

DISSERTATION

**THE ROLE OF ORGANIC MATTER AND OTHER SOIL PROPERTIES IN Zn²⁺
ACTIVITY AND AB-DTPA-EXTRACTABLE Zn IN SOILS**

Submitted by

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY KATHRYN M. CATLETT ENTITLED THE ROLE OF ORGANIC MATTER AND OTHER SOIL PROPERTIES IN Zn^{2+} ACTIVITY AND AB-DTPA-EXTRACTABLE Zn IN SOILS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTORATE OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

THE ROLE OF ORGANIC MATTER AND OTHER SOIL PROPERTIES IN Zn^{2+} ACTIVITY AND AB-DTPA EXTRACTABLE Zn IN SOILS

Zinc is a plant micronutrient as well as a potential heavy metal contaminant in soils. In soil solution, the free Zn activity determines the availability of Zn as a micronutrient and its characteristics as a heavy metal contaminant. A better understanding of the mechanism that controls free Zn activity could improve soil treatments of Zn deficiency or toxicity. In this study, Zn^{2+} activity (measured by chelation) was related to soil properties for 18 alkaline soils from three farms in eastern Colorado. Organic carbon and pH were statistically significant parameters in a regression with $\log Zn^{2+}$ activity. Principal component analysis and path analysis were studied and applied to these soils. Results of principal component analysis showed that the first principal component, summing clay and total soil Zn and subtracting soil carbon, accounted for 52 % of the variability in the soils. Soil pH and inorganic carbon dominated the second principal component, which accounted for 32 % of the variability. Results of path analysis showed that direct effects of pH, total soil Zn, and organic carbon are important in predicting free Zn activity in these soils. Indirect effects of clay through organic carbon, of inorganic carbon through pH, and between pH and organic carbon were also important.

Results from statistical analyses indicate that adsorption of Zn on organic matter may control Zn solubility in soils. To further explore this potential mechanism, Zn adsorption to organic matter was modeled using the chemical equilibrium model, MINTEQA2, and model results were compared to experimental data from the three Colorado farms. Experimental and model results were in close agreement. Adsorption onto organic matter may control Zn solubility in acidic to neutral soils, while precipitation may control Zn in alkaline soils.

The AB-DTPA soil test can also be used as a measure of the availability of micronutrients to plants. AB-DTPA-extractable Zn was measured and correlated to soil chemical properties for soil samples described above. Soil organic carbon and total soil Zn were statistically significant parameters in a linear regression with AB-DTPA-extractable Zn. Organic matter and clay contents were positively correlated with AB-DTPA-extractable Zn.

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CHAPTER 1

INTRODUCTION

The availability of zinc as a micronutrient has been the subject of much research in soil science. Zinc is known to be deficient in plants, especially those grown in alkaline soils. Despite all the research, a full understanding of the interaction of Zn with soil is not established. Advances in the understanding of the behavior of Zn in soils can help agriculturists understand how to prevent plants from becoming Zn-deficient.

From a different perspective, Zn may be considered as a heavy metal contaminant in soils. Concern for Zn contamination can be found in areas of acid mine drainage and in soils amended with biosolids. Increased knowledge of Zn solubility could be applied in these situations to decrease the mobility of Zn.

Several soil properties may influence Zn solubility and availability in soils. In this study, the relationships between Zn solubility and pH, organic matter, inorganic carbon, clay, CEC, and total soil Zn are investigated. The roles of organic matter and pH are the primary focus of this research.

Zinc solubility is examined in terms of Zn^{2+} activity and AB-DTPA (ammonium bicarbonate-diethylenetriaminepentaacetic acid)-extractable Zn. Free Zn (written " Zn^{2+} ") activity is important in solubility diagrams. These diagrams are typically graphs of log metal activity versus pH. They can be used to explore possible solid phases that control metal solubility in soil. In addition, Zn^{2+} is the form of Zn adsorbed by plants. AB-

DTPA-extractable Zn is also a measure of the availability of Zn to plants. This extraction procedure is used to test soils for Zn deficiency.

Metal solubility can be given in terms of activity and concentration. The activity of a metal equals the concentration times an activity coefficient. This activity coefficient depends on the ionic strength of the solution. Activity is represented with parentheses (e.g., “ (Zn^{2+}) ”) and concentration is represented with brackets (e.g., “ $[\text{Zn}^{2+}]$ ”).

Hypotheses addressed in this study are: (1) free Zn activity in soil increases as organic matter decreases; (2) soil pH, organic matter content, clay content and total soil Zn are important soil parameters in predicting Zn solubility in soils; (3) adsorption to organic matter could control Zn solubility in soils.

This paper is divided into six chapters. Chapter 1 is the introduction and the other chapters explore different aspects of the roles of soil parameters in Zn solubility. Chapter 2 discusses the estimation of Zn^{2+} activity in soil and explores relationships between soil properties and Zn^{2+} activity by multiple regression analysis. Chapter 3 explores the relationships between soil properties and Zn^{2+} activity using the advanced statistical techniques of principal component analysis and path analysis. Chapter 4 demonstrates the use of a chemical speciation model to develop solubility diagrams for Zn adsorption by organic matter and for Zn precipitation in soils. Chapter 5 shows the relationships between soil properties and AB-DTPA-extractable Zn and compares these results to the regression results for Zn^{2+} activity from Chapter 2. Chapter 6 concludes this manuscript with a discussion of the results presented in previous chapters and an exploration of ideas for future research.

CHAPTER 2

EFFECTS OF SOIL CHEMICAL PROPERTIES ON Zn^{2+} ACTIVITY

Summary

Zinc is a plant micronutrient as well as a potential heavy metal contaminant in soils. In soil solution, the free metal ion activity determines the availability of Zn as a micronutrient and its characteristics as a heavy metal contaminant. In this study, Zn^{2+} was measured by a chelation method and compared to soil chemical properties, such as pH, soil organic carbon and clay content in eighteen alkaline soils from three farms in eastern Colorado. Soil organic carbon and pH were statistically significant parameters in a linear regression with $\log Zn^{2+}$ activity. This relationship suggests that adsorption of Zn to organic matter may control Zn solubility in these soils. The results from this study were compared to previous studies of Zn solubility.

Introduction

Zinc (Zn) has been the subject of much research in agriculture because it is an essential micronutrient and thus important for plant growth. Zinc deficiencies commonly occur in Colorado and other states in the West because of high soil pH. However, Zn in high concentrations can also be toxic to plants and animals. Thus it is becoming the subject of environmental research (e.g., Lerch et al., 1990; Barbarick et al., 1997).

Biosolids and manure applied to agricultural lands as fertilizer may contain higher concentrations of Zn than commonly found in soils. These amendments may supply sufficient Zn for plant growth, but there is concern that Zn and other heavy metals may present a problem with contamination. Zinc is also a possible contaminant in areas of acid mine drainage. To understand bioavailability and transport of Zn in soils, the solubility and speciation of Zn in soil solution must be understood. Several mechanisms have been proposed to describe Zn solubility in soil. These include solid forms or phases of Zn and interactions with organic matter and pH.

Zinc solubility in soil

Solid forms or phases of Zn may control its solubility in soil. When an element in solution exceeds the equilibrium concentration related to a mineral or solid phase, that mineral can precipitate. Similarly, when the concentration of an element decreases below the equilibrium solubility, that mineral can dissolve to increase the concentration back to the equilibrium value. The solid phase that controls Zn solubility in soil is not well understood, but is referred to as “soil-Zn” by Lindsay (1979). There is some evidence that this solid phase may be franklinite (Sinha et al., 1978; Norvell et al., 1987; Ma and Lindsay, 1990; Ma, 1991). Other studies indicate a possible mineral phase solubility control, but one that may not be franklinite. Pulford (1986) suggests that a possible precipitation reaction involving Zn and Fe could occur independently of pH. Zinc also may precipitate on the surface of calcium carbonate or co-precipitate with the Ca to form a carbonate of the form $Zn_xCa_{1-x}CO_3$ (Papadopoulos and Rowell, 1989).

The solubility control is usually considered to be the precipitation or dissolution of a mineral phase such as Zn_2SiO_4 , but it could also be adsorption onto a mineral such as iron oxide, or adsorption onto clay or organic matter. Adsorption may occur at low pH, and precipitation may occur at high pH. Gupta et al. (1987) suggest that at high pH, precipitation reactions control Zn solubility, whereas at neutral to acidic pH, specifically adsorbed Zn may control Zn solubility. McBride and Blasiak (1979) suggest that adsorption to oxide surfaces, which have a high affinity for Zn, may be important in controlling Zn solubility. Their data are close to expected soil-Zn values between pH 5.5 and 7.0. They also state that “a single adsorption mechanism is not likely to control solubility over a wide pH range” (McBride and Blasiak, 1979). Singh and Abrol (1985) found that precipitation of willemite (Zn_2SiO_4) was likely at $pH > 7.9$ in the sodic soils studied. They also found that precipitation or adsorption may occur between pH 6 and 7.9, and that the slopes were close to zero below pH 6, indicating a possible adsorption mechanism. Jeffrey and Uren (1983) conclude that at neutral to alkaline pH, specific adsorption of a hydrolyzed form of Zn (e.g., $Zn(OH)^+$) may account for the low soluble Zn concentrations. Yet, Randhawa and Broadbent (1965) state that in their studies of Zn and Cu with known organic compounds, Cu was adsorbed as $CuOH^+$, but Zn was adsorbed as Zn^{2+} .

The actual mechanism of Zn adsorption in soils is not clear. Zinc may bind to Fe, Mn and Al oxides, clays, organic matter or any combination of these. Iron, Mn and Al oxides have negatively charged surfaces and thus may strongly bind metals, even in neutral to alkaline soils. Adsorption by these oxides has been suggested by several studies (McBride and Blasiak, 1979; Dang et al., 1996; Loganathan et al., 1977). In

addition, Fe or Al oxides could possibly coat clay surfaces and alter the adsorption of Zn to the soil (Shuman, 1976). Zinc adsorption by clays has been shown to be pH dependent (Kurdi and Doner, 1983; Cavallaro and McBride, 1984). Other research on adsorption of Zn by clays includes studies on the effects of solution composition on adsorption (Bartal et al., 1988; Elrashidi and O'Connor, 1982) and the effects of cation exchange capacity (CEC) on adsorption (Brigatti et al., 1996; Choudhari, 1984; Maguire et al., 1981).

Organic matter may affect Zn solubility in soils (e.g., Kerndorff and Schnitzer, 1980; Senesi et al., 1989; Shuman, 1976). Organic matter and pH are important factors that influence metal solubility. It is difficult to separate their influences because pH affects variable charge on organic matter as well as metal precipitation reactions. It is expected that additions of organic matter will decrease metal solubility (McBride et al., 1997), but many questions still remain about the influence of organic matter on Zn solubility.

Caution should be used when comparing experimental results from different studies. Many different methods are used to estimate Zn solubility. For example, some researchers measure total soluble Zn concentrations, whereas others calculate free Zn ion concentrations or labile Zn concentrations. In acidic soils these concentrations may be similar, but in neutral to alkaline soils these concentrations are different. Figure 2.1 illustrates the contribution of hydrolysis, carbonate and organic species to the total Zn concentration. At low pH the total soluble Zn and free Zn activity are nearly the same, but at high pH they are different. Measurements of free Zn activity and Zn speciation are discussed in the next sections.

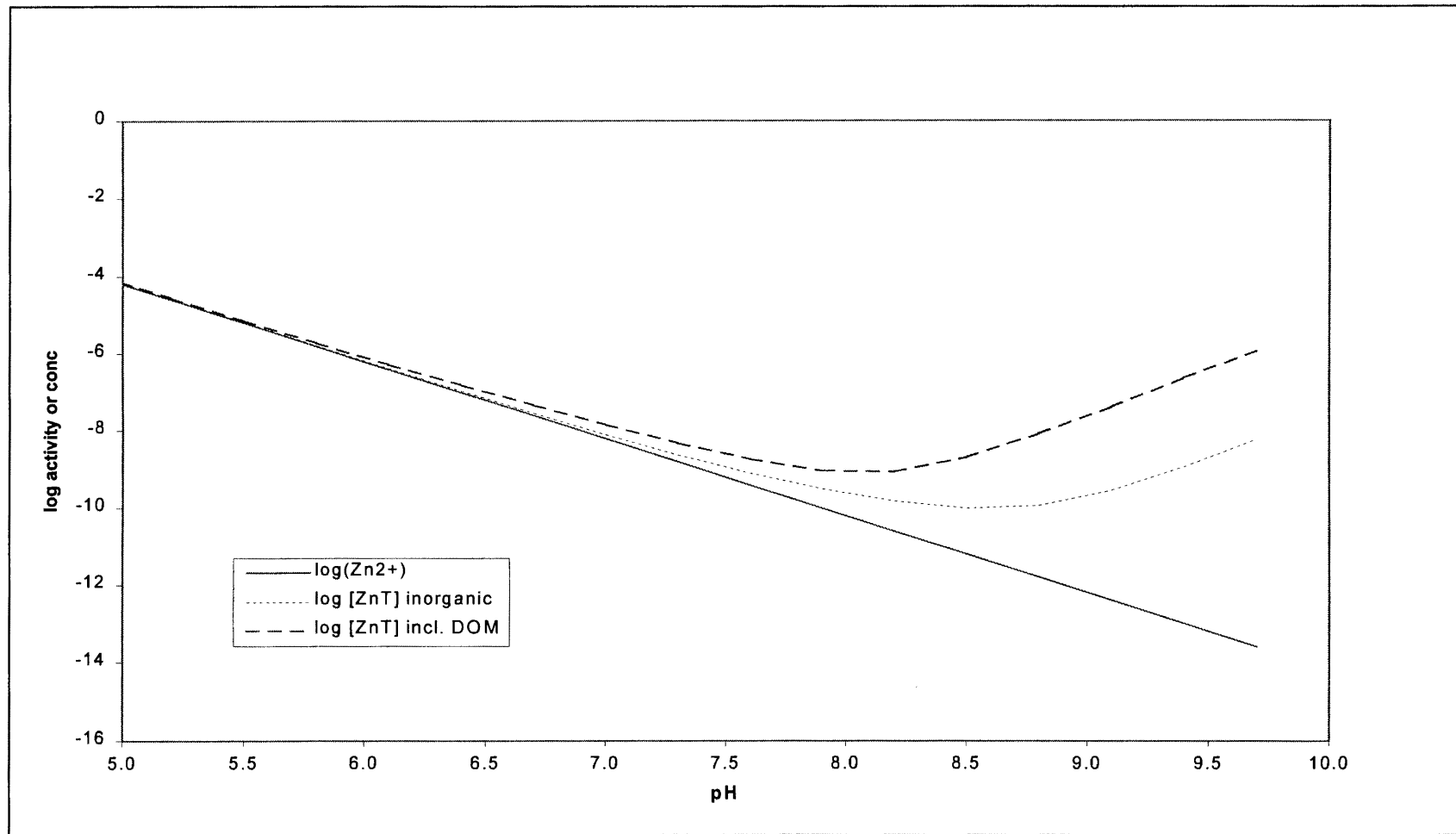


Fig. 2.1. Total Zn concentrations and free Zn activity are plotted with pH, as calculated by MINTEQA2. Zinc is controlled by soil-Zn (Lindsay, 1979). The total Zn concentration with only inorganic species includes hydrolysis species and carbonate species at atmospheric CO_2 (g), i.e., 0.0003 atm. A concentration of $5.0 \times 10^{-6} \text{ M}$ DOM was included to produce the third and upper line. The binding constant used for DOM was the default constant in MINTEQA2.

Free Zn activity measurement

Measurement of free Zn activity in soils is important in the study of Zn solubility in soils. However, there are two significant difficulties in estimating Zn^{2+} activities. One problem is that the Zn^{2+} activity in a water extract is usually too small to measure directly with an ion selective electrode, especially at high pH values. So total Zn is often measured instead. The second problem is that the heterogeneity of organic matter makes it difficult to account for organically-complexed Zn. Total Zn can be measured and then speciated with MINTEQA2 (Allison et al., 1991) or another speciation model such as GEOCHEM (Mattigod and Sposito, 1979) to estimate organically-complexed Zn. However, binding constants change with pH, with solution composition, or with characteristics of organic matter in soil.

Experimental methods using voltammetry and ion-exchange resins can provide a value for "labile" Zn. "Labile" is defined by the method used and typically represents the most easily dissociated species of Zn in solution. Most organic complexes are not easily dissociated, so "labile" or "easily labile" concentrations may provide a maximum value for inorganically-complexed Zn.

Total soluble Zn can be measured and then speciated accurately in some situations. Studies have shown that most Zn is not complexed by dissolved organic matter (DOM) in acidic soils (Brown et al., 1997; Curtin and Smillie, 1983; Jeffery and Uren, 1983). However, in neutral to alkaline soils ($pH > 6$), organic-Zn complexes may account for 4 – 8 % of the total soluble Zn (Dang et al., 1996; Holm et al., 1995; McBride and Blasiak, 1979). Sanders (1983) suggested that dissolved organic-Zn complexes could be forming since the ratio of $[Zn^{2+}]/[Zn]_T$ decreased above pH 6 and hydrolysis

species are insignificant at this pH. Thus, it is justifiable to speciate total Zn without including a dissolved organic Zn species, especially in soils below pH 6.

Chelation can account for some of the difficulties inherent in other methods of measuring free Zn activity in alkaline soils. The Zn^{2+} activity can be measured to very low values ($<10^{-11}M$) using the chelation method of Norvell and Lindsay (1969). In addition, organically-complexed Zn is accounted for in the chelation method, although it is not calculated. More details of this method are included below.

Application of chelation to free metal ion measurement

Competitive chelation uses a chelate such as EDTA or DTPA to estimate the free metal activity in a soil solution. To use chelation to estimate free metal activities one must assume that there is a solid phase in the soil such as a precipitate or an adsorbed phase that controls the metal activity in soil solution. It is assumed that the free metal activity for the solution with the chelate is the same as the free metal activity without the chelate. For example, perhaps franklinite ($ZnFe_2O_4$) controls Zn solubility in soil solution, and amorphous $Fe(OH)_3$ controls Fe. The Zn solubility is controlled by this solid phase, assuming there is enough of the solid phase to supply sufficient metal ion to solution, so that the free metal activity will be the same without EDTA and with a small concentration of EDTA. Soil properties such as pH and redox may affect the free metal activity. However, if these properties are kept constant, the free metal activity will also be constant. Thus, if you add a small amount of EDTA to a soil solution, for example, the solid phase will allow more metal to come into solution to equilibrate with the EDTA,

and the free metal activity at equilibrium will be the same as that in the solution without EDTA.

The solid phase that controls the free metal activity can be predicted by measuring the free metal activity. For different soils, there are different solid phases that control the solubility of a single metal. For example, amorphous $\text{Fe}(\text{OH})_3$ may control Fe solubility in one soil, but in another soil, goethite ($\text{Fe}(\text{OH})_3$) may control Fe solubility. One would expect different Fe^{3+} activities for these different soils for given soil solution properties (Lindsay, 1979).

Soluble organic complexes of metals are taken into account by chelation. EDTA can compete with DOM for free metal ion in solution, but calculations (shown below) of metal activity only depend on metal-EDTA concentrations and counter-ion concentrations. As long as the metal-organic complexes are at least 100 times less than the metal-EDTA complexes, these calculations are valid.

The chelation method uses the concept of a solid phase that controls solubility by assuming that the free metal solubility will not change if a small amount of EDTA is added to solution. In addition, the EDTA is loaded with different mole fractions of the metal of interest and a counter ion to insure that the equilibrium of the system is not greatly disturbed. Then when the initial mole fraction is the same as the final mole fraction, no Zn will dissolve or precipitate. For alkaline or calcareous soils, calcium is often chosen as a counter ion because of its high solubility and good competition for EDTA at high pH. (See Fig. 15-4 in Lindsay 1979.)

Zinc and organic matter

Total Zn in a soil solution is divided into species through a process called speciation. In general, total Zn could be divided into inorganic and organic fractions and each of these fractions could be further subdivided. For example, inorganic Zn could be the sum of several species such as Zn^{2+} , $ZnOH^+$, and $ZnSO_4^0$.

Several factors affect both the solubility and speciation of Zn in soil, including pH, anion and cation concentrations, and the concentration and type of organic matter. As the pH of a soil increases, the Zn concentration in the soil solution decreases because mineral forms of Zn are less soluble at high pH (Lindsay, 1979). Soil pH also affects Zn speciation. At low pH, Zn^{2+} is the dominant species and at high pH, $Zn(OH)_2^0$ becomes dominant (Lindsay, 1979). Dissolved organic Zn species may become important at high pH. Anion concentrations can affect Zn solubility by causing Zn minerals to dissolve or precipitate. For example, at high phosphate concentrations, hopeite (a Zn-phosphate mineral) may precipitate (Lindsay, 1979). In addition, both anion and cation concentrations can affect Zn speciation. High concentrations of sulfate could make $ZnSO_4^0$ species dominant over Zn^{2+} (Lindsay, 1979). High concentrations of calcium may compete for sulfate and result in the formation of more $CaSO_4^0$ and less $ZnSO_4^0$ (Lindsay, 1979).

The effects of organic matter on Zn solubility and speciation are uncertain. If organic matter is soluble, the solubility of Zn-organic species could increase. If organic matter is insoluble, the concentration of Zn-organic species could decrease. There are indications in the literature that total soluble Zn is not affected by organic matter (McBride et al., 1997). However, as McBride et al. (1997) indicated, such studies are

limited by narrow ranges in organic matter concentrations and by the heterogeneity of organic matter in soils.

Part of the difficulty in understanding the effects of organic matter on Zn solubility and speciation is the heterogeneity of soil organic matter. The solubility of soil organic matter varies between and within soils. Some forms of organic matter in soil are soluble, while others are not. In addition, soil organic matter derived from different vegetation sources can have different concentrations and types of functional groups and thus different effects on metal solubility.

The problem addressed in this study is to explore the effects of organic matter on free Zn activity and add to the understanding of Zn interactions with organic matter. In different research studies, various methods used for measuring free Zn activity resulted in slopes of the $\log(\text{Zn}^{2+})$ vs. pH regression line ranging from -0.32 to -2 (Dang et al., 1996). These results do not adhere to the -2 value that is expected from Lindsay (1979) and Norvell and Lindsay (1969) for a precipitation reaction. I hypothesize that an adsorption reaction with organic matter may control Zn solubility instead of a precipitation reaction involving a mineral such as franklinite.

There are problems with comparing different studies because of the differences in methods and experimental design. Different methods were used to obtain Zn^{2+} activity, including chelation (Ma and Lindsay, 1990; Ma and Lindsay, 1993; Norvell et al., 1987; Sinha et al., 1978), ion-exchange resins (Curtin and Smillie, 1983; Dang et al., 1996; Fotovat et al., 1997; Holm et al., 1995; Jeffery and Uren, 1983), and speciation of total soluble Zn with computer models (Dang et al., 1996; Fotovat and Naidu, 1997).

To elucidate the relationship between organic matter and Zn solubility in soils, Zn^{2+} activity must be measured accurately. Also, the experiment must be designed to minimize the effects of the heterogeneity of organic matter in soils and to maximize the range of organic matter concentrations.

For this study, the chelation method was chosen as the best method of estimating Zn^{2+} activity in alkaline soils, even though it is time-consuming. Neutral and alkaline soils from eastern Colorado were chosen as soil samples. These soils were from agricultural areas that grow similar crops and have similar climate but exhibit a range of organic matter concentrations.

The objectives of this experiment are to: (i) estimate the Zn^{2+} activity in neutral and alkaline soils of similar organic matter composition; (ii) investigate the relationships between the Zn^{2+} activity and soil chemical properties of these soils; and (iii) relate the estimated Zn^{2+} activity to potential solid phases in the soils.

Methods and Materials

The soil samples were from farms used in a study by Davis and coworkers (Iversen et al., 1998). The purpose of that study was to explore the variation in crop quality across farms in a relatively small area. They separated each field into three sections by the quality of crops that grew on the farm. Healthy crops comprised the group labeled "A", crops of intermediate quality were labeled "B", and crops of poor quality were labeled "C". Three farms, CF, LP, and Weld, were chosen out of the 18 farms based on their range of organic matter contents and similarities in soil chemical properties. The goal in selecting the farms was to choose soils of neutral to alkaline pH

that had a relatively wide range of organic carbon concentrations but similar expected organic matter composition. Each farm was divided into three parts and sampled at two depths (surface and sub-surface) in a location near to Davis' sampling locations. Two of the farms, CF and LP, were sampled along a toposequence from hilltop, to sideslope and footslope. For these two farms, the hilltop corresponded to the poorest quality crop or Group C soils, the sideslope to intermediate quality or Group B soils and the footslope to the highest quality or Group A soils. The Weld farm was flat overall. Samples were taken across that field approximately where the crop conditions indicated Group A, B, and C soils. The farm was cleared of crop and residue at the time of sampling, and the three sections could not be assigned to a group unambiguously. Instead of Group A, B, or C assignments, they were assigned "1, 2, 3." Three locations at three farms and at two depths (surface and sub-surface) were sampled for a total 18 soil samples. Surface samples were taken from about 0 to 6 cm and subsurface samples were from about 6 to 16 cm. The soils were air-dried, ground lightly with a mortar and pestle, and shaken gently through a 2-mm sieve.

Soil chemical properties

The pH of the soil samples was measured in a 1:2 soil to solution ratio after equilibration for 24 hours and as part of the chelation method at 5 days. The 5-day pH measurement is represented in two ways. The 5-day pH is the pH of the blank from the chelation method. The 5-day average pH is the average pH over all solutions from a particular soil, including the solutions with chelate added. These two values are very close for the soils sampled (see Table 2.1) because the pH of the water extracts is close to

Table 2.1. Soil properties and soil taxonomy for the 18 soils. Horizontal lines separate the 3 farms.

soil #	farm	location	depth	24-hr pH	5-d pH	average	% IC	% OC	% clay	total soil Zn mg kg ⁻¹	CEC cmol _c kg ⁻¹	soil taxonomy*
						5-d pH						
1	CF	A	top	7.84	8.24	8.19	0.000	0.86	16.9	64.0	30.6	1
2	CF	A	bottom	7.61	8.16	8.04	0.000	0.73	23.1	66.5	27.9	1
3	CF	B	top	7.74	8.50	8.45	0.030	0.90	29.4	78.4	35.1	1
4	CF	B	bottom	7.77	8.72	8.67	0.67	0.86	30.0	71.9	39.1	1
5	CF	C	top	7.76	8.57	8.57	0.42	0.80	26.3	74.8	39.1	2
6	CF	C	bottom	7.85	8.76	8.73	1.32	0.62	27.5	65.7	35.3	2
7	LP	A	top	7.29	7.66	7.76	0.015	1.25	15.6	55.2	19.2	3
8	LP	A	bottom	7.61	8.45	8.47	0.021	1.04	19.4	60.2	27.7	3
9	LP	B	top	6.77	7.59	7.47	0.0035	1.42	16.3	57.9	22.8	3
10	LP	B	bottom	6.99	7.30	7.38	0.0073	1.26	21.3	64.6	25.3	3
11	LP	C	top	8.32	8.69	8.64	1.05	1.09	13.1	29.7	15.2	3
12	LP	C	bottom	7.94	8.68	8.69	2.55	1.86	16.3	25.3	18.8	3
13	Weld	1	top	7.50	8.43	8.42	0.019	0.92	21.3	61.7	28.3	4
14	Weld	1	bottom	7.70	8.59	8.58	0.43	0.65	28.8	71.3	37.3	4
15	Weld	2	top	7.24	7.85	7.80	0.011	0.82	30.0	65.4	27.7	4
16	Weld	2	bottom	7.75	8.56	8.49	0.015	0.48	23.8	64.7	30.5	4
17	Weld	3	top	7.26	7.62	7.57	0.022	0.70	23.1	61.7	28.7	4
18	Weld	3	bottom	8.04	8.56	8.52	0.013	0.43	23.8	66.0	29.0	4

* Key to soil taxonomy:

1 = Fine-silty, mixed, mesic Aridic Argiustoll (Petersen et al., 1986)

2 = Fine-silty, mixed (calcareous), mesic Ustic Torriorthent (Petersen et al., 1986)

3 = Fine, montmorillonitic, mesic Aridic Paleustoll (Petersen et al., 1986)

4 = Fine, montmorillonitic, mesic Aridic Argiustoll (Crabb, 1982)

the pH of the chelate extracts. The 5-day pH average was used for all graphs and statistical analyses.

Several soil properties were measured for each of the samples. Total soil Zn was measured from a HNO_3 - HClO_4 digest, and the solution was analyzed by inductively coupled plasma (ICP) (Hossner, 1996). Percent inorganic carbon was measured by a modified volumetric method (Wagner et al., 1998; L. Sherrod, personal communication). Total carbon was measured by a Dorhmann DC-190 High-Temperature Total Carbon Analyzer. Percent organic carbon was estimated by the difference in total carbon and inorganic carbon. Cation exchange capacity was measured by a method for soils with carbonates (Sumner and Miller, 1996). Percent clay was measured by the hydrometer method (Gee and Bauder, 1986).

Chelation method

The free Zn activity was measured by a modified chelation method (Norvell and Lindsay, 1969; Ma and Lindsay, 1990). The method is described below in detail. Soil suspensions were prepared with 10 g of soil and a final solution volume of 20 mL to yield a 1:2 soil to solution ratio. Initially, 10 g of soil were added to a 125-mL Erlenmeyer flask along with 12 mL of deionized (DI) water. Samples were covered with parafilm slightly folded back at the top to allow equilibration with the atmosphere. These samples were placed on an oscillating shaker for 24 hours at about 150 revolutions per minute. Subsequently, 8 mL of chelate solution (described below) were added to each of the samples, and the samples were shaken for 4 more days. A blank treatment was prepared for each soil by adding 8 mL of DI water to the flask, instead of a chelate solution.

Samples were weighed daily and adjusted for water loss via evaporation. Duplicates and in some cases triplicates of each soil were used.

In this study EDTA was chosen as the chelating agent because of the affinity of EDTA for Zn at neutral pH. Calcium was chosen as the competing ion because the pH of the soils was neutral to alkaline. Chelate solutions of different mole fractions of Zn- and Ca-EDTA were prepared so that the total concentration of EDTA was 100 μM in the soil solution. A stock solution of reagent grade $\text{Na}_2\text{H}_2\text{EDTA}$ was used. Different amounts of ZnCl_2 and CaCl_2 standards were added to flasks containing the EDTA stock solution to create a range of mole fractions of Zn- and Ca-EDTA from approximately 0 to 1. The pH of these solutions was adjusted to about 7 with NaOH to reduce dissolution of the soil due to acidity. Then the solutions were allowed to shake overnight and the pH was again adjusted to 7.0.

In previous experiments at neutral to alkaline pH values (Ma and Lindsay, 1990; Ma and Lindsay, 1993; Sinha et al., 1978), the Zn-EDTA equilibrium mole fraction was small (<0.1) in uncontaminated soils. Zinc-EDTA mole fractions from 0.0001 to 0.2 and 0.005 to 0.9 (for more acidic soils) were used.

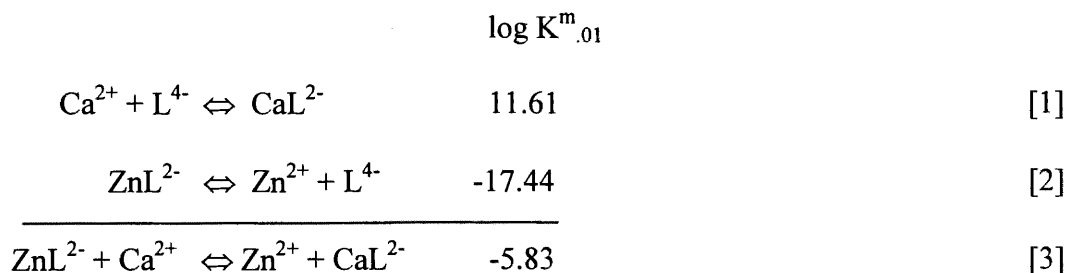
At the end of the 5-day shaking period, the pH of each suspension was measured with a combination pH electrode. The suspensions were then centrifuged at 18,000 rpm for 10 minutes using a Sorvall RC-5B refrigerated superspeed centrifuge. The supernatant solutions were filtered through a 0.45- μm nylon syringe filter. The electrical conductivity (EC) of the filtrates was measured using a conductivity meter and the Ca^{2+} ion activity was measured with an Orion Ca ion selective electrode (ISE). Concentrations of Fe, Zn, Ca, Mn, and Cu were measured in the extract by inductively coupled plasma

spectroscopy (ICP). Iron, Mn, and Cu are the metals most likely to compete with Zn and Ca for EDTA in these soils.

The concentration of EDTA in the extract was measured by adding excess ZnCl_2 to the solution and measuring ZnEDTA^{2-} by ion chromatography. The variation in EDTA concentrations was small within each soil and replication, so only half of the samples were analyzed for each replication due to time constraints. Note that there were 5-7 solutions involved in each replication for each soil. Then the EDTA concentration was averaged for each soil over all replications. There was some error associated with the calibration of the EDTA curve. Replications within a soil had a smaller standard deviation than that of the calibration standards. The EDTA concentration is probably the source of the greatest error in this method. More detail on error analysis is included in the Appendix.

Chelation method theory and calculations

To calculate the Zn activity, equilibrium dissociation equations for CaEDTA and ZnEDTA are needed (Lindsay, 1979). An equation for Zn activity was obtained as follows. First, the competition between Ca and Zn for EDTA must be expressed (L = EDTA):



where $\log K_{.01}^m$ is the mixed equilibrium constant for the given reaction at an ionic strength of 0.01. “Mixed” indicates that hydrogen ion and electrons are expressed in activities and everything else is in concentrations.

Rearranging this equation and recognizing that activity coefficients of Ca and Zn are equal yields:

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

Then dividing the numerator and the denominator on the right-hand side by $([ZnL^{2-}] + [CaL^{2-}])$ yields:

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

And finally,

$$(Zn^{2+}) = 10^{-5.83} (Ca^{2+}) * \theta / (1-\theta) \quad [6]$$

$$\text{where } \theta = [ZnL^{2-}] / ([ZnL^{2-}] + [CaL^{2-}]). \quad [7]$$

Here, θ is the equilibrium mole fraction of ZnEDTA²⁻, with respect to Zn and Ca.

The Ca²⁺ activity in solution and the equilibrium mole fraction of ZnEDTA are needed to calculate Zn²⁺ activity. The Ca²⁺ activity is calculated by taking the Ca²⁺ concentration (measured by ISE using a concentration curve) and multiplying by the activity coefficient. The activity coefficient is estimated by the Davies equation which uses the ionic strength of the solution (Lindsay, 1979; Davies, 1962). The ionic strength (IS) is estimated by the equation: IS = 0.013 EC, where EC is the electrical conductivity (Lindsay, 1979; Griffin and Jurinak, 1973). The Ca²⁺ activity for a soil was estimated as the average Ca²⁺ activity for the samples used to calculate the equilibrium mole fraction.

For example, if two data points were used to calculate the equilibrium MF, then the Ca^{2+} activities of those two points were averaged. If a regression equation was used to calculate the equilibrium MF, then all the data points of the regression were used to calculate the Ca^{2+} activity.

To calculate the equilibrium mole fraction (MF) of ZnEDTA, a graph is made of the final MF vs. initial MF of ZnEDTA. The final MF is calculated by:

$$\text{MF}_f = \text{ZnEDTA}/(\text{ZnEDTA} + \text{CaEDTA}) \quad [8]$$

The total Ca concentration in solution cannot be considered as CaEDTA because there is likely a significant amount of free calcium ion and inorganic calcium complexes in solution. Thus total EDTA concentration is measured and then CaEDTA is calculated by taking the total EDTA concentration and subtracting the sum of the metal-EDTA concentrations:

$$[\text{CaEDTA}] = [\text{EDTA}]_T - [\text{ZnEDTA}] - [\text{FeEDTA}] - [\text{CuEDTA}] - [\text{MnEDTA}] \quad [9]$$

The metal-EDTA concentrations can be measured by inductively coupled plasma (ICP). The total metal concentration, as measured by ICP, is assumed to be metal-EDTA since free metal concentrations are low in calcareous soils and do not form inorganic complexes of even 1/100th of the concentration of EDTA. So, for example, $[\text{ZnEDTA}^{2-}]$ is the Zn concentration measured by ICP minus the Zn concentration in the blank for that soil. The metal concentration in the water extract is subtracted because sometimes there are measurable colloidal concentrations in the blank and thus also in the EDTA extracts. High concentrations in the blank were primarily observed with Fe.

The equilibrium mole fraction (MF) of ZnEDTA is estimated from a plot of final ZnEDTA mole fractions versus initial ZnEDTA mole fractions. See Figs. 2.2 through

2.4. The equilibrium mole fraction of ZnEDTA is the point of intersection of that graph with the line defined by: initial ZnEDTA MF = final ZnEDTA MF (i.e., the line $y = x$). This makes sense from the soil chemistry perspective because the closer the final MF is to the initial MF, the less the MF changes and the closer it is to equilibrium. If the final MF were the same as the initial MF, that value would be the equilibrium MF. For most soils, a line was constructed with the two points nearest the intersection to determine the equilibrium point (Fig. 2.2). Linear regressions were used when the scatter of the data was relatively large (Fig. 2.3). For some soils the point of intersection was just below the range of the data points. A linear regression was extrapolated to where it intersects the $y = x$ line (Fig. 2.4).

Analysis of EDTA

The final EDTA concentration can be measured by ion chromatography. The soil adsorbs some of the EDTA that is added, thus the final EDTA concentration is usually lower than what was added initially. Previous studies (Norvell et al., 1987, Ma and Lindsay, 1990) have shown that up to about 20% of the original EDTA could be adsorbed to the soil. Thus the final solution concentration of EDTA for this study should be between 80 and 100 μM . An ion chromatograph (IC) can detect this concentration. In the final soil solution, not all of the EDTA will be in the same form. It will be a combination of CaEDTA, ZnEDTA and other metal-EDTA. By adding excess Zn to solution as ZnCl_2 , the CaEDTA and other metal-EDTA can be converted to ZnEDTA.

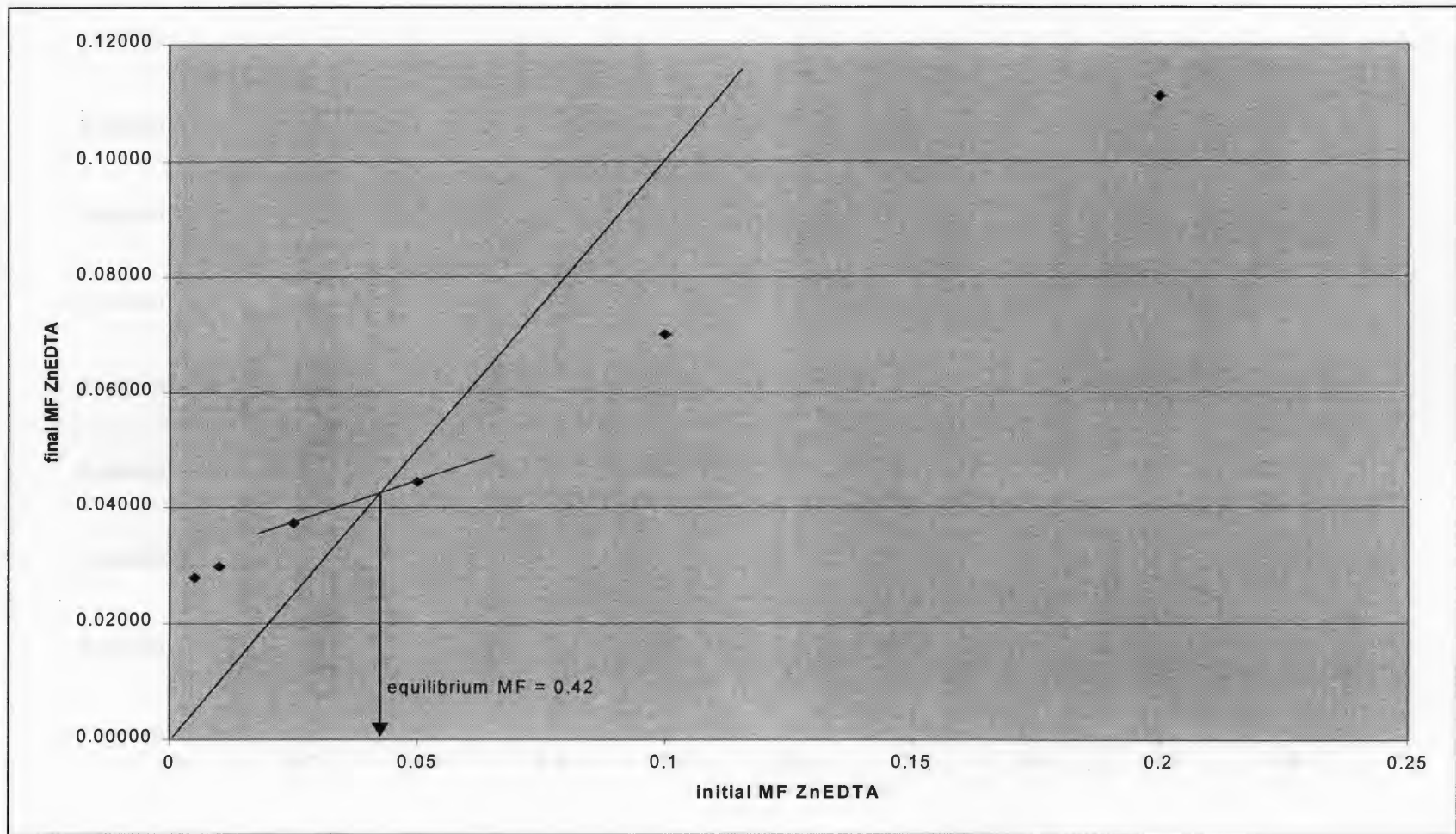


Fig. 2.2. Final MF ZnEDTA²⁻ versus initial MF ZnEDTA²⁻ for soil 1, first replication.

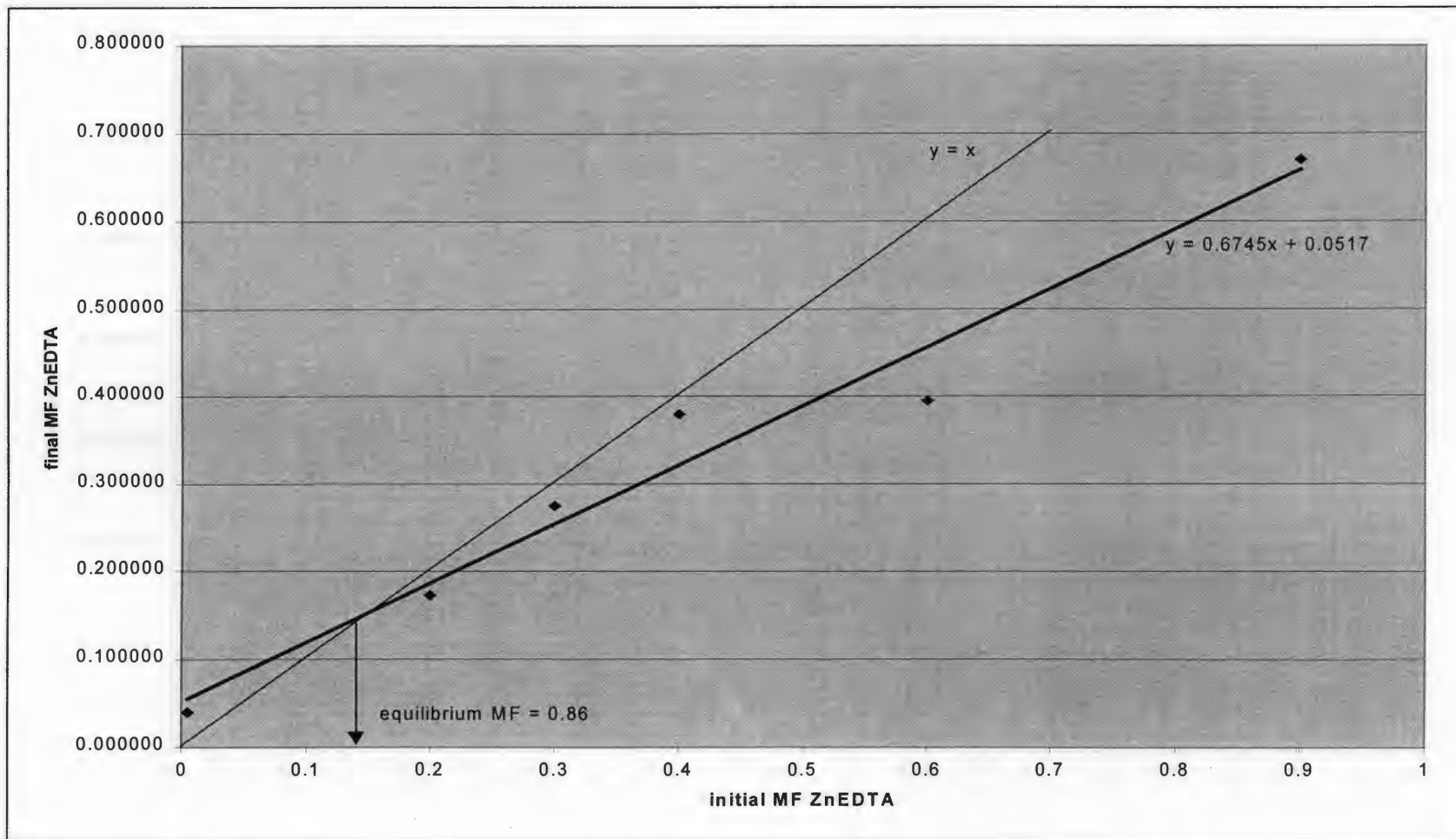


Fig. 2.3. Final MF ZnEDTA²⁻ versus initial MF ZnEDTA²⁻ for soil 10, replication 1.

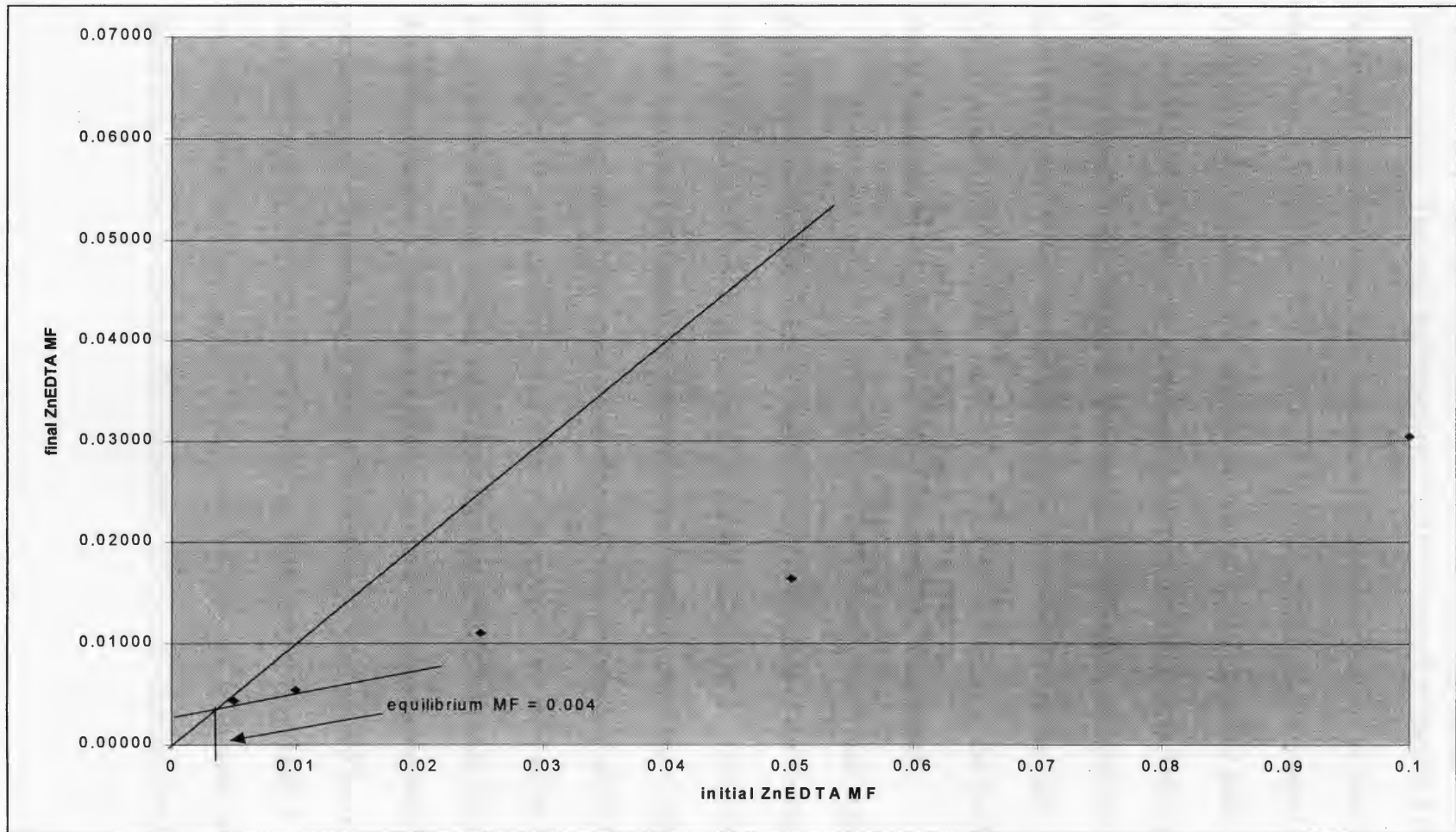


Fig. 2.4. Final MF ZnEDTA²⁻ versus initial MF ZnEDTA²⁻ for soil 16, replication 1.

Solutions of approximately 100 μM were run on the IC using Orion AS4A and AS4G columns. The peak that represents ZnEDTA occurred at about 8.4 minutes. It is a fairly wide peak that sometimes overlaps with the sulfate peak. The $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent was diluted using 70 % eluent and 30 % DI water, which separated the sulfate and ZnEDTA peaks well, but didn't always result in completely separate peaks.

There was some error associated in how the ZnEDTA peak area was calculated by the ion chromatography software. The integration software calculated the area only under the ZnEDTA peak, not including any overlap with the sulfate peak. Also, the CaEDTA and H_2EDTA peaks came out at about the same time as the ZnEDTA peak. ZnCl_2 was added to the solutions to help distinguish the desired peak.

There were some difficulties with the ion chromatograph used in this research. So the EDTA concentrations were not measured in the solutions of the first replication of the chelation method. They were measured in the second replication of the chelation method within a month of extracting the solution. Some of the solutions were measured within 10 days of extraction. The measurement results from the same soil at 10 days and at one month after extraction (different replications) were within the error of the IC standards. To get a second set of data, an initial mole fraction solution was added to each soil, as in the chelation method. After shaking for 5 days, only EDTA was measured. These EDTA concentrations were measured a week after extraction. They agreed fairly well with the other EDTA data, although they tended to be a little higher. (See Table 2.2.) The larger concentrations could have resulted because the analysis was run a week after extraction rather than 10 days to a month after extraction. EDTA may degrade in soil solution over

Table 2.2. First and second EDTA extract concentrations (mol L⁻¹) for the 18 soils. Horizontal lines separate the 3 farms.

soil #	EDTA 1	EDTA 2	average
1	82.8	105.6	94.2
2	83.2	87.2	85.2
3	82.8	85.3	84.1
4	90.3	86.5	88.4
5	86.3	85.0	85.6
6	88.1	84.2	86.2
7	75.6	82.9	79.2
8	87.8	67.9*	87.8
9	66.9	72.0	69.4
10	68.5	79.9	74.2
11	88.2	90.4	89.3
12	86.9	59.6*	86.9
13	91.1	93.0	92.0
14	92.5	93.7	93.1
15	80.9	70.6*	80.9
16	90.4	93.1	91.8
17	77.1	90.4	83.8
18	90.8	94.0	92.4

* low estimate due to error in peak area calculation
(not used in average)

time. However, the agreement was still within the range of the error in the method for most of these soils.

One source of error in the chelation method relates to the adsorption of EDTA by soil. Different EDTA species (e.g., FeEDTA and CaEDTA) appear to adsorb at different rates. In general, FeEDTA chelates adsorb faster than CaEDTA chelates, which adsorb faster than ZnEDTA or CuEDTA chelates (Norvell, 1970; Norvell and Lindsay, 1982; Wallace and Lunt, 1956). Previous studies have both considered and not considered this differential adsorption with Zn^{2+} activity measurements in soils (e.g., Norvell, 1987; Ma and Lindsay, 1990, respectively). The current study did not include the differential adsorption of ZnEDTA and CaEDTA.

Statistical analysis

Statistical analyses were performed using the statistical analysis package SAS (SAS Institute, 1988). Model selection was performed by stepwise selection as well as Akaike's Criteria (AIC) and adjusted R-squared criteria (Neter et al., 1990). Stepwise selection begins with the parameter with the largest correlation coefficient with log (Zn^{2+}). Then each of the other parameters is paired with the first variable and the model with the best R-squared is chosen, provided that the variables are all significant at an alpha of typically 0.15. The selection process continues until no other variables can be added. Variables can also be deleted from the model if the p-values associated with those variables become greater than 0.15 by additions of other variables to the model. AIC and adjusted R-squared selection criteria account for the number of parameters in the model, while calculating the criteria values for every possible model using one to all predictors.

The best adjusted R-squared is the highest value, whereas the best AIC is the lowest value (most negative). See Table 2.3 below for an example. Table 2.3 was sorted by adjusted R-squared values and not AIC values, although they are often similarly ranked for a data set.

Differences in adjusted R-squared and AIC criteria are often small for different models. The variation in the data may be larger than these small differences. Thus choosing the best model for a data set can often be ambiguous. It is the researcher's responsibility to consider all aspects of the problem in the choice of the best model.

Two other statistical indicators were used to explore correlation between parameters and to explore whether or not an outlier was an influential observation. A variance inflation factor (VIF) is a measure of how correlated the predictors are. A VIF greater than 10 indicates a possible collinearity problem (Neter et al., 1990). The Cook's distance is a measure of how influential a data point is for determination of parameter coefficients in a regression model. An outlier observation may be considered influential in parameter coefficient estimates if the Cook's distance is much greater than 1.

Results and Discussion

Soil chemical properties for the 18 soil samples are listed in Table 2.1 along with the farm, location and depth for each sample. The 24-hour suspension pH ranged from 6.77 to 8.32 for these soils. The 5-day average pH ranged from 7.38 to 8.75. Total carbon ranged from 0.44 % to 4.41 % and inorganic carbon from 0 % to 2.55 %. Organic carbon (OC) ranged from 0.43 % to 1.86 %, a factor of about 4.3. Clay content ranged

Table 2.3. Table of adjusted R-square and Akaike's Information Criteria (AIC) values for the full data set. N is the number of variables in the model. The largest adjusted R-square and the most negative AIC correspond to the best models.

N	Adjusted R-Square	R-Square	AIC	Variables in Model
6	0.734	0.8279	-38.1574	pH OC clay Zn _T log(IC+1) CEC
4	0.7329	0.7958	-39.081	pH OC clay Zn _T
5	0.7261	0.8066	-38.0651	pH OC clay Zn _T log(IC+1)
5	0.7135	0.7977	-37.2535	pH OC clay Zn _T CEC
5	0.7077	0.7937	-36.897	pH clay Zn _T log(IC+1) CEC
3	0.6956	0.7493	-37.3899	pH OC Zn _T
4	0.6956	0.7672	-36.7224	pH OC Zn _T CEC
4	0.6929	0.7652	-36.5667	pH clay Zn _T log(IC+1)
5	0.6768	0.7719	-35.0893	pH OC Zn _T log(IC+1) CEC
4	0.6754	0.7518	-35.5696	pH OC Zn _T log(IC+1)
4	0.662	0.7415	-34.8389	pH OC clay CEC
3	0.6536	0.7148	-35.0662	pH clay Zn _T
3	0.6518	0.7132	-34.9696	pH OC CEC
4	0.6489	0.7315	-34.1537	pH OC log(IC+1) CEC
2	0.6469	0.6884	-35.4779	pH OC
5	0.6456	0.7498	-33.4258	pH OC clay log(IC+1) CEC
3	0.645	0.7077	-34.6236	pH OC log(IC+1)
3	0.6382	0.7021	-34.2825	pH clay CEC
1	0.6371	0.6585	-35.8239	pH
4	0.6276	0.7152	-33.097	pH clay Zn _T CEC
2	0.6238	0.6681	-34.3373	pH clay
3	0.6217	0.6885	-33.4788	pH OC clay
4	0.6188	0.7085	-32.6738	pH OC clay log(IC+1)
2	0.6161	0.6612	-33.9713	pH Zn _T
2	0.6134	0.6589	-33.8458	pH CEC

from 15.6 % to 30.0 %. Total soil Zn concentration ranged from 25.3 to 78.4 mg kg⁻¹. CEC ranged from 15.2 to 39.1 cmol_c kg⁻¹.

Table 2.4 shows a summary of the results from the chelation method. The pH used in this table and in the regression analysis is the average 5-day pH for the soils. The equilibrium MF, log (Zn²⁺) and log (Ca²⁺) are averages of the 2 or 3 replications. The average log Zn²⁺ activities ranged from -11.23 to -9.12. Table 2.5 lists the log (Zn²⁺) replication values, the averages, and the standard deviations for each soil. Standard deviations were all small, and the largest standard deviation was 0.30 log units. Soil 9 was the only soil without a replication, and thus has no standard deviation.

Log Zn²⁺ activity ranged from -11.23 to -9.12. A plot of the average log Zn²⁺ activity versus pH is included below (Fig. 2.5). This plot is fairly linear, with an R-squared of 0.53 and regression line given by:

$$y = - 1.04 x - 1.96 \quad [10]$$

Figure 2.6 shows a plot of log Zn²⁺ activity versus percent organic carbon (OC) content. This graph is also nearly linear; as log Zn²⁺ activity increases so does organic carbon. However, soil 12 appears to be an outlier. The regression analysis describes in more detail whether or not this soil is actually an outlier. If this possible outlier is removed, the range of percent organic carbon is only a factor of about 3.4, which is lower than originally intended.

Log Zn²⁺ activity versus total soil Zn is plotted in Fig. 2.7. Soils 11 and 12 appear to be outliers in this graph. The total Zn in these two soils is less than the other soils, possibly because of the visible chunks of carbonates in these soils. Note that soil 11 is the surface soil that corresponds to soil 12, and there is not much of a trend in this plot.

Table 2.4. Average 5-day pH, equilibrium mole fractions, and Zn^{2+} and Ca^{2+} activities for the 18 soils. Horizontal lines separate the 3 farms.

soil #	5-day pH	equilibrium MF	$\log (Zn^{2+})$	$\log (Ca^{2+})$
1	8.19	0.0408	-10.22	-3.01
2	8.04	0.0260	-10.49	-3.08
3	8.45	0.0342	-10.18	-2.90
4	8.67	0.0055	-10.92	-2.82
5	8.57	0.0161	-10.31	-2.69
6	8.73	0.0040	-10.97	-2.71
7	7.76	0.0486	-9.92	-2.79
8	8.47	0.0053	-10.98	-2.81
9	7.47	0.3250	-9.12	-2.97
10	7.38	0.1604	-9.58	-3.02
11	8.64	0.0070	-10.62	-2.62
12	8.69	0.0018	-11.23	-2.62
13	8.42	0.0103	-10.71	-2.89
14	8.58	0.0033	-11.20	-2.87
15	7.80	0.0447	-10.30	-3.12
16	8.49	0.0049	-11.06	-2.91
17	7.57	0.0432	-10.40	-3.20
18	8.52	0.0043	-11.13	-2.93

Table 2.5. Log Zn²⁺ activities by replication, including average and standard deviation.

soil #	rep 1 log (Zn ²⁺)	rep 2 log (Zn ²⁺)	rep 3 log (Zn ²⁺)	ave log (Zn ²⁺)	st dev
1	-10.28	-10.16		-10.22	0.09
2	-10.60	-10.38		-10.49	0.16
3	-10.27	-10.09		-10.18	0.13
4	-11.11	-10.76	-10.89	-10.92	0.18
5	-10.33	-10.29		-10.31	0.03
6	-10.87	-10.81	-11.23	-10.97	0.23
7	-9.98	-9.86		-9.92	0.08
8	-10.85	-10.79	-11.29	-10.98	0.27
9	-9.12			-9.12	
10	-9.71	-9.46		-9.58	0.18
11	-10.84	-10.51	-10.51	-10.62	0.19
12	-11.07	-11.43	-11.19	-11.23	0.18
13	-10.75	-10.66		-10.71	0.06
14	-11.41	-10.99		-11.20	0.30
15	-10.49	-10.11		-10.30	0.27
16	-11.20	-10.92	-11.05	-11.06	0.14
17	-10.33	-10.46		-10.40	0.09
18	-11.34	-11.03	-11.03	-11.13	0.18

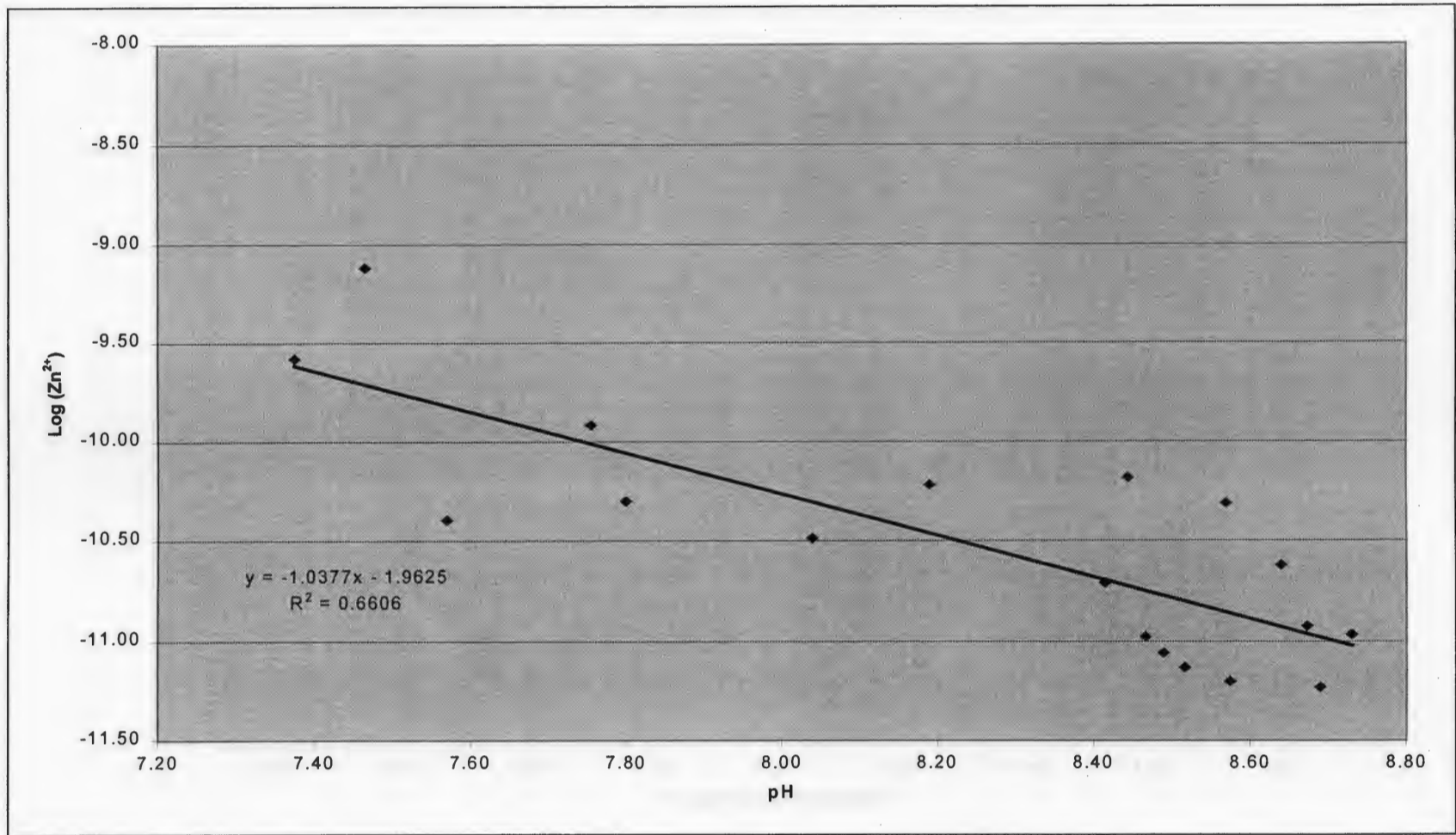


Fig. 2.5. Log Zn²⁺ activity versus 5-day average pH. The regression line is plotted with the data.

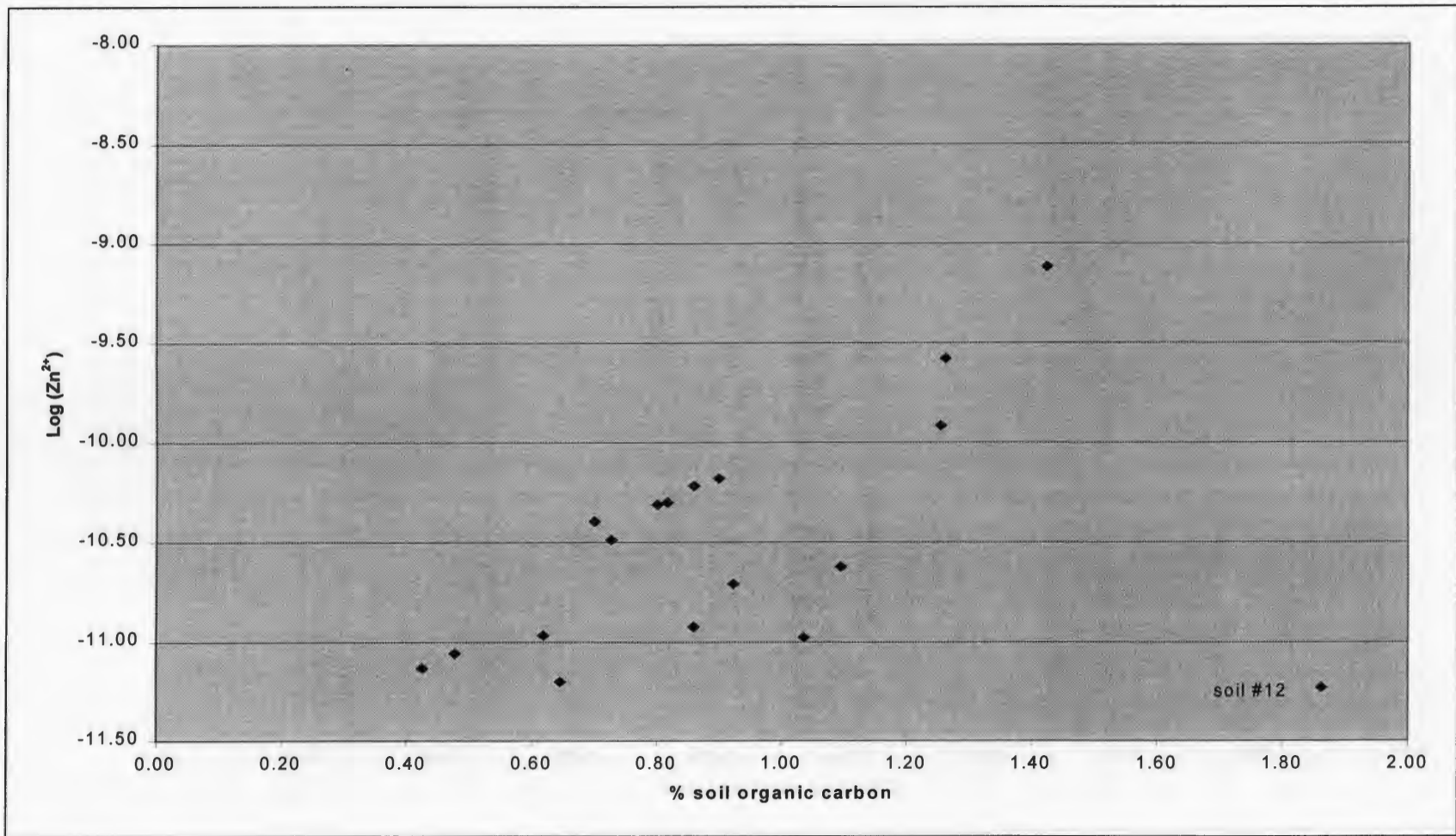


Fig. 2.6. Log Zn²⁺ activity versus percent soil organic carbon. Soil 12, the outlier, is labeled.

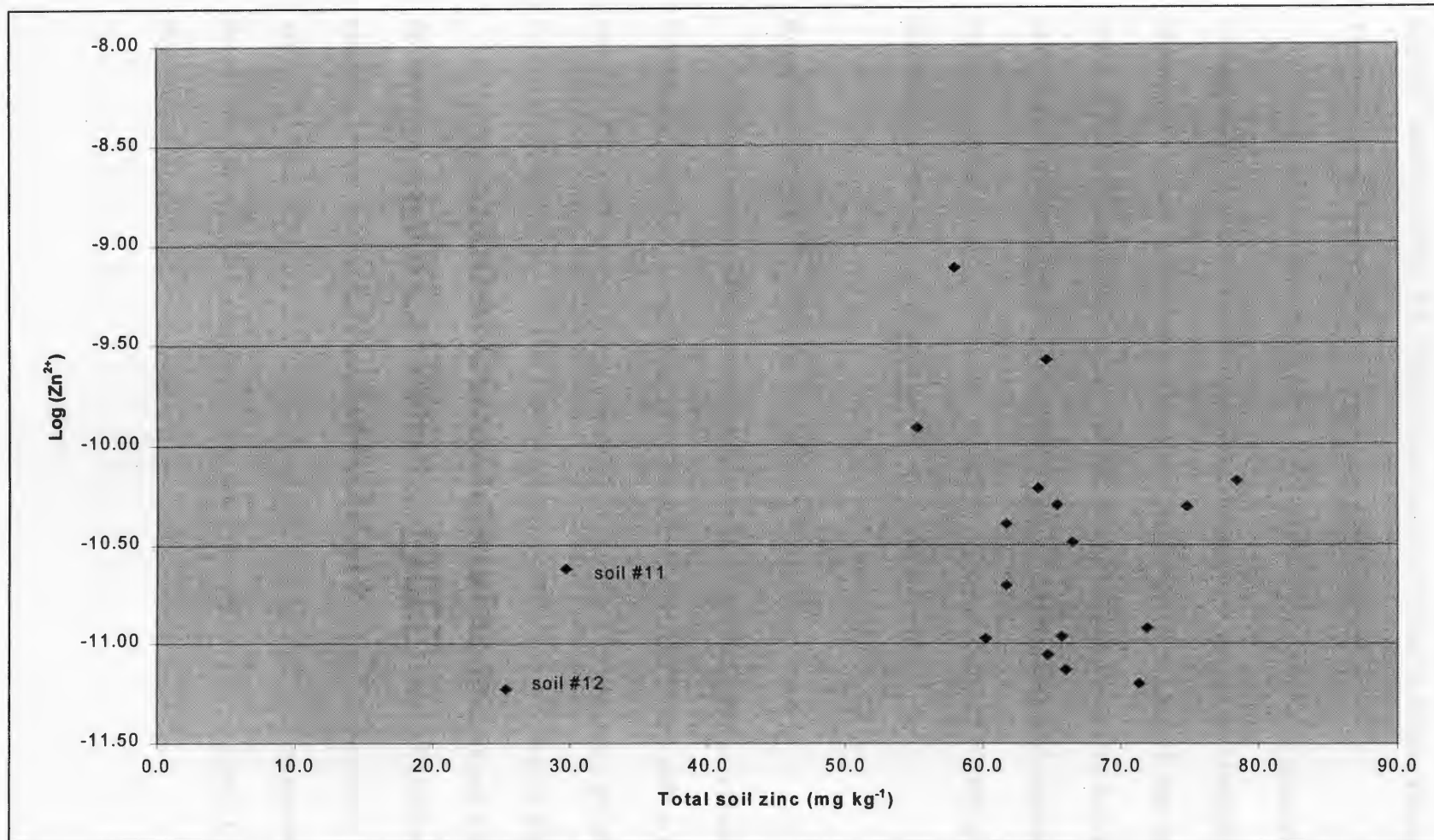


Fig. 2.7. Log Zn²⁺ activity versus total soil Zn. The two outliers, soils 11 and 12, are labeled.

Clay content is plotted with $\log \text{Zn}^{2+}$ activity in Fig. 2.8, and CEC is plotted with $\log \text{Zn}^{2+}$ activity in Fig. 2.9. There is not much of a trend in either of these plots with Zn. The percent clay and CEC only range over a factor of about 2.

Figure 2.10 shows $\log \text{Zn}^{2+}$ activity plotted with the log of percent inorganic carbon plus 1 ($\log(\text{IC}+1)$). The logarithm was taken of the percent inorganic carbon because the spread of the inorganic carbon was large. A value of 1 was added because some of the soils contained no measurable inorganic carbon, and the log of zero is undefined. In this figure it appears that Zn may be decreasing with increasing inorganic carbon. It is difficult to ascertain a definite trend in the data since there are a disproportionate number of soils at low inorganic carbon.

Regression results

In this section correlation coefficients and regression analysis results are reported. Correlation coefficients are listed in Table 2.6. Recall, the “5-day pH” is the average 5-day pH. In all regressions the pH always refers to the average 5-day pH since it corresponds to the Zn^{2+} activity measurement more so than the 24-hour pH.

Below, a full regression model using all possible predictors and soil samples is developed to describe $\log \text{Zn}^{2+}$ activity. Selection criteria are used to refine the full model. Several models are examined that describe the data. The positive and negative aspects of the models are discussed. A significance level of 0.1 was generally used to decide whether a model was significant. Models with p-values below 0.1 are considered statistically significant.

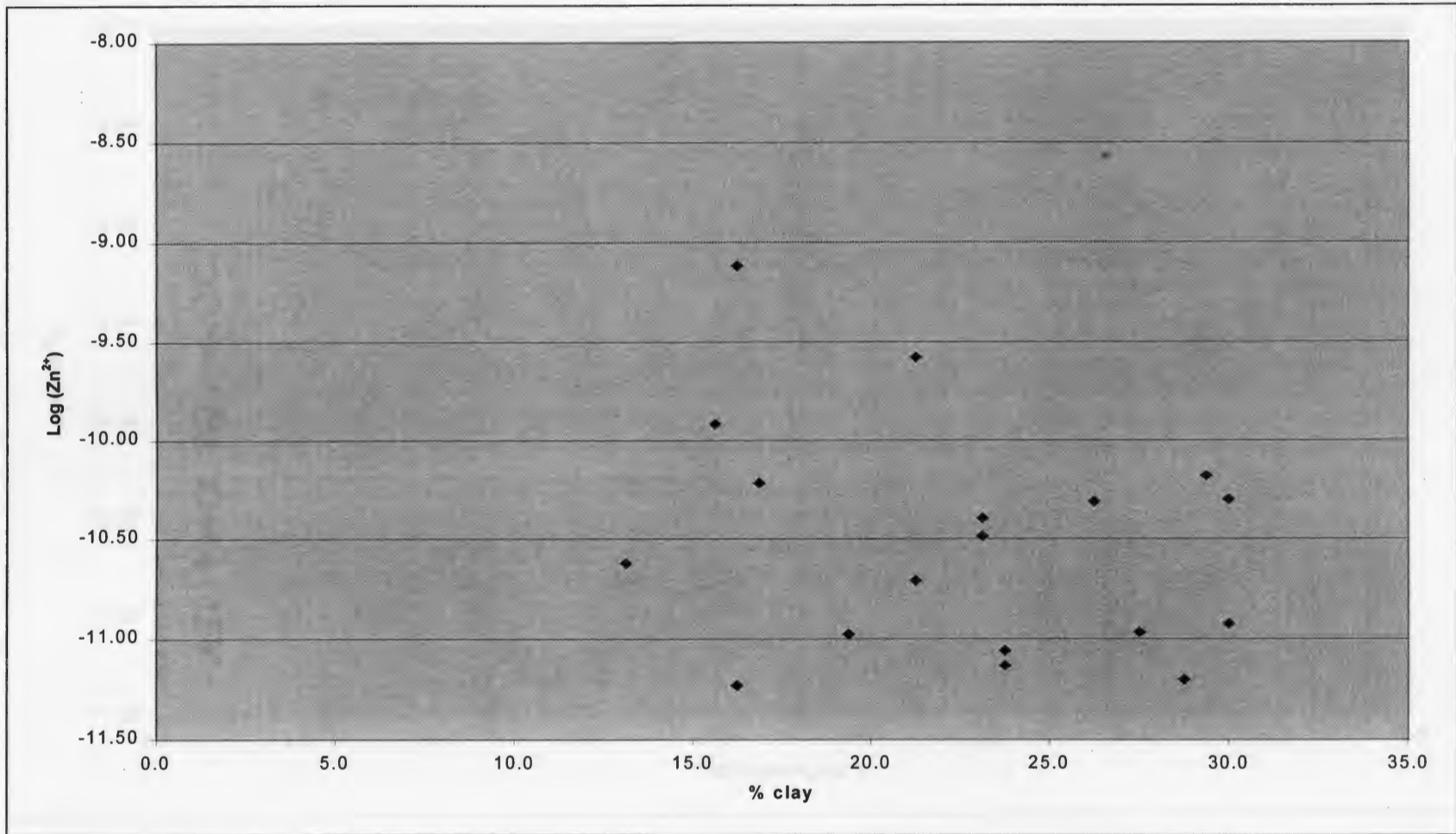


Fig. 2.8. $\text{Log } Zn^{2+}$ activity versus percent clay for the 18 soils.

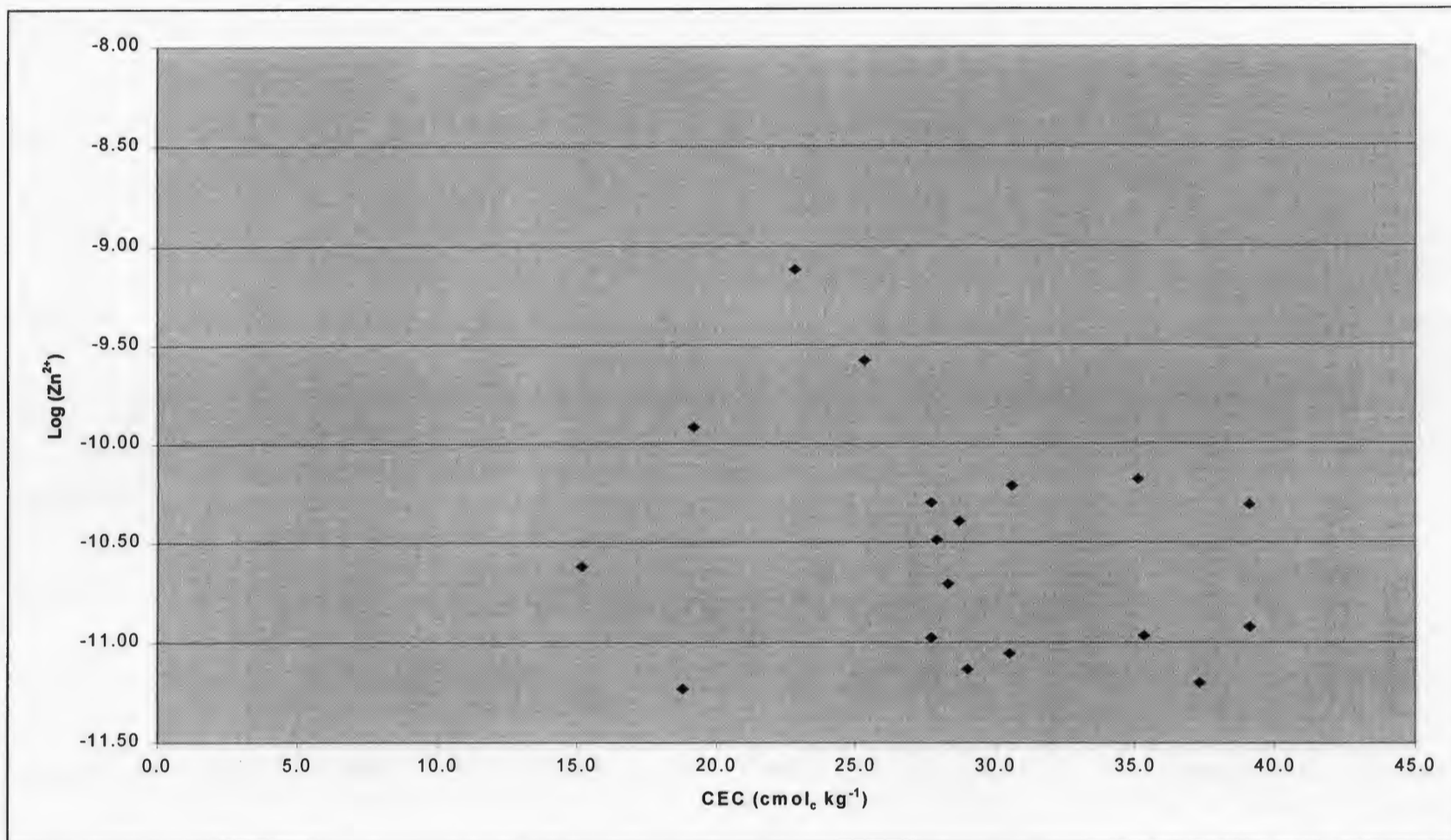


Fig. 2.9. Log Zn²⁺ activity versus cation exchange capacity for the 18 soils.

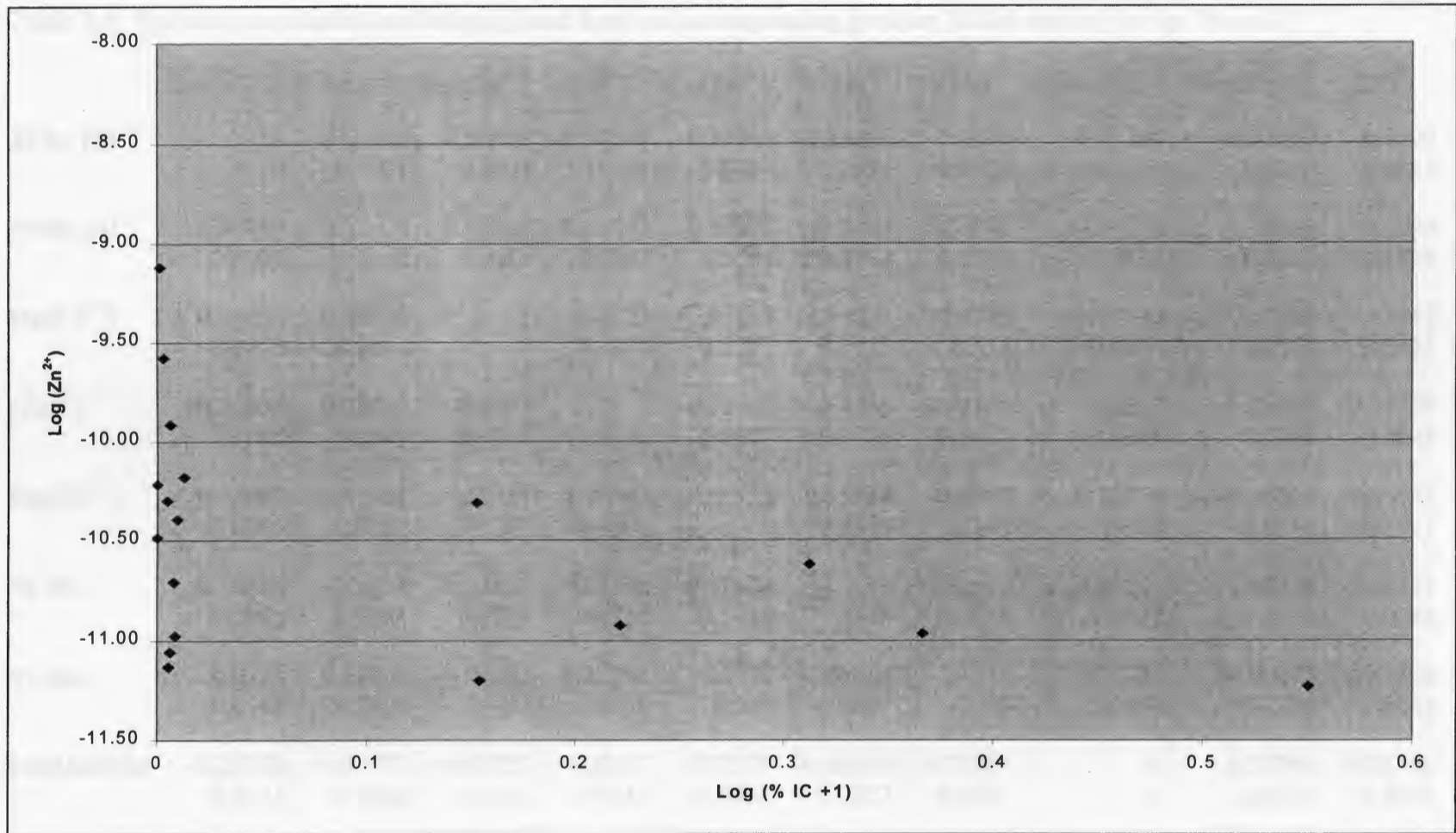


Fig. 2.10. Log Zn²⁺ activity versus log (% inorganic carbon + 1).

Table 2.6. Pearson's correlation coefficients (listed first) and corresponding p-values (listed second) for the 18 soils.

	24-hr pH	5-day pH	log(Ca ²⁺)	(Zn ²⁺)	log(Zn ²⁺)	% OC	% clay	total soil Zn	log(IC+1)	CEC
24-hr pH	1 0	0.86863 0.0001	0.58636 0.0105	-0.70836 0.001	-0.73863 0.0005	-0.26466 0.2885	0.0135 0.9576	-0.25248 0.3121	0.53127 0.0233	0.1102 0.6633
5-day pH	0.86863 0.0001	1 0	0.69315 0.0014	-0.63442 0.0047	-0.81351 0.0001	-0.2494 0.3183	0.23906 0.3394	-0.06972 0.7834	0.58320 0.0111	0.3624 0.1394
log(Ca²⁺)	0.58636 0.0105	0.69315 0.0014	1 0	-0.2123 0.3977	-0.37147 0.1291	0.33621 0.1725	-0.24213 0.333	-0.45727 0.0564	0.74285 0.0004	-0.11543 0.6483
(Zn²⁺)	-0.70836 0.001	-0.63442 0.0047	-0.2123 0.3977	1 0	0.79941 0.0001	0.4346 0.0715	-0.32165 0.1931	-0.0212 0.9335	-0.25849 0.3004	-0.27779 0.2644
log(Zn²⁺)	-0.73863 0.0005	-0.81351 0.0001	-0.37147 0.1291	0.79941 0.0001	1 0	0.35884 0.1436	-0.2752 0.269	0.12376 0.6247	-0.46571 0.0514	-0.2602 0.2971
% OC	-0.26466 0.2885	-0.2494 0.3183	0.33621 0.1725	0.4346 0.0715	0.35884 0.1436	1 0	-0.60614 0.0077	-0.66229 0.0027	0.38184 0.1179	-0.63351 0.0048
% clay	0.0135 0.9576	0.23906 0.3394	-0.24213 0.333	-0.32165 0.1931	-0.2752 0.269	-0.60614 0.0077	1 0	0.75387 0.0003	-0.09083 0.7200	0.83886 0.0001
total soil Zn	-0.25248 0.3121	-0.06972 0.7834	-0.45727 0.0564	-0.0212 0.9335	0.12376 0.6247	-0.66229 0.0027	0.75387 0.0003	1 0	-0.58796 0.0103	0.83764 0.0001
log(IC+1)	0.53127 0.0233	0.58320 0.0111	0.74285 0.0004	-0.25849 0.3004	-0.46571 0.0514	0.38184 0.1179	-0.09083 0.7200	-0.58796 0.0103	1 0	-0.11291 0.6555
CEC	0.1102 0.6633	0.3624 0.1394	-0.11543 0.6483	-0.27779 0.2644	-0.2602 0.2971	-0.63351 0.0048	0.83886 0.0001	0.83764 0.0001	-0.11291 0.6555	1 0

Full regression model

A regression was fit to the data using the following parameters to predict $\log(\text{Zn}^{2+})$: pH, % OC, % clay, $\log(\text{IC} + 1)$ and total soil Zn (Zn_T). The model is:

$$\log(\text{Zn}^{2+}) = -0.88 \text{ pH} + 0.55 \text{ OC} - 0.054 \text{ clay} + 0.034 \text{ Zn}_T + 0.84 \log(\text{IC}+1) - 4.76 \quad [11]$$

Table 2.7 shows that this model is significant with a p-value of 0.0006. The R-squared value of this model is 0.81, and indicates that the model accounts for 81 % of the variation in $\log(\text{Zn}^{2+})$. The VIFs are greater than 1, which indicates that the predictors are related to each other. This can be confirmed by looking at the correlation coefficients. Since the VIFs are smaller than 10, collinearity may not be a problem. When CEC was also included in the model, the VIFs were greater than 10. This large value indicated a problem with collinearity, so CEC was not included in the full model. Typically, CEC is strongly related to organic matter and clay content, so the observation above is not surprising.

The soil with the largest percent OC value (soil 12) is an outlier for this data. The Cook's distance for soil 12 is 1.8 for this model. So, soil 12 is near to being influential for this model. Below models are examined with and without this data point. Also given below is a plot of the residuals for these data (Fig. 2.11).

Model refinement and selection

The regression model above can be refined to identify the parameters that best predict $\log(\text{Zn}^{2+})$ for this data. By doing so, a better understanding of the soil chemical factors that influence $\log(\text{Zn}^{2+})$ can be developed.

Table 2.7. Analysis of variance table for the full regression model for the 18 soils.

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	5	4.65	0.93045	10.01	0.0006
Error	12	1.12	0.09293		
C Total	17	5.77			
Root MSE		0.305	R-square	0.8066	
Dep Mean		-10.519	Adj R-sq	0.7261	
C.V.		-2.898			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T	Variance Inflation
intercept	1	-4.760	2.299	-2.07	0.0606	0.000
pH	1	-0.878	0.256	-3.43	0.0050	2.487
LOGIC	1	0.835	1.017	0.82	0.4267	4.971
OC	1	0.552	0.344	1.60	0.1346	2.693
CLAY	1	-0.054	0.029	-1.85	0.0898	4.615
Zn _T	1	0.034	0.014	2.47	0.0296	6.532

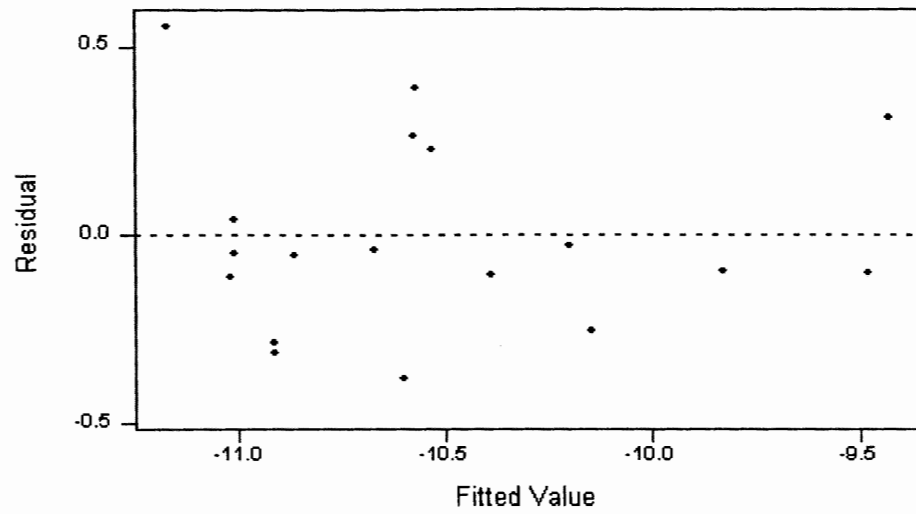


Fig. 2.11. Residual plot for the full regression model, 18 soils.

There are two soils that might be considered outliers for one or more of the variables. Soil 12 is an outlier for % OC and total soil Zn. Soil 11 is an outlier for total soil Zn. (See Fig. 2.7.) There could be an error in the total carbon measurement because of the large carbonate concentrations in soil 12. For soil 12, approximately 1 mg of soil was used for the total carbon measurement. For other soils 10-20 mg soil was used. This fraction of soil 12 was from the finest fraction of the soil with likely the highest percentage of carbonate and possibly organic carbon (based on the appearance of the soil sample). In comparison, the inorganic carbon measurements required 1 g of soil, which could give a better representation of the soil as a whole. The inorganic carbon content of soil 12 may also have been slightly underestimated since it was outside of the calibration curve where the curve begins to level off for large carbonate contents. However, the inorganic carbon content did not change much when a calibration curve with a wider range was used. The total soil Zn analysis used 10 g of soil, which would also give a better overall picture of the soil than the total carbon measurement.

It seems likely that the total carbon measurement is in error, but not the total soil Zn measurement. The total soil Zn of those two soils could reasonably be less than the others because of a dilution effect of the soils due to a large amount of carbonates. It does not seem reasonable that the organic carbon content of soil 12 would be so large because soils 11 and 12 are located at the top of an eroded slope and the erosion would have removed the A horizons that contained organic carbon. Soil 11 is the sample of the upper soil horizon and soil 12 is the lower soil horizon at that location. An unusually large value for organic carbon in the lower horizon at the top of a hillslope does not seem likely.

Multiple regression analyses of the data are presented below using the full data set, the data set without soil 12, and the data set without soils 11 and 12. Models are selected using stepwise selection, adjusted R-squared criteria and AIC criteria, as described in the Methods section above.

Model selection using full data set

A stepwise selection was performed to see which variables of the 5 in the full model would be selected or rejected at an alpha of 0.15. CEC was included in the selection process to evaluate CEC as a significant predictor. For the full data set, only the pH was a significant parameter in predicting $\log(\text{Zn}^{2+})$. The model is

$$\log(\text{Zn}^{2+}) = -1.96 - 1.04 \text{ pH} \quad [12]$$

The R-squared is 0.66, and the p-value is < 0.0001 . No other variables were significant at the 0.15 level. The residuals are graphed below (Fig. 2.12).

In addition to stepwise selection, adjusted R-squared and Akaike's information criteria (AIC) were used to select models (Table 2.3). The adjusted R-squared criteria show the best model includes pH, organic carbon, inorganic carbon, clay, total soil Zn and CEC as predictors. However, the VIF's are greater than 10 for this model, so it is not good. The model with the most negative AIC criterion of -39.08 was a model with pH, organic carbon, clay and total soil Zn as predictors. This model is:

$$\log(\text{Zn}^{2+}) = -0.74 \text{ pH} + 0.68 \text{ OC} - 0.039 \text{ clay} + 0.027 \text{ Zn}_T - 5.80 \quad [13]$$

and has an R-squared of 0.80. The second best model according to the adjusted R-squared criteria is shown in Eq. [13] with an adjusted R-squared of 0.733. Both models are good according to the selection criteria, but model [12] is better, since it is simpler.

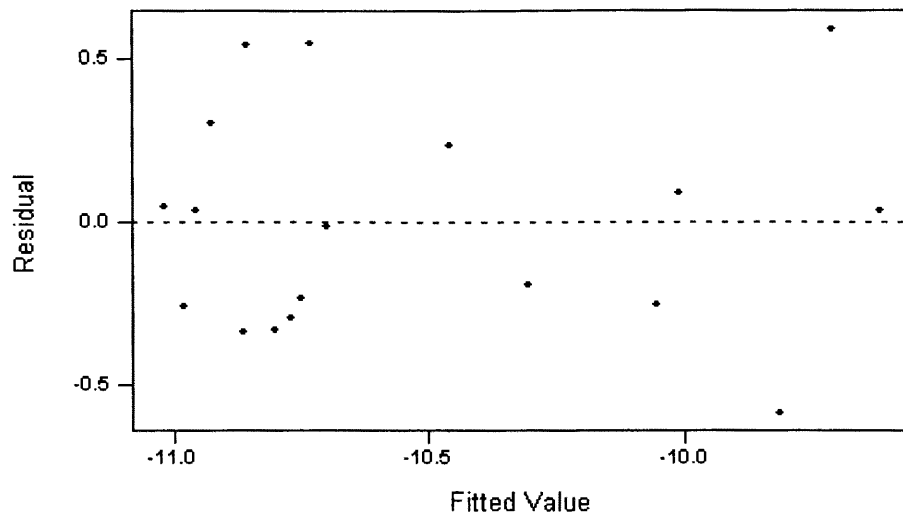


Fig. 2.12. Residual plot for the stepwise selection model using the full data set.

Model selection omitting soil 12

It is appropriate to repeat a model selection for $\log(\text{Zn}^{2+})$ without soil 12, since it is an outlier in the $\log(\text{Zn}^{2+})$ vs. organic carbon plot and an influential observation in the full model. With the data for soil 12 included, the R-squared value for the relationship between $\log(\text{Zn}^{2+})$ and percent organic carbon was 0.13. This is a small value and indicates almost no relationship between the variables and $\log(\text{Zn}^{2+})$. Without soil 12 the R-squared value is 0.61, which indicates some relationship. Soil 12 is also an influential observation in a model with pH and organic matter when the full data set is considered with a Cook's D value of 3.7.

A stepwise selection was performed with the same 6 variables as above (pH, percent OC, percent clay, total soil Zn, $\log(\text{IC} + 1)$, and CEC). In this case, both pH and organic carbon were found to be significant in predicting Zn activity. The model is:

$$\log(\text{Zn}^{2+}) = -0.66 \text{ pH} + 1.04 \text{ OC} - 5.92 \quad [14]$$

with an R-squared value of 0.81 and a p-value of < 0.0001 . The residual graph is shown in Fig. 2.13.

Adjusted R-squared and AIC values were calculated for these soils. The best model according to these criteria is a model including pH, organic carbon, and total soil Zn. The model is:

$$\log(\text{Zn}^{2+}) = -0.63 \text{ pH} + 1.22 \text{ OC} + 0.0094 \text{ Zn}_T - 6.97 \quad [15]$$

For this model, the adjusted R-squared value is 0.80 and the AIC is -42.7 . The R-squared value is 0.84 and the p-value is < 0.0001 . The previous model (Eq. [14]) has an adjusted R-squared value of 0.78 and an AIC of -42.3 .

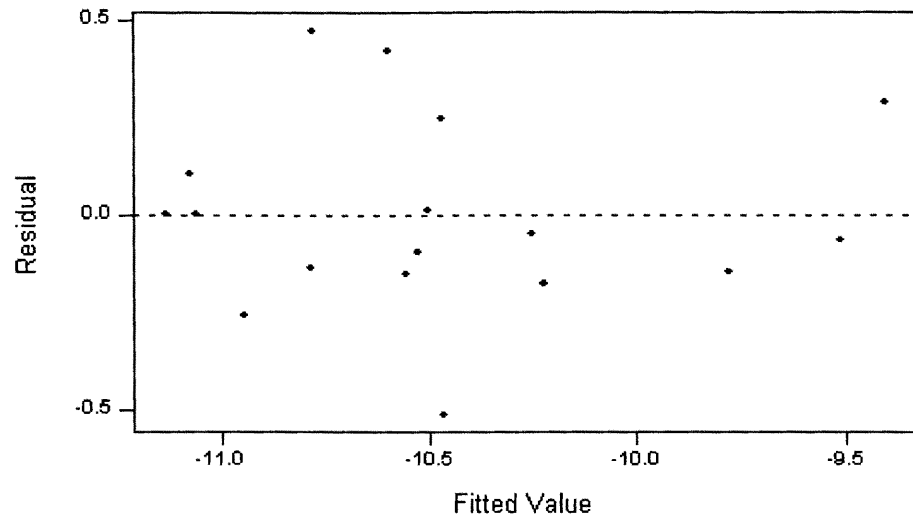


Fig. 2.13. Residual plot for regression equation including pH and organic carbon, omitting soil 12.

Model selection omitting soils 11 and 12

Because soil 11 was an outlier with total soil Zn, the same statistical selections were conducted without soils 11 and 12 in the data set. The stepwise selection for this data set showed that pH, percent organic matter, total soil Zn, and percent clay were the best predictors for $\log(\text{Zn}^{2+})$. The model is:

$$\log(\text{Zn}^{2+}) = -0.83 \text{ pH} + 0.96 \text{ OC} - 0.038 \text{ clay} + 0.049 \text{ Zn}_T - 6.75 \quad [16]$$

with an R-squared value of 0.89 and a p-value of < 0.0001 . The best model based on AIC criteria also included these four parameters. For this model, the adjusted R-squared is 0.856 and the AIC is -44.0 . The model with the largest adjusted R-squared criterion (0.860) included $\log(\text{IC}+1)$ in addition to the other four parameters:

$$\log(\text{Zn}^{2+}) = -0.96 \text{ pH} + 0.85 \text{ OC} - 0.051 \text{ clay} + 0.055 \text{ Zn}_T - 0.83 \log(\text{IC}+1) - 5.76 \quad [17]$$

Apparently, the presence or absence of soil 11 does make some difference in the selected regression equation. The model without both soils 11 and 12 had four predictors in it, whereas without soil 12 the models had two or three predictors.

It is reasonable to remove soil 12 for the purpose of modeling, but removal of soil 11 is not so obvious. Soil 12 can be removed because of possible measurement error with organic carbon content and because it is an influential observation. Soil 11 is not influential, and the total soil Zn concentrations for both of these soils seems reasonable, although less than the other data.

Equations [14] and [15] are probably the best models for these data since they are the best models for these soils, without soil 12. The model with only pH and organic carbon (Eq. [14]) may be most meaningful in terms of the soil chemistry of these soils. The use of the regression equation must be considered when choosing the best model.

A model with fewer parameters may be more useful for thermodynamic interpretation. For example, an interpretation of the model of Eq. [14] might be that an adsorption reaction of Zn on organic matter controls the Zn solubility in the soils. On the other hand, if the purpose of developing a regression equation was to predict bioavailability of Zn or mobility of Zn in similar soils with a wider range of soil Zn concentrations, Eq. [15] might be better because it accounts for more of the variability in the soils. Equation [14] is a better model for this study, since one purpose of this study was to explore the solubility control of Zn in alkaline soils.

Summary of regression analyses

Regression analyses can be used to represent relationships between a parameter of interest and explanatory variables. In this study eighteen soils were sampled and various soil chemical properties were measured, including $\log(\text{Zn}^{2+})$, pH, inorganic carbon, organic carbon, clay content, total soil Zn and CEC. The simplest regression model for the entire data set uses pH to predict Zn^{2+} activities in these soils.

There were two outliers in the data set: soil 11 was an outlier with total soil Zn, and soil 12 was an outlier with organic carbon and total soil Zn. Soil 12 can be justifiably removed from the data set because of possible error in the total carbon measurement for that soil as stated above. Soil 12 is an influential observation, whereas soil 11 is not influential. Model selection using a stepwise selection procedure on the modified data set (without soil 12) yields:

$$\log(\text{Zn}^{2+}) = -0.66 \text{ pH} + 1.04 \text{ OC} - 5.92 \quad [14]$$

with an R-squared value of 0.81 and a p-value of < 0.0001 . This model accounts for 81% of the variability in the data. A 3-dimensional mesh plot of the data is depicted in Fig. 2.14. In this figure the largest Zn^{2+} activities occur at low pH and high organic matter. This figure shows that Zn^{2+} activity decreases as pH increases and as organic matter decreases. There is a slight bulge in the graph at high pH and low organic matter.

The model of Eq. [14] is different from some previous studies (Anderson and Christensen, 1988; McBride et al., 1997) because it shows that organic carbon is important in predicting Zn solubility in soils. Anderson and Christensen (1988) reported that pH is more important than any other single property in predicting Zn mobility and that organic matter did not have much effect. McBride et al. (1997) concluded that organic matter did not affect total Zn solubility. They developed the regression equation:

$$\log[Zn]_s = -0.71 \text{ pH} + 0.68 \log Zn_T + 4.44 \quad [17]$$

with an R-squared of 0.86. McBride et al. (1997) used contaminated soils in their study, which may explain why total soil Zn was a significant predictor. The soils used in the current study did not have a wide range of total Zn, so Zn_T may not have the same importance for the current study as compared to the study of McBride et al. (1997). In addition, McBride et al. (1997) modeled total soluble Zn whereas in this study free Zn activity was measured.

The current study shows a relationship between Zn solubility and organic matter that is opposite to what is usually expected. Zinc deficiency often occurs in muck or peat soils (Adriano, 1986). Organic matter in the soil may contribute to the CEC of the soil and thus depress Zn solubility with increasing organic matter (McBride et al., 1997). In the current study, the organic matter content increased as the Zn^{2+} activity increased. A

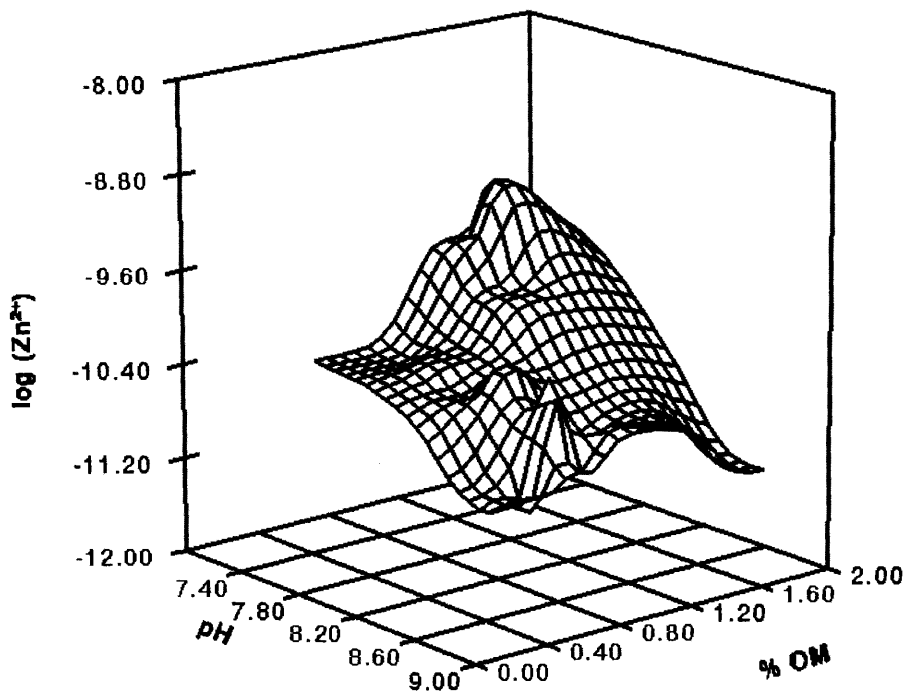


Fig. 2.14. 3-Dimensional plot of $\log (Zn^{2+})$ versus pH and organic matter for the 18 soils.

threshold for organic matter content may exist such that for soils with little organic matter: a slight increase in organic matter may increase Zn availability, but Zn solubility is suppressed if the organic matter content is too large. In addition, there may be a similar threshold for total soil Zn content.

Other studies have shown an organic matter-Zn trend similar to that of the current study. Sinha et al. (1978) also show increased $\log \text{Zn}^{2+}$ activity with increased soil organic matter. The previous investigators used a chelation method with soils of pH 7 – 8 to estimate Zn^{2+} activity. The organic matter contents of their soils were fairly low. Ma and Lindsay (1990) also show a trend of increased $\log \text{Zn}^{2+}$ activity with increased organic matter. Figure 2.15 combines the $\log \text{Zn}^{2+}$ activity and organic carbon data from the current study with that of Sinha et al. (1978) and Ma and Lindsay (1990). The percent organic matter values from the latter two studies were multiplied by 0.58 to convert from organic matter to organic carbon.

Thermodynamic relationships

Data from the present research were plotted with the solubility relationships for soil-Zn and franklinite, where Fe was controlled by soil-Fe or maghemite (Fig. 2.16). Willemite (Zn_2SiO_4) in equilibrium with soil-Si is much more soluble than the Zn in these soils. Some of the data fall close to the soil-Zn line and others are closer to a franklinite line. All the data appear to be within 1.2 log units of the soil-Zn line. It is possible that soil-Zn or franklinite controls the free Zn activity for these soils. The franklinite lines could shift up or down depending upon which Fe mineral

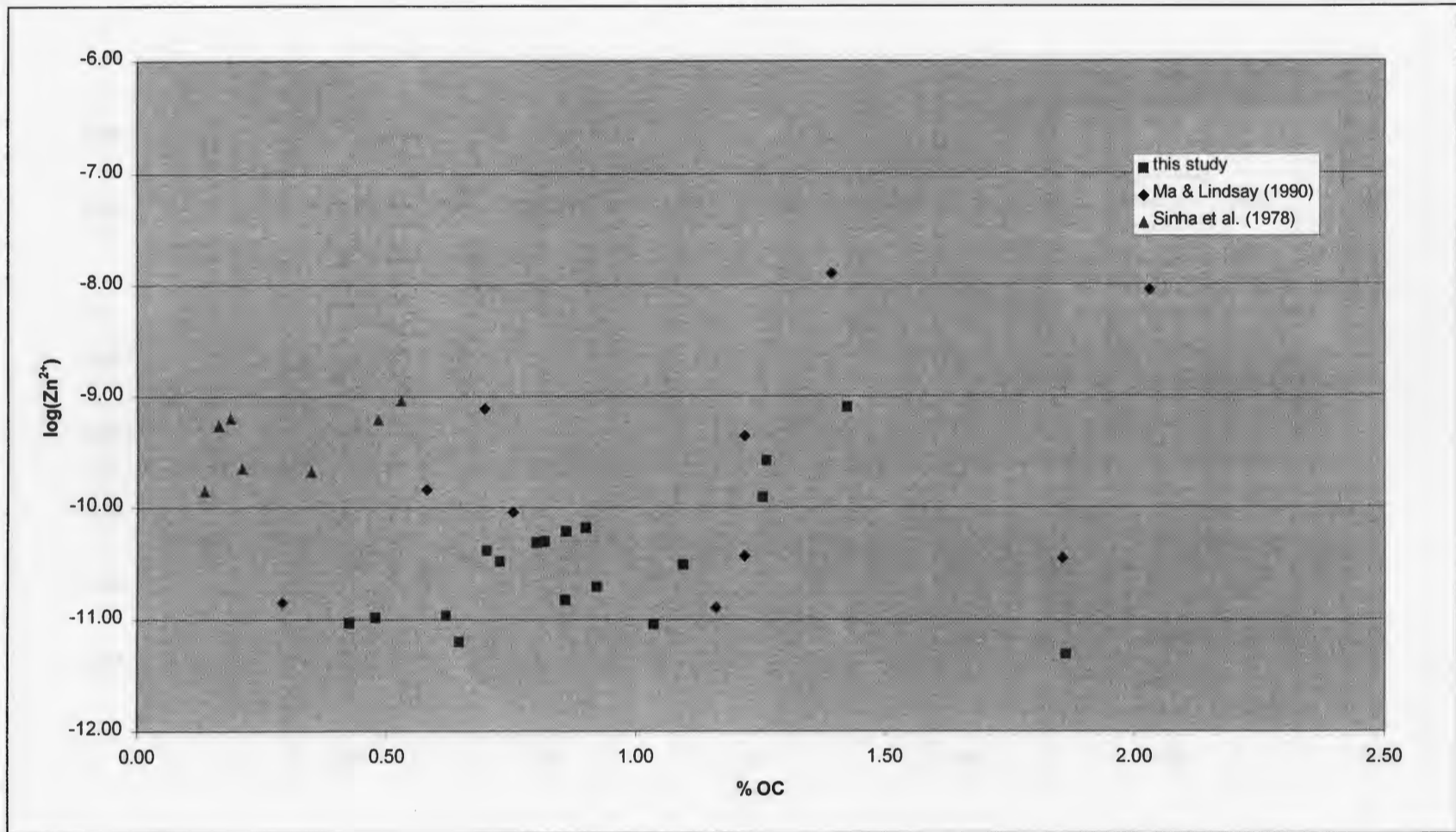


Fig. 2.15. Log Zn²⁺ activity plotted with percent organic carbon for the current study, Ma and Lindsay (1990), and Sinha et al. (1978).

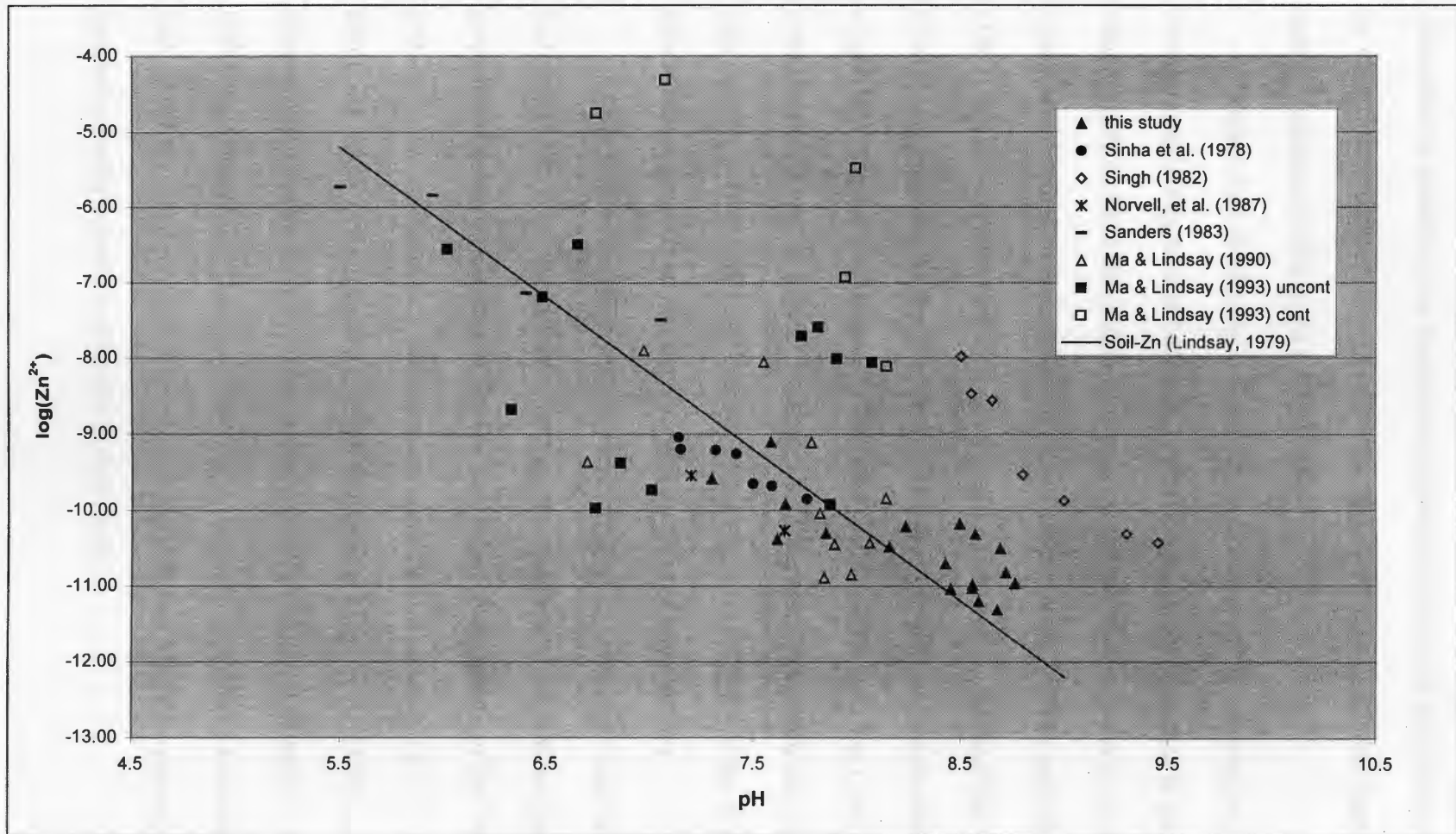


Fig. 2.16. Log Zn^{2+} activity versus pH including data from this study and other data from the literature. The solid line corresponds to the soil-Zn line of Lindsay (1979). Data from Ma and Lindsay (1993) were separated by contaminated (cont) and uncontaminated (uncont) soils.

controls Fe solubility. For example, if a more amorphous maghemite (i.e., more soluble) controlled Fe solubility, the franklinite-maghemite line would shift down, since increased Fe solubility would decrease Zn solubility. The solubility could also change if other cations substitute for Fe or Zn in franklinite.

Figure 2.16 shows $\log \text{Zn}^{2+}$ activity data versus pH for several studies from the literature, including the current study. All of the studies represented in this graph, except Sanders (1983), used the chelation method to estimate Zn^{2+} activities. Sanders (1983) used a resin method to distinguish Zn^{2+} from total soluble Zn. The soils from Singh (1982) and the contaminated soils of Ma and Lindsay (1993) fall near the willemite (Zn_2SiO_4) solubility line or a franklinite solubility line with iron controlled by maghemite or goethite. Most of the other soils are close to the soil-Zn line. Ma (1991) showed that franklinite may vary somewhat in composition, depending on conditions of its synthesis. The possible variation in frankinite formation may explain some of the different Zn solubilities in the soils of this study as well as those of other studies.

Data from some other studies, especially the ion-exchange resin studies, were not included in Fig. 2.16. One reason was that data were not listed in those papers, although graphs were present. Curtin and Smillie (1983) had lower values of Zn^{2+} activities than soil-Zn in acid soils and Zn^{2+} activities near soil-Zn for soils of pH 6 – 7. Their soils had a slope of -0.57 in the graph of $\log \text{Zn}^{2+}$ versus pH. Dang et al. (1996) showed a slight relationship between Zn^{2+} activities and pH, with slopes of -0.56 and -0.32 for unfertilized and fertilized soils, respectively. The Zn^{2+} activities were near soil-Zn for soils of pH 6 – 7 and more soluble than soil-Zn at higher pH. Fotovat et al. (1997) showed a similar behavior with soils in their study.

A collection of the linear relationships for each of the studies is summarized in Table 2.8, and the studies are grouped by method. Dang et al. (1996) collected some of these regression relationships. It is interesting to observe that with two exceptions, the slopes for the data collected using a chelation method are all greater than 1.0, whereas the slopes for the data collected using a resin method were all less than 1.0. The exceptions are the uncontaminated soils of Ma and Lindsay (1993) and the soils of Sanders (1983). The observed differences in slope between the two methods brings into question whether or not both chelation and ion-exchange resin methods measure the same thing. Does one method measure free Zn activity, while another method measures a different soluble form of Zn? To pursue the issue of what activity or species is actually measured by the different methods is a subject for future study.

Interpretation of slope

Since the slope of the $\log(\text{Zn}^{2+})$ versus pH data for this study is closer to -1 than to -2 , there may be a different mechanisms at work besides precipitation and dissolution. One possibility is that organic matter may play a role in the free Zn solubility control, as indicated by Eq. [14]. In neutral to alkaine soils, $\text{Zn}(\text{OH})^+$ is a dominant solution species of Zn that may adsorb to soil and replace one H^+ :

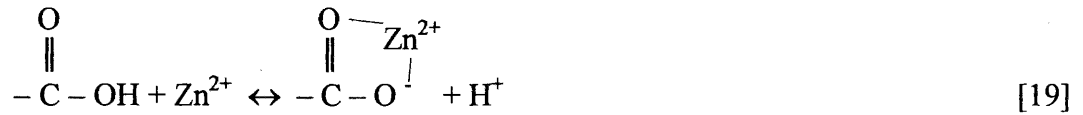


where L is an organic ligand in the soil capable of complexing Zn. The resulting slope of $\log(\text{Zn}^{2+})$ versus pH should be -1 . Jeffrey and Uren (1983) concluded that at neutral to alkaline pH, specific adsorption of a hydrolyzed form of Zn (e.g. $\text{Zn}(\text{OH})^+$) may control Zn solubility. My results point to a similar possible conclusion.

Table 2.8. Regression equations for Zn^{2+} activity or total soluble Zn concentration versus pH from various studies. Soils used from Ma and Lindsay (1993) were the uncontaminated soils.

method	regression equation	reference
chelation	$\log (Zn^{2+}) = 5.8 - 2 \text{ pH}$	soil-Zn, Lindsay (1979)
chelation	$\log (Zn^{2+}) = -2.0 - 1.0 \text{ pH}$	this study
chelation	$\log (Zn^{2+}) = 1.1 - 1.4 \text{ pH}$	Ma and Lindsay (1990)
chelation	$\log (Zn^{2+}) = -5.7 - 0.36 \text{ pH}$	uncont. soils, Ma and Lindsay (1993)
chelation	$\log (Zn^{2+}) = 0.02 - 1.3 \text{ pH}$	Sinha et al. (1978)
chelation	$\log (Zn^{2+}) = 12.9 - 2.5 \text{ pH}$	Singh, (1982)
ion exchange resin	$\log (Zn^{2+}) = 1.4 - 1.3 \text{ pH}$	Sanders, (1983)
ion exchange resin	$\log (Zn^{2+}) = -3.0 - 0.57 \text{ pH}$	Curtin and Smillie (1983)
ion exchange resin	$\log (Zn^{2+}) = -3.5 - 0.56 \text{ pH}$	Dang et al. (1996)
ion exchange resin	$\log (Zn^{2+}) = -3.5 - 0.67 \text{ pH}$	Fotovvat et al. (1997)
total Zn	$\log [Zn_T] = 6.5 - 0.75 \text{ pH}$	Jeffrey and Uren (1983)

On the other hand, if Zn^{2+} adsorbs to organic matter, two other mechanisms could occur. Zn may adsorb to organic matter and replace only one proton by adsorption to a carboxyl group:



Another possibility is to have an ion-exchange reaction occur (with a zero slope) such as:



Different reactions may occur in soils, depending upon pH, solution composition, organic matter content, CEC or other soil properties.

A different perspective on the slope of the $\log(Zn^{2+})$ versus pH graph is to represent the data by two different regions. (See Fig. 2.17.) In region 1, at $\text{pH} < 8.4$, the plot of $\log(Zn^{2+})$ versus pH has a small slope of about -1.1 . In region 2, at $\text{pH} > 8.4$, the slope is closer to -2 , as it is for soil-Zn. Hence at higher pH these soils may be controlled by a precipitation reaction involving soil-Zn or franklinite, and at lower pH an adsorption reaction may control Zn solubility. This observation is similar to several previous studies (e.g., Gupta et al., 1987; Singh and Abrol, 1985). Brennan and Lindsay (1996) and Lindsay and Catlett (1998) illustrate that the slope may level off at low pH for all metals, including Zn.

Zinc solubility could also be controlled by other reactions in the soils of this study. Those reactions include other mineral precipitation reactions, such as the precipitation of a calcium-zinc carbonate, or other adsorption reactions, such as adsorption onto iron or manganese oxides or clay.

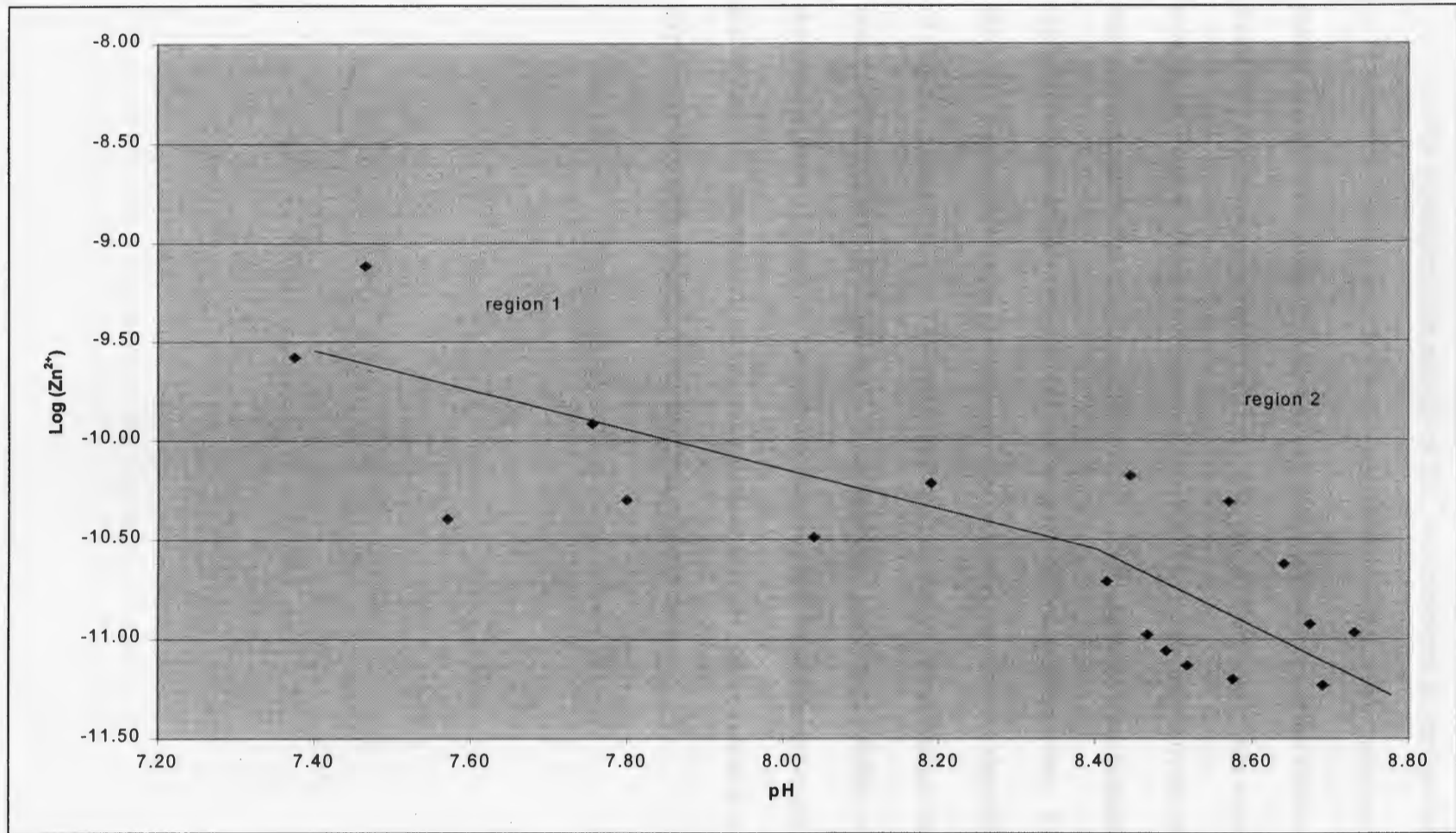


Fig. 2.17. Log of Zn²⁺ activity versus pH with possible region 1 and region 2 denoted. Regions 1 and 2 may have different solubility controls for Zn.

Conclusions

In this experiment, the activity of Zn^{2+} was measured at very low concentrations in 18 neutral to alkaline soils from eastern Colorado farms using chelation. The organic matter composition of the soils should be similar because of similar crops grown in these fields and similar management practices. The range of organic matter concentrations was a factor of about 4, which is narrow but could still illustrate trends in the relationship between organic matter and Zn solubility. $\log Zn^{2+}$ activities were predicted by a regression equation that included pH and organic carbon as parameters. $\log Zn^{2+}$ activities were plotted with pH near the soil-Zn line. However, the data fall along a line of slope -1 rather than -2 . This result indicates that another mechanism besides precipitation and dissolution of soil-Zn could occur. Another possibility is that two different regions of solubility happen, one below pH 8.4 and one above pH 8.4. Free Zn ion or $Zn(OH)^+$ may adsorb on organic matter at low pH. More research is needed to explore the possible adsorption mechanisms of Zn in soils.

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CHAPTER 3

**USE OF PRINCIPAL COMPONENT ANALYSIS AND PATH ANALYSIS TO
EXPLORE RELATIONSHIPS BETWEEN SOIL PARAMETERS AND FREE Zn
ACTIVITY**

Summary

Principal component analysis (PCA) and path analysis methods were studied and applied to 18 soil samples from three farms in eastern Colorado. Both methods help researchers understand the dynamics of complex systems. Results of PCA showed that the first principal component, a linear combination summing clay and total soil Zn and subtracting soil carbon, accounted for 52 % of the variability in the soils. Soil pH and inorganic carbon dominated the second principal component, which accounted for 32 % of the variability. Results of path analysis showed the importance of direct effects of soil pH, total soil Zn, and organic carbon in predicting free Zn activity in these soils. Indirect effects of all variables were also explored. The results of these methods were compared with the results from multiple regression analysis.

Introduction

The dynamics of natural systems are often complex, and multiple regression analysis may not address all the interactions involved in these systems. Other statistical

techniques can be applied with multiple regression to help understand the entire system better. Principal component analysis (PCA) and path analysis are two statistical techniques that can provide information on the dynamics of complex systems such as water chemistry (e.g. Duffy and Brandes, 1999), ecological systems (e.g. Smith et al., 1997), and soil science (e.g. Basta et al., 1993).

PCA explains the variance – covariance structure of the data through linear combinations of the original data (i.e. principal components). PCA can serve as an intermediate step in a much larger investigation. PCA can be used to reduce the dimensions of the data or to help interpret the data by observing natural groupings or clusters in the data set. Analysis of principal components often reveals relationships not previously expected and allows interpretations that would not ordinarily be expected (Johnson and Wichern, 1988).

Path analysis was developed by Sewall Wright to explore direct and indirect effects of predictor variables hypothesized to have a causal effect on response variables (Wright, 1921; Wright, 1934). This method allows the researcher to observe if a causal model agrees or disagrees with the data. Construction of a path diagram is key to building the hypotheses of the method. The path coefficients associated with this diagram help determine the relative importance of direct and indirect effects. Path analysis is also called causal analysis and is a specific type of analysis in a more general group of analyses called structural equation modeling.

In this chapter, the use of PCA and path analysis is explored with data previously analyzed by multiple regression (see Chapter 2). First, the two methods will be explained

in some detail. Then the results of the two methods will be discussed and compared to the results of the multiple regression analysis.

Methods

As discussed in Chapter 2, several soil properties were measured for 18 soils from eastern Colorado. Zn^{2+} activity was measured by chelation (Ma and Lindsay, 1990; Norvell and Lindsay, 1969). Soil pH was measured along with the chelation method at 5 days in a 1:2 soil to solution ratio. Total soil Zn was measured from a $HNO_3 - HClO_4$ digest, and the solution was analyzed by inductively coupled plasma (ICP) (Hossner, 1996). Percent inorganic carbon was measured by a modified volumetric method (Wagner et al., 1998; L. Sherrod, personal communication). Total carbon was measured by a Dorhmann DC-190 High-Temperature Total Carbon Analyzer. Percent organic carbon was estimated by the difference between total carbon and inorganic carbon. Percent clay was measured by hydrometer method (Gee and Bauder, 1986).

The logarithm was taken of the percent inorganic carbon because the spread of the inorganic carbon was small. Since some of the soils contained no inorganic carbon and the log of zero is undefined, 1 was added before taking the logarithm.

Statistical analyses were performed using SAS (SAS Institute, 1988). Specific commands or procedures are explained in the text below.

Principal component analysis

Principal components are linear combinations of the original variables. These linear combinations are orthogonal and uncorrelated, have unit length, and explain the maximum possible variance. In mathematical terms:

let \mathbf{x} = vector of original variables,

\mathbf{l}_i = vector of coefficients of a linear combination of \mathbf{x} ,

superscript “T” = the transpose of the vector or matrix.

Then the first principal component is defined as:

the linear combination $\mathbf{l}_1^T \mathbf{x}$ that maximizes $\text{Var}(\mathbf{l}_1^T \mathbf{x})$

subject to $\mathbf{l}_1^T \mathbf{l}_1 = 1$

and the second principal component is:

the linear combination $\mathbf{l}_2^T \mathbf{x}$ that maximizes $\text{Var}(\mathbf{l}_2^T \mathbf{x})$

subject to $\mathbf{l}_2^T \mathbf{l}_2 = 1$ and $\text{Cov}(\mathbf{l}_1^T \mathbf{x}, \mathbf{l}_2^T \mathbf{x}) = 0$

(Johnson and Wichern, 1988).

It can be shown that these linear combinations are the eigenvectors of the variance-covariance or correlation matrix. The eigenvalues associated with the eigenvectors represent the amount of variation explained by each eigenvector. The variance-covariance matrix is a matrix with the variance of each variable along the diagonal and the covariance of two variables in the corresponding off-diagonal position. The correlation matrix has 1's along the diagonal and correlation coefficients in the off-diagonal positions. Both of these matrices are symmetrical, which means the eigenvectors will be orthogonal.

When variables are of different scales of measurement, it is usually desirable to “standardize” the variables. To standardize a variable (x_i), the mean (\bar{x}_i) is subtracted from the value and this difference is divided by the standard deviation (s_x) of that variable, so that the mean of the standardized variable is 0 and the variance is 1. The standardized value is given by $\frac{x_i - \bar{x}_i}{s_x}$. When the variables are standardized, the variance-covariance matrix becomes the correlation matrix of the original variables. So, if standardization of units is desired, the correlation matrix is used instead of the variance-covariance matrix. One drawback of standardization is that it tends to inflate variables with small variance and reduce the influence of variables with large variance.

Eigenvectors are solutions to the equation: $A\mathbf{x} = \lambda\mathbf{x}$ where A is the correlation (or variance-covariance matrix), λ is an eigenvalue, and \mathbf{x} is an eigenvector. The eigenvector corresponding to the greatest λ_i is the first principal component. The second greatest λ_i corresponds to the eigenvector which is the second principal component, and so on. More information on principal components can be found in Davis (1986); Gnanadesikan (1977); and Johnson and Wichern (1988).

In this study, the original variables are pH, percent organic carbon (OC), the logarithm of percent inorganic carbon ($\log(\text{IC}+1)$), percent clay (clay), and total soil Zn content (Zn_T). Since the units of measurement for these variables differ, the correlation matrix was used to obtain the principal components. The SAS procedure called PRINCOMP was used with the “standard” option to calculate the principal components (eigenvectors), eigenvalues, and to evaluate the principal components for each of the soils (SAS Institute, 1988).

Path analysis

One of the first steps in the method of path analysis is the construction of a path diagram. See for example, Fig. 3.1. Variables are connected by one-headed or two-headed arrows. Path coefficients correspond to the one-headed arrows and are written P_{ij} , where the arrow is drawn from variable i to j . So P_{ij} is the effect of one unit change in variable i on variable j . Two-headed arrows represent correlation coefficients between variables i and j . These correlations are designated by r_{ij} . The variables are numbered so that coefficients can be designated by numbers instead of variables.

Path analysis operates under several assumptions. First, all important variables are assumed to be identified and to be measured without error. The effects are assumed linear, additive and unidirectional. In addition, the residuals are not to be correlated. See Pedhazur (1982) and Smith et al. (1997) for more information.

Some path models may resemble a multiple regression analysis, such as that depicted in Fig. 3.1. In this simple path model, several independent variables are used to predict one dependent variable. Correlations are drawn between each of the predictor variables. This model is the type of path analysis used in this paper.

The total contribution of each predictor variable on the response is the sum of all paths from that variable to the response variable (e.g., see Fig. 3.1). There are five effects of each predictor variable on the response, one direct and four indirect. For example, the effects of pH on $\log(Zn^{2+})$ are summed as: the direct effect (P_{16}), the indirect effect of pH through organic carbon ($r_{12}P_{26}$), the indirect effect of pH through clay ($r_{13}P_{36}$), the indirect effect of pH through total soil Zn ($r_{14}P_{46}$), and the indirect effect of pH through inorganic carbon ($r_{15}P_{56}$). So the total effect of pH on $\log(Zn^{2+})$ is:

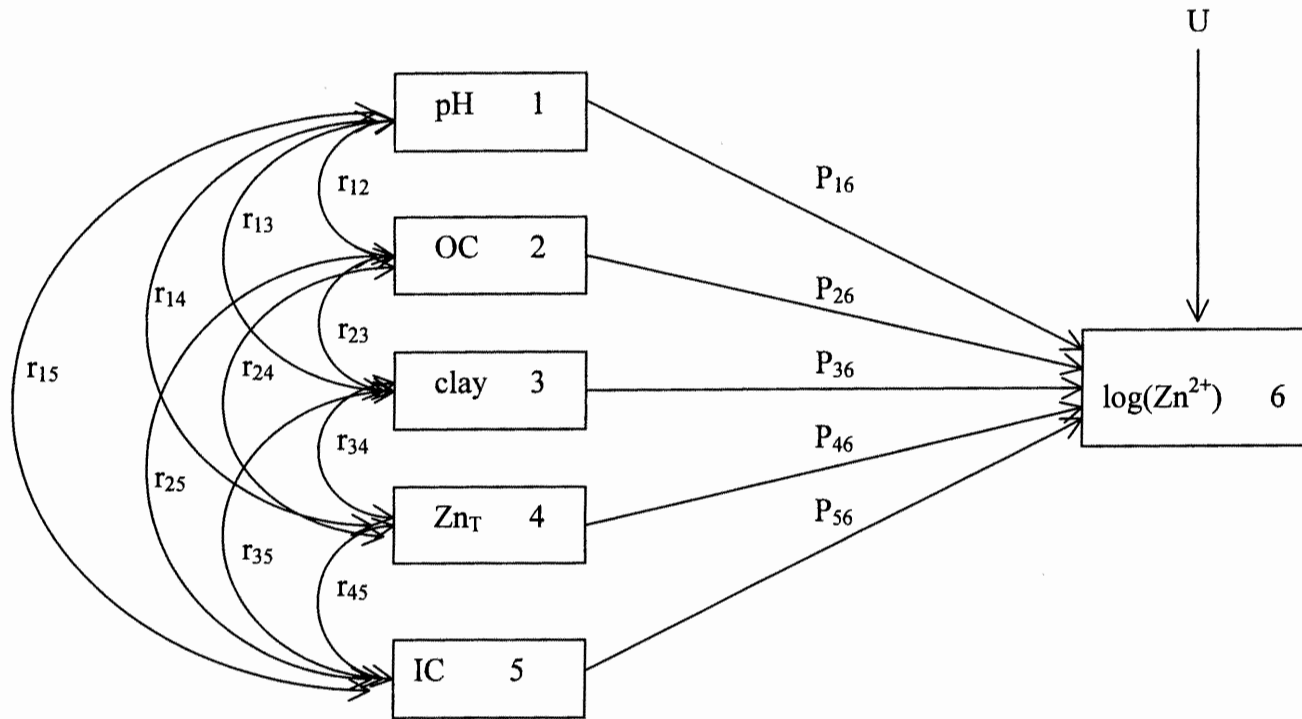


Fig. 3.1. Path diagram for the model of five soil parameters to predict $\log(\text{Zn}^{2+})$ – Model 1. Numbers in the boxes with variable names represent the number associated with that variable in the subscripts of r and P . The variable U represents the standardized residual.

$$r_{16} = P_{16} + r_{12}P_{26} + r_{13}P_{36} + r_{14}P_{46} + r_{15}P_{56}.$$

Similar equations can be derived for the other predictor variables:

$$r_{26} = r_{12}P_{16} + P_{26} + r_{23}P_{36} + r_{24}P_{46} + r_{25}P_{56}$$

$$r_{36} = r_{13}P_{16} + r_{23}P_{26} + P_{36} + r_{34}P_{46} + r_{35}P_{56}$$

$$r_{46} = r_{14}P_{16} + r_{24}P_{26} + r_{34}P_{36} + P_{46} + r_{45}P_{56}$$

$$r_{56} = r_{15}P_{16} + r_{25}P_{26} + r_{35}P_{36} + r_{45}P_{46} + P_{56}$$

Note from Fig. 3.1 that 1 = pH, 2 = organic carbon, 3 = clay, 4 = total soil Zn, 5 = inorganic carbon, 6 = free Zn activity. The total effect of each variable is given by r_{i6} , where $i = 1$ to 5. So each term on the right-hand side of the above equations is either a direct or an indirect effect of the predictor variable on $\log(Zn^{2+})$.

The path coefficients can be calculated by performing a multiple regression analysis including all the predictor variables in a model with $\log(Zn^{2+})$. In SAS, the command “proc reg” is used. The correlation coefficients can be determined in SAS by using the command “proc corr.” As an alternative command for this regression-type of path model, and for more complicated models, “proc calis” can be used.

More information on path analysis can be found in the works of Johnson and Wichern (1988) and Pedhazur (1982). Those references give different perspectives on interpreting indirect effects. Pedhazur (1982) suggests that some of the indirect effects described above are either spurious or undetermined effects instead of indirect effects. Pedhazur’s approach may be more rigorous than the one described above. Johnson and Wichern (1988) agree with the presentation above regarding indirect effects (no effect is spurious or undetermined). In this paper, path analysis is used as an exploratory tool, so that the approach of Johnson and Wichern (1988) is acceptable, if not entirely rigorous.

Basta et al. (1993) and Williams et al. (1990) follow the approach of Johnson and Wichern (1988) in applying path analysis to adsorption of metals in soils and to general agriculture, respectively.

Results

Principal component analysis

Eigenvalues of the correlation matrix for the five principal components or eigenvectors (PC1-PC5) are given in Table 3.1. The proportion of variance explained by each principal component is given (the eigenvalue) along with the cumulative variance. For example, the eigenvalue corresponding to principal component 1 (PC1) shows that PC1 accounts for 52 % of the total variance. The first two principal components account for 84 % of the total variance. Since the first three principal components account for most of the total variance, these are the components of interest.

Table 3.2 gives the principal components (or eigenvectors) of the correlation matrix as linear combinations of the original variables. The principal components read down in each column. For example

$$PC1 = -0.026 \text{ pH} - 0.38 \log(\text{IC} + 1) - 0.52 \text{ OC} + 0.49 \text{ clay} + 0.59 \text{ Zn}_{\text{soil}} \quad [1]$$

The soil parameters in this equation are standardized to a mean of zero and a variance of one. The principal component is also standardized to unit variance.

The results of the PCA are explored using three different perspectives. First, one can examine the principal components themselves to determine how the soil properties contribute to each principal component. Second, the principal components can be plotted against each other for each soil sample, and data from groups of soils can be

Table 3.1. Eigenvalues of the correlation matrix for the five principal components or eigenvectors (PC1-PC5). The proportion of variance explained by the principal component is given, along with the cumulative variance.

	Eigenvalue	Proportion of variance	Cumulative variance
PC1	2.595915	0.5192	0.5192
PC2	1.615688	0.3231	0.8423
PC3	0.502262	0.1005	0.9428
PC4	0.212598	0.0425	0.9853
PC5	0.073537	0.0147	1

Table 3.2. Eigenvectors of the correlation matrix as linear combinations of the original variables (in columns). PC1 through PC5 are the eigenvectors.

	PC1	PC2	PC3	PC4	PC5
pH	-0.02603	0.73250	-0.363110	0.54143	-0.19432
log(IC+1)	-0.37809	0.56660	0.351783	-0.35734	0.53346
OC	-0.51771	-0.19594	0.582353	0.57389	-0.15842
clay	0.49237	0.31959	0.595984	-0.19305	-0.51281
Zn_T	0.58815	-0.04336	0.223754	0.46102	0.62417

analyzed for patterns. Third, principal components can be used in a linear regression with another variable of interest, in this case $\log(\text{Zn}^{2+})$.

Figures 3.2 through 3.4 show the importance of each soil parameter on the first three principal components. For PC1 (Fig. 3.2), soil pH is not an important factor, as shown in the coefficient for pH in Eq. [1] above. The first principal component appears to be related to the sum of clay content and total soil Zn with carbon content subtracted. Soil pH and inorganic carbon dominate PC2 (Fig. 3.3). The interpretation of PC3 is less clear (Fig. 3.4). Organic carbon and clay are most strongly related to PC3. Soil pH, inorganic carbon and soil Zn contribute slightly less to PC3, with pH in a negative direction.

In Figs. 3.5 through 3.7, the first three principal components are plotted against each other. The numbers near each data point correspond to the soil sample number (see Table 3.3). Figure 3.5 shows PC2 versus PC1. Soils 11 and 12 have strong negative values because the concentration of total soil Zn of these soils is low and the concentration of soil Zn plays a strong role in PC1. Figure 3.6 shows PC3 versus PC1. Soils 11 stands apart from the other soils because of its low concentration of soil Zn, and soil 12 stands out because of its low soil Zn content and its disproportionately high organic carbon content. Soils 7, 9, and 10 also stand slightly apart from the other soils. Figure 3.7 shows a wide gap separating soils 3, 4, 5, 6, 12, 14, and 15 from the soils on the bottom half of the graph of PC3 versus PC2, but it is not entirely clear why the soils are grouped as such. Soils 4, 5, 6, 12, and 14 contain large concentrations of inorganic carbon that might explain the large values of PC2 for those soils. In addition, each of those soils has a high clay content, except soil 12.

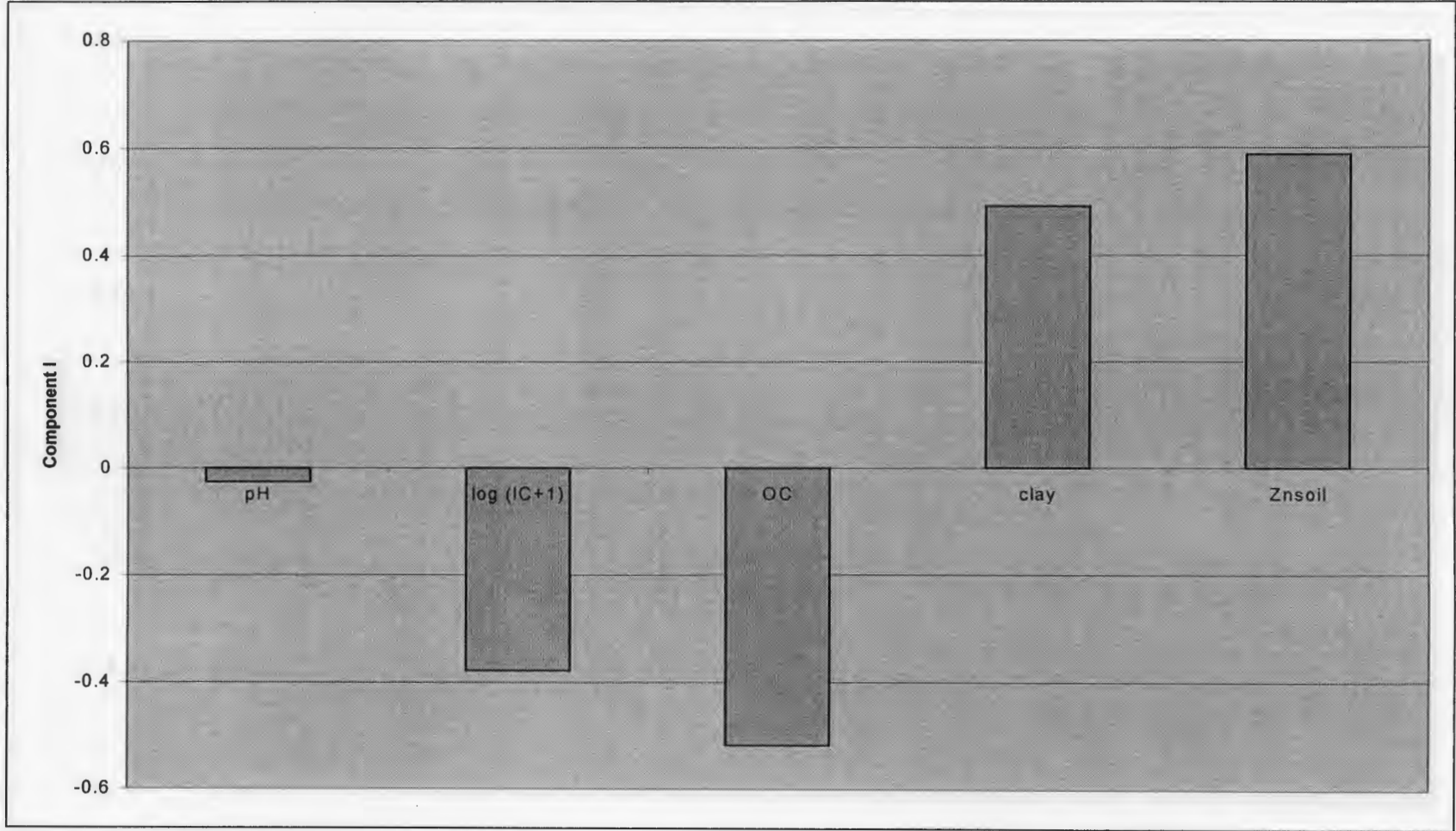


Fig. 3.2. Principal component 1 plotted with the five soil parameters.

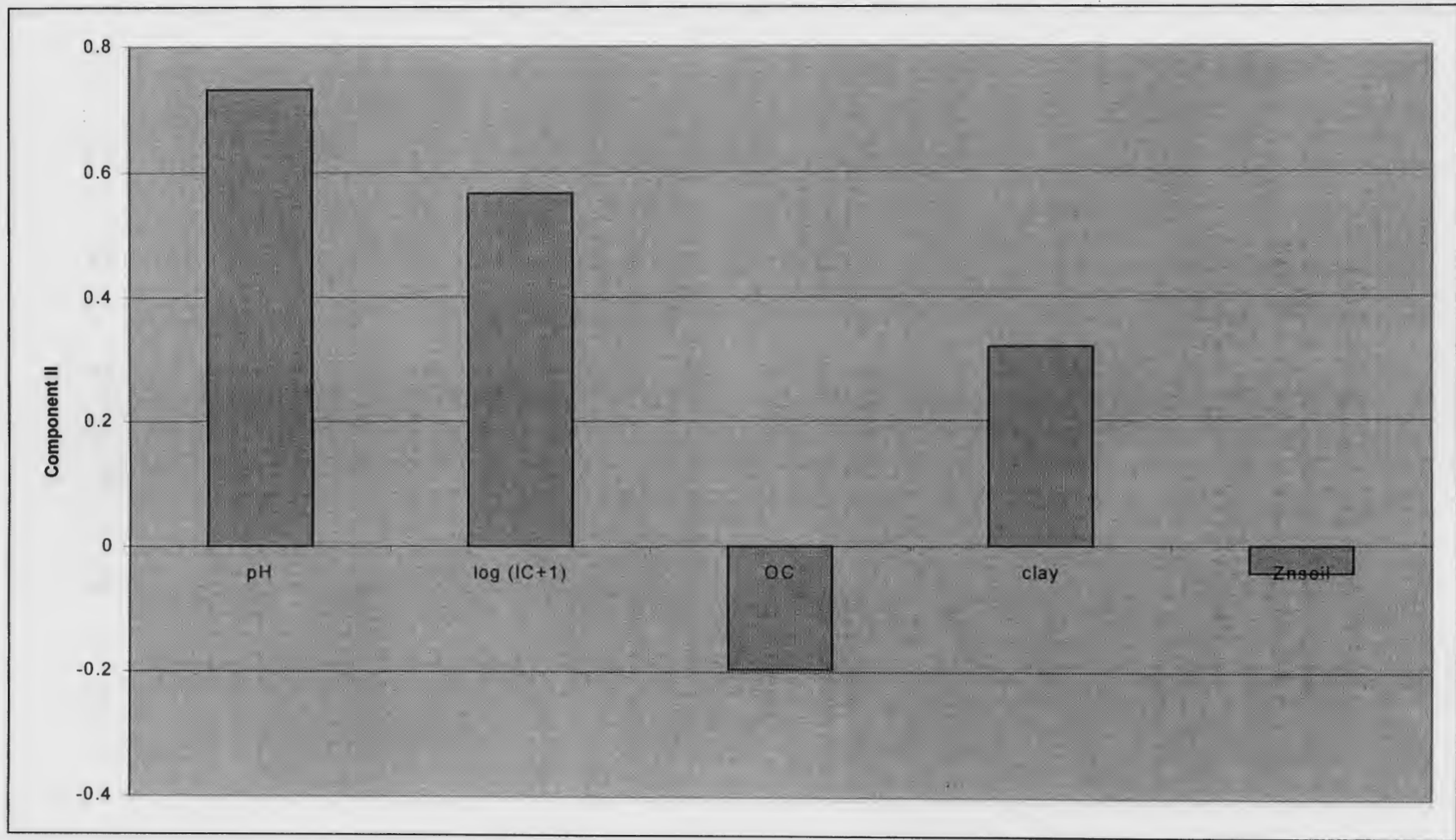


Fig. 3.3. Principal component 2 plotted with the five soil parameters.

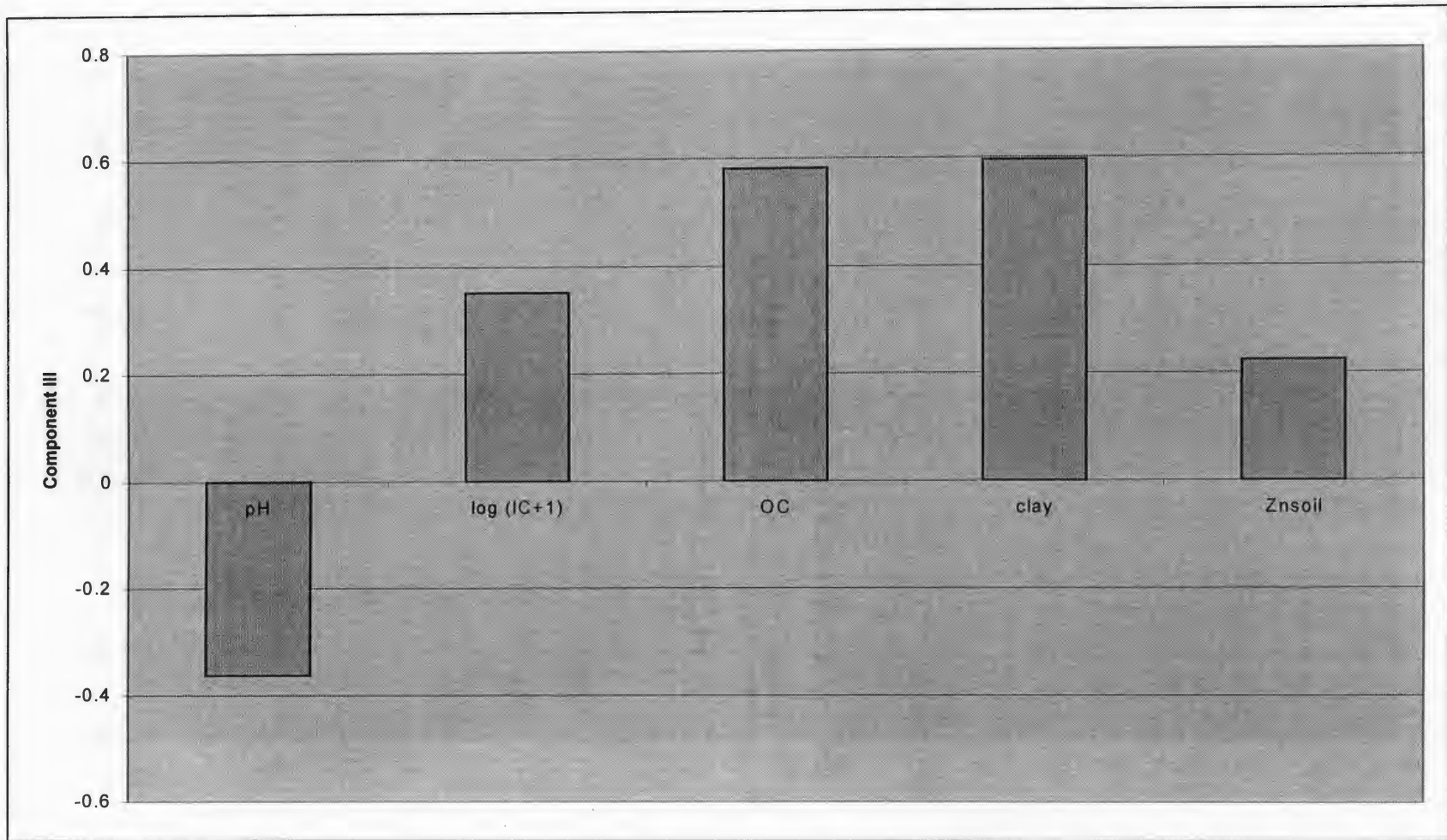


Fig. 3.4. Principal component 3 plotted with the five soil parameters.

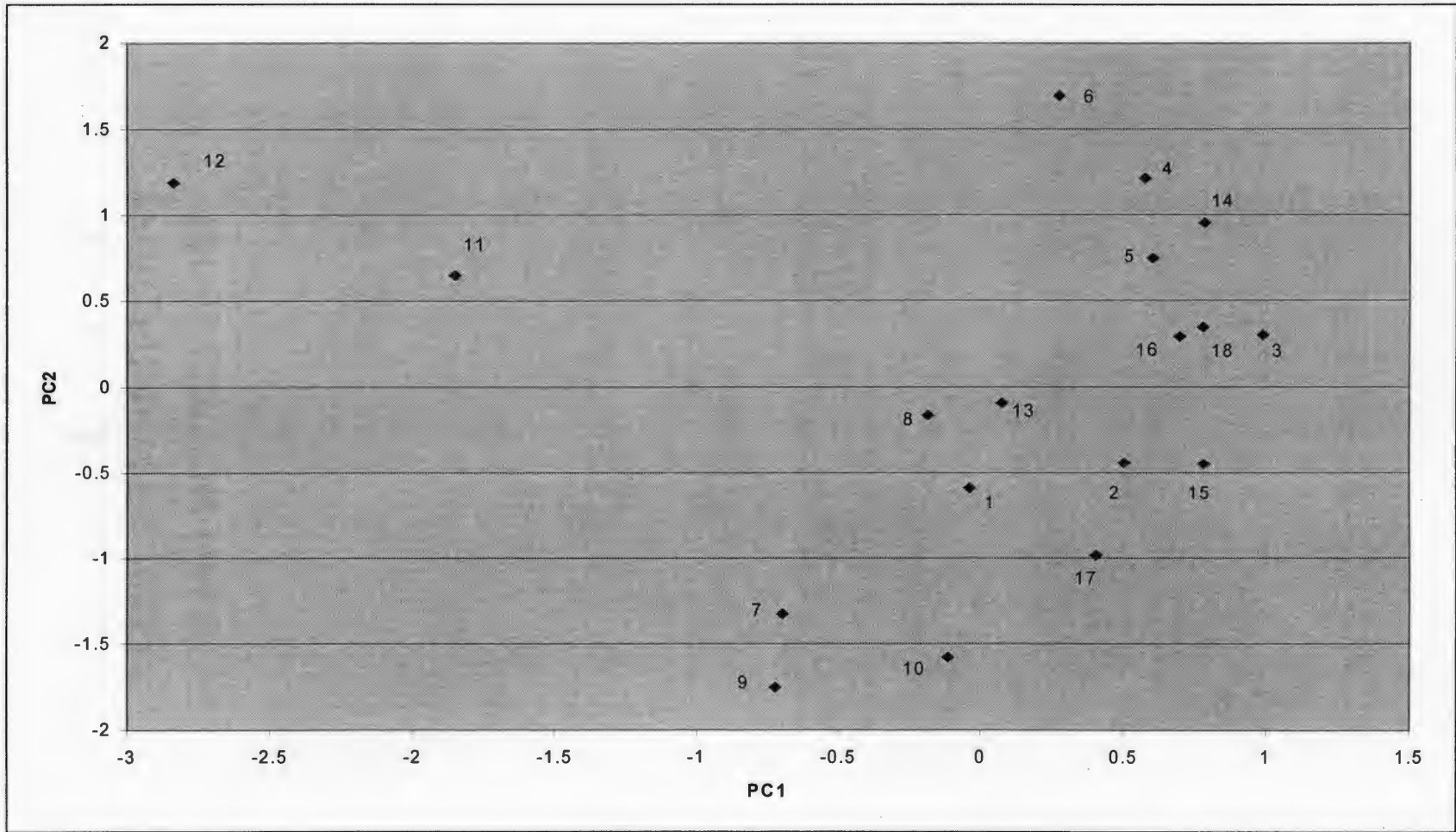


Fig. 3.5. Principal component 2 (PC2) plotted against principal component 1 (PC1). Numbers in the figure correspond to soil sample numbers.

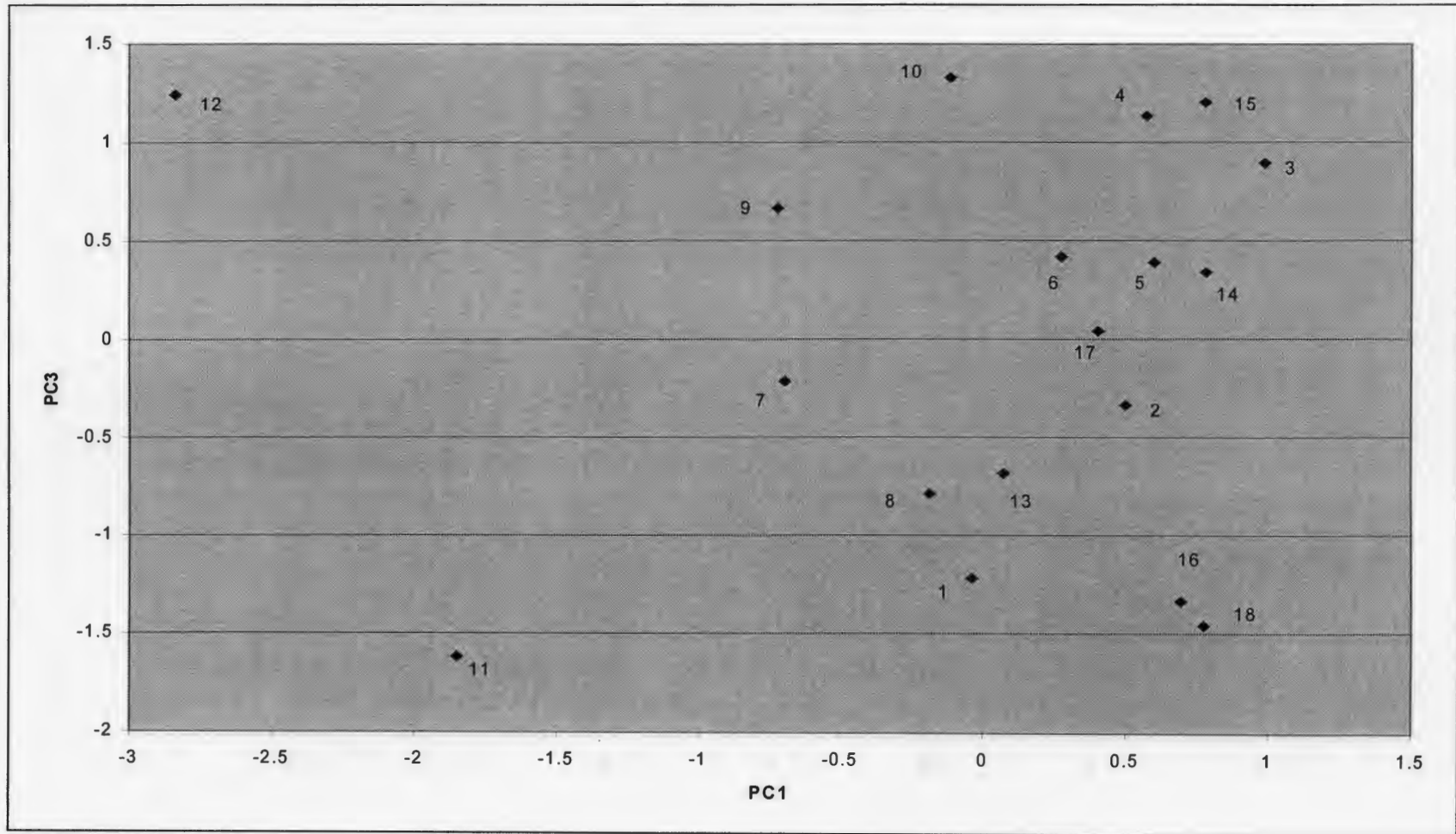


Fig. 3.6. Principal component 3 (PC3) plotted with principal component 1 (PC1). Numbers in the figure correspond to soil sample numbers.

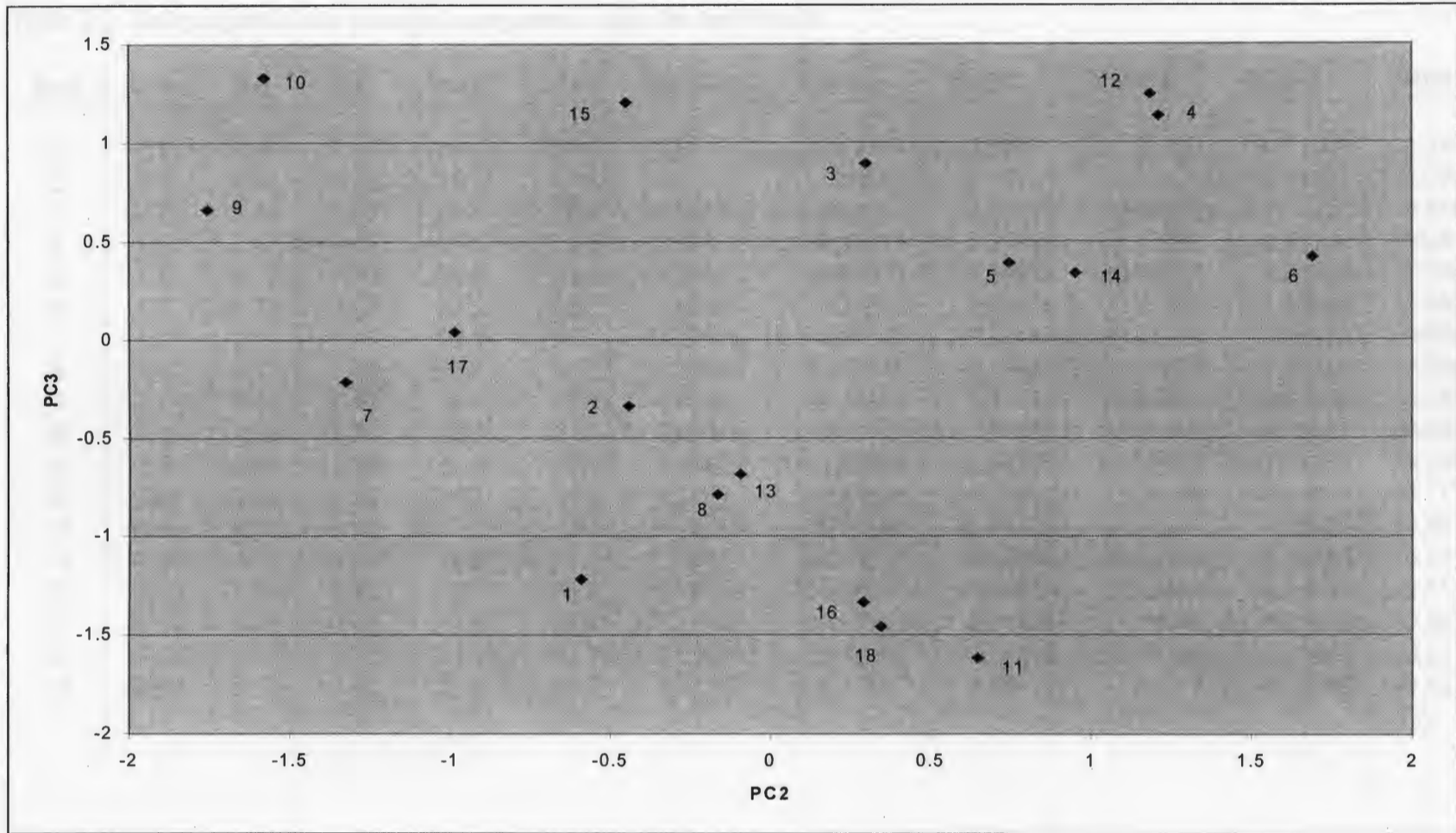


Fig. 3.7. Principal component 3 plotted with principal component 2. Numbers in the figure correspond to soil sample numbers.

Table 3.3. Soil properties and principal component values for the 18 soils.

Soil	farm	pH	OC	clay	Zn _T	log(IC+1)	PRIN1	PRIN2	PRIN3	PRIN4	PRIN5
1	CF	8.19	0.86	16.9	64.0	0.0	-0.03854	-0.58992	-1.21989	0.73009	1.38351
2	CF	8.04	0.73	23.1	66.5	0.0	0.50169	-0.44163	-0.33476	-0.41031	0.09582
3	CF	8.45	0.90	29.4	78.4	0.26236	0.98793	0.30015	0.89277	1.57317	-0.85839
4	CF	8.67	0.86	30.0	71.9	2.03471	0.57395	1.21374	1.13327	0.47740	0.08505
5	CF	8.57	0.80	26.3	74.8	1.6525	0.60071	0.74622	0.38957	0.83434	1.29079
6	CF	8.73	0.62	27.5	65.7	2.65605	0.27359	1.69256	0.41856	-1.17041	1.96925
7	LP	7.76	1.25	15.6	55.2	0.13976	-0.69743	-1.32468	-0.21348	0.42132	0.45664
8	LP	8.47	1.04	19.4	60.2	0.19062	-0.18665	-0.16422	-0.78814	1.57164	-0.76013
9	LP	7.47	1.42	16.3	57.9	0.0344	-0.72301	-1.75371	0.66483	0.44209	0.78367
10	LP	7.38	1.26	21.3	64.6	0.07046	-0.11487	-1.57806	1.32900	-0.25612	0.60024
11	LP	8.64	1.09	13.1	29.7	2.44495	-1.85090	0.64780	-1.61822	-1.01970	-0.39077
12	LP	8.69	1.86	16.3	25.3	3.2779	-2.83688	1.18871	1.24338	0.11815	-0.71515
13	Weld	8.42	0.92	21.3	61.7	0.17395	0.07302	-0.09302	-0.68474	0.98681	-0.90177
14	Weld	8.58	0.65	28.8	71.3	1.66013	0.78225	0.95248	0.33894	-0.12544	0.07453
15	Weld	7.80	0.82	30.0	65.4	0.10436	0.78060	-0.44879	1.20384	-1.34739	-2.21028
16	Weld	8.49	0.48	23.8	64.7	0.13976	0.69535	0.29155	-1.33680	-0.35033	-0.66779
17	Weld	7.57	0.70	23.1	61.7	0.19885	0.40322	-0.98492	0.04140	-2.12541	0.18737
18	Weld	8.52	0.43	23.8	66.0	0.12222	0.77597	0.34574	-1.45951	-0.34988	-0.42260

Figure 3.8 is a 3-dimensional graph of the first three principal components and shows several groupings of soils. Soils 3, 4, 5, 6, and 14 form the first group. Group 1 soils have medium to high pH, large soil Zn concentrations, and the largest clay contents. Soil 15 also has a high clay content, but is just outside this group because of a lower pH. Soils 16 and 18 form Group 2. These soils have the lowest organic carbon content of all soils by a difference of at least 0.14 %. Group 3 is composed of soils 1, 2, 8, and 13. These soils have small concentrations of inorganic carbon, and near average organic carbon, clay and soil Zn contents. Soil 17 has similar characteristics to Group 3 soils but has a lower pH. Soils 9 and 10 form Group 4. These two soils have high organic carbon, low inorganic carbon and low pH. Soil 7 is close to Group 4 but has a higher pH and inorganic carbon content. Soils 11 and 12 may be considered a group if the organic carbon content of soil 12 were lower. Otherwise these two soils share low clay and soil Zn contents and high pH.

It appears that pH, organic carbon, inorganic carbon, and clay contents must be measured in order to distinguish these groups. It is not clear from the graphs that soil Zn content is critical in grouping these soils.

Another observation of the groups of soils described above is that the farms did not describe these groups as well as soil properties. There is some dominance of different farms in different groups, but not all soils from one farm formed a group. Thus the soils within each of the farms may be somewhat independent or at least vary independently of other soils from the same farm.

Comparison of principal component results with Zn^{2+} activities can show relationships of the above groups to the activity of Zn. Figure 3.9 presents a plot of log

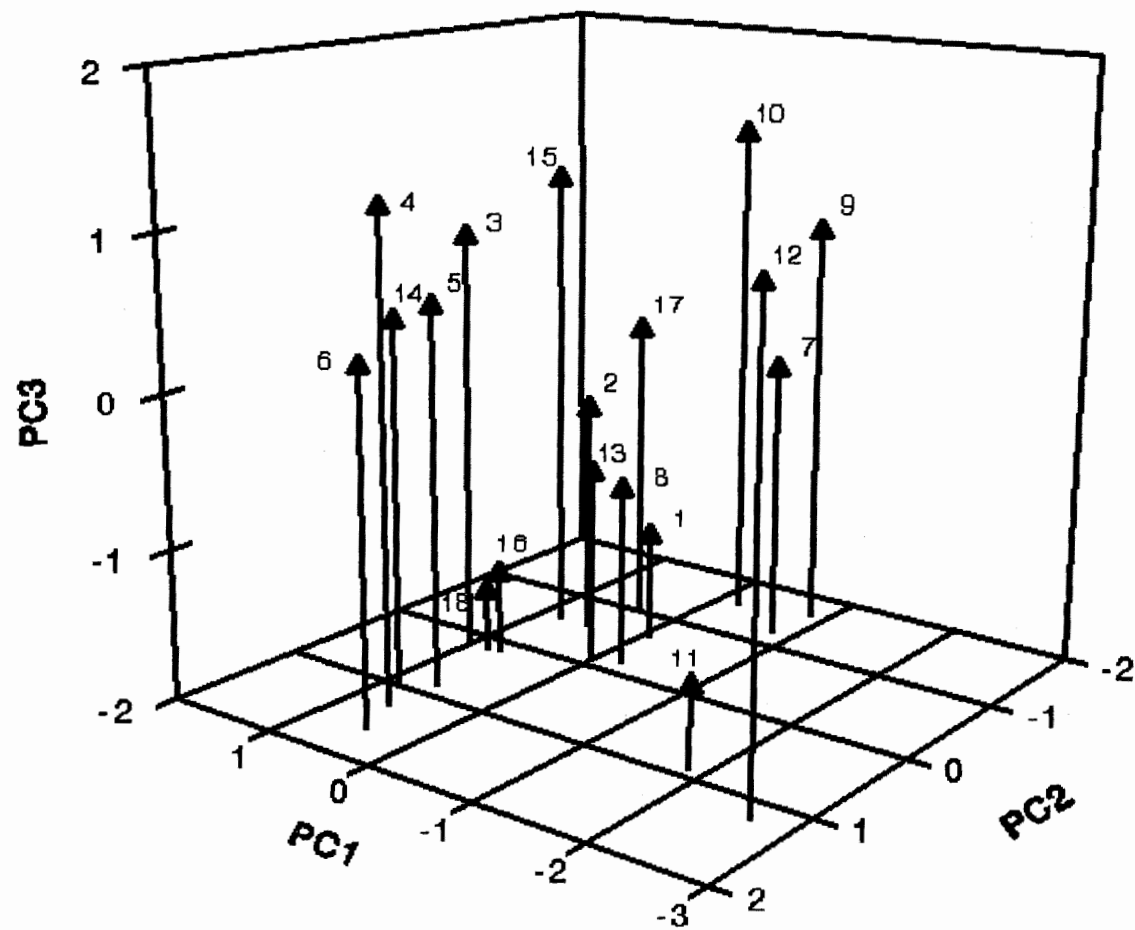


Fig. 3.8. 3-Dimensional plot of the first three principal components. Numbers correspond to the soil sample.

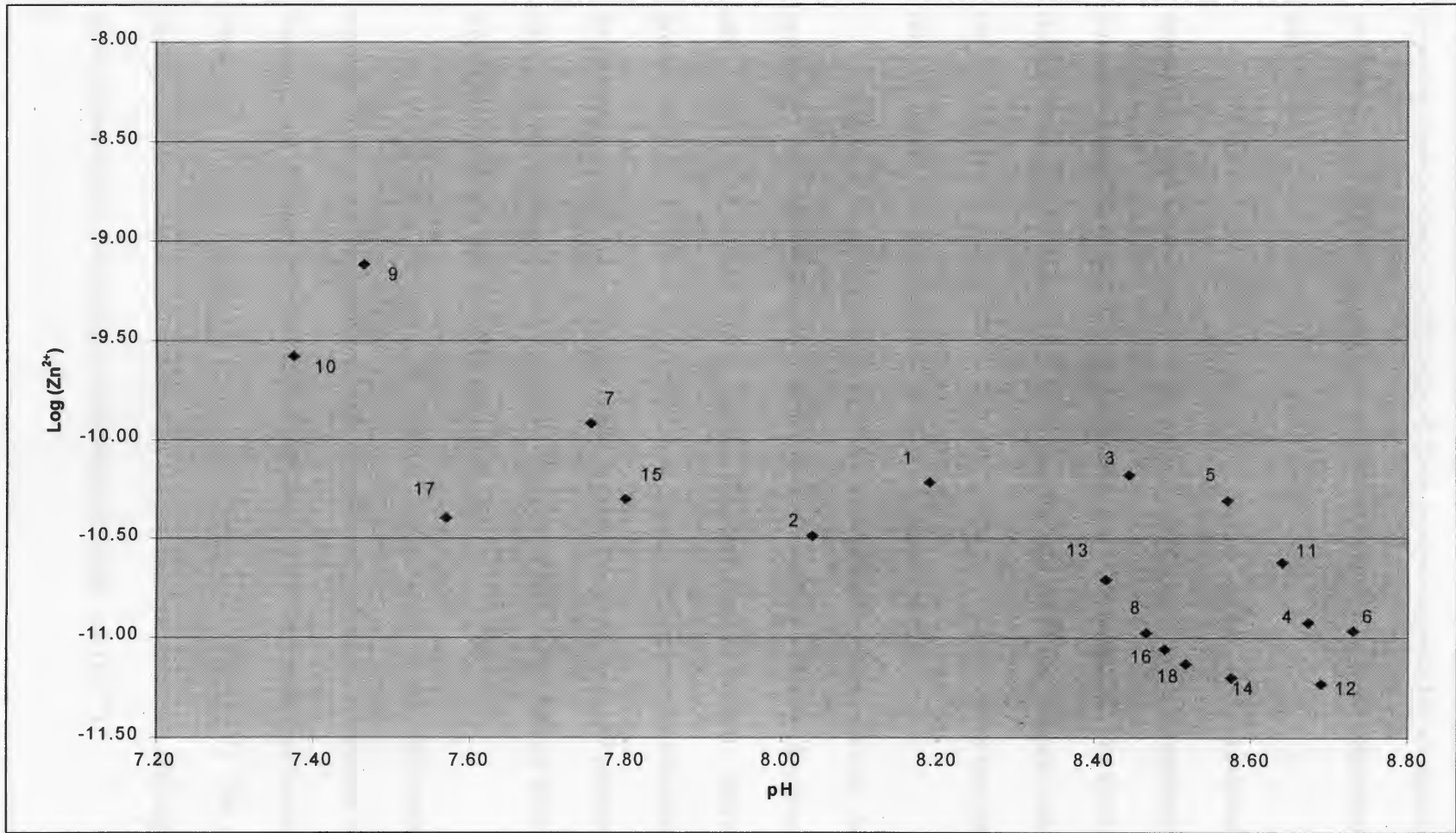


Fig. 3.9. $\text{Log}(\text{Zn}^{2+})$ plotted with pH. Numbers in figure correspond to soil sample numbers.

(Zn^{2+}) versus pH, with the soils numbered and groups designated. Because of the close grouping there is some significance of these groups suggested in a comparison of soil pH and free Zn activity. Thus, pH may play an important role in distinguishing these soils and the subsequent availability of Zn in these soils.

Figure 3.9 also shows some indication that there could be a relationship between depth of the soil sample and free Zn activity. Recall that the odd numbered soils are the top sample and the even numbered soils are the bottom sample. The even numbered (lower) soils may have a steeper slope than the odd numbered (upper) soils. However, the odd numbered soils also tend to have a lower pH. So the effect may be pH or depth related. There may also be some other confounding factor.

Figure 3.10 shows the $\log (Zn^{2+})$ versus percent organic carbon. Some of the groups are still close together, such as Group 2 with soils 16 and 18 at low organic carbon and Group 4 with soils 9, 10 and possibly 7 at high organic carbon. However, the other groups are intertwined in the middle of the figure. Perhaps organic carbon is important in some groups but not all. If this exercise were continued for all soil properties, we would expect to see some soil groups together and others not, depending on the relative importance of each soil property with each group.

In Figs. 3.11 through 3.13, $\log (Zn^{2+})$ is plotted with principal components 1 through 3. Regression equations were fit with each principal component and $\log (Zn^{2+})$. Soils 11 and 12 were left out of the regression for the first principal component because these soils are very negative in PC1 and relatively low in $\log (Zn^{2+})$. The purpose of fitting regression equations with each of the principal components and $\log (Zn^{2+})$ was done to examine if the principal components describe $\log (Zn^{2+})$.

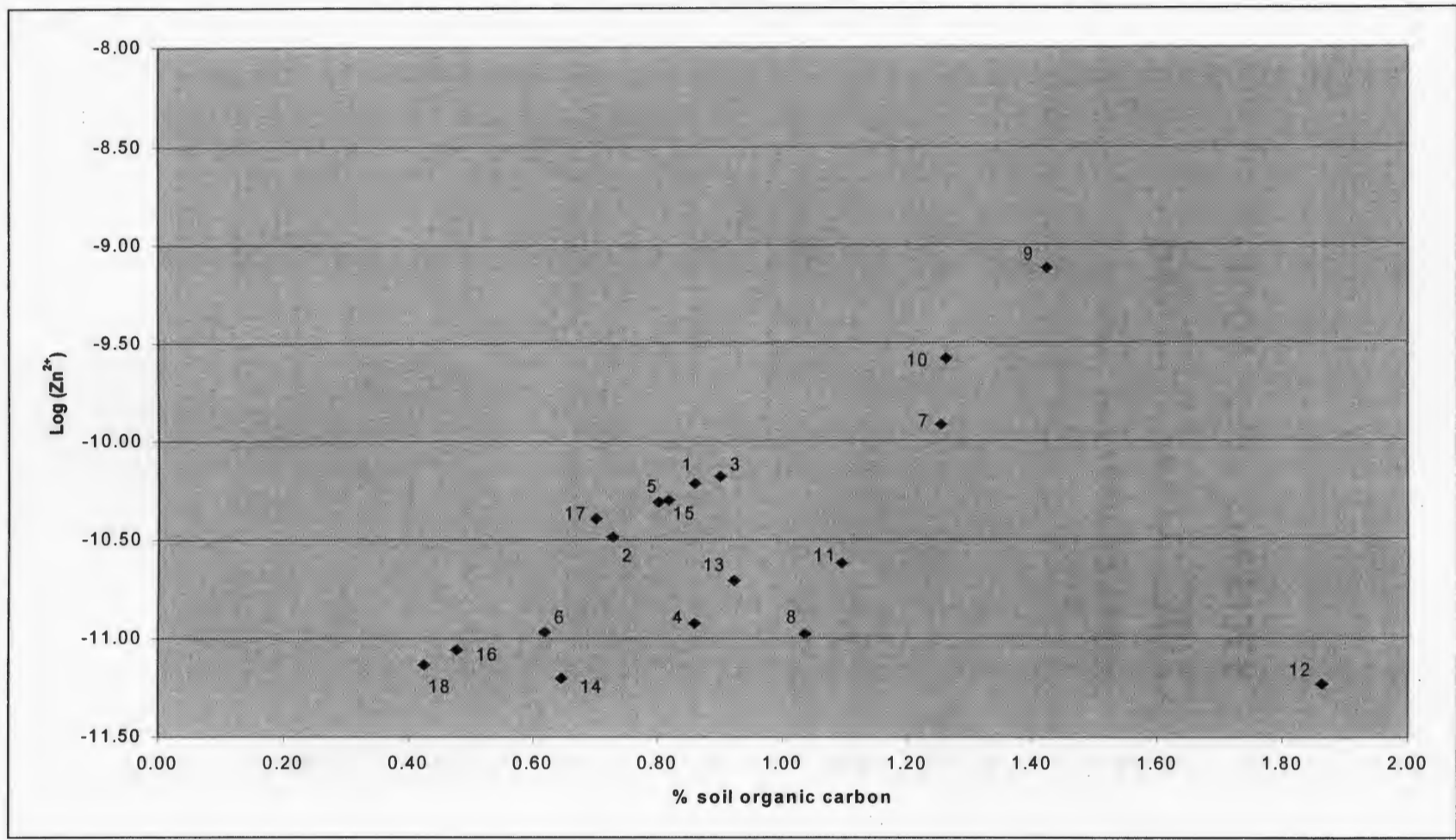


Fig. 3.10. $\text{Log}(Zn^{2+})$ plotted with percent soil organic carbon. Numbers correspond to soil sample numbers.

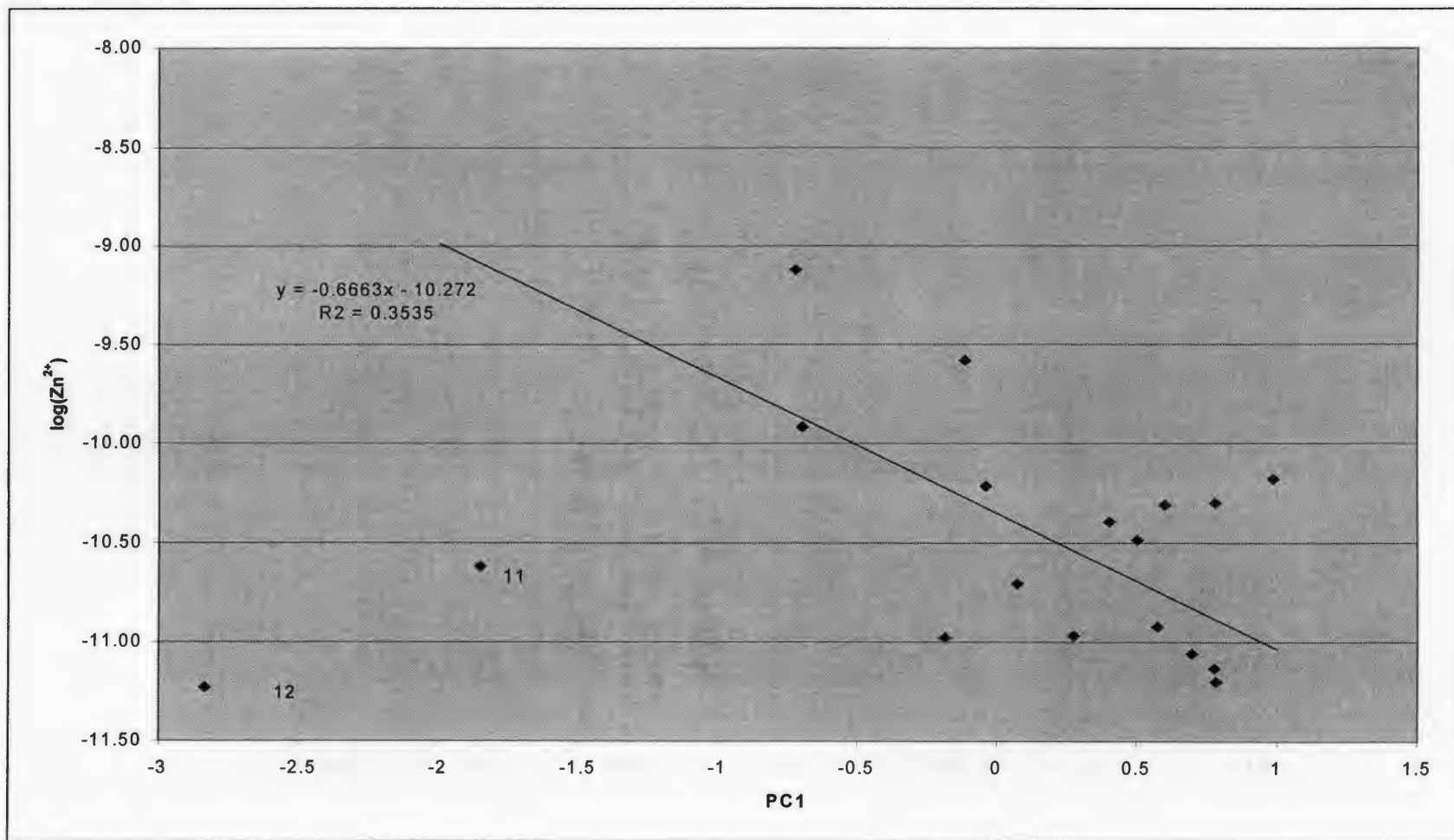


Fig. 3.11. Log (Zn^{2+}) plotted with principal component 1. The regression equation was fit without soils 11 and 12.

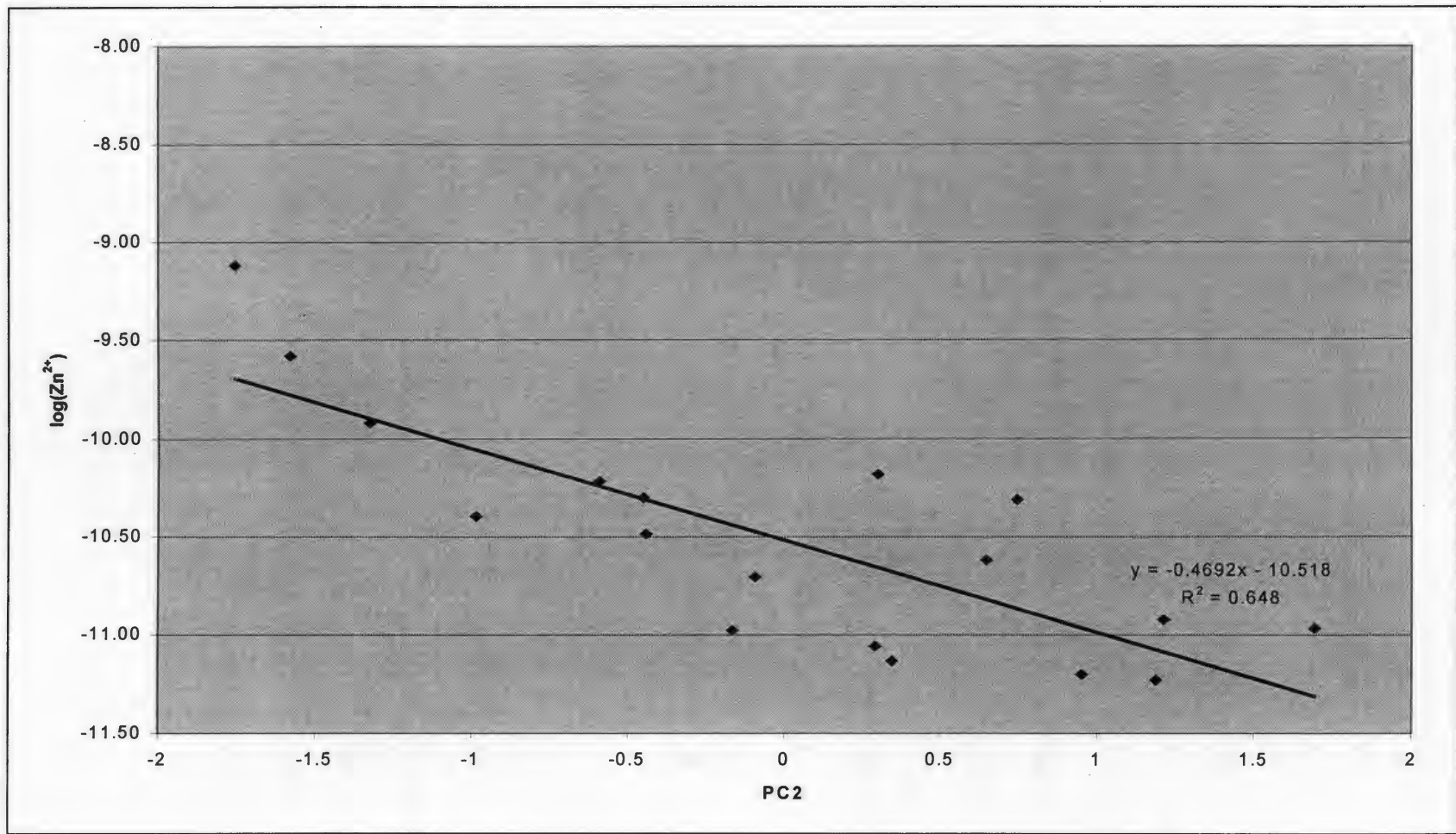


Fig. 3.12. $\log(\text{Zn}^{2+})$ plotted with principal component 2.

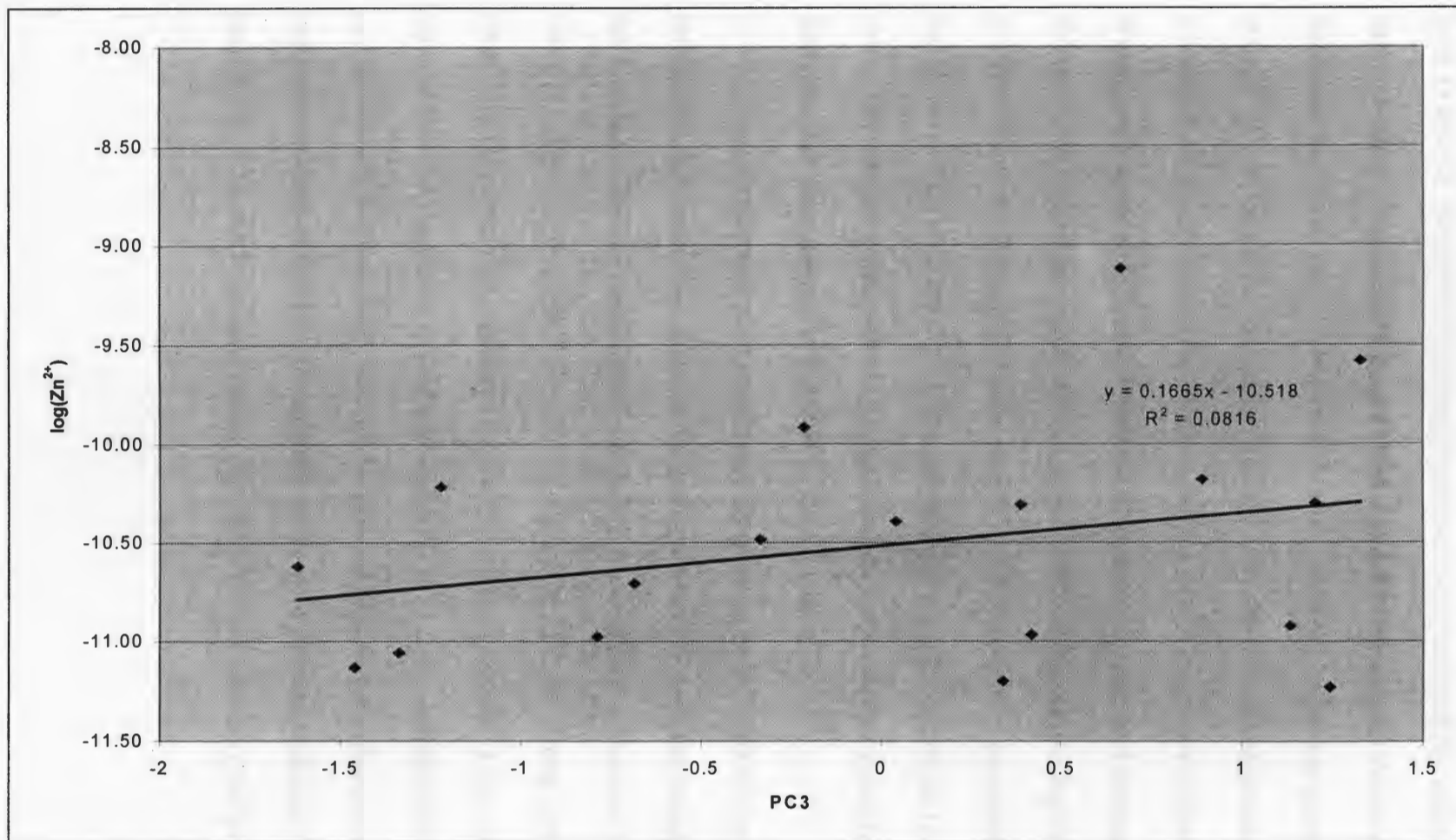


Fig. 3.13. $\log(\text{Zn}^{2+})$ plotted with principal component 3.

Figure 3.11 shows a decrease in free Zn activity as PC1 increases in all soils except for soils 11 and 12. Recall PC1 is strongly positive in clay and soil Zn, and negative in carbon content. These results suggest that increased clay and soil Zn are related to decreased free Zn activity, and increased carbon content is related to increased free Zn activity. These results are somewhat different from the multiple regression results in Chapter 2. Correlation coefficients show that $\log(\text{Zn}^{2+})$ is positively correlated with organic carbon and soil Zn and negatively correlated with clay and inorganic carbon. However, the regression coefficient of inorganic carbon is positive (Eq. [11] of Chapter 2). The R-squared for this regression with PC1 is 0.35, which is somewhat low. So, the regression of PC1 with $\log(\text{Zn}^{2+})$ does not describe the behavior of $\log(\text{Zn}^{2+})$ in these soils. The multiple regression of Chapter 2 may be more relevant to $\log(\text{Zn}^{2+})$ than the first principal component is to $\log(\text{Zn}^{2+})$.

Similar results are seen in the regressions of $\log(\text{Zn}^{2+})$ with the second and third principal components. The second principal component is the most strongly correlated of the first three principal components with $\log(\text{Zn}^{2+})$ with an R-squared of 0.65 (Fig. 3.12). Since pH plays a strong role in free Zn activity and in PC2, the strong relationship is not surprising. However, the regression of pH by itself with $\log(\text{Zn}^{2+})$ has a greater R-squared than the regression of PC2 with $\log(\text{Zn}^{2+})$. PC2 also incorporates inorganic carbon strongly and positively, and this trend could explain the differences in the regressions. There is significant variability in inorganic carbon with free Zn activity. As seen in Fig. 3.13, the R-squared for the regression of PC3 with $\log(\text{Zn}^{2+})$ is small at 0.08.

Summary of PCA

PCA of the 18 soils from eastern Colorado farms showed that 84 % of the variability in the soils was accounted for by the first two principal components. Four groups of soils emerged when the principal components were plotted against each other. The groups could be seen in plots of soil properties versus $\log \text{Zn}^{2+}$ activity.

Principal components may help illustrate the sources of variability in soils. PCA can also introduce groupings in soils by soil chemical properties. However, relationships between principal components and $\log \text{Zn}^{2+}$ activities were weaker than the relationships between soil chemical properties and $\log \text{Zn}^{2+}$ activities described by multiple regression analysis.

The lack of strong relationships involving Zn solubility and principal components does not mean that there are no relationships between principal components and nutrient availability in these soils. Future investigations may use PCA to explore relationships between soil properties and nutrient availability in soils. Larger data sets may be more applicable to PCA and more enlightening in terms of nutrient availability.

Results of path analysis

The results of the correlation and multiple regression for the standardized variables are given in Tables 3.4 and 3.5. The correlation coefficients in Table 3.4 are used in the equations above as the r_{ij} 's ($i=1$ to 5, $j=1$ to 5). The direct effects of the path coefficients are shown in Table 3.5 as the parameter estimates of the multiple regression. These values are also the P_{i6} values in the equations above ($i=1..5$).

Table 3.4. Correlation coefficients and corresponding p-values of standardized variables in Model 1. These values correspond to the two-way arrows of the path diagram.

	pH	OC	clay	Zn_T	log(IC+1)
pH	1	-0.23479	0.22137	-0.08772	0.5832
	0	0.3483	0.3773	0.7293	0.0111
OC	-0.23479	1	-0.60614	-0.66229	0.3818
	0.3483	0	0.0077	0.0027	0.1179
clay	0.22137	-0.60614	1	0.75387	-0.0908
	0.3773	0.0077	0	0.0003	0.7200
Zn_T	-0.08772	-0.66229	0.75387	1	-0.58796
	0.7293	0.0027	0.0003	0	0.0103
log(IC+1)	0.5832	0.3818	-0.0908	-0.58796	1
	0.0111	0.1179	0.7200	0.0103	0

Table 3.5. Analysis of variance table from SAS for the standardized variables in Model 1. The parameter estimates are the direct effects of the variables on $\log(\text{Zn}^{2+})$.

Analysis of Variance					
Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	5	13.71104	2.74221	10.01	0.0006
Error	12	3.28652	0.27388		
C Total	17	16.99756			
Root MSE		0.52333		R-square	0.8066
Dep Mean		0.00002		Adj R-sq	0.7261
C.V.		2743569			

Parameter Estimates					
Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	-0.0000701	0.1234	-0.001	0.9996
pH	1	-0.687	0.2002	-3.43	0.0050
OC	1	0.334	0.2083	1.60	0.1346
clay	1	-0.503	0.2727	-1.85	0.0898
Zn _T	1	0.801	0.3244	2.47	0.0296
log(IC+1)	1	0.232	0.2830	0.82	0.4276

Path analysis results are given in Table 3.6 as suggested by Williams et al. (1990). The effects of the predictor variables are read across each row, with direct effects in the column of the same variable name as the row title and indirect effects in the columns corresponding to the other variables. To help distinguish direct from indirect effects, the direct effects are italicized. For example, the direct effect of pH on $\log(\text{Zn}^{2+})$ is -0.69 and the indirect effect of pH through organic carbon has a value of -0.078 . These values represent the change in $\log(\text{Zn}^{2+})$ as pH increases 1 unit.

The correlation coefficients listed in the “r” column in Table 3.6 represent the sum of all relationships between the variable of that row and $\log(\text{Zn}^{2+})$. For example the correlation between pH and $\log(\text{Zn}^{2+})$ is -0.81 . Note that this value is the correlation coefficient of the standardized variables with $\log(\text{Zn}^{2+})$ as well as the sum of each row (within round-off error). Thus the rows represent the decomposition of the effects of each predictor on $\log(\text{Zn}^{2+})$.

The overall R-squared for this model is 0.81 and indicates that 81 % of the variability of the standardized $\log(\text{Zn}^{2+})$ is explained by the five variables of pH, organic carbon, inorganic carbon, clay and total soil Zn. A large part of the variability of $\log(\text{Zn}^{2+})$ is explained by the model.

Examination of the direct effects reveals that the greatest values are for pH (-0.69) and total soil Zn (0.80). As expected, an increase in pH corresponds to a decrease in $\log(\text{Zn}^{2+})$ and an increase in total soil Zn corresponds to an increase in $\log(\text{Zn}^{2+})$. Also from the table one can see that the direct effect of clay is relatively large at -0.50 , where increased clay content corresponds to decreased $\log(\text{Zn}^{2+})$. The direct effect of organic

Table 3.6. Results of path analysis for Model 1. The effects of the predictor variables are read across each row, with direct effects in the column of the same variable name (along the diagonal) and indirect effects in the columns corresponding to the other variables. Direct effects are italicized.

	pH	OC	clay	Zn_T	IC	r
pH	<i>-0.69</i>	-0.078	-0.11	-0.070	0.14	-0.81
OC	0.16	<i>0.33</i>	0.30	-0.53	0.089	0.36
clay	-0.15	-0.20	<i>-0.50</i>	0.60	-0.021	-0.28
Zn_T	0.060	-0.22	-0.38	<i>0.80</i>	-0.14	0.12
IC	-0.40	0.13	-0.046	-0.47	<i>0.23</i>	-0.47

carbon is a positive correlation with $\log(\text{Zn}^{2+})$. Inorganic carbon has a small positive relation with $\log(\text{Zn}^{2+})$.

Interpretation of the indirect effects of the soil parameters on $\log(\text{Zn}^{2+})$ is more subjective. An interpretation of these effects is presented below. It is interesting to note that large values of the indirect effects may mean something, but it is up to the researcher to decide what that significance might be and to design further studies to pursue some of these interpretations.

The indirect effects of pH are small, and the total effect of pH on $\log(\text{Zn}^{2+})$ is similar to the direct effect of pH. The overall correlation coefficient of pH and $\log(\text{Zn}^{2+})$ is the largest of all variables chosen in this model.

Organic carbon has intermediate values for indirect effects through clay (0.30) and total soil Zn (-0.53). The positive indirect effect of organic carbon through clay results mathematically from the product of the negative correlation between these variables and the negative direct effect of clay ($r_{23} * p_{36}$ in Eq. [2]). For the soils sampled, the surface soil generally had more organic carbon and less clay, whereas the subsurface layer had more clay and less organic carbon. Because the negative correlation between organic carbon and clay may be more circumstantial than causal, the indirect effect may not be meaningful. One interpretation might be that the organic carbon fraction associated with clay particles might increase the $\log \text{Zn}^{2+}$ activity. The indirect effect of organic carbon through total soil Zn (-0.53) indicates that organic carbon may decrease Zn solubility through some fraction of Zn in soil. However, this interpretation may not be valid, since it contradicts the direct effect of OC on $\log(\text{Zn}^{2+})$ as positive.

The largest indirect effect of clay is through soil Zn (0.60). This value is positive, which suggests that clay may contribute to a large portion of the soluble Zn in the total pool of soil Zn. This seems to be in contrast to the direct effect of clay on $\log(\text{Zn}^{2+})$ and the overall effect of clay on $\log(\text{Zn}^{2+})$ which are both negative.

The total effect of inorganic carbon on $\log(\text{Zn}^{2+})$ is the opposite relationship between inorganic carbon and $\log \text{Zn}^{2+}$ activity (a negative value) from what is expected from the direct effect (a positive value). The indirect effects of inorganic carbon through pH and Zn_{soil} are fairly large and negative, indicating that an increase of inorganic carbon can result in a decrease in $\log(\text{Zn}^{2+})$. The overall effect of inorganic carbon on $\log(\text{Zn}^{2+})$ is negative because the magnitudes of the indirect effects through pH and Zn_{soil} are large and negative. One interpretation of the indirect effect through pH might be that the presence of inorganic carbon could increase pH, which then results in a decrease in $\log(\text{Zn}^{2+})$. Also, the presence of inorganic carbon in soil may decrease the total pool of Zn in the soil effectively by "diluting" the rest of the soil. Soil carbonates may not contain a large source of Zn, so a soil with carbonates may have a smaller fraction of elements such as Zn. Thus inorganic carbon may decrease total soil Zn and result in decreased Zn^{2+} activity. However, this effect may be more circumstantial than causal. The mechanism of the indirect effect of inorganic carbon on Zn^{2+} activity, through total soil Zn content is not entirely clear. Perhaps a different path diagram will allow a more clear interpretation.

Results of path diagram 2

Path diagram 2 (Fig. 3.14) illustrates a different model of Zn^{2+} activity in soils. In the above section, it was clear that interpretations that involved total soil Zn in the first

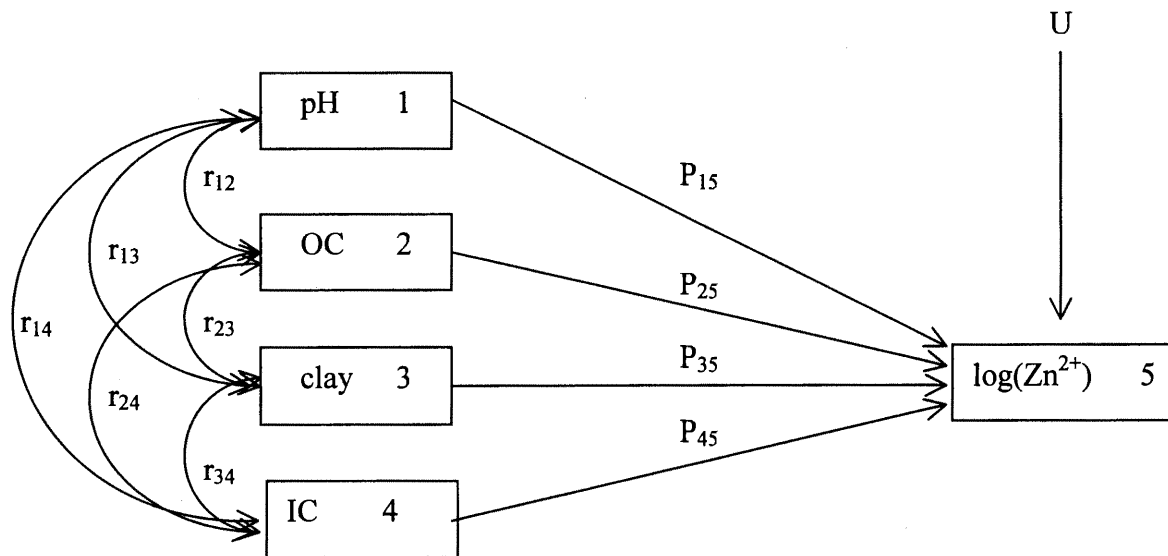


Fig. 3.14. Path diagram for the model of four soil parameters to predict $\log(\text{Zn}^{2+})$ – Model 2. Numbers in the boxes with variable names represent the number associated with that variable in the subscripts of r and P . The variable U represents the standardized residual.

model were difficult. This result may have been expected since organic carbon, clay and inorganic carbon may contribute to the overall pool of Zn in the soil. So, the soil Zn term may be redundant in a causal diagram and may be removed. Model 2 (Fig. 3.14) shows the new path diagram with only the four remaining variables predicting $\log(\text{Zn}^{2+})$.

This new model was analyzed for two different situations. First, all soils were included. Second, soil 12 was removed. From previous analysis of this data (Chapter 2), it was concluded that soil 12 was likely an outlier in the organic carbon data, as well as an influential observation in a linear regression with $\log(\text{Zn}^{2+})$. Since the method of path analysis uses similar assumptions and methods as linear regression, it is appropriate to explore the data with and without soil 12.

Table 3.7 gives the results of the path analysis for Model 2, including soil 12. The correlation coefficients (r) between the variables and $\log(\text{Zn}^{2+})$ are the same as in Table 3.6. These coefficients do not change because a correlation coefficient does not change with the number of variables in a model. Regression coefficients, however, do change with different variables. Hence the direct effects of the variables change with the removal of soil Zn as a predictor variable.

Table 3.7 is easier to interpret than Table 3.6 because most of the values in Table 3.7 are small. Soil pH has the largest direct and overall effects on free Zn activity, whereas other variables have small direct effects on $\log(\text{Zn}^{2+})$. Organic carbon has a moderately positive direct effect on free Zn activity. The only other large value in Table 3.7 is the indirect effect of inorganic carbon through pH on $\log(\text{Zn}^{2+})$. As interpreted above, this value suggests that the presence of inorganic carbon may increase pH and thus decrease $\log(\text{Zn}^{2+})$.

Table 3.7. Results of path analysis for Model 2, including soil 12. The effects of the predictor variables are read across each row, with direct effects in the column of the same variable name (along the diagonal) and indirect effects in the columns corresponding to the other variables. Direct effects are italicized.

	pH	OC	clay	IC	r
pH	<i>-0.61</i>	-0.077	0.0081	-0.14	-0.81
OC	0.14	<i>0.33</i>	-0.022	-0.090	0.36
clay	-0.13	-0.20	<i>0.037</i>	-0.021	-0.28
IC	-0.35	0.13	0.0033	<i>-0.23</i>	-0.47

Results of path diagram 2, without soil 12

Results of the correlation and regression analyses of the standardized variables with soil 12 removed from the data are given in Tables 3.8 and 3.9. One can see a benefit of path analysis and decomposition of total effects by comparing these two tables. The final column of Table 3.8 shows the correlation coefficients of each of the predictor variables with $\log(\text{Zn}^{2+})$. Table 3.9 shows the parameter estimates, which correspond to the direct effects of the variables. The parameter estimates are much smaller than the correlation coefficients, indicating that there are some fairly large indirect effects in this model. The results of this path analysis are given in Table 3.10. The direct effects are shown in bold on the diagonal, and the direct effects of pH and OC are large. The direct effect of pH (-0.5) indicates that an increase in pH results in a decrease in $\log(\text{Zn}^{2+})$. The direct effect of OC (0.54) suggests an increase in $\log(\text{Zn}^{2+})$ with an increase in OC. These two independent variables also have large total correlation coefficients with $\log(\text{Zn}^{2+})$.

Several relatively large indirect effects exist in this model. Soil pH has a negative indirect effect of -0.29 on free Zn activity through organic carbon. Increasing pH may decrease Zn activity by an interaction with binding sites on organic matter. This result agrees with the current understanding of metal interactions with organic matter. As pH increases Zn can better compete with protons for binding sites. The positive indirect effect on Zn activity of organic carbon through pH may indicate that increasing organic matter in soil may decrease pH and thus increase $\log(\text{Zn}^{2+})$ or it may increase pH and thus decrease $\log(\text{Zn}^{2+})$.

Table 3.8. Correlation coefficients and corresponding p-values of standardized variables. These values correspond to the two-way arrows of the path diagram in Model 2 without soil 12.

	pH	OC	log (IC)	clay	log (Zn²⁺)
pH	1	-0.54228	0.59268	0.31353	-0.79817
	0	0.0245	0.0122	0.2204	0.0001
OC	-0.54228	1	-0.13785	-0.57847	0.78282
	0.0245	0	0.5978	0.015	0.0002
log (IC)	0.59268	-0.13785	1	0.15653	-0.37066
	0.0122	0.5978	0	0.5485	0.1430
clay	0.31353	-0.57847	0.15653	1	-0.39787
	0.2204	0.015	0.5485	0	0.1137

Table 3.9. Analysis of variance table from SAS for the standardized variables for Model 2 without soil 12. The parameter estimates are the direct effects of the variables on log (Zn²⁺).

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	13.04249	3.26062	13.23	0.0002
Error	12	2.95732	0.24644		
C Total	16	15.99981			
Root MSE		0.49643		R-square	0.8152
Dep Mean		0.00007		Adj R-sq	0.7536
C.V.		689420			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	0.0000712	0.12040	0.000	0.9995
pH	1	-0.53556	0.18926	-2.83	0.0152
OC	1	0.54070	0.17985	3.01	0.0109
log(IC+1)	1	0.000855	0.16128	0.05	0.9586
clay	1	0.08149	0.15329	0.53	0.6047

Table 3.10. Results of path analysis for Model 2 without soil 12. The effects of the predictor variables are read across each row, with direct effects in the column of the same variable name (along the diagonal) and indirect effects in the columns corresponding to the other variables. Direct effects are italicized.

	pH	OC	clay	IC	r
pH	<i>-0.54</i>	-0.29	0.026	0.0051	-0.80
OC	0.29	<i>0.54</i>	-0.047	-0.0012	0.78
clay	-0.17	-0.31	<i>0.081</i>	0.0013	-0.40
IC	-0.32	-0.075	0.013	<i>0.0086</i>	-0.37

The direct effects of clay and inorganic carbon are small, 0.081 and 0.0086, respectively. There is a small negative indirect effect of clay through pH on free Zn activity (-0.17). This result suggests that increased clay content may be associated with decreased pH and thus increased $\log(\text{Zn}^{2+})$, or with increased pH and decreased $\log(\text{Zn}^{2+})$. A larger indirect effect on free Zn activity is the effect of clay through organic carbon (-0.31). Increased clay in these soils may be associated with decreased organic matter, and this could result in a decrease in $\log(\text{Zn}^{2+})$. The negative indirect effect of inorganic carbon through pH on $\log(\text{Zn}^{2+})$ suggests (as above) that the presence of inorganic carbon could increase the pH and thus decrease free Zn activity.

Summary of path analysis

Three different situations were examined by path analysis to investigate the cause and effect of soil parameters on $\log(\text{Zn}^{2+})$. Model 1 included five soil parameters to explain free Zn activity in soils: pH, organic carbon, inorganic carbon, clay and total soil Zn. Of these five soil parameters, pH and total soil Zn had the largest direct and total effects on free Zn activity. Indirect effects of organic carbon, inorganic carbon and clay through total soil Zn were large. Other relatively large indirect effects were the effect of inorganic carbon through pH, the effect of organic carbon through clay, and the effect of total soil Zn through clay.

The second model included only four of the soil parameters of the first model. Total soil Zn was discarded because of difficulties interpreting the indirect effects that involved total soil Zn. The results from this analysis showed that pH had the largest

direct and total effects on $\log(\text{Zn}^{2+})$. There was a strong indirect effect of inorganic carbon through pH on $\log(\text{Zn}^{2+})$. The other effects were relatively small.

The third simulation used Model 2, but did not include soil 12. Soil 12 is an outlier with respect to organic carbon and $\log(\text{Zn}^{2+})$. With soil 12 discarded, both pH and organic carbon had large direct and total effects on $\log(\text{Zn}^{2+})$. Indirect effects of pH through organic carbon, organic carbon through pH, clay through organic carbon, and inorganic carbon through pH were strong. It is interesting that the largest effects of clay and inorganic carbon were through another variable, organic carbon and pH, respectively.

Model 2 without soil 12 seems to be the most important of the cases examined. There is less ambiguity in the interpretation of results when total soil Zn is discarded from the model. It is appropriate to remove soil 12 since it was justifiably removed from the multiple regression analysis.

The relationships between organic carbon, pH and metal solubilities, the effect of clay on organic carbon and metal solubilities, or the effects of inorganic carbon on pH and metal solubilities could be addressed through future research evolving from this path analysis. These analyses suggest important interactions between soil properties and micronutrient solubilities in soils.

Further exploration of path analysis in soils may also be the subject of future research. Other more complicated models may be conceived and developed in future study. (See, for example, Fig. 3.15.)

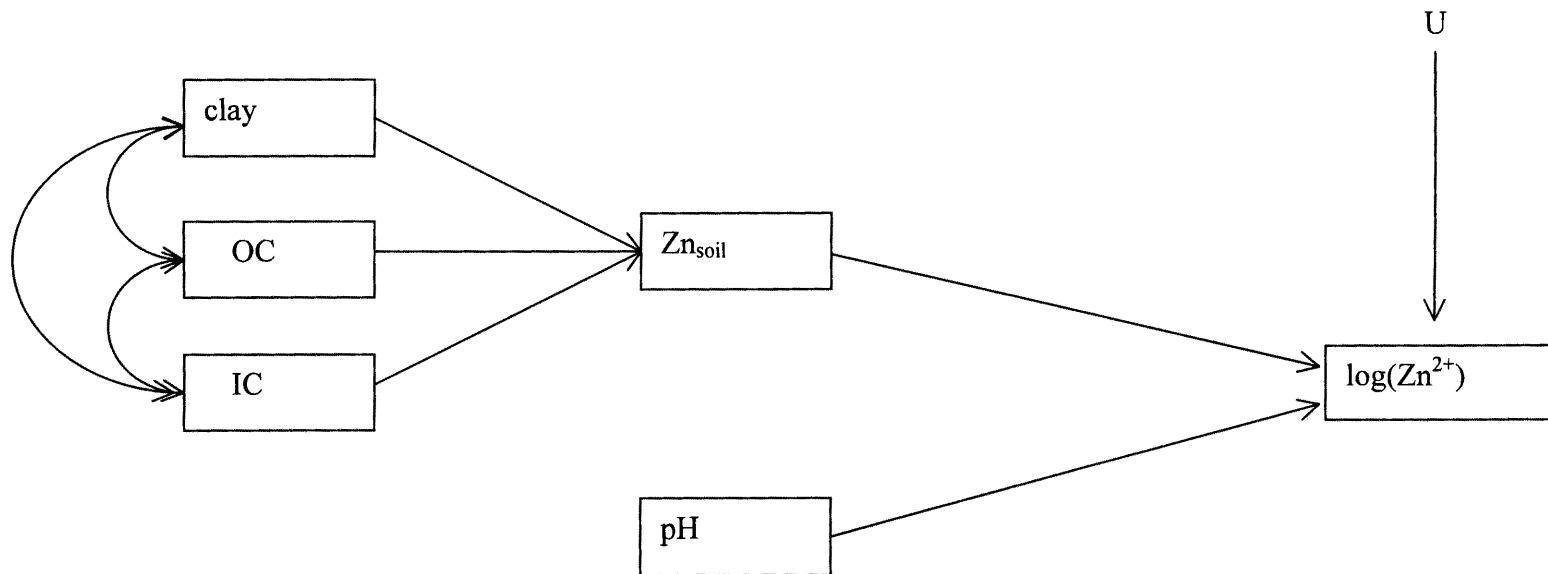


Fig. 3.15. A potential path diagram for the model of five soil parameters to predict $\log(\text{Zn}^{2+})$ with total soil Zn predicted by three parameters. The variable U represents the standardized residual.

Conclusions

PCA and path analysis have some similar conclusions. Results from both methods suggest that total soil Zn content is not important for these analyses in these soils when pH, organic carbon, inorganic carbon and clay content are measured. Soil Zn content may be an important predictor in soluble Zn concentrations; however, when trying to understand the mechanisms involved in Zn solubility (for path analysis) or when grouping soils based on soil properties (for PCA), total soil Zn concentrations are not as important as other soil parameters.

Both of these methods have some advantages over multiple regression analysis. PCA and path analysis account more for the interactions between variables than does multiple regression analysis. Multiple regression analysis can include interactions as the product of two or more variables. However, path analysis decomposes interaction terms in more detail than does regression analysis. PCA allows many different relationships between the variables, especially when certain principal components are dominated by certain input variables. For example, in this study, pH and inorganic carbon dominated PC2. From this grouping and from path analysis results, one can see that there may be a relationship between pH and inorganic carbon for these soils.

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CHAPTER 4

MODELING THE SOLUBILITY CONTROL OF Zn BY ORGANIC MATTER IN SOIL WITH MINTEQA2

Summary

Adsorption of Zn on organic matter may be an important solubility control mechanism of Zn in soils. Previous work has shown there are statistically significant relationships between $\log \text{Zn}^{2+}$ activities and organic matter in soils. (See Chapters 2 and 3.) The objective of this study is to explore the adsorption of Zn to organic matter using the chemical equilibrium model, MINTEQA2 and to compare the model results with experimental data. To model Zn adsorption to organic matter, the equilibrium dissociation constants for the Suwannee River dissolved organic matter (DOM) were used. Experimental and modeling results agreed well. Adsorption onto organic matter may control Zn solubility in acidic to neutral soils, while precipitation reactions may control Zn in alkaline soils.

Introduction

The heterogeneity of soil organic matter makes it difficult to understand the mechanisms involved in the adsorption of metals to organic matter. Soil organic matter (SOM) includes detrital organic particulates, organic coatings on clays and minerals, and

soil microorganisms. It is composed mostly of carbon, with different functional groups contributing to interactions with the soil environment. The most significant functional groups in soils are carboxyl, carbonyl, phenolic OH, amino (-NH₂), imidazole (ring NH), and thiol (-SH) groups. Most of these functional groups allow protons to exchange with the soil solution, which makes adsorption of metals to these ligand sites pH dependent. Metal adsorption is also dependent on the number and environment of each type of site. In addition, the physical structure of organic matter can vary in solution, which can change metal adsorption and solubility. As pH increases, the molecule can stretch out because of the repulsion of negatively charged functional groups. But when a metal is added, the molecule can collapse around the metal, possibly occluding it and decreasing the metal solubility. For more information on the structure and binding of soil organic matter see Sposito (1984) and Stevenson (1994).

There are two different approaches that can be used in modeling the adsorption of trace metals to soil organic matter. An empirical approach fits mathematical expressions to experimental data that typically describe concentration of adsorbed metal as a function of metal concentration in solution. This approach may be considered unsatisfactory because it is often not applicable to solution conditions other than those of the experiment (Davis and Kent, 1990).

An alternative approach is to use a mechanistic model of adsorption. These models tend to express binding of the metal to organic matter in terms of a reaction of the form: $SOM + M \leftrightarrow SOM-M + H$. These models can take into account changes in ionic strength, pH, and ligand concentration. An example of this type of model is the one used

in MINTEQA2 (Allison et al., 1991), which models the complexation of trace metals with DOM.

Adsorption of Zn on organic matter may be an important solubility control mechanism of Zn in soils. Previous work has shown there are statistically significant relationships between $\log \text{Zn}^{2+}$ activities and organic matter in soils. (See Chapters 2 and 3.) The objectives of this current study are to model the adsorption of Zn on organic matter using MINTEQA2 and to compare the model results with experimental data of $\log \text{Zn}^{2+}$ activity versus pH.

Methods

The soils

Eighteen soils were collected from three farms in eastern Colorado: CF, LP, and Weld farms. These farms appeared to have three different sections, as decided by crop health. Each farm was divided into the three sections and sampled at two depths to result in 18 soil samples. More information on the soils and farms can be found in Chapter 2. $\log \text{Zn}^{2+}$ activity was measured by chelation (Ma and Lindsay, 1990; Norvell and Lindsay, 1969). Soil pH was measured along with the chelation method at 5 days in a 1:2 soil to solution ratio.

The model

The chemical speciation model, MINTEQA2 (Allison et al., 1991) was used to model Zn precipitation and adsorption to organic matter over a range of pH. The adsorption model used in MINTEQA2 is based on work by Dobbs et al. (1989). This

model treats organic matter as a complex substance that contains many different ligand sites. The model assumes that humic substances contain a large number of sites that are normally distributed about an average formation constant ($\log K$). It includes the competition of protons and metals for ligand sites. The mean $\log K$ values in the MINTEQA2 database describe the reactions of protons and trace metals with Suwannee River dissolved organic matter (DOM). These constants were determined using lanthanide ion probe spectroscopy (Perdue et al., 1984; Susetyo et al., 1991).

To apply model calculations to data from the laboratory in the current study, it was assumed that the Suwannee River DOM is a good analogue of the solid organic matter in the soils of this study. Thus the binding constants of protons and Zn to the Suwannee River DOM were applicable to soil organic matter. Little other data are available for binding of metals to SOM. This assumption allows the use of MINTEQA2 to model the adsorption of organic matter without measuring binding constants in the laboratory. In addition, this assumption allows dissolved organic matter (a solution species) to represent soil organic matter (a solid). The solution species Zn-DOM was considered to be a solid phase instead of a dissolved phase. An exact replication of the soil data by the model is not expected, although general trends may be seen.

Input to MINTEQA2 included total DOM concentration, total Zn concentration, and a sweep of pH from 4.3 to 10. The total DOM concentration was taken partially from Suwannee River data and partially from the soil data. For the Suwannee River organic matter, the site density was 5.0×10^{-4} moles of sites per gram organic matter, with 48.79 % carbon. The soils had an average of 0.9 % organic carbon. The soil to solution

ratio was 1:2. Hence the total DOM concentration was estimated to be 0.0046 moles of sites per liter.

The total Zn concentration was the same for all pH with a value of 10^{-8} mol L⁻¹. This value is intermediate for what is expected over the pH range of the input. The value of total Zn includes the Zn adsorbed to organic matter, which is different from what is considered when Zn forms a mineral precipitate. The mineral form of Zn is not included in total soluble Zn. There could be error in the calculations for Zn²⁺ activity because of this assumption; however, general trends should be observed.

In order to account for the possibility of a Zn precipitate forming, soil-Zn (Lindsay, 1979) was entered as a possible solid. When the ion activity product exceeds the stability constant, soil-Zn will precipitate.

Two databases were used with MINTEQA2. The Lindsay revised database (Lindsay and Ajwa, 1995) was used for the solution species and for the equilibrium constants for soil-Zn. The complig.dbs database (MINTEQA2 Version 3.11) was used for the constants of the adsorption reactions involving Suwannee River DOM.

Results and Discussion

The speciation of Zn for the MINTEQA2 simulation of Zn adsorbed to organic matter is plotted with pH in Fig. 4.1. Zn²⁺ is the dominant species in acidic and neutral solutions. The ZnOH⁺ species is dominant from roughly pH 7.5 to 9, and Zn(OH)₂⁰ becomes dominant at pH greater than 9. At low to neutral pH, Zn solubility is controlled by adsorption to organic matter. In alkaline conditions, soil-Zn controls Zn solubility.

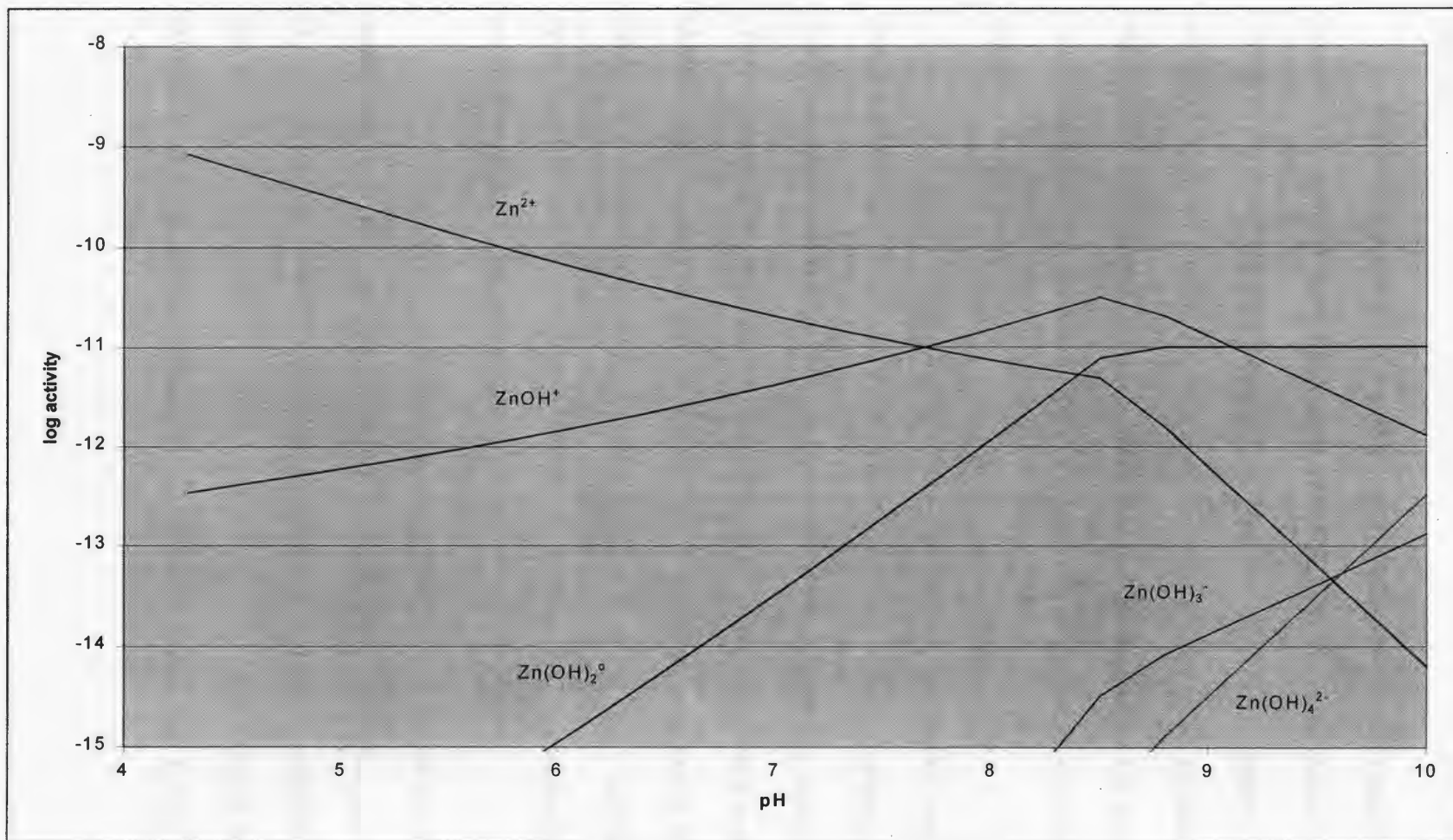


Fig. 4.1. Speciation of Zn plotted with pH for a model simulation of Zn adsorption to organic matter. Total soluble Zn concentration was 10^{-8} mol L⁻¹, with soil-Zn allowed to precipitate. Concentration of OM was 0.046 mol sites L⁻¹.

The change of slope of the $\log(\text{Zn}^{2+})$ line at about pH 8.5 indicates the precipitation of soil-Zn.

Figure 4.2 is a graph of $\log(\text{Zn}^{2+})$ activity with pH when organic matter (OM) controls Zn solubility (OM-Zn) and when soil-Zn controls Zn solubility (soil-Zn). In addition, the data from the current study of Zn^{2+} activity in 18 Colorado soils are included. One can see that the data do not lie exactly along either of these lines, but are closer to the soil-Zn line. However, it appears that the data might fall along the solubility lines if the lines were shifted up and to the right. This shift could occur with changes in equilibrium constants.

Figure 4.3 illustrates the alignment of the data with solubility lines that are parallel to the OM-Zn and soil-Zn lines of Fig. 4.2. A possible solubility control for Zn that fits the data well at high pH is franklinite with Fe controlled by amorphous magnetite (Fe_3O_4 amorp) at redox conditions ($pe + pH$) of 12.5. This Fe mineral was recently characterized by Brennan and Lindsay (1998). A pH diagram including several possible Zn solids in soils is given in Fig. 4.4. The franklinite- Fe_3O_4 amorp solubility line shifts up or down depending on redox conditions. A $pe + pH$ of 12.5 is within the realm of reasonable redox conditions for soil.

The OM-Zn line (Fig. 4.3) either corresponds to the adsorption of Zn to organic matter with a greater dissociation constant than that of Zn with Suwannee River DOM or to a solution which contains a larger concentration of total Zn. It is reasonable to believe that the total Zn concentration could be different from the input value of 10^{-8} M. This value was chosen somewhat arbitrarily. To obtain a better number for the total soluble

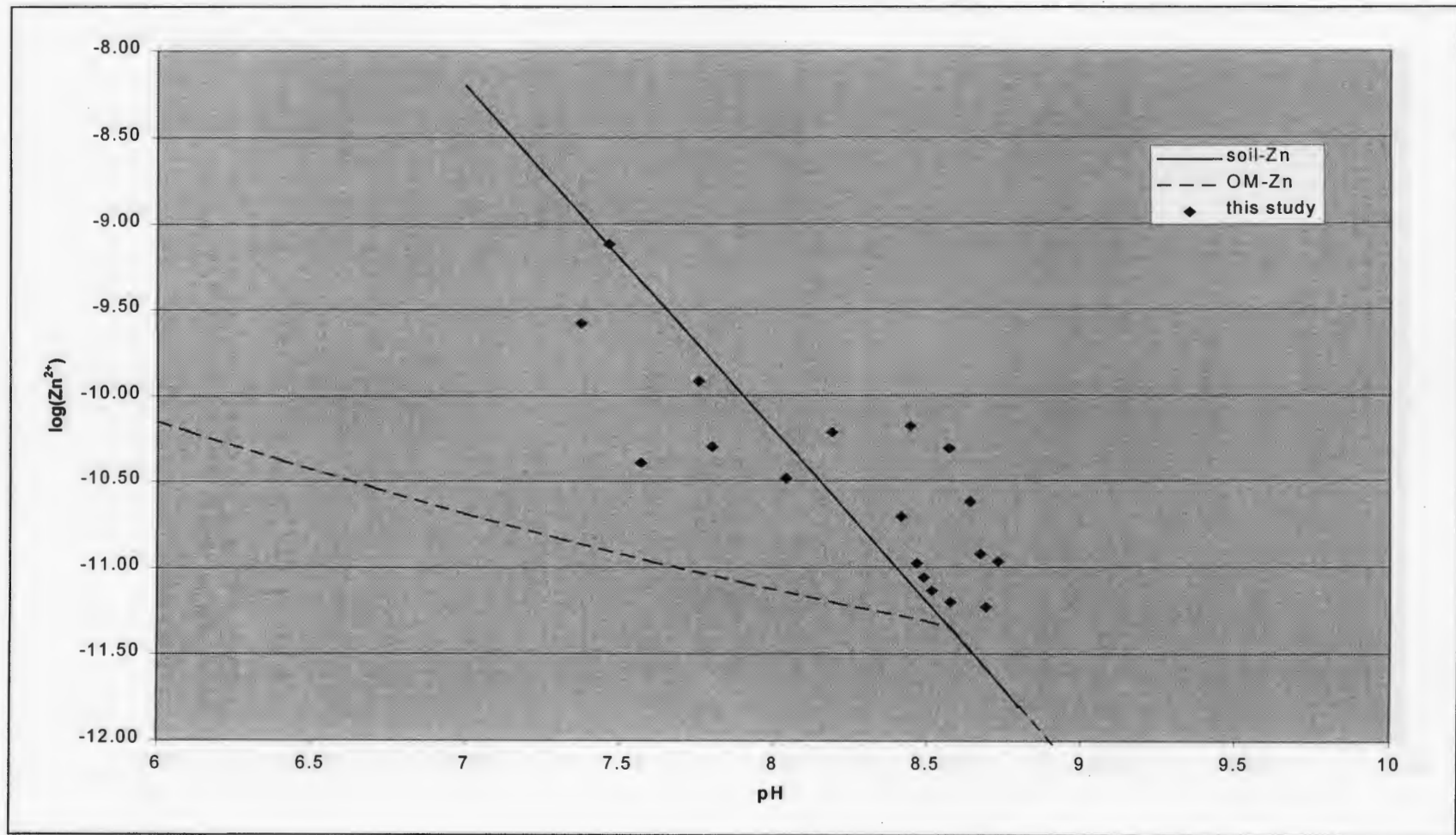


Fig. 4.2. Log Zn²⁺ activity plotted with pH for soil-Zn, the simulated organic matter control of Zn, and for the soils of this study. For the organic matter simulation, total soluble Zn concentration was fixed at 10⁻⁸ mol L⁻¹ with soil-Zn allowed to precipitate. Soil-Zn precipitated at a pH just over 8.5.

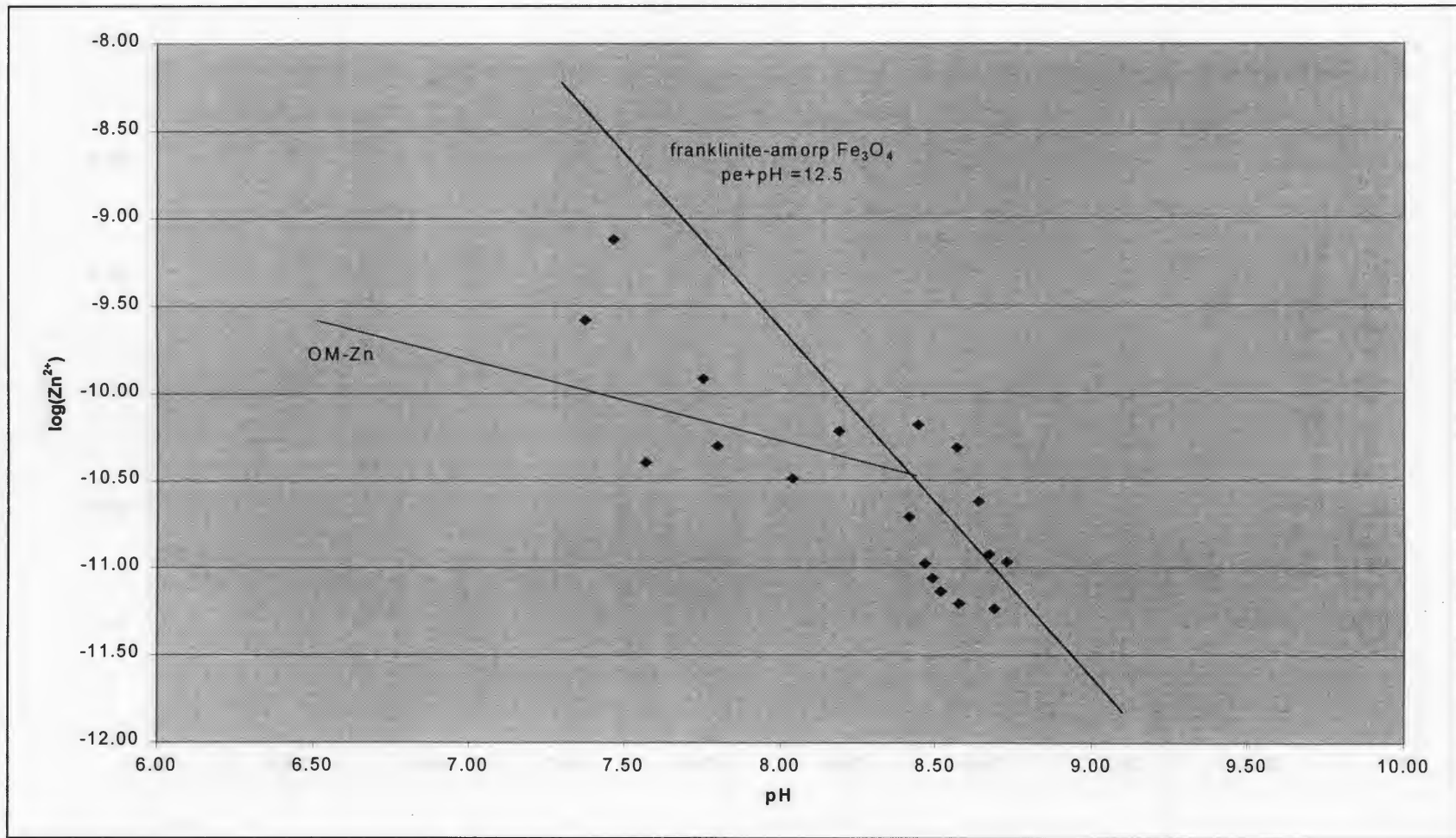


Fig. 4.3. Log Zn²⁺ activity is plotted with pH for the data from this study. Franklinite with Fe controlled by amorphous magnetite (Brennan and Lindsay, 1998) at pe + pH 12.5 is included with an organic matter control of Zn similar to the Suwannee River fulvic acid, but with a greater dissociation constant or greater total Zn concentration. These lines are parallel to those of Fig. 4.2.

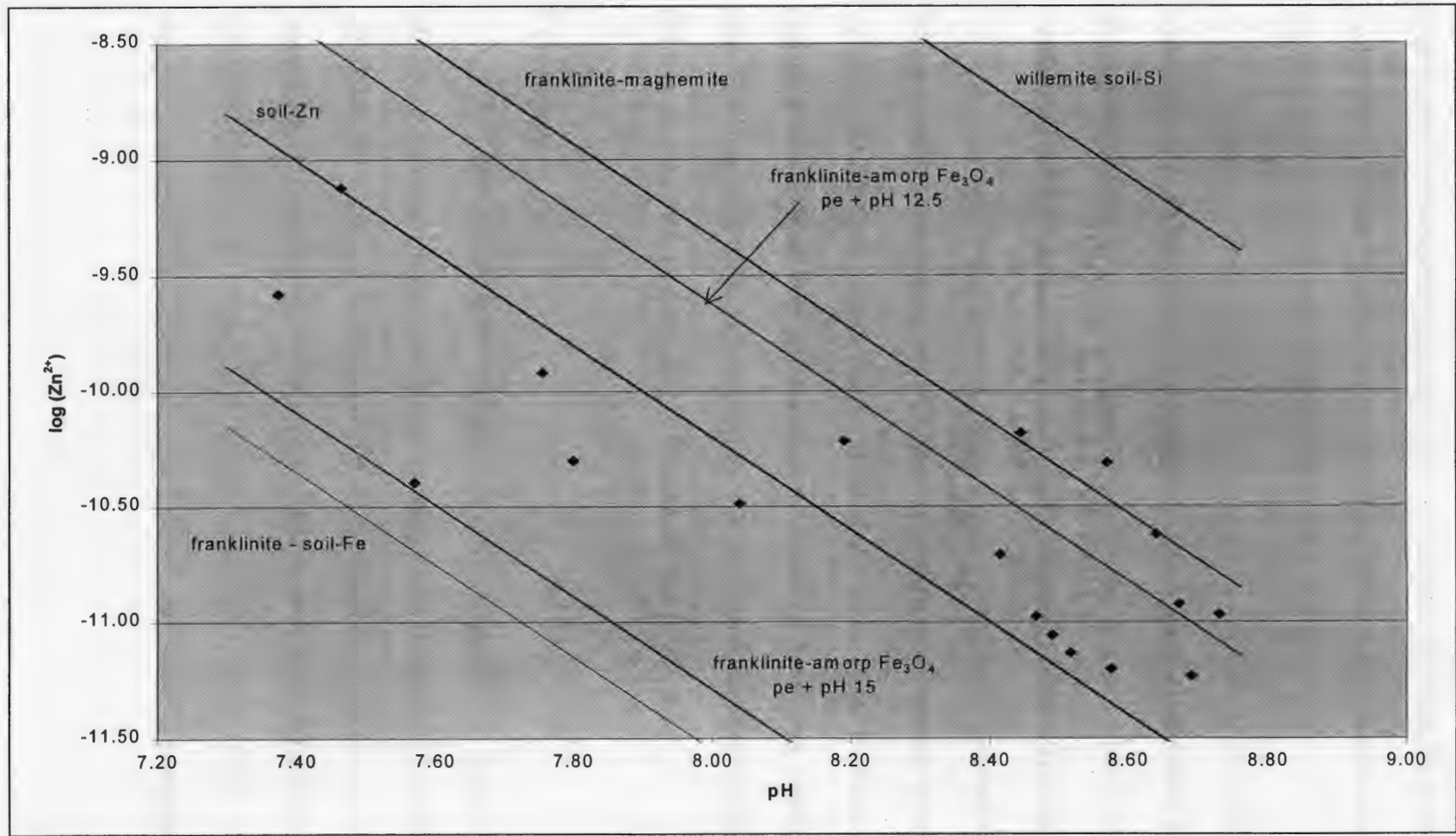


Fig. 4.4. Solubility lines for possible Zn solids in soils. The data from this study fall near the franklinite line with Fe controlled by magnetite at pe + pH 12.5 (Brennan and Lindsay, 1998).

Zn concentration, which includes Zn adsorbed to organic matter, some kind of extraction must be used that would measure this value. In addition, this total Zn concentration would likely vary for the different soils and these values would have to be averaged to compare model results to the experimental soil data set.

It is reasonable to assume that the SOM in the Colorado soils is different from the Suwannee River DOM. First, aquatic and soil organic matter could have different properties and different binding constants with metals. Xia et al. (1997) showed O-containing functional groups complex Zn in the Suwannee River fulvic and humic acids, but S- and O- containing functional groups complex Zn in soil humic substances. Thus different binding constants would be expected between the Suwannee River organic substances and the soil organic matter. Second, the source of the Suwannee River organic matter is likely very different from the source of the organic matter in the soils from Colorado. The difference in vegetation in these areas could contribute to different binding constants and thus the shift in the OM-Zn line in Fig. 4.3.

Conclusions

Zn²⁺ activity data from Colorado soils were compared with simulations of Zn adsorption to organic matter and Zn precipitation using the chemical speciation model MINTEQA2. The model simulations and experimental data support two different solids controlling Zn solubility in two pH regions. At low to neutral pH (below pH 8.5), Zn solubility appears to be controlled by adsorption of Zn to organic matter. At neutral to high pH (above pH 8.5), Zn solubility appears to be controlled by precipitation of

franklinite, with Fe controlled by amorphous magnetite at pe + pH 12.5 or with Fe controlled by maghemite.

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CHAPTER 5

INFLUENCE OF SOIL FACTORS ON AB-DTPA-EXTRACTABLE Zn

Summary

The NH_4HCO_3 – DTPA (AB-DTPA) soil test is used to identify soils of neutral to alkaline pH which may be deficient in micronutrients. There is evidence that extractable Zn is related to soil properties. In this study, AB-DTPA-extractable Zn was measured and correlated to soil chemical properties, such as pH, soil organic carbon and clay content for eighteen neutral to alkaline soils from three farms in eastern Colorado. Soil organic carbon and total soil Zn were statistically significant parameters in a linear regression with AB-DTPA-extractable Zn. Organic matter and clay contents were positively correlated with AB-DTPA-extractable Zn. Results were compared to previous studies to explore the effects of soil properties on extractable Zn.

Introduction

DTPA and NH_4HCO_3 – DTPA (AB-DTPA) soil tests are used to identify soils of neutral to alkaline pH that may be deficient in micronutrients (Lindsay and Norvell, 1978; Soltanpour and Schwab, 1977; Soltanpour and Workman, 1979). These two extraction methods could be considered to measure the bioavailability of micronutrients in soils.

Soil properties can influence extractable Zn and availability of Zn to plants (Benbi and Brar, 1992; Haq and Miller, 1972; Soltanpour et al., 1976). Havlin and Soltanpour (1984) established relationships between the extractability of fertilizer Fe and Zn and various soil properties. Others have illustrated relationships between critical levels of DTPA-extractable Zn and soil properties (Brennan, 1992; Brennan and Gartrell, 1990).

In a previous study (see Chapter 2) Zn^{2+} activity was significantly correlated with pH and soil organic carbon content. Zn^{2+} activity and AB-DTPA-extractable Zn may be correlated with the same soil properties since they are both thought to be related to plant uptake of Zn. Thus AB-DTPA-extractable Zn may also related to pH and organic carbon, although the pH of the AB-DTPA extract is somewhat buffered. The pH begins at 7.6 and rises to about 8.5 because of exposure to atmospheric carbon dioxide.

The goal of this study was to discover if the soil properties that best predict Zn^{2+} activity (Chapter 2) are the same soil properties that best predict AB-DTPA-extractable Zn in soils. The objectives are to measure AB-DTPA-extractable Zn concentrations and to investigate the relationships between AB-DTPA extractable Zn and soil chemical properties for neutral to alkaline soils.

Methods

As discussed in Chapter 2, several soil properties were measured for 18 soils from eastern Colorado. Zn^{2+} activity was measured by chelation (Ma and Lindsay, 1990; Norvell and Lindsay, 1969). The pH of the soil samples was measured in a 1:2 soil to solution ratio at 24 hours. Total soil Zn was measured from a $HNO_3 - HClO_4$ digest, and the solution was analyzed by inductively coupled plasma (ICP) (Hossner, 1996). Percent

inorganic carbon was measured by a modified volumetric method (Wagner et al., 1998; L. Sherrod, personal communication). Total carbon was measured by a Dorhmann DC-190 High-Temperature Total Carbon Analyzer. Percent organic carbon was estimated by the difference between total carbon and inorganic carbon. Cation exchange capacity was measured by the method for soils with carbonates (Sumner and Miller, 1996). Percent clay was measured by hydrometer method (Gee and Bauder, 1986). The concentrations of AB-DTPA-extractable Zn were also measured (Soltanpour and Schwab, 1977; Soltanpour and Workman, 1979).

Statistical analyses were performed using the statistical analysis package SAS (SAS Institute, 1988). Model selection was performed by stepwise selection as well as Akaike's Criteria (AIC) and adjusted R-squared criteria (Neter et al., 1990). Stepwise selection begins with the parameter with the largest correlation coefficient with log (Zn^{2+}). Then each of the other parameters is paired with the first variable and the model with the best R-squared is chosen, provided that the variables are all significant at an alpha of typically 0.15. The selection process continues until no other variables can be added. Variables can also be deleted from the model if the p-values associated with those variables become greater than 0.15 by additions of other variables to the model. AIC and adjusted R-squared selection criteria account for the number of parameters in the model, while calculating the criteria values for every possible model using one to all predictors. The best adjusted R-squared is the highest value, whereas the best AIC is the lowest value (most negative).

Results

Soil properties measured for the eastern Colorado soils are given in Table 5.1. The 24-hour suspension pH ranged from 6.77 to 8.32 for these soils. Total carbon (total C) ranged from 0.44 to 4.41% and inorganic carbon (IC) from 0 to 2.55 %. Organic carbon (OC) ranged from 0.43 to 1.86%. Clay content ranged from 15.6 to 30.0%. Total soil Zn concentration ranged from 25.3 to 78.4 mg kg⁻¹, and the CEC ranged from 15.2 to 39.1 cmol_c kg⁻¹.

AB-DTPA-extractable Zn ranged from 0.10 to 0.77 mg kg⁻¹. These values are all relatively small. Some plants grown on these soils may be Zn-deficient, especially at the lower levels of extractable Zn. Soltanpour (1991) suggests that AB-DTPA-extractable Zn concentrations less than 0.9 mg Zn kg⁻¹ are too small for healthy production of Zn-sensitive crops. Previous studies indicate that the critical level for DTPA-extractable Zn is about 0.8 mg Zn kg⁻¹ for corn (Lindsay and Norvell, 1978), 0.12 - 0.27 mg Zn kg⁻¹ for wheat (Brennan, 1992), and 0.13 to 0.55 mg Zn kg⁻¹ for clover (Brennan and Gartrell, 1990). Critical levels of DTPA-extractable Zn tend to be slightly less than AB-DTPA-extractable Zn (Reed and Martens, 1996).

Correlation coefficients are given for AB-DTPA-extractable Zn and soil properties in Table 5.2. The largest correlation coefficients were between AB-DTPA-extractable Zn and total soil Zn, CEC and percent clay, and CEC and total soil Zn.

Table 5.1. Soil chemical properties for the 18 soils. Horizontal lines separate the 3 farms.

soil #	farm	location	depth	24-hr pH	% total C	% IC	% OC	% clay	total soil Zn mg kg ⁻¹	CEC cmol _c kg ⁻¹	AB-DTPA Zn mg kg ⁻¹
1	CF	A	top	7.84	0.86	0.000	0.86	16.9	64.0	30.6	0.53
2	CF	A	bottom	7.61	0.73	0.000	0.73	23.1	66.5	27.9	0.22
3	CF	B	top	7.74	0.93	0.030	0.90	29.4	78.4	35.1	0.77
4	CF	B	bottom	7.77	1.52	0.67	0.86	30.0	71.9	39.1	0.22
5	CF	C	top	7.76	1.22	0.42	0.80	26.3	74.8	39.1	0.50
6	CF	C	bottom	7.85	1.94	1.32	0.62	27.5	65.7	35.3	0.18
7	LP	A	top	7.29	1.27	0.015	1.25	15.6	55.2	19.2	0.31
8	LP	A	bottom	7.61	1.06	0.021	1.04	19.4	60.2	27.7	0.12
9	LP	B	top	6.77	1.43	0.0035	1.42	16.3	57.9	22.8	0.57
10	LP	B	bottom	6.99	1.27	0.0073	1.26	21.3	64.6	25.3	0.25
11	LP	C	top	8.32	2.15	1.05	1.09	13.1	29.7	15.2	0.16
12	LP	C	bottom	7.94	4.41	2.55	1.86	16.3	25.3	18.8	0.08
13	Weld	1	top	7.50	0.94	0.019	0.92	21.3	61.7	28.3	0.25
14	Weld	1	bottom	7.70	1.07	0.43	0.65	28.8	71.3	37.3	0.15
15	Weld	2	top	7.24	0.83	0.011	0.82	30.0	65.4	27.7	0.27
16	Weld	2	bottom	7.75	0.49	0.015	0.48	23.8	64.7	30.5	0.10
17	Weld	3	top	7.26	0.72	0.022	0.70	23.1	61.7	28.7	0.25
18	Weld	3	bottom	8.04	0.44	0.013	0.43	23.8	66.0	29.0	0.11

Table 5.2. Pearson's correlation coefficients and corresponding p-values for soil properties.

	pH	AB-DTPA Zn	% OC	% clay	total soil Zn	log (IC + 1)	CEC
pH	1	-0.29071	-0.26466	0.0135	-0.25248	0.58320	0.1102
	0	0.2419	0.2885	0.9576	0.3121	0.0111	0.6633
AB-DTPA Zn	-0.29071	1	0.1019	0.07961	0.40398	-0.34604	0.22799
	0.2419	0	0.6874	0.7535	0.0964	0.1595	0.3629
% OC	-0.26466	0.1019	1	-0.60614	-0.66229	0.38184	-0.63351
	0.2885	0.6874	0	0.0077	0.0027	0.1179	0.0048
% clay	0.0135	0.07961	-0.60614	1	0.75387	-0.09083	0.83886
	0.9576	0.7535	0.0077	0	0.0003	0.7200	0.0001
total soil Zn	-0.25248	0.40398	-0.66229	0.75387	1	-0.58796	0.83764
	0.3121	0.0964	0.0027	0.0003	0	0.0103	0.0001
log (IC + 1)	0.58320	-0.34604	0.38184	-0.09083	-0.58796	1	-0.11291
	0.0111	0.1595	0.1179	0.7200	0.0103	0	0.6555
CEC	0.1102	0.22799	-0.63351	0.83886	0.83764	-0.11291	1
	0.6633	0.3629	0.0048	0.0001	0.0001	0.6555	0

Regression analysis

A regression model was fit to the data in order to predict AB-DTPA-extractable Zn (extr-Zn) with the parameters: pH, percent organic carbon (OC), percent inorganic carbon (log (IC +1)), percent clay content (clay) and total soil Zn in mg kg⁻¹ (Zn_T). The logarithm of the percent inorganic carbon was taken because of the narrow range of the inorganic carbon measurements. One was added because some of the soils contained no inorganic carbon, and the log of zero is undefined. The full model, including all parameters is:

$$\text{extr-Zn} = 0.17 \text{ pH} + 0.46 \text{ OC} - 0.21 \log (\text{IC}+1) - 0.011 \text{ clay} + 0.017 \text{ Zn}_T - 2.16 \quad [1]$$

and has an R-squared of 0.51 and a p-value of 0.093. This model is significant at the 0.1 alpha level.

Model selection techniques reduce the number of parameters in the model. For each of the model selections below, the possible predictors included: pH, organic carbon, clay, CEC, total soil Zn, and inorganic carbon. Stepwise selection and AIC criteria showed the best model for predicting AB-DTPA-extractable Zn as:

$$\text{extr-Zn} = 0.35 \text{ OC} + 0.012 \text{ Zn}_T - 0.77 \quad [2]$$

which has an R-squared of 0.41 and a p-value of 0.02. The AIC criterion is -64.2.

Adjusted R-squared criteria showed the best model includes the parameters organic carbon, total soil Zn, and clay content. The model is:

$$\text{extr-Zn} = 0.32 \text{ OC} + 0.015 \text{ Zn}_T - 0.013 \text{ clay} - 0.64 \quad [3]$$

and has an R-squared of 0.46 and a p-value of 0.03. The adjusted R-squared for this model is 0.35.

Equation [2] and Eq. [3] have similar AIC and adjusted R-squared criteria. The AIC for Eq. [2] is -64.2 and for Eq. [3] is -64.0. The adjusted R-squared value for Eq. [2] is 0.33 and for Eq. [3] is 0.35. These differences in the criteria are much smaller than the variation in the data. Both models are good representations of the data.

There could be some confusion about the effect of clay content on AB-DTPA extractable Zn for these soils. The correlation coefficient of clay with extractable Zn is positive, indicating that an increase in clay produces an increase in extractable Zn. (See Table 5.2.) However, in the model above (Eq. [3]), the coefficient of clay is negative, indicating the opposite interaction. In Eq. [3] increased clay results in decreased extractable Zn. This apparent contradiction occurs because clay and organic matter are inversely correlated and because organic carbon is more strongly correlated with extractable Zn than clay content. Perhaps organic carbon and clay are inversely related for these soils because organic matter is higher in the surface soils, but clay is greater in the subsurface soils. Thus the surface soils have more organic matter and less clay, whereas the subsurface soils have more clay and less organic matter. The inverse relationship then may be more circumstantial than causal. The interaction between clay and organic matter results in a counter-intuitive interaction between clay and extractable Zn in Eq. [3]. For the sake of clarity, it may be better to use Eq. [2] than Eq. [3] to model AB-DTPA extractable Zn for these soils.

In previous analysis of these data (see Chapter 2), the validity of the organic carbon measurement of soil 12 was questioned. The current analysis does not support or refute the removal of that data point. In the graph of AB-DTPA-extractable Zn versus organic carbon, there is more spread to the data than in the $\log(\text{Zn}^{2+})$ versus organic

carbon graph (see Fig. 5.1). In addition, for the models given above, soil 12 is not an influential observation according to the Cook's D values for each of those models. Thus, it is not appropriate to remove soil 12 from the data set for this analysis.

Both soils 11 and 12 are outliers in the graph of AB-DTPA-extractable Zn versus total soil Zn (Fig. 5.2). Because total soil Zn is a factor in the regression equations above, it is worthwhile to examine the effect of removing both of these soils. Organic carbon content, total soil Zn and clay content were chosen as important predictors in each of the selection procedures. The resulting model is similar to the one above in Eq. [3]:

$$\text{extr-Zn} = 0.36 \text{ OC} + 0.032 \text{ Zn}_T - 0.024 \text{ clay} - 1.54 \quad [4]$$

and has an R-squared of 0.59 and a p-value of 0.011. Since the removal of soils 11 and 12 did not change the model much, they are not true outliers and should be left in the data set.

Discussion

In this study, AB-DTPA-extractable Zn was correlated most strongly with total soil Zn, organic carbon content and clay content. Regression equations that predict AB-DTPA-extractable Zn included these parameters. Unlike Zn^{2+} activity, AB-DTPA-extractable Zn was not strongly related to pH.

Other studies have explored relationships of soil properties to DTPA-extractable Zn. Li and Mahler (1992) related DTPA-extractable Zn to pH, organic carbon and the interaction term pH x OC (the product of pH and OC) for soils in northern Idaho. They found DTPA-extractable Zn was significantly correlated with OC and the pH x OC interaction term. Joshi et al. (1983) found that pH was a significant predictor of DTPA-

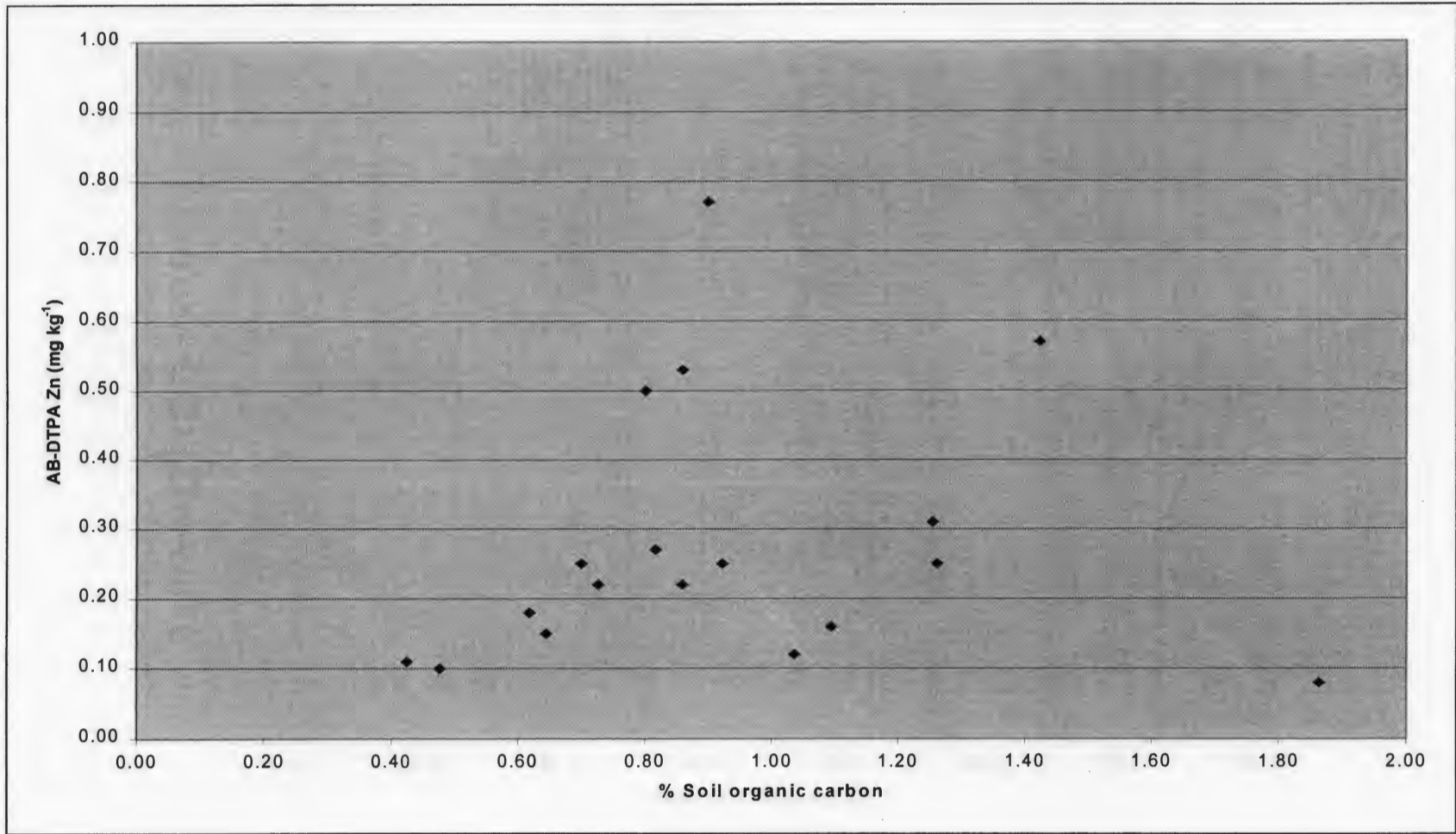


Fig. 5.1. AB-DTPA extractable Zn plotted with soil organic carbon. Soil 12 is the point with the highest measured soil organic carbon content.

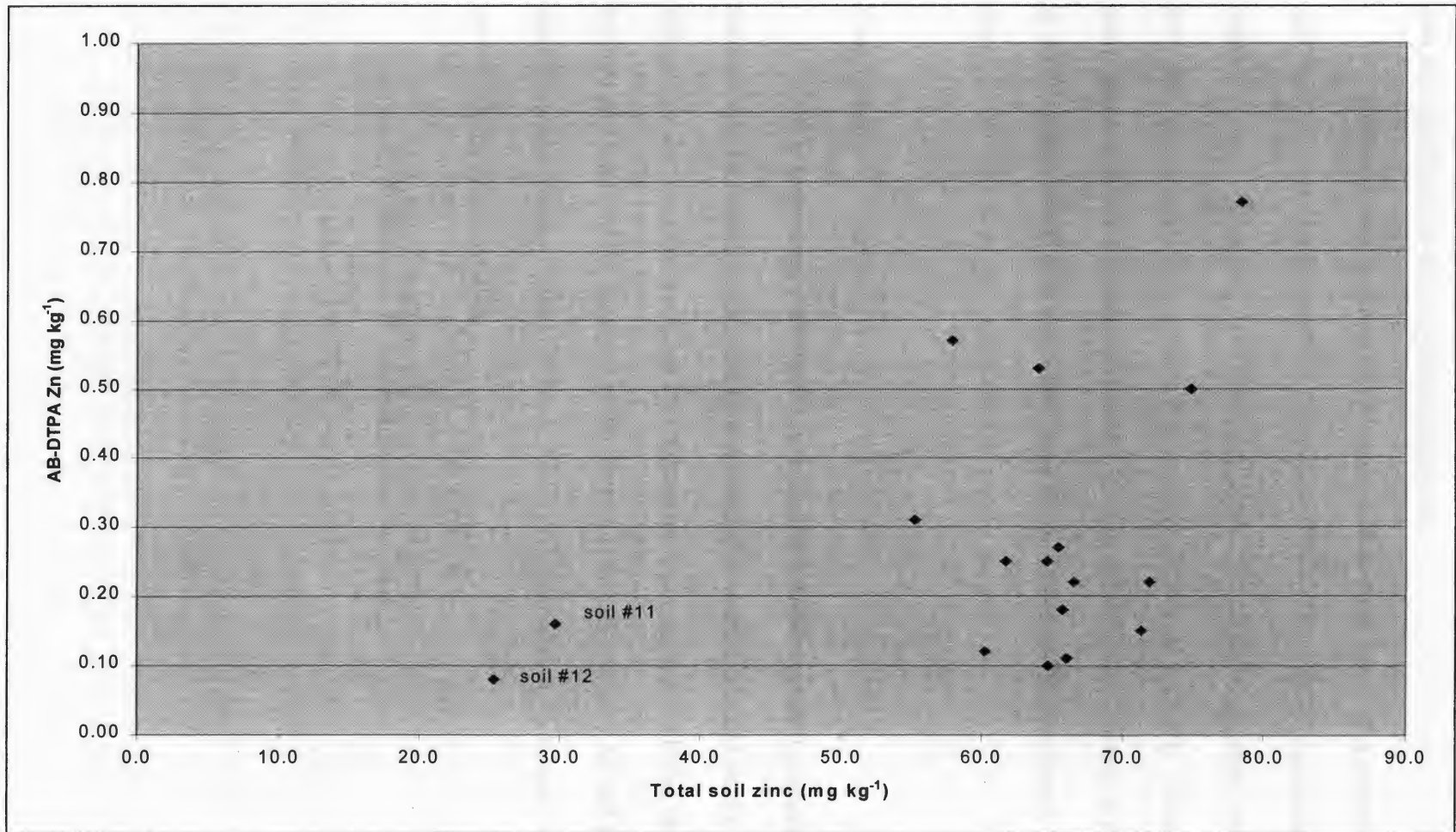


Fig. 5.2. AB-DTPA extractable Zn plotted with total soil Zn. Soils 11 and 12 have a much lower value of Zn in the soil than the other soils.

extractable Zn in a multiple regression analysis of course-textured soils. Organic carbon was not significant in their regression analyses.

The multiple regression results were different for AB-DTPA-extractable Zn and Zn^{2+} activity with soil properties for the soils of this study. Both regressions included organic carbon. However, AB-DTPA-extractable Zn was also strongly correlated with total soil Zn, whereas Zn^{2+} activity was strongly correlated with pH. These differences seem reasonable since metal activities are known to be strongly related to pH in general. In addition, the AB-DTPA extraction method uses a pH buffered solution, which may decrease the effects of pH on AB-DTPA-extractable Zn.

Conclusions

In this experiment, AB-DTPA-extractable Zn and other soil properties were measured in 18 neutral to alkaline soils from three eastern Colorado farms. AB-DTPA-extractable Zn was best predicted by a regression equation that included organic carbon content and total soil Zn for these soils. Organic carbon, total soil Zn and pH may all be significantly correlated with DTPA- or AB-DTPA-extractable Zn in soils, based on current and previous studies.

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CHAPTER 6

CONCLUSIONS

In this study, Zn^{2+} activity and AB-DTPA-extractable Zn were measured in 18 soils from three farms in eastern Colorado. The first hypothesis from Chapter 1 states that free Zn activity in soil increases as organic matter decreases. The results of this study show the opposite is true. Free Zn activity increased as organic matter increased. Hypothesis 2 states that soil pH, organic matter, clay content, and total soil Zn are important predictors of Zn solubility. This is true to some extent. Soil pH was a significant predictor for Zn^{2+} activity, and total soil Zn was a significant predictor for AB-DTPA-extractable Zn. Multiple regression analysis showed that organic matter was a significant factor in the prediction of both free Zn activity and AB-DTPA-extractable Zn. Principal component and path analyses were used to further explore the effects of soil properties on Zn^{2+} activity. Path analysis demonstrated the importance of pH and organic matter on Zn^{2+} activity. The third hypothesis is supported by results of these statistical analyses and the modeling results of MINTEQA2. The importance of organic matter to free Zn activity was shown by the significance of organic matter in the statistical analyses. The modeling showed that organic matter could be a solubility control for Zn below pH 8.5. Organic matter may be an important soil property to consider in the study of Zn availability to plants.

This research demonstrated that at least two regions of Zn solubility occur in soils. At high pH a precipitation-dissolution reaction occurs. At low to neutral pH, an adsorption reaction occurs. The pH at the inflection point was 8.5 for the soils of this study. The adsorption reaction for these soils was very likely adsorption to organic matter, as demonstrated by statistical analysis and mathematical modeling. In other soils, adsorption to clay or Fe, Mn, or Al oxides may occur. The pH would affect Zn adsorption to most of these materials, unless a pure cation exchange reaction was occurring and H^+ was not involved. In either case, the adsorption reaction would control Zn solubility at lower pH and the precipitation reaction would control Zn solubility at high pH. The pH at the inflection point would depend upon the mineral solubility control, the adsorptive material, characteristics of the adsorptive material, and characteristics of the soil environment (e.g., ionic strength, cation and anion concentrations).

To observe such an inflection point in a $\log(M^{n+})$ versus pH graph, the characteristics of the adsorptive material must be similar for the soils involved. Crops, climate and parent material were fairly constant across the soils of this study. So the soil organic matter likely had similar types of functional groups and a similar number of functional groups in proportion to the amount of organic matter present. The inflection point will be more clear the more similar the characteristics of the adsorptive material across soils.

If Zn has at least two regions with a different solubility control, then other metals likely behave similarly. Other researchers have shown metal-pH slopes leveling off to near zero at low pH values (see Chapter 2). Significant advances in understanding metal

solubilities can be made in the near future, especially considering the improvements in computer modeling and analytical techniques.

Future studies will make great advances in understanding metal solubilities in soil by combining metal solubility data with data on the properties of adsorptive material. With X-ray absorption spectroscopy (e.g., EXAFS, XANES) and ^{13}C nuclear magnetic resonance, the binding of metals to different functional groups in organic matter, Fe oxides and clays can be examined. Also, the key functional groups for adsorptive material in different soil environments can be understood. The influence of the adsorptive material and functional groups can be related to metal solubilities and free metal ion activity data. Recent improvements in models of complex surfaces, such as organic matter, can enhance the development of solubility diagrams that involve metal interactions with these complex surfaces. This type of research will increase our knowledge of how adsorption reactions control metal solubilities in soils.

For example, organic matter in agricultural soils and grasslands could be characterized and compared by vegetation type and climate. Then micronutrient activities could be measured and related to organic matter characteristics and pH. If we can determine which functional groups are important for which metals and increase that type of functional group in the soil, we may better control the metal solubility. So micronutrient availability could be increased for plants in deficient soils by additions of organic matter or some other adsorptive material. On the other hand, metal solubilities could be decreased if it is desired to reduce the mobility and the effects of contamination.

More advanced future work could explore how microorganisms affect the functional groups of organic matter (and of other surfaces) and thus metal solubility.

Then, if some adsorptive material is added to a soil, we may be able to predict what will happen to the metal solubility in the long term.

In addition, advanced statistical techniques such as principal component and path analyses can provide another perspective on the effects of soil properties on metal solubility. The current study showed interactions between organic carbon and pH, and clay and organic carbon on Zn solubility in soil. These types of interaction increase the complexity involved in understanding metal solubilities. However, advanced statistical techniques can simplify some of the complexity or at least indicate the important aspects of the complex behavior of soil. Then the researcher has a better idea of where to go for the next study. In this case, future work may examine interactions between pH and organic carbon, pH and inorganic carbon, or clay and organic carbon and the effects of these factors on metal solubility.

Future studies of metal solubility in soils will be exciting. New analytical techniques, new mathematical models, and new applications of statistical analyses can be combined with old and respected approaches to develop a greater understanding of Zn and other metal solubilities in soils.

APPENDIX

Error in the concentration of EDTA

As mentioned in Chapter 2, the EDTA concentration is likely the source of the greatest error in the Zn^{2+} activity measurements. This section discusses in detail the measurement of EDTA in the soils and the error in $\log(Zn^{2+})$ associated with the measurement.

It is important to understand the error in the Zn^{2+} activity as a factor of the error in the EDTA. Will the error affect the results of the regression selection? Two factors must be considered in exploring the effect of the error in EDTA concentration on the Zn^{2+} concentration. First we must consider the magnitude of the error in the EDTA concentration. Then we must discuss how an error of that size will effect the Zn^{2+} activity.

One source of error in the EDTA concentration occurred because every time I used the ion chromatograph to run a set of samples for a full day, the standards that were run in the morning did not match the standards run later in the day. A set of standards (with 3 replications) was run at the beginning of the day; then, sets of 2 or 3 standards were run after every 9-10 samples, as well as at the end of all the samples. The original standard curve predicted much lower (up to 20% lower) concentrations for the standards that were run later in the day. This error was even greater for the lowest 3 standards of the set than for the highest 2.

Possible reasons for this error may be that I did not let the machine warm up enough. Typically I let the machine warm up for about a half and hour. This was enough time to produce an apparently consistent baseline for the DI water blank. An observable change in the instrument was that the pressure decreased from around 1450 to 1320 by the end of the day. It doesn't seem like this pressure change should make a difference in the measurement of the EDTA concentration, but maybe it did.

To compensate for this change in the areas measured for the standards, I used the initial standard curve for the first 5-10 samples and then used the standards at the end of the run to create a second standard curve for the rest of the data. The samples had a difference of around 5-10% of the EDTA concentration, depending on which standard curve I used. The standards that were run in the middle of the samples agreed well with the standard curve using the final set of standards.

This error in the standard curve causes an error of about 10 % in the EDTA concentration. Error was inversely related to concentration. Lower concentrations had a little higher error, and higher concentrations had a little lower error.

The consistency of the standards could also produce an error in the EDTA concentration. For the first estimation of EDTA concentration, the standards were replicable to within about 1.4%. For the second estimation they were within about 3.9%. So we could assume that this error would result in an average of about plus or minus 2.7% of the EDTA concentration.

Adding the two types of errors above gives us an error of about plus or minus 13% of the EDTA concentration. Next we must determine how that error gets transferred to error in Zn^{2+} activity or $\log (Zn^{2+})$.

Error in Zn^{2+} associated with the determination of EDTA

It is important to calculate the effect of the error in the EDTA concentration on the Zn^{2+} activity. However, it is difficult to get an analytical relationship for this effect. The EDTA concentration is used to calculate the final MF of ZnEDTA. Then the MF final is plotted against the MF initial to get the MF equilibrium. The MF equilibrium is the variable used in the calculation for Zn^{2+} activity. The effect of error in the EDTA concentration must be determined by recalculating MF equilibria for a range of EDTA concentrations for several (if not all) of the soils. Then the error in (Zn^{2+}) can be calculated from error in equilibrium MF ZnEDTA by an analytical equation.

Below is a table of 6 of the soils from my study, changes made to the EDTA concentration, and the resulting new equilibrium MF ZnEDTA (Table A.1). The new Zn^{2+} activities were calculated using equation 15 from Appendix B. The average resulting error in the equilibrium MF was 17%. This value is greater than the original 10% error in the EDTA. However, this error does not affect $\log (Zn^{2+})$ by much. The error in $\log (Zn^{2+})$ is about 0.7 %. This error is slightly greater than the standard deviation for the soils, but it is still not a large error. Thus error in EDTA does not contribute much to the error in $\log (Zn^{2+})$.

Calculations of error in (Zn^{2+})

Below are calculations for error in (Zn^{2+}) using a mathematical analysis of the formula:

$$(Zn^{2+}) = 10^{-5.83} (Ca^{2+}) \frac{\theta}{1 - \theta} \quad [1]$$

Table A.1. Effect of error in EDTA concentrations on equilibrium MF and $\log(\text{Zn}^{2+})$. The new equilibrium MF was calculated by using the new EDTA concentrations to produce new graphs for the soils listed in the table. The new $\log(\text{Zn}^{2+})$ was calculated by using the equations in Appendix B to calculate new Zn^{2+} activities from the changes in equilibrium MF.

soil #	eq MF ave	original (Zn^{2+})	$\log(\text{Zn}^{2+})$	error in EDTA	new eq MF	delta eq MF	new (Zn^{2+})	$\log(\text{Zn}^{2+})$
5	0.0150	4.90E-11	-10.31	+ 10%	0.0132	-0.0018	4.30E-11	-10.37
5	0.0150	4.90E-11	-10.31	- 10%	0.0174	0.0024	5.70E-11	-10.24
6	0.0054	1.07E-11	-10.97	+ 10%	0.0050	-0.0004	9.92E-12	-11.00
6	0.0054	1.07E-11	-10.97	- 10%	0.0060	0.0006	1.19E-11	-10.92
7	0.0481	1.20E-10	-9.92	+ 10%	0.0394	-0.0087	9.76E-11	-10.01
7	0.0481	1.20E-10	-9.92	- 10%	0.0617	0.0136	1.56E-10	-9.81
8	0.0071	9.12E-12	-11.04	+ 10%	0.0061	-0.0010	7.83E-12	-11.11
8	0.0071	9.12E-12	-11.04	- 10%	0.0086	0.0015	1.11E-11	-10.96
15	0.0548	5.01E-11	-10.30	+ 10%	0.0435	-0.0113	3.93E-11	-10.41
15	0.0548	5.01E-11	-10.30	- 10%	0.0742	0.0194	6.93E-11	-10.16
16	0.0062	1.05E-11	-10.98	+ 10%	0.0056	-0.0006	9.45E-12	-11.02
16	0.0062	1.05E-11	-10.98	- 10%	0.0069	0.0007	1.17E-11	-10.93

1. Addition of an error, ΔCa in the (Ca^{2+}) .

The new (Zn^{2+}) , denoted as $(\text{Zn}^{2+})'$ can be calculated by

$$(\text{Zn}^{2+})' = 10^{-5.83}[(\text{Ca}^{2+}) + \Delta\text{Ca}] \frac{\theta}{1-\theta} \quad [2]$$

This gives us

$$(\text{Zn}^{2+})' = 10^{-5.83}(\text{Ca}^{2+}) \frac{\theta}{1-\theta} + 10^{-5.83}(\Delta\text{Ca}) \frac{\theta}{1-\theta} \quad [3]$$

Substituting (Zn^{2+}) from above yields

$$(\text{Zn}^{2+})' = (\text{Zn}^{2+}) + 10^{-5.83}(\Delta\text{Ca}) \frac{\theta}{1-\theta} \quad [4]$$

Then $(\text{Zn}^{2+})' = (\text{Zn}^{2+}) + \Delta\text{Zn}$, where

$$\Delta\text{Zn} = 10^{-5.83}(\Delta\text{Ca}) \frac{\theta}{1-\theta} \quad [5]$$

So error in the free Ca activity results in error in the free Zn activity, which depends on the equilibrium mole fraction of ZnEDTA as well as the error in (Ca^{2+}) .

2. Addition of error of $\Delta\theta$ to the equilibrium MF of ZnEDTA, θ .

The (Zn^{2+}) which includes error, denoted as $(\text{Zn}^{2+})'$ can be calculated by

$$(\text{Zn}^{2+})' = 10^{-5.83}(\text{Ca}^{2+}) \frac{\theta + \Delta\theta}{1 - (\theta + \Delta\theta)} \quad [6]$$

To make the equations more simple, let $k = 10^{-5.83}(\text{Ca}^{2+})$. Then

$$(\text{Zn}^{2+})' = k * \frac{\theta + \Delta\theta}{1 - (\theta + \Delta\theta)}. \quad [7]$$

Multiplying both sides by $1 - (\theta + \Delta\theta)$ and dividing both sides by $1 - \theta$ yields

$$(\text{Zn}^{2+})' * \frac{[1 - (\theta + \Delta\theta)]}{1 - \theta} = k \frac{(\theta + \Delta\theta)}{1 - \theta} = \frac{k\theta}{1 - \theta} + \frac{k\Delta\theta}{1 - \theta}. \quad [8]$$

Substituting $(\text{Zn}^{2+})'$ from equation 1, we have

$$(\text{Zn}^{2+})' * \frac{[1 - (\theta + \Delta\theta)]}{1 - \theta} = (\text{Zn}^{2+}) + \frac{k\Delta\theta}{1 - \theta}. \quad [9]$$

Solving for $(\text{Zn}^{2+})'$ gives us

$$(\text{Zn}^{2+})' = (\text{Zn}^{2+}) * \frac{1 - \theta}{[1 - (\theta + \Delta\theta)]} + \frac{k\Delta\theta}{[1 - (\theta + \Delta\theta)]}. \quad [10]$$

Substituting in for k yields

$$(\text{Zn}^{2+})' = (\text{Zn}^{2+}) * \frac{1 - \theta}{[1 - (\theta + \Delta\theta)]} + \frac{10^{-5.83}(\text{Ca}^{2+})\Delta\theta}{[1 - (\theta + \Delta\theta)]}. \quad [11]$$

We can leave the new $(\text{Zn}^{2+})'$ in this form, or else we can factor out a $(\text{Zn}^{2+})'$ from both terms on the right-hand side:

$$(\text{Zn}^{2+})' = (\text{Zn}^{2+}) * \left(\frac{1 - \theta}{[1 - (\theta + \Delta\theta)]} + \frac{10^{-5.83}(\text{Ca}^{2+})\Delta\theta}{[1 - (\theta + \Delta\theta)]} * \frac{1}{(\text{Zn}^{2+})} \right) \quad [12]$$

and

$$(\text{Zn}^{2+})' = (\text{Zn}^{2+}) * \left(\frac{1-\theta}{[1-(\theta+\Delta\theta)]} + \frac{10^{-5.83}(\text{Ca}^{2+})\Delta\theta}{[1-(\theta+\Delta\theta)]} * \frac{1-\theta}{10^{-5.83}(\text{Ca}^{2+})\theta} \right) \quad [13]$$

Simplifying gives us

$$(\text{Zn}^{2+})' = (\text{Zn}^{2+}) * \left(\frac{1-\theta}{[1-(\theta+\Delta\theta)]} + \frac{\Delta\theta}{[1-(\theta+\Delta\theta)]} * \frac{1-\theta}{\theta} \right) \quad [14]$$

$$\text{and } (\text{Zn}^{2+})' = (\text{Zn}^{2+}) * \left(\frac{(1-\theta)(\theta+\Delta\theta)}{[1-(\theta+\Delta\theta)]\theta} \right). \quad [15]$$

So we have $(\text{Zn}^{2+})' = (\text{Zn}^{2+}) * f$, where $f = \left(\frac{(1-\theta)(\theta+\Delta\theta)}{[1-(\theta+\Delta\theta)]\theta} \right)$.

3. We can combine both of the situations above to predict error in (Zn^{2+}) as a function of both error in (Ca^{2+}) , ΔCa , and error in equilibrium MF ZnEDTA, $\Delta\theta$. By following similar mathematical reasoning we have the result:

$$(\text{Zn}^{2+})'' = 10^{-5.83}[(\text{Ca}^{2+}) + \Delta\text{Ca}] \frac{(\theta+\Delta\theta)}{[1-(\theta+\Delta\theta)]} \quad [16]$$

that can also be expressed in the form

$$(\text{Zn}^{2+})'' = (\text{Zn}^{2+}) \frac{(1-\theta)}{[1-(\theta+\Delta\theta)]} + \frac{10^{-5.83}[(\text{Ca}^{2+})\Delta\theta + \theta\Delta\text{Ca} + \Delta\text{Ca}\Delta\theta]}{[1-(\theta+\Delta\theta)]} \quad [17]$$