bound to reducible oxides, as follows:

e1. Twenty-five ml of 0.04M hydroxylamine hydrochloride in 25% acetic acid solution were added to the residue and heated at 90°C for 3 h and then cooled and the supernatant was separated.

e2. Twenty ml of 0.3M Na-citrate and 2.5 ml of 1M NaHCO₃ were added to the residue. The temperature was brought to 80°C and 0.5 g of solid Na₂S₂O₄ was added and the mixture was stirred constantly for 1 min and then occasionally for 15 min, while still being heated at 80°C. The system was then cooled and the supernatant was separated.

The total elemental concentration in the soil was measured after digestion with HF + HClO₄ acids (Chapman and Pratt, 1961).

Elemental concentration in the extraction solutions from the various steps were measured by atomic absorption spectroscopy. A Perkin-Elmer Model 5000 Spectrophotometer was used with acetylene flame for the determination of Fe, Mn, Mg, Ni, and Zn, and with N₂O flame for Al, Ca and Si. Cadmium was measured by flameless AA using PE 500 HGA and deuterium lamp as a background correction source.

In calculating the amount of elements which were liberated in each step, the carry-over of elements between successive steps was taken into account. The loss of weight due to the dissolution of a major soil constituent (carbonates in soil 1) was also considered. Assuming that the main carbonate species was calcite (CaCO₃) and measuring the

dissolved Ca in step b, which amounts to about 14% of the soil weight (Table 2), a value of 35% weight loss was obtained, and entered into the calculations. Minor changes in soil weight due to extraction of minor soil components were not taken into account.

Differential Infrared Spectroscopy and Difference XRD

A parallel sequential extraction procedure, similar to the one described above, was carried out in order to get samples for infrared and x-ray spectroscopy. Four g of dry soil were used and were extracted with 100 ml solution in 250 ml centrifuge tubes, thus the ratio of solution to soil was kept the same as described above. At the beginning of the sequential extraction 14 centrifuge tubes were prepared for each soil. Two test tubes were separated from the others after each decantation step, and the soil sediments were washed 3 times with distilled water in order to leach-out the remaining reagents. Then the soil was freeze-dried, the contents of the two tubes were mixed and ground to a fine powder. Spectroscopic measurements were performed on this powdered soil.

1.5 mg to 2.5 mg of powdered and ground untreated soil and of each of the soil residues from steps (a) to (e) were mixed with 90 mg of spectroscopic grade KBr and pressed into a pellet at a pressure of 16 t cm^{-2} . Light absorbance spectra were measured, using these pellets, in the range 4000 to 400 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer, Nicolet Model MX-S, equiped with a computation package enabling spectra averaging, normalization and subtraction. To obtain a representative spectrum for a given residue, 120 spectra were recorded over a time period of 2 min and an averaged spectrum was obtained. X-ray diffraction (XRD) was measured with Philips PW 1720 x-ray generator

equipped with a Co-x-ray tube. An iron filter was not used because it suppressed signals that originated from minor components in the soils. Spectra were recorded, converted to digital form and transformed for further processing (baseline correction, normalization and subtraction) to a software package based on a spreadsheet (Lotus 123). Resolution of digital data was 0.026 degrees (2θ). Preliminary tests revealed that slight changes in internal orientation, due to differences in packaging of the soil in the sample carrier, can cause variations in the relative height of peaks of the same soil component. Both patterns in Fig. 1 are of soil 1, the lower one was obtained without pressing the powder while the upper one was obtained when it was firmly pressed. The ordering of the intensity at the two peaks of calcite at $d=1.87\text{\AA}$ and $d=1.91\text{\AA}$ is reversed dependent on the packaging. Subtraction of two spectra, in which the proportion between peaks of the same component are not the same due to variation in sample handling, may lead to erroneous results. Pressing the powder firmly against a flat glass was found to improve the reproducibility of XRD measurements, and was adopted as a routine step in the procedure.

Differences between the spectra of residues from any two sequential extraction steps, (A) and (B), were obtained by the following procedure both for the IR and x-ray spectra. First the two spectra were normalized by multiplying the subtracted spectrum (B) by a factor which equals the ratio between the absorbance of a reference peak in both spectra. This was done in order to correct for absorbance differences resulting from variations in length of the optical pathway (pellet thickness), residue concentration and variations in scattering due to differences in particle size distribution. Since quartz is an abundant and highly resistant component in most soils, and is assumed not to be dissolved or altered by

any of the extraction steps of the present procedure, the quartz doublet at 800 cm^{-1} and its diffraction peak at $2\theta = 31.1$ ($d=3.34\text{\AA}$) were selected as the reference features. After normalization, spectrum B was subtracted from spectrum A, to obtain the difference spectrum which magnifies the spectral differences and can be looked upon as the characteristic spectrum of the phase removed by the given extraction step.

The difference spectra should be cautiously analyzed, since artifact features can be produced in the procedure. For example, artificial peaks may appear in the difference-spectrum at the position of a strong and wide band, e.g. the Si-O stretching at $900\text{--}1100\text{ cm}^{-1}$ or quartz peak at $3.31\text{\AA}$. A very slight change in the slope of the edges of the band or a slight shift in the baseline in spectrum B relative to A, can cause the appearance of an artificial absorbance feature with a shifted peak in the difference spectrum. This artificial feature is characterized by uneven, steep and smooth slopes. Schultze (1986) outlines a correction procedure for 2θ shifts. We preferred not to correct these shifts because in most cases one can not determine a priori whether such a shift results from technical reasons or it represents a real deformation in the structure of a phase. The signal to noise ratio (S/N) of the original spectra is another important deciding factor in interpreting the difference spectra. High noise levels limit the ability to identify, unambiguously, weak features in the difference spectrum. Slight variations in background or baseline shifts due to particle size variation, packing changes, temperature changes or lack of stability of the measuring instrument may produce artificial bands that should be ignored. However, presence of accompanying peaks which can be related to another vibration mode or diffraction mode of the same soil component, may help in more valid identification. Absence of a series of

characteristic features of a component can result either from the fact that they are too small to be detected or because the suspected peak is really an artificial one. Looking for a supporting clue in the solution composition does not always give clear answers either, because bands that appear in the difference spectrum can result from changes in the crystalline structure that are not accompanied by liberation of elements into the solution. In judging whether a particular peak is an artificial one, subjectivity can not be completely avoided.

RESULTS

Concentrations of the elements extracted in the various steps, the sum extracted in the five-steps procedure, and the total elemental content in the soil, are given in Table 2a and 2b. Combined together, the five steps of the procedure extracted a major portion of the Ca, Mg and Mn from the two soils, varying proportions of Fe and representative trace metals of the soil, but only minor portions of the Si and Al. This indicates that while the reagents used, effectively dissolved the carbonates, organic matter and free oxides, they virtually did not dissolve the silicate and aluminosilicate minerals.

The IR and XRD spectra of the untreated soil and the soil residues from the various extraction steps, are presented in Figs. 2 and 4 for soil 1 and Figs. 3 and 5 for soil 2, respectively. The spectrum of the untreated soil 1 (Fig. 2-I) depicts pronounced and characteristic bands for carbonates (1431 , 877 and 713 cm^{-1}) and somewhat less pronounced features of clay minerals (1035 , 990 , 940 and 472 cm^{-1}) and quartz (800 , 513 cm^{-1}). Features at 3441 and 1647 cm^{-1} are assigned to OH stretching and OH bending in H_2O , respectively. Other

features due to OH stretching are found at 3600 cm^{-1} . As might be expected, the peaks of carbonates in the carbonate-poor soil 2 (Fig. 3-I), are much less pronounced, but those of the silicate minerals are equally or more strongly shown.

The same picture is depicted by the XRD patterns. Presence of calcite in soil 1 (Fig. 4-I) is shown by the major peak at $d=3.01\text{ A}$ and the accompanying peaks ($1.47, 1.52, 1.60, 1.62, 1.87, 1.91, 2.09, 2.27, 2.48, 3.82\text{ A}$), while quartz is represented by the feature at 3.32 A and those at $1.52, 1.91, 2.09, 2.27, 2.48, 3.82\text{ A}$. Clay minerals present in this soil are montmorillonite (14.4 A) and attapulgite (10.2 A). The dominant mineral in the XRD pattern of soil 2 is quartz and as expected, carbonates are much less pronounced. The XRD pattern clearly indicates that the main carbonate mineral in soil 2 (Fig. 5-I) is dolomite ($\text{CaMg}(\text{CO}_3)_2$) and that montmorillonite (14A) and kaolinite (7A) are the dominant clay minerals. Hematite ($\alpha\text{ Fe}_2\text{O}_3$) is identified by the peaks at $1.69, 2.22, 2.51, 2.69\text{ A}$. The presence of feldspars is indicated by the peaks at 3.17 and 4 A .

Each step in the sequential dissolution procedure alters, reduces or completely eliminates certain features of the spectrum. Throughout the extraction sequence, features characteristic of the clay minerals and quartz are virtually not affected and the spectra of the soil residue at the end of the extraction procedures (Figs. 2-VII, 3-VII, 4-VII and 5-VII) are characterized by their dominance. This supports the chemical findings shown in Table 2 and Fig. 6.

Difference spectra, characterizing the extracted phases, obtained by subtracting the spectrum of the soil residue after a given extraction step from the spectra obtained at the previous step, are also given in Figs. 2-

5, a to e. For example, the spectrum of the extracted carbonate in soil 1 was obtained by subtracting spectrum 2-III from spectrum 2-II, to give spectrum 2b, and spectrum 4b was obtained by subtracting 4-III from 4-II. The difference spectra magnify the subtle changes occurring at each extraction step and enable a more critical evaluation of its effects as discussed below.

DISCUSSION

Soluble+Exchangeable Ions Replacement

The most frequently employed reagents to replace exchangeable cations are NH_4OAc (Jackson, 1958; Chapman, 1965) and MgCl_2 (Tessier et al., 1979; Kuo et al., 1983; Gibbs, 1973). For arid zone soils we preferred to use NH_4Cl . Ammonium acetate (NH_4OAc) was rejected since (even buffered to pH 7) it is known to dissolve carbonates (Tessier et al., 1979 and ref. cited therein), and to attack metal-coatings of particles (Gibbs, 1973). MgCl_2 was rejected in order to enable the measurement of Mg release from the soil as an important indicator for a possible attack of clays or dolomite, and because Mg is an abundant cation adsorbed to clays in semi-arid soils.

Only small spectral intensity differences were observed following this step. The appearance of three characteristic peaks at 1458, 873 and 713 cm^{-1} (Fig. 2a) indicates however some attack and removal of carbonates from soil 1, showing that NH_4Cl (buffered to pH 7) also attacks carbonates. This conclusion is strengthened by the presence of the main calcite peak (3.01 Å) and five accompanying peaks (1.87, 1.91, 2.09, 2.17, 2.48 Å) in the DXRD pattern (Fig. 4a). From the extraction results (Table 2a) we find that the total amount extracted is $0.18\text{ meq g}^{-1}\text{ Ca}$

and $0.03 \text{ meq g}^{-1} \text{ Mg}$. The cation exchange capacity of the soil is 0.217 meq g^{-1} , thus much of the extracted Ca and Mg may result from the exchangeable ions. If one assumes that $0.1 \text{ meq g}^{-1} \text{ Ca}$ resulted from dissolved calcite, it corresponds to only about 0.5% CaCO_3 , indicating a very high sensitivity of the difference method for the detection of this mineral. Experience shows that 2-3% of carbonate (calcite) can be detected in IR spectra of soils (White, 1974). Carbonate fingerprints in the carbonate-poor soil No. 2 are not detected in the difference IR spectrum (Fig. 3a) nor in the DXRD pattern (Fig. 5a).

The sensitivity of the differential spectroscopy method is also demonstrated by the appearance of a negative peak at 1404 cm^{-1} in Figs. 2a and 3a. It is attributed to adsorbed NH_4^+ on clay surfaces in the soil, added during the extraction step. Adsorbed NH_4^+ on a synthetic clay was detected by Van Olphen and Fripiat (1976) by a feature at 1404 cm^{-1} , and IR absorption spectra of NH_4Cl and NH_4Br show features at 1403 cm^{-1} and 1401 cm^{-1} , respectively (Ryskin, 1974). Assuming that NH_4^+ occupies all the exchangeable sites after the first SSD step, its concentration is only 0.4% and 0.7% by weight in soil 1 and soil 2, respectively. Liberation of adsorbed or, probably, fixed NH_4^+ continue in successive steps as can be seen from the appearance of the 1404 cm^{-1} peak in the difference spectra 3c and 3d.

Using potassium instead of NH_4 as the displacing cation (Silviera and Sommers, 1977; Emmerich et al., 1982; Miller et al., 1983) could have eliminated or reduced the fixation of NH_4^+ and alteration of clay minerals, because K is a much more abundant cation in soil than NH_4 . On the other hand, this hypothesis

can not be validated spectroscopically because IR spectroscopy is not sensitive towards adsorbed or fixed K.

Carbonate Removal

The difference IR spectrum in Fig. 2b shows the strong and diagnostic bands of carbonates removed from soil 1 during this step. The mineral removed appears to be mostly calcite (CaCO_3). The diagnostic features at 1431, 877 and 715 cm^{-1} agree quite well with the values reported for calcite (White, 1974). These bands are attributed to the carbonate group and assigned to planar, out-of-plane and internal asymmetric out-of-plane vibrations, respectively. Calcite features also appear in the DXRD pattern of soil 1 (Fig. 4b) at 1.66, 1.70, 1.90, 2.09, 2.27, 2.48 and 3.01 Å. Calcium dissolved during this step amounts to 14.1% out of soil mass corresponding to 35.2% by weight of calcite. Dissolution of carbonates, in this carbonate-rich soil continues in the following step (step c).

In soil 2, a molar ratio of $\text{Ca/Mg} = 0.85$ was found. This suggests dissolution of dolomite whose main feature is clearly recognized in the DXRD pattern at $d=2.87\text{Å}$ (Fig. 5b). Although the mass of dissolved dolomite is 4.3% of total soil weight, its dissolution is not detected in the difference IR spectrum (Fig. 3b) probably because of its low concentration and low extinction coefficient.

Silicate minerals were not attacked in this step by the buffered sodium acetate ($\text{pH} = 5$) treatment, as evidenced by the low concentration of Si and Al in the extracts (Tables 2a and b, Fig. 6), and the absence of spectral features of silicate minerals in the difference spectra. Similar observations were reported by Tessier et al. (1979). Dissolution of

carbonates was accompanied by liberation of 46.5% of the total Mn in soil 1 and 17.8% of the total in soil 2. Iron was not present in the extracted solution. The amount of Fe and Mn extracted from sediments at this step, reported by Tessier et al. (1979), are about ten-fold higher than those extracted from soils in the present study.

Three modes of association of trace metals (e.g. Ni, Zn and Cd) to carbonates include adsorption, precipitation and coprecipitation. Adsorption prevails at low metal concentrations while precipitation and coprecipitation are dominant at higher concentrations (McBride, 1980; Dudley, 1988). The excess NH_4 concentration in step a should have replaced the adsorbed metals on carbonate surfaces while metals that are associated to carbonates by precipitation and coprecipitation should have been liberated in the present step. The significant amount of trace metals, particularly of Cd released at this step from the calcareous soil 1 (Fig. 6), suggests that the most important association modes of the metals to carbonates in this soil are precipitation and coprecipitation.

Removal of Easily Reducible Oxides

In the difference spectra of the phase extracted at step c by hydroxylamine hydrochloride, defined as easily reducible oxides (ERO), the following minerals may be detected: Manganite ($\gamma\text{-MnOOH}$) with peaks at 1084 cm^{-1} and $596\text{-}600\text{ cm}^{-1}$ (Van der Mar1, 1976) in both soils (Figs. 2c, 3c); Possibly and tentatively, traces of an aluminosilicate phase, perhaps kaolinite with the characteristic peaks at 1000 cm^{-1} and 470 cm^{-1} , in soil 2, and montmorillonite (1028 cm^{-1} and 526 cm^{-1}) in soil 1, and a carbonate phase, probably dolomite + calcite, with peaks at 1433 cm^{-1} and 887

cm^{-1} in soil 1. The extracted elements include Mn, Ca, Si and Al. Only negligible amounts of iron were extracted.

Manganite, in which Mn is at an intermediate oxidation of +3, is predicted to appear in soils under partial reduction, where the redox potential (pe+pH) is poised at 16.62 (Lindsay, 1979). The direct identification of this mineral in the IR difference spectra of these forest top-soils, which are rich in organic matter and biologically active, is not surprising, but to the best of our knowledge such direct identification has not been reported yet. About 31% and 35% of total Mn in the soils has been extracted in this step in soil No. 1 and 2, respectively.

Continued carbonate removal from soil 1 during this step is evidenced by typical peaks in both difference spectra 1c (1433, 877, 713 cm^{-1}) and 3c (3.01, 2.48, 2.09, 1.90, 1.87 $\text{\AA}$). This is possibly because the acid-capacity of the reagent used was too low for such a carbonate-rich soil. However, applying one more carbonate dissolution step with buffered acidic Na-acetate (identical to step b), resulted in dissolution of additional 6% of total calcium (from soil 1), whereas in step c, 10.7% of total Ca were dissolved (Fig. 6). It is noticed also that the carbonate features in the IR difference spectrum from this step (Fig. 2c) are not as sharp as those resulting from the exchangeable cations replacement in step a (Fig. 2a), in which much less Ca was extracted (Table 2a). From these observations, it may be concluded that the more aggressive reagent employed in the present step, i.e. hydroxylamine hydrochloride in 25% acetic acid, dissolves additional calcite as well as less soluble carbonates with somewhat different structural characteristics from those extracted both in step a and step b.

Even though carbonate signatures are not observed in the difference

spectra of soil 2, dissolution of high quantities of Ca and Mg, with a molar ratio of Ca/Mg of 0.96 suggests that dolomite, the dominant carbonate mineral in this soil, was extracted.

Peaks at 576 and 1028 cm^{-1} in the IR difference spectrum of soil 1, may suggest montmorillonite while the bands at 470 and 1000 cm^{-1} in difference spectrum of soil 2, may suggest an attack of kaolinite. However, evidence for such attack of clay minerals is not observed in the DXRD patterns and only slight dissolution of aluminosilicates is indicated by Si and Al extraction in this step. The Si/Al molar ratio of 0.46 and 0.47 in soils 1 and 2 respectively, is lower than the expected ratio for both the 2:1 and 1:1 phyllosilicates and indicates either contribution from Al rich phases (Al-oxides) or noncongruent dissolution of the clays.

Customarily, selective dissolution of Mn oxides from soils was done using hydroxylamine hydrochloride at low concentrations, at low temperature and for short extraction time (Chao, 1972; Agemian and Chau, 1976). Selectivity of this treatment in terms of removal of easily reducible oxides i.e. Mn oxides, with only small dissolution of iron minerals is indicated (Table 2). The identification of the manganite spectral features in the difference spectra strengthens the fact that the selective dissolution of Mn-oxides was achieved.

Organic Matter Oxidation and Removal

The IR difference spectra for this step (Figures 1d and 2d) show bands that indicate organic matter removal. The bands in the region of 1400 cm^{-1} are assigned to C-H deformation of CH_2 or CH_3 groups, and the bands near 1250 cm^{-1} are assigned to C-O

stretching and OH deformation of COOH or CO stretching of aryl ethers. The broad band at 3400 cm^{-1} and the prominent peak at 1650 cm^{-1} belong to OH stretching of water and groups which are present in clays and oxides, as well as in organic matter. As expected, no signs for removal of the amorphous organic matter are detected in the DXRD patterns of both soils (Figs. 4d and 5d). An attack of clay minerals was not detected neither in DXRD patterns nor in DIR spectra. Hence it is reasonable to assume that the dissolved Fe, Mg, Al, and Si were complexed with organic matter prior to its destruction. Tessier et al. (1979) concluded both from the low concentration of Si and Al in solution and from changes in XRD patterns of smectite and chlorite, that clay minerals in sediments were slightly attacked by this treatment.

The absence of C=O stretching mode of COOH at 1720 cm^{-1} , raises the possibility that partial reduction of organic matter occurred in the previous step during removal of the easily reducible oxides (Stevenson, 1982).

Reducible Oxide Removal With Hydroxylamine Hydrochloride (HAHC) at 90°C

Dissolution of the iron oxides liberates significant amounts of Fe in soils 1 and 2 (Table 2). In soil 2, crystalline iron oxide extraction is achieved, as evidenced by the hematite ($\alpha\text{-Fe}_2\text{O}_3$) features in the DXRD pattern (Fig. 5e1). Two out of the 3 characteristic peaks of hematite appear at $d = 2.51\text{ \AA}$ and $d = 2.22\text{ \AA}$. The extracted iron oxide in the calcareous soil 1 (probably goethite) could not be clearly identified in the DXRD spectra possibly because of its low content.

Slight attack of clay minerals during this step is evident in soil 2

from the absorbance bands at 3622, 1000-1050, 914 and 831 cm^{-1} in the DIR spectra (Fig. 3e1). Such a combination of features appears in the spectra of smectites, illites and in S/I interstratified minerals (Van der Mar1, 1976). It is thus difficult to identify the exact mineral attacked in this stage - but it is quite clear that aluminosilicate minerals in the soil have been structurally modified by the treatment. The amount of Si actually extracted at this stage amounts to only 1.6% and 0.8% of total Si in soils 1 and 2, respectively. Librational frequencies of OH in dioctahedral clays give a clear indication of octahedral composition. AlAl(OH) liberation lies in the range 915-951 cm^{-1} and MgAl(OH) near 840 cm^{-1} (Farmer, 1974). The attacked clay in soil 2 contained Al and Mg in the octahedral position and probably this is the source for the high amounts of Si, Al and Mg extracted at this step. The amount of extracted Mg is higher than that of Al. Octahedral Mg appears to be preferentially released into solution over Al upon acid attack of clay minerals (Singer, 1977). Clay fingerprints are not easily observed in the DIR spectrum of soil 1 (Figure 2e1), perhaps due to lower aluminosilicate content in this soil. Evidence regarding clay dissolution in similar treatments is contradicting: Whereas Tessier et al. (1979) reported a slight attack, both Chester and Hughes (1967) and Gupta and Chen (1975) found that in their case, clays were not damaged.

Reducible Oxides Removal With Dithionite- Citrate- Bicarbonate (DCB)

Iron dissolution in soils 1 and 2 by this treatment is 2 and 4 times, respectively, higher than in the hydroxylamine hydrochloride at 90°C treatment (e1). These findings are contrary to those of Gupta and Chen (1975), who found DCB to be less effective for extraction of iron

from sediments.

Dissolution of hematite in soil 2 is clearly seen: Typical features of hematite occur in the DIR spectrum at 1153 and 1192 cm^{-1} (Fig. 3e2) and in the DXRD spectrum at 1.70, 2.22 and 2.51 Å (Fig. 5e2). Possibility for silicate minerals attack by DCB is indicated by the appearance of a peak at 3620 cm^{-1} and a shoulder at 918 cm^{-1} in the DIR spectrum. It is possible that the attacked mineral is feldspar with the main XRD peak at $d = 4.00$ Å (Fig. 5e2). Although DCB is found to be more efficient than hydroxylamine hydrochloride in selective dissolution of iron oxides as realized by the higher amount of extracted Fe and lower amounts of extracted Si and Al, less metals such as Zn (Table 2) and Cu (unpublished data) were extracted with it. Similar findings were reported by Gupta and Chen (1975). The lower ability of the DCB treatment to extract heavy metals is explained by its high pH, the low ability of citrate to complex heavy metals (Gupta and Chen, 1975) and possibly by metal-sulfide precipitation (Tessier et al., 1979). It is also possible that most of the heavy metals in the studied soil are not associated with iron oxides but with another phase that can be extracted more efficiently with hydroxylamine hydrochloride.

SUMMARY AND CONCLUSIONS

One of the major limitations of sequential selective dissolution techniques is the limited knowledge of their specificity. It is widely accepted that absolute selective dissolution of a component of a complex matrix such as soils, is almost impossible. There is, however, lack of quantitative information on the degree of specificity of various extractants.

In the present study, we employed differential spectroscopic methods (DXRD and DIR) together with chemical data, to characterize the extracted phases in a 5-step SSD procedure. The first step is exchangeable cation replacement with 1M NH_4Cl adjusted to pH 7. DXRD and DIR spectra reveal that this reagent slightly attacks calcite in a carbonate-rich soil, and that NH_4 from the extracting solution is adsorbed and fixed by the soil. Sodium acetate (buffered to pH 5 with acetic acid), that was used in the second step designed to dissolve the carbonate phase, has not attacked any of the other major phases of the soil as evidenced by lack of clay and iron oxide features in DXRD and DIR spectra, and the low concentrations of extracted Si, Al and Fe. Although it was selective toward carbonates, this step failed to completely dissolve calcite in a carbonate-rich soil, and dolomite in both soils. Carbonate dissolution continued, and was completed, in the following step(s).

Hydroxylamine hydrochloride (0.04M in 25% acetic acid at 25°C) was found to selectively extract Mn oxides and to leave iron oxides virtually intact. This was confirmed chemically by a relatively large amount of extracted Mn, and spectroscopically by detection of manganite features in the DIR spectrum. The difference IR spectroscopy revealed that undesired organic matter reduction occurred at this step. Organic matter removal by oxidation with acidified H_2O_2 in the fourth step did not damage iron oxides or clay minerals. Reduction and dissolution of iron oxides in the last step is done more efficiently and selectively with DCB than with hydroxylamine hydrochloride (0.04M in 25% acetic acid at 90°C). This is evident by the larger amount of Fe and lower Si and Al that were extracted with the former reagent. In both treatments an attack of clay minerals is observed. The DCB treatment was, however, less

efficient in heavy metal extraction either because the pH was high, and/or citrate has low ability to complex heavy metals; and/or because of metal sulfide precipitation. The use of infrared difference spectra and DXRD, together with chemical data, provides in-depth analysis of the nature and exact composition of the phase(s) extracted by a given reagent from a particular soil. Characterizing the extracted phases may enable further optimization of SSD procedures for soils in the future.

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Table 1. Some selected properties of the studied soils.

Soil No.	Soil Type	Clay	Silt	Sand	Carbonates	Organic Matter	CEC	Specific Surface	pH
		-----g k ⁻¹				----- meq kg ⁻¹		m ² g ⁻¹	
1	Xerothent	337	100	563	513	107	217	181	7.8
2	Xerachrept	325	150	525	22	114	381	269	8.15

Table 2a. Concentrations of extracted elements in each step of the selective sequential dissolution procedure of Soil 1.

Element	Si	Al	Fe	Mn	Ca	Mg	Ni	Zn	Cd
	-----mg kg ⁻¹ -----								
Phases									
Soluble + Exchangeable (a)	0	0	0	3609	347	0	0	0	0
Carbonates (b)	130	11.9	4	511	141105	750	8.3	7.2	0.26
Easily- Reducible (c)	128	270	30	447	21481	321	25.5	8.5	0.009
Organic Matter (d)	815	442	342	137	6300	1792	33.8	17.7	0.072
Reducible Oxides (e1)	1900	774	1422	66	1194	1482	20.2	77.4	0.017
(e2)	1819	309	2604	32	794	721	16.4	18.0	*
Total extracted (a to d)+e1	2974	1498	1798	1160	173700	4692	87.8	111	0.358
(a to d)+e2	2892	1033	2980	1127	173300	3931	84.0	51.6	*
Total in soil	117600	23450	25000	1100	200000	6700	148	155	0.52
% Extracted out of total in soil (a to d)+e1	2.5	6.4	7.2	106	86.8	70	59.3	71.6	67.7
(a to d)+e2	2.5	4.4	11.9	103	86.7	58.7	56.8	33.3	*

*Cd in DCB extraction (e2) was not determined because of analytical problems with measuring its concentration with flameless AAS.

Table 2b. Concentrations of extracted elements in each step of the sequential selective dissolution procedure of Soil 2.

Element	Si	Al	Fe	Mn	Ca	Mg	Ni	Zn	Cd
	-----mg kg ⁻¹ -----								
Phases									
Soluble + Exchangeable (a)	0	0	0	0	5213	1115	0	0	0
Carbonates (b)	398	54.7	4.5	146	8752	6170	0	0	0.06
Easily- Reducible (c)	217	447	32.4	287	2186	1359	0	1.7	0.05
Organic Matter (d)	851	1655	590	105	5792	4571	7.4	16.5	0.067
Reducible Oxides (e1)	1796	1762	3564	41.7	839	2113	3.9	37.8	0.027
(e2)	868	798	14904	72.2	564	834	6.1	11.1	*
Total extracted (a to d)+e1	3262	3919	4190	578	22782	15328	11.3	56	0.204
(a to d)+e2	2334	2955	15530	609	22507	14049	13.5	29.3	*
Total in soil	224000	65000	57000	822	28000	19000	54	142	0.65
% Extracted out of total in soil									
(a to d)+e1	1.5	6.0	7.4	70.3	81.4	80.7	20.9	39.4	31.4
(a to d)+e2	1.0	4.5	27.2	74.1	80.4	73.9	25.0	20.6	*

*Cd in DCB extraction (e2) was not determined because of analytical problems with measuring its concentration with flameless AAS.

FIGURE CAPTIONS

- Fig. 1. Effect of sample packaging in the carrier on the XRD pattern.
- Fig. 2. Infrared spectra of the untreated soil 1, of the residues after each step of the SSD procedure, and difference spectra that represent the extracted soil components. The spectra are: I - untreated soil, II - after exchangeable ions replacement, III - after carbonates extraction, IV - after reducible oxide reduction, V - after organic matter oxidation, VI - after reducible oxides reduction with hydroxylamine hydrochloride, and VII - after reducible oxides removal with DCB. The difference spectra represent the following phases: a - exchangeable ions, b - carbonates, c - easily reducible oxides, d - organic matter, e1 - reducible oxides (hydroxylamine hydrochloride), e2 - reducible oxides (DCB).
- Fig. 3. Infrared spectra of the untreated soil 2, of the residues after each step of the SSD procedure and difference spectra that represent the extracted soil components. Symbols as in Fig. 2.
- Fig. 4. XRD spectra of the untreated soil 1, of the residues after each step of the SSD procedure, and difference spectra that represent the extracted soil components. Symbols as in Fig. 2.

Fig. 5. XRD spectra of the untreated soil 2, of the residues after each step of the SSD procedure, and difference spectra that represent the extracted soil components. Symbols as in Fig. 2.

Fig. 6. Extracted elements, as percent out of total in the soil, extracted at each step of the SSD procedure in two soils.

Fig. 1

Fig. 2.

Fig. 2

INTENSITY (CPS)

Fig. 4

Fig. 5

Fig. 6

13. PARTITION AND TRANSFORMATIONS OF ADDED CADMIUM AMONG SOLID-PHASE COMPONENTS OF SOILS

D. HIRSCH AND A. BANIN

ABSTRACT

Two soils were treated with increasing loads of soluble Cd (0.1, 1.0; and 10.0 mg/kg). Partitioning of Cd among various solid phase components was highly perturbed (as compared to the native soil) by the addition. Partition pattern returned almost completely to that of the native soil after a few days of incubation of the saturated soil pastes at 25°C. the same trend was found in soils maintained at field capacity moisture and stored at 25°C for several months. It is proposed that the partition pattern of Cd (or other trace elements) among the solid phase components of a non-polluted soil represents an "equilibrium" state, determined by the competing binding mechanisms operating in that soil. The soil will tend to return to this equilibrium partitioning pattern after perturbation by addition of Cd at trace levels. The rate of reattainment of equilibrium strongly depends on soil moisture.

INTRODUCTION

Cadmium adsorption and participation onto solid soil components are the major mechanisms responsible for decreasing the metal concentration in soil solutions, hence decreasing its toxicity (Street et al., 1977; Christensen, 1984).

Cadmium added to soils associates with various soil constituents such as clays, carbonates, organic matter, oxides and silicates. Its distribution among these constituents was reported in a number of studies (Gupta and Chen, 1975; Silviera and Sommers, 1977; Sposito et al., 1982; Emmerich et al., 1982; Miller et al., 1983; Lake et al., 1984; Tiller et al., 1986; Feijtel et al., 1988). Results show large variation among soils in Cd partition related to soil parameters.

Brief references are found in the literature to the fact that following an initial rapid sorption, the partitioning of cadmium and other trace metals among soil constituents, changes with time. Cadmium imported with sewage-sludge is generally repartitioned after addition to soils. Silviera & Sommers (1977) found that the amounts of Cu, Cd and Zn extracted with DTPA change with time because of slow transformations of the elements to less extractable forms. Banin et al. (1981) found that Pb, Cd, Cu and Ni added in the organic fraction with non-filtered reclaimed sewage water tended to accumulate in an inorganic soil phase that is hydroxylamine hydrochloride extractable.. Emmerich et al. (1982) found the organic matter and carbonates to fix metals (Cu, Cd, Zn, Ni), in sludge amended soils. The hypothesis of Sposito et al. (1983) was that the

observed decrease of Cd availability with time is due to decomposition of the sludge and transformations of Cd to the soils' inorganic phases.

These transformations affect plant availability of trace metals. Uptake of Cd and Zn to corn plants grown in sludge-amended field-plots diminished from year to year for several consecutive years after termination of sludge additions (Bidwell and Dowdy, 1987). The total Cd extractable by aggressive extractants (DTPA or 1M HNO₃) did not change, however, suggesting that subtle changes are taking place in Cd binding to the soil components which are sensed by plants but not by the extractants.

The objective of the present study was to test the following hypothesis: Cadmium partition in a non-polluted soil represents an equilibrium state. The distribution pattern depends on the competing mechanisms of binding at that particular soil. Addition of Cd (at the trace level) to the soil perturbs equilibrium and a series of processes is initiated, tending to restore equilibrium. Due to the differences in the rate of the various binding reactions, sequential transformations from one soil phase to another may continue for long periods, resulting of shifting of the partition pattern with time. Ultimately, the soil will return to the original relative distribution pattern, with Cd redistributed among the various natural Cd-pools according to their abundance, but at a higher total Cd load.

EXPERIMENTAL

Soils: Samples were collected from the top 5 cm horizon of two non-disturbed forested sites in the Judea Hills in Israel. Full characterization of the soils was done as reported by Hirsch and Banin (submitted; see Chapter 9 of this report). Soil 1 is highly calcareous (Rendzima type) with relatively low iron oxide content. Soil 2 is low in carbonates and relatively rich in clays and iron oxides (Terra-rossa type). Organic matter in both soils is medium-low ($\sim 10 \text{ g.kg}^{-1}$).

Cd addition: Two kg (DW) aliquots of the soils were placed in a plastic jar, brought to the saturated-paste water content with distilled water, and left for equilibration for 24h at 10°C . Volumes of 100 ml $\text{Cd}(\text{NO}_3)_2$ solutions of various concentrations were added to the jars to obtain Cd loads of 0.1, 1.0, and $10.0 \text{ mg Cd} \cdot \text{kg}^{-1} \text{ soil}$. The non-loaded, control soil was treated similarly with 100 ml of distilled water. The solutions were added slowly from a burette while the paste was continuously and thoroughly stirred.

Cd partitioning analyses: The sequential selective dissolution (SSD) procedure was used to measure Cd partition. Details of the method are given in Hirsch and Banin (submitted, Chapter 12 of this report). Analyses were conducted on aliquots of the saturated soil pastes (SP) immediately after addition of the Cd, and after a few days (8 and 26 days for soil 1 and 2, respectively), of storing at $25 \pm 2^{\circ}\text{C}$.

Analyses were also conducted on the same Cd-amended soils stored at the field-capacity (FC) moisture content for several

months at a temperature of $25 \pm 2^\circ\text{C}$. The saturated pastes were spread in a thin layer on a tray and dried for several hours in a forced air oven at 40°C . Drying was stopped when the soils were slightly below the field capacity moisture content. The soils were then returned to FC by spraying them with distilled water while continuously mixing. The moist soils were stored in covered, but not sealed, jars. The soils were sampled once every 4-6 weeks, moisture content was analyzed and distilled water was added to restore them to the original moisture content.

SSD analyses were conducted at least in duplicate (frequently in triplicate). Cd in the extracts from the various steps of the SSD procedure was analyzed by GFAA. Cd partitioning is reported as percent in each soil fraction of the total extracted and the total added, in the non-amended soil and Cd-amended soils, respectively.

RESULTS AND DISCUSSION

Cadmium partitioning among the exchangeable (EXCH), carbonate (CARB), easily reducible oxides (ERO), organic matter (OM), and reducible oxides (RO) phases in the non-amended and Cd-amended soils immediately after addition, after a few days of incubation as saturated pastes and after a few months of incubation at the field capacity moisture content, are shown in Figure 1 a, b, and c respectively.

The native, non-amended soil 1 (calcareous) is characterized by dominance of the Cd-CARB fraction (~80%) followed by the OM fraction. The non-calcareous soil 2 shows a more even distribution

among the CARB, ERO, OM, and RO phases. Exchangeable Cd was not found in both soils.

More than 99% of the added Cd disappeared from solution immediately after addition and associated with the solid phase (Banin and Hirsch, 1990; Chapter 7, this report). In both soils exchangeable Cd became a dominant component, its relative content increasing with the added load of Cd (Figure 1a). Most of the rest of the added Cd was bound to carbonates. This fraction either stayed constant with the load (soil 1) or decreased (soil 2). Practically no Cd was associated with any of the other phases in soil 1. In soil 2 some of the added Cd associated with the ERO and OM phases. When compared to the non-amended soil, the overall distribution pattern was highly perturbed by the addition of Cd.

After a few days of incubation as saturated paste, Cd fractional partitioning returned almost completely to that of the non-amended soil (Figure 1b). Obviously, the absolute total concentration in each phase was higher as Cd load increased, but the fraction found in each phase out of total Cd in the soil was roughly the same as in the non-amended soil. Notable departure from that is the still higher relative content in the carbonate phase of both soils.

Incubation at field-capacity moisture content resulted also in reattainment of the "equilibrium" distribution typical of the non-amended soil (Figure 1c). The rate was, however, considerably slower. The transformation of exchangeable Cd to the carbonate phase in soil 1 and to the various other phases in soil 2 continued for months. Slower attainment of equilibrium at the field capacity moisture content may be due both to diminished diffusional fluxes

and lower rate of dissolution-precipitation reactions. The later affects the neoformation of new phases (oxides particularly) in which the added Cd may be incorporated.

SUMMARY AND CONCLUSIONS

Cd added to soils as a soluble salt was immediately sorbed to the solid phase. Initially it was bound electrostatically as an exchangeable ion and on the exposed carbonate surfaces in the soils. Increased Cd-load invariably resulted in increased Cd fraction in the exchangeable phase but constant (soil 1) or decreasing (soil 2) fraction in the carbonate phase. The immediately observed distribution pattern is presumably controlled by the rate of the specific retention reactions and the availability of sorbing surfaces and/or necessary reactants.

After a few days of incubation of the soil as a saturated paste, exchangeable Cd disappeared, and the distribution pattern returned, almost completely, to that typical of the non-amended soil. Some enrichment in the carbonate phase and deficiency in the organic matter phase were still observed.

A similar trend was observed in the soils incubated at the field capacity moisture content. The transformations were, however, much slower and continued for months. The rate of attainment of equilibrium in the systems was limited, apparently by diffusional flux and overall lower rates of dissolution-precipitation reactions.

Cadmium added in loads above the capacity of a given soil component are stored initially as exchangeable Cd and then, more permanently, as carbonate-bound Cd. If incorporation in a soil-phase is kinetically limited, accumulation in the exchangeable or carbonate phases takes place. Slow transfer, limited probably by the rate of formation of the new phase (oxides, organic matter), then proceeds over long periods of time. It appears that such processes may continue for years after Cd was added to the soil.

We conclude that the hypothesis presented earlier in this paper has not been rejected by the present results. Further studies are needed, however, to fully validate it and examine its limits of applicability.

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Figure 1. Partition of Cd among the solid phase components of two soils treated with Cd (NO₃)₂ solutions.

- (a) Immediately after Cd addition.
- (b) After a few days of incubation as saturated paste (SP) at 25°C.
- (c) After several months of incubation at field capacity (FC) moisture content. (EXCH - exchangeable; CARB - carbonate-bound; ERO - bound to easily reducible oxides; OM - bound to organic matter; RO - bound to reducible oxides).

F. DESCRIPTION OF COOPERATION

The principal investigators first met each other at an International Workshop in Germany in 1985. While at the workshop they discovered joint interests in the chemistry of heavy metals in soils. They decided to prepare a joint research proposal for submission to BARD and to focus on Zn and Cd. While at the conference they outlined their interests, sketched a first draft of the proposal and assigned each other areas of responsibility. The proposal was eventually funded by BARD in 1987. Our cooperation began from the very beginning of our acquaintance.

During the first year of the project Dr. Banin came to the U.S. and visited at Colorado State University for several days. The BARD project was reviewed and our approaches were discussed. Work for the first year was reported and plans were made to continue our scientific exchanges for the next year.

During the second year Dr. Lindsay visited Israel for several days during which our cooperative studies were discussed in great detail. Assignments were made to be sure we were accomplishing the objectives stated in the proposal. Plans were made for the second progress report and how it would be handled.

During the last year of the project Dr. Banin was in the U.S. and visited Colorado once again. We reviewed our progress and exchanged results and findings. We made plans for winding up our work and for preparing the final report. Shortly after that visit soil samples from the U.S. were sent to Israel for analysis by the sequential selective dissolution and differential IR and

XRD spectroscopy method developed in Israel. These analysis and comparisons on these soils will be pursued in future cooperative studies involving the two laboratories.

During preparation of the final report exchanges were made by telephone and by FAX. Joint parts of the report were prepared by each of us, exchanged, and finalized. This cooperative work had been mutually beneficial to both institutions, the principal investigators, and the several students associated with the work.

All of the major areas outlined in the initial research proposal have been dealt with, and significant progress has been made in each area. The many scientific contributions that have resulted from this project will be useful to other contemporary scientists who study these subjects.

G. EVALUATION OF ACCOMPLISHMENTS

The research reported herein has provided a better understanding of the solid-phase controls of Zn^{2+} and Cd^{2+} in arid-zone soils. This information is useful to soil and environmental scientist concerned with the accumulation of heavy metals in agricultural crops and their entry into the food chain. By knowing the solid-phase controls of various elements in soils, we are better equipped to understand solubility relationships and to predict their effect on the availability and toxicity of Cd and Zn. The activity measurements reported herein can be entered into chemical speciation models and used to predict the behavior of Zn^{2+} and Cd^{2+} in many kinds of environments. These findings will also help to assess the potential hazards of growing agricultural crops in soils contaminated with Zn and Cd.

Zn^{2+} Activity Measurements

The chelation method was used successfully to measure the activity of Zn^{2+} in a number of natural arid-zone soils. The results indicate that Zn^{2+} activity can often be expressed by the equilibrium relationship: $(\text{Zn}^{2+}) = 10^{5.8} (\text{H}^+)^2$, which we refer to as soil-Zn. Contaminated soils, on the other hand, show higher Zn^{2+} activities closer to those expected for ZnSiO_3 in moderately polluted soils and to ZnCO_3 in more heavily polluted soils. Because of these solid phase controls, severe Zn toxicities are not expected in arid-zone soils above pH 6.5, but they are expected on highly polluted soils of lower pH.

Franklinite Solubility Relationships

The solubility of Zn^{2+} in unpolluted soils, referred to here as soil-Zn, is generally very near the solubility of ZnFe_2O_4 (franklinite). To examine the possibility that franklinite may control the solubility of Zn in soils, synthetic franklinite was prepared and carefully characterized in the laboratory. Its solubility, along with that of natural franklinite obtained from the Smithsonian Institution, was measured in the laboratory. Various franklinite samples prepared in different ways were added to soils to determine solubility relationships in soil environments when equilibrium was approached from both undersaturation and supersaturation. The findings support the hypothesis that the activity of Zn^{2+} in many natural soils tends to approach that of well-characterized synthetic franklinite. When soluble Zn salts are added to soils, Zn rapidly precipitates, but maintains a higher Zn^{2+} activity than that of natural soil-Zn or well-characterized synthetic franklinite. The slightly higher solubility of added Zn is very near the measured solubilities of natural franklinite and more poorly formed synthetic franklinite. This higher solubility persisted for more than 105 days in the study report here. Franklinite may indeed be the mineral controlling Zn^{2+} activity in uncontaminated soils often referred to as soil-Zn.

Fe^{3+} Activity Measurements in Soils

Since franklinite contains both Fe and Zn, the solubility of

Zn^{2+} that it maintains depends upon the activity of Fe^{3+} . For this reason the activity of Fe^{3+} as well as Zn^{2+} was measured in a number of soils. The activity of Fe^{3+} found in most of these soils was between that of soil-Fe and that of amorphous Fe hydroxide. These findings are important for predicting and interpreting the solubility relationships of Zn^{2+} and franklinite in soils.

Cd^{2+} Activity in Soil Solutions

The Cd ion selective electrode (Cd-ISE) was used to directly measure Cd^{2+} activity in water and in soil solutions in a number of studies in the past. The electrode is recommended for use in the range of 10^{-1} to 10^{-7} M cadmium and its response drops considerably below the theoretical 29.6 mV/10-fold change in concentration, between 10^{-6} M and 10^{-7} M.

In many cases total cadmium concentration (Cd_t) in soil solutions is in the range of 10^{-9} to 10^{-7} M and free Cd^{2+} constitutes between 20 to 80% of the total. Therefore, the direct measurement of Cd^{2+} in extracted soil solutions did not yield meaningful data except for cases of high non-realistic additions of Cd. In the present project we have shown that free Cd^{2+} in extracted soil solutions can be accurately measured with Cd-ISE, using an addition method. The activity of Cd^{2+} in the non-treated soil solutions can then be calculated from measurements of Cd_t , assuming excess complexing agents in solution. In aqueous soil solutions Cd_t can be measured down to

$5 \cdot 10^{-9}$ M (~0.5 ppb) using GFAA. Thus the "limit of detection" for Cd^{2+} activity in soil solutions by the addition method may be in the range of $1 \cdot 10^{-9}$ to $4 \cdot 10^{-9}$ assuming $\text{Cd}^{2+}/\text{Cd}_t$ of 0.2 to 0.8.

This represents an improvement of about 2 orders of magnitude in our ability to measure directly Cd^{2+} activity in water and in soil and sediment solutions. The method enables the direct measurement of Cd^{2+} activity in non-polluted soil solutions or following the addition of realistic pollution loads of this metal, such as may develop after prolonged irrigation with reclaimed sewage water.

A study of a large group of non-polluted soils from Israel has shown that Cd_t concentration in the saturated-paste extract was in the range from $6 \cdot 10^{-9}$ M to $1 \cdot 10^{-7}$ M and Cd^{2+} varied between $7 \cdot 10^{-10}$ M and $6 \cdot 10^{-8}$ M. The pH range was 6.8 to 8.4. Free cadmium (Cd^{2+}) activity did not show a negative dependence on pH, which was expected from the newly defined soil-Cd solubility measurements reported herein by Workman and Lindsay (1990). It appears that Cd^{2+} activity in this group of non-polluted soils is controlled by sorption mechanisms rather than by a single solid-phase mineral. The difference between the group of Colorado soils and the group of Israeli soils may be related to differences in the mineralogical compositions of the soils and the various solid-phase Cd-adsorption sites present.

Modelling and Prediction of Cadmium Complexation in Solution and Adsorption to Clay

In view of the importance of adsorption processes in

controlling Cd^{2+} activity in soil solutions, a model system was studied, and a computational model was employed for predicting Cd adsorption under different ionic strengths, ionic composition, and clay to water ratios (Hirsch et al., 1989).

Increasing ionic strength decreased Cd adsorption by montmorillonite. The presence of a complexing ion, such as Cl^- also inhibits Cd adsorption. When the complexing anion was HCO_3^- , disappearance of Cd from solution was enhanced compared to the case where the anion was ClO_4^- , which does not form complexes with Cd. Two possible explanations of the latter phenomenon are 1) strong binding of the CdHCO_3^- complex to the clay, or 2) surface precipitation of otavite (CdCO_3). Increasing clay concentration enhances Cd adsorption. A model that predicts cation binding and cation exchange in clay suspensions and calculates the surface potential, the concentrations of the species bound to the clay surface, in the double layer and in the equilibrium solution, was coupled with a subroutine to calculate complexation reactions in solution. Agreement between observed and calculated values of adsorbed Cd was fairly good. The binding coefficient that best fit the data are 1, 10, and 30 for Na^+ , Cd^{2+} , and CdCl^+ , respectively.

Cd^{2+} Activity Measurements in Soils

The chelation method were used to examine Cd^{2+} activity in a number of natural and polluted soils. In most cases DTPA was used as the chelating agent and Pb^{2+} was used as the counter ion

under the conditions that added PbCO_3 maintained a known activity of Pb^{2+} . In most unpolluted soils above pH 6.5 the measured Cd^{2+} activities showed a strong pH dependence and followed the relationship: $(\text{Cd}^{2+}) = 10^{7.61} (\text{H}^+)^2$. This activity of Cd is approximately two orders of magnitude lower than the activity of Cd in equilibrium with CdCO_3 (otavite) and atmospheric CO_2 . The measurements of Cd activities in many non-polluted soils is often referred to as soil-Cd. No known Cd mineral has a solubility this low; however concurrent work in our laboratory (El-Falaky et al. (1991) points out the possibility that CdFe_2O_4 may be such a mineral, but its solubility is not well known.

In polluted soil the measured activities of Cd^{2+} are generally above the soil-Cd solubility line. They approach the solubility of Cd_2SiO_4 in moderately polluted soils and CdCO_3 in highly polluted soils. Although there is still much uncertainty about the solid phases that control Cd^{2+} activities in soils, the present study has opened the arena and given some guidelines for understanding the solubility of Cd in soils.

Cd Partitioning Between Components of the Solid-Phase of Soils

A procedure for sequential selective dissolution (SSD) of trace components in soils was tested using chemical and spectroscopical analyses. The procedure includes 5 sequential steps designed to selectively dissolve and extract the following phases: a) soluble and exchangeable ions, b) carbonates, c) easily-reducible oxides, d) organic matter and e) reducible

oxides. Although most of the extractants, and the adapted sequence, are based on already used techniques, in the present project we characterized the selectivity and specificity of each step both chemically and spectroscopically. Spectral data included x-ray diffractometry (XRD) and infrared (IR) absorption measurements as well as differential XRD and differential IR spectra obtained by subtracting the soil spectra obtained at two consecutive steps. It was found that replacement of the exchangeable cations with IM NH_4Cl ($\text{pH} = 7$) in the first step resulted in a mild attack of calcite and some NH_4^+ fixation. Sodium acetate ($\text{pH} = 5$) used in the second step failed to completely dissolve dolomite and calcite in a carbonate-rich soil. Reduction of Mn oxides with 0.04 M hydroxylamine hydrochloride (in 25% acetic acid at 25°C) in the third step is confirmed both from relatively high concentration of Mn in the extract solution and from tentative direct identification of manganite (MnOOH) in the difference spectra. Organic matter dissolution has also occurred in this step. Oxidation of organic matter with H_2O_2 did not damage clay minerals or iron oxides. Reduction of iron oxides in the last step was found to be done more efficiently and selectively with DCB than with hydroxylamine hydrochloride (in 25% acetic acid at 90°C). However, the DCB treatment was less efficient in the extraction of trace metals. In both treatments, some dissolution of clay minerals was detected by both the chemical and spectroscopic analyses. In general the protocol adopted is suitable for characterization of

the partition of trace metals among solid phase components of soils.

The transformations of Cd among solid-phase components of two soils from Israel amended with various levels of soluble Cd were followed using the SSD method. The addition of Cd perturbed the native pattern of distribution causing increased exchangeable and carbonate-bound Cd. With time the soils tended to return to the original pattern of distribution of the non-amended soil. The rate of return depended on the moisture content of the soil. Equilibrium was regained in a few days when the soils were saturated, but took more than a year when the soils were maintained at field capacity.

The observations reported here lead us to propose that the partition pattern of Cd (and possibly other trace metals) among various solid phase components of a non-polluted soil represents an "equilibrium" state poised by the different binding mechanisms operating in that soil. The soil will tend to return to this equilibrium partitioning pattern after perturbation by addition of trace levels of soluble Cd. Since the transformations are slow, the soil may be removed from the "equilibrium state" for relatively long periods of time, but ultimately will return. The availability of Cd to plants may be affected by the slow transformation of added Cd in soils. This helps to explain the slow decrease of Cd availability to plants with time that has been observed in field experiments. These findings open new possibilities for the development of methods to characterize Cd availability to plants.

LIST OF PUBLICATONS

Published Manuscripts

- Hirsch, D. and A. Banin. 1990. Cadmium speciation in soil solutions. J. Environ. Qual. 19:366-372.
- Hirsch, D., S. Nir, and A. Banin. 1989. Prediction of cadmium complexation in solution and adsorption to montmorillonite. Soil Sci. Soc. Am. J. 53:716-721.
- Ma, Qiying and W. L. Lindsay. 1990. Divalent zinc activity in arid-zone soils obtained by chelation. Soil Sci. Soc. Am. J. 54:719-722.
- Workman, S. M. and W. L. Lindsay. 1990. Estimating divalent cadmium activities measured in arid-zone soils using competitive chelation. Soil Sci. Soc. Am. J. 54:987-993.

Manuscripts in Preparation and Review

- Hirsch, D. and A. Banin. Studies of a combined sequential selective dissolution/differential IR and XRD spectroscopy procedure for soils.
- Hirsch, D. and A. Banin. Partion and transformations of added cadmium among solid-phase soil components.
- Ma, Qiying and W. L. Lindsay. Measurements of free Zn^{2+} activities in normal and contaminated soils using chelation.
- Ma, Qiying and W. L. Lindsay. Determination of Fe^{3+} activities in normal and contaminated soils using chelation.
- Ma, Qiying and W. L. Lindsay. Franklinite synthesis and solubility measurements
- Ma, Qiying and W. L. Lindsay. Franklinite equilibrium studies in soils.
- Ma, Qiying and W. L. Lindsay. Measurement of cadmium activities using chelation.
- Hirsch, D. and A. Banin. Cadmium activities in non-polluted arid-zone soil solutions.
- Workman, S. M., R. L. Jump, and W. L. Lindsay. Cadmium activities measured in contaminated soils using competitive chelation.