A GEOCHEMICAL EQUILIBRIUM MODELING APPROACH TO ASSESSING SOIL ACIDIFICATION IMPACTS DUE TO DEPOSITIONS OF INDUSTRIAL AIR EMISSIONS

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Abstract. Soil acidification impacts arising from depositions of industrial air emissions may become a serious environmental concern. Currently, in the literature quantitative mechanistic modeling and the experimental acid neutralizing capacity (*ANC*) approach and a qualitative evaluation approach classifying soils into various levels of sensitivity to acid additions have been reported to assess the long-term soil acidification impacts due to industrial air emissions. Another alternative quantitative approach proposed by this study is the geochemical modeling approach that can be used to similate an *ANC* curve based on relevant soil chemistry data by calculating the equilibrium distributions of chemical species in the soil solution according to the specified geochemical processes. The purpose of this syudy was essentially to illustrate the potential applications and practical utility of the proposed geochemical modeling approach to assessing soil acidification impacts due to industrial air emissions. The application of the geochemical modeling apprach was illustrated by comparisons of the experimental and simulated *ANC* curves for a calcareous and a noncalcareous soil representing insensitive and sensitive soil cases, respectively. Results obtained from these comparisons reveal that, in terms of producing the ANC curve for the soil solution, the geochemical modeling approach seems to perform well and produce more reliable results for calcareous soil than for noncalcareous soil. However, the approach can also be used for noncalcareous soils when the air emission rates are low and may need further testing with additional measured data for a wide range of soils other than those presented in this study.

Keywords: acid deposition, geochemical modeling, industrial air emissions, soil acidification

1. Introduction

The soil acidification problem may arise from the air emissions originating from industrial facilities such as thermal power plants, petroleum refineries and petrochemical industries. Long term atmospheric wet and dry depositions of these industrial effluents, such as sulfur and nitrogen oxide gases, may become a serious environmental concern.

Recent case studies (Soyupak *et al.*, 1993a, b) have identified three different approaches to assess the long-term acidification impacts of air emissions from various industrial complexes on agricultural and forest soils. Among these, mechanistic modeling approach (De Vries *et al.*, 1989) and experimental acid neutralizing

capacity (*ANC*) approach are quantitative in nature. The mechanistic modeling approach developed by De Vries *et al.* estimates the temporal changes in soil pH considering acid deposition rates, soil properties and various processes causing proton additions into soil solution. The experimental *ANC* curves can be obtained by titration of soil using an acid (Page *et al.*, 1982). The third approach, qualitative evaluation approach (Holowaychuck and Fessenden, 1987), however, classifies soils into various levels of sensitivity to acid additions based on values of pH and cation exchange capacity (CEC) prior to acid deposition. A related work by Soyupak *et al.* (1993b), an EIA study for a coal fueled power plant, compared the results of these three approaches in terms of estimating the number of years to reach predetermined critical pH values in noncalcareous and calcareous soils under proposed rates of air emissions. They concluded that although results of the quantitative approaches agreed well with indications of the qualitative approach, the two quantitative approach, both for calcareous and non calcareous soils, yielded significantly different estimates for the number of years required for soil pH to drop to a critical value.

Another alternative approach that can be used to assess soil acidification impacts is the use of a geochemical equilibrium modeling approach. Geochemical equilibrium models can essentially be used to produce an *ANC* curve based on relevant soil chemistry data by calculating the equilibrium distribution of chemical species in the soil solution according to the specified geochemical processes (Allison *et al.*, 1990; Yeh and Tripathi, 1990). This paper presents a geochemical equilibrium modeling approach (an alternative tool) to assessing soil acidification impacts due to industrial air emissions. The main objective of the paper is to illustrate the potential applications and practical utility of the geochemical modeling approach. For this purpose, experimental *ANC* curves for calcareous and noncalcareous soils were compared with respective *ANC* curves produced by the geochemical modeling approach. The paper also intends to present the estimation and implications of various significant parameters relevant to the evaluation of soil acidification impacts.

2. Soil Acidity

Major air pollutants determining soil acidity via dry and wet deposition processes are sulfur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) gases. The relationship between the emissions of primary pollutants and the resultant acid deposition is complex (Carmichael and Shin, 1992). In general, for emissions from coal-fired power plants it is conservatively assumed that SO_2 emissions are three times of total NO_x and NH_3 emissions and that one mole of SO_2 produces two moles of hydrogen ion H^+ (Soyupak *et al.*, 1993b). Such addition of H^+ to soil via dry and wet depositions will cause a decrease in the pH value of soils.

By definition, a soil is considered to be acidic if the pH value of its aqueous-solution phase is less than 7.0. The pH of the soil solution will be determined by the combined effects of various different natural processes. Some of these processes increase the pH value of the soil solution while some decrease.

In soils, the mechanisms acting as a buffer against pH decrease by the added H^+ ions includes the dissolution (weathering) of carbonates, slicates and/or Al hydroxides and cation exchange (De Vries *et al*., 1989). In calcareous soils, the free H^+ input by acid depositions is neutralized by the dissolution of calcite, known as carbonate buffer range (pH $\approx$ 6.8). In noncalcareous soils, or upon depletion of the carbonates, added H^+ can be neutralized by exchange with base cations released from mineral weathering. The adsorption of H^+ by solid surfaces in soil is known as exchange buffer range (pH $\approx$ 5.5). Upon further acidification and a decrease in base saturation, free H^+ can be neutralized by Al^{3+} dissolution, known as Al buffer range (pH $\approx$ 4.0). The buffering capacity of soils decreases with decreasing CEC and contents of minerals such as carbonates, slicates and/or Al hydroxides. Upon depletion of minerals pH can drop as low as near 3.0 in soils (De Vries *et al*., 1989).

The changes in the chemical composition of soil solution in terms of soil pH can quantitatively be described by the concept of *acid-neutralizing capacity (ANC)* and its derivative with respect to pH, the *buffer intensity*, β_H. The *ANC* is the moles of H^+ per unit mass (or volume) required to change the pH values of a soil solution to the pH at which the net charge due to *free ions* is zero (Sposito, 1989). Thus, the *ANC* of a soil solution can be expressed in terms of free-ion concentrations and in the presence of dissolved (CO_2(g), in terms of the alkalinity. For the soil adsorbent, the *ANC* can be defined as

$$ANC = CEC - TA \tag{1}$$

where *CEC* is the *cation exchange capacity* representing the negative surface charge that can be balanced by dissolved cations; and *TA* is the *total acidity* representing the fraction of negative surface charge that can be balanced by acidifying cations such as H^+, Al^{3+}, $AlOH^{2-}$ and $Al(OH)_2^+$. The ratio of *TA/CEC* is usually near zero for mineral soils having a pH value of 5.5 or greater while this ratio increases sharply in acid soils as pH decreases from 5.5 to lower values (Sposito, 1989).

If the *TA* of the soil exceeds about 15% of its *CEC*, then the pH of soil may cause a variety of problems for plant growth due to metal toxicity or deficiency. The netralization of soil acidity requires addition of Ca^{2+} ions to the soil. In acid soils, the added Ca^{2+} will replace Al^{3+} at the exchange site and increase the *ANC* of soil absorbent. If the Al^{3+} that exchanges for Ca^{2+} precipitates in the soil solution the *ANC* of soil solution will remain unchanges, otherwise it will decrease (Sposito, 1989). The activities of Ca^{2+} ion both in the soil solution and in the soil adsorbent will have a significant role determining the *ANC* of soils. This situation leads to the concept of *lime potential(LP)* defined as

$$LP = pH + \log(Ca^{2+}) \tag{2}$$

where (·) represents the ion activity in the soil solution. Soils that have *LP* values greater than 3.0 will usually exhibit a minimum Ca^{2+} fraction of 0.5 at the exchange site and thus an adequate *ANC*.

The buffer intensity, β_H, can be expressed as the number of moles of H^+ per unit mass or volume that are dissociated from (or adsorbed by) a soil when the pH value of soil solution increases (or decreases) by one pH unit. Thus, having known the β_H and the number of moles of H^+ added to or removed from per unit mass of soil, Δn_H, the general relationship to calculate the change in the pH of the soil solution, ΔpH, is given by

$$\Delta pH = \Delta n_H / \beta_H. \tag{3}$$

In addition, the number of years, *T*, required to bring the soil pH to a preset pH value can be calculated by

$$T = (\Delta pH)(\beta_H)/R_H \tag{4}$$

where R_H is the acid deposition rate [moles H^+ gm^{-1} soil.year^{-1}] due to air emissions. In general, β_H exhibit a typical pH dependence. However, depending on the shape of the *ANC* curves, β_H can be assumed constant at some characteristic pH ranges.

3. Geochemical Equilibrium Model

The geochemical models essentially calculate the equilibrium distribution of chemical species in soil solution according to the specified geochemical processes, namely speciation, complexation, dissolution-precipitation, oxidation-reduction, ion exchange and gas equilibria. Calculations are accomplished by solving the mass balance equations under the constraint of mass action expressions describing the formation of each chemical species present in the soil solution (Ünlü, 1998).

The thermodynamic equilibrium calculations in this study are based on the MINTEQA2 geochemical model of Allison *et al.* (1990). Computational procedure proceeds as follows. Concentration of a chemical species *k* is expressed in terms of its molality, S_k [mole kg^{-1}], which is related to the activity X_k [mole kg^{-1}] by the activity coefficient, γ_k, as

$$X_k = \gamma_k S_k. \tag{5}$$

The Davies equation of the form

$$\log \gamma_k = -Az_k^2 \left(\frac{1^{1/2}}{1 = 1^{1/2}} - 0.24I \right) \tag{6}$$

is used to calculate the activity coefficients of charged species; where A is a constant (0.5092), z_k is the charge of species k, and I is the ionic strength of the solution defined by

$$I = \frac{1}{2} \sum_k Sk z_k^2. \tag{7}$$

For neutral species, activity coefficients are calculated as $\log \gamma_k = 0.1I$, while the activity of adsorbates is calculated based on Vanselow convention using their mole fractios.

The relationship between the chemical components present in the soil solution and the species that can be formed by combination of these components is expressed by a set of mass action expression of the form

$$K_k = X_k \prod_l X_l^{-a_{kl}} \tag{8}$$

where K^k is the equilibrium constant for the formation of species k, X_k is the activity of species k, X_l is the activity of component l, a_{kl} is the stoichiometric coefficient of component l in species k, and $\prod$ represents the product over all components in species k. Substituting (5) in (8) and rearranging yield

$$S_k = \frac{K_k}{\gamma_k} \prod_l X_l^{a_{kl}}. \tag{9}$$

In addition to the mass action expressions defined by (9), the concentration distribution of each species in the system must satisfy a set mass balance equations of the form

$$Y_l = \sum_k a_{kl} S_k - T_l \tag{10}$$

where T_l is the known total dissolved concentration of component l and Y_l is a tolerance criteria, i.e., the difference between the calculated and known total dissolved concentration of component l. The value of Y_l is set to 10^{-4} in the geochemical code.

The mass balance Equations (10) are solved under the constraint of mass extion expressions (9) by replacing S_k in (10) via (9). This substitution leads to a set of nonlinear algabraic equations with unknowns expressed as equilibrium component acivities X_l. The solution is obtained using an iterative Newton-Raphson scheme. The procedure starts with an initial guess for X_l and continues with iterations by recalating S_k and Y_l until the final values of Y_l satisfy the convergence criteria.

TABLE I

Some physical and chemical properties of calcareous and noncal-carous soils

Parameter	Calcareous soil	Noncalcareous soil
Sand (%)	28.6	47.6
Silt (%)	21.6	29.6
Clay (%)	49.8	22.8
Texture	Clay	Loam
Water Saturation (%)	67	41
EC (mmhos cm^{-1})	0.72	1.60
CEC (Meq 100 g^{-1})	20.0	13.6
PH	7.65	6.93
$CaCO_3$ (%)	26.3	0.0
Organic matter (%)	1.39	1.27

4. Laboratory Measurement of ANC Curve

The *ANC* curves of a calcareous and a noncalcareous soil were experimentally determined in the laboratory. Some physical and chemical properties of these soils are presented in Table I. The calcareous soil has a $CaCO_3$ content of 26.3% and a clay texture with a CEC value of 20 meq 100 g^{-1}. The noncalcareous soil, on the other hand, has no free $CaCO_3$, a loam texture with a CEC value of 13.6 meq 100 g^{-1}. The pH values, measured on saturation paste, of calcareous and noncalcareous soils are slightly basic and slightly acidic, respectively. Additional data for both soils involving total dissolved amounts of major anion and cations are given in Table II and exchangeable amounts of major cations are shown in Table III. Based on the available data, the dissolved phase compositions of both soils appear very similar, while the exchangeable phase compositions differ in terms of Ca^{2+}.

To measure the *ANC* curves for calcareous and noncalcareous soils, respective soil samples air dried and passed through a 2 mm sieve. For calcareous soils, seventeen (17) soil samples, each weighing 100 g, were subjected to additions of H_2SO_4 solutions at various concentrations ranging between 0 and 1800 meq L^{-1} (0, 5, 10, 15, 20, 25, 50, 100, 250, 500, 750, 1000, 1250, 1500, 1700 and 1800 meq L^{-1}). For noncalcareous soil, however, twenty two (22) soil samples, each weighing 100 g again, were subjected to additions of H_2SO_4 solutions at different concentrations ranging between 0 and 100 meq L^{-1} (0, 5, 10, to 100 with 5 meq L^{-1} increments). Based on water saturation values given for both soils in Table I, each set of 100 g soil samples received H_2SO_4 solution, with a different but known concentration within the specified ranges, at an amount sufficient to saturate

TABLE II

Dissolved phase concentrations of major cation and anions for calcareous and noncalcareous soils

Parameter	Calcareous soil (meq 100 g^{-1})	Noncalcareous soil (meq 100 g^{-1})
Na$^+$	0.050	0.030
K$^+$	0.004	0.004
Ca^{2+}	0.030	0.030
Mg^{2+}	0.010	0.020
Cl$^-$	0.020	0.020
HCO$_3^-$	0.030	0.020
CO$_3^{2-}$	0.000	0.000
SO$_4^{2-}$	0.044	0.044

TABLE III

Exchangeable phase concentrations of major cations for calcareous and noncalcareous soils

Parameter	Calcareous soil (meq 100 g^{-1})	Noncalcareous soil (meq 100 g^{-1})
Na$^+$	0.030	0.010
K$^+$	0.147	0.218
Ca^{2+}	13.290	7.970
Mg^{2+}	2.290	2.880

the 100 g soil sample. In other words, each of the 17 100-g calcareous soil samples received 67 mL of H$_2$SO$_4$ solution while each of the 22 100-g noncalcareous soil samples received 41 mL of H$_2$SO$_4$ solution with different concentrations within the specified respective ranges. This way, each soil sample was subjected to additions of increasing amounts of H$^+$ and, in turn, the change in soil pH in response to additions of H$^+$ was observed.

The pH of each soil sample was measured on duplicate samples of both saturation paste and saturation extract using a digital pH meter. Saturation paste of a soil sample was prepared, as described in the previous paragraph, by adding H$_2$SO$_4$ solution at an amount (67 and 41 mL for calcarous and noncalcareous soils, respectively) sufficient for the complete saturation of the soil sample. Saturation extract, which represents the soil solution, was obtained by suction-filtration of H$_2$SO$_4$
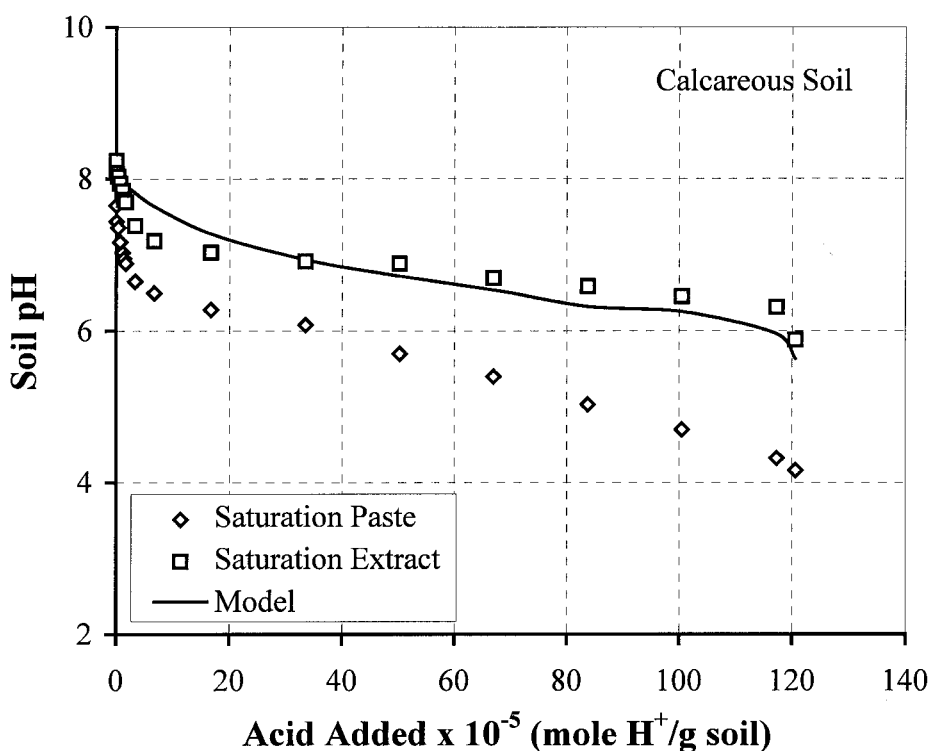
Figure 1. Measured and simulated acid neutralizing capacity curves for the calcareous soil.

solution-saturated paste of the soil samole. For pH measurements, a Swiss-made digital pH meter, Methrom 645, was used. The electrode was an Ingold 4402–57/120 combination pH electrode. Before measurements, pH meter was calibrated using pH 4 and pH 7 buffer solutions and the temperature of sample (saturation paste or extract) was recorded. The electrode of the pH meter was submerged properly into the sample and the pH was measured after adjusting the pH meter for the temperature of the sample. Between the consecutive measurements, the electrode was cleaned with distilled was and dried with soft tissue paper. Reproducibility of pH values measured on duplicate samples was very high such that a meaningful statistical analysis of the data was not justifiable.

Results of the experimental study were presented as soil pH versus the amount of acid added in Figures 1 and 2 for calcareous and noncalcareous soils, respectively. For both soils, pH values measured in saturation extract were always greater than those measured in saturation paste, and the difference between pH measurements in saturation extract and saturation paste increased gradually with the decrease of pH. It was also observed that for both soils pH drop (the difference between the initial and final pH values) due to H^+ addition was much less in saturation extract than in saturation paste. All these observations can be explained
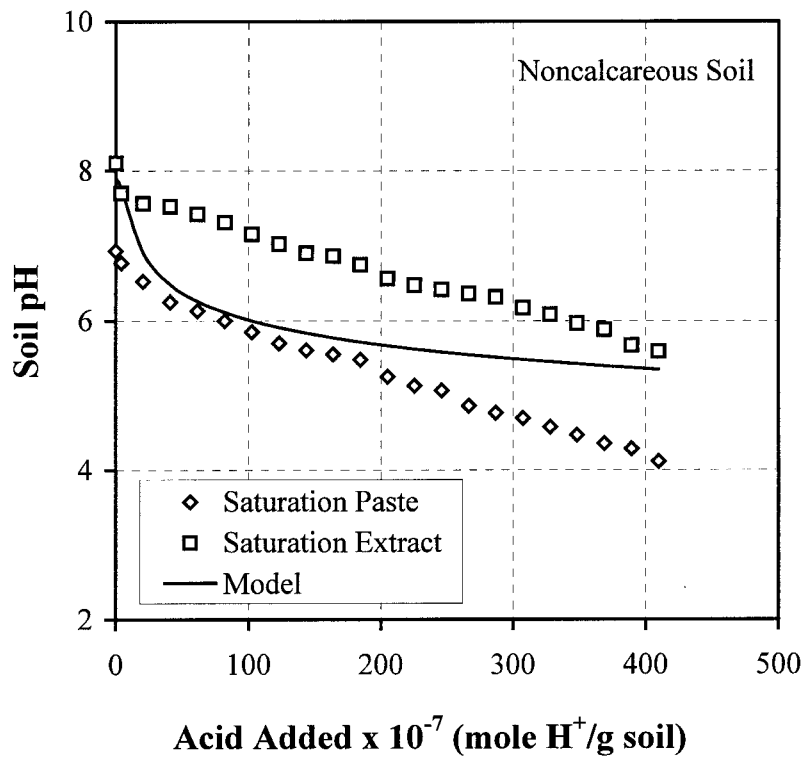
Figure 2. Measured and simulated acid neutralizing capacity curves for the noncalcareous soil.

by the effect of exchangeable acidity in the saturation paste. In calcareous soil, as a result of adding a total of 1.206×10^{-3} mole H^+ g^{-1} of soil, pH value in saturation paste is dropped from 7.65 to 4.16 and in saturation extract from 8.24 to 5.88. In noncalcareous soil, similar pH drops (from 6.93 to 4.12 in saturation paste and from 8.10 to 5.59 in saturation extract) were observed as a result of adding nearly two orders of magnitude less acidity (a total of 4.1×10^{-5} mole H^+ g^{-1} of soil). This shows that the acid neutralizing capacity of calcareous soil is significantly greater than that of noncalcareous soil due to the presence of free $CaCO_3$. This situation is also reflected by the respective *LP* values of both soils, being 5.63 for calcareous soil and 5.01 for noncalcareous soil. Free H^+ additions in calcareous soil were consecutively neutralized by the carbonate and exchange buffers. Neutralization of free H^+ in noncalcareous soil, however, is accomplished only by the exchange buffer. Because the final pH values were not below 4, the Al buffer range were not activated for both soils.

TABLE IV

Ion exchange reactions and selectivity coefficients used for geo-chemical modeling

Ion exchange	Selectivity coefficient
$1/2\,CaX_2 + Na^+ \Leftrightarrow 1/2\,Ca^{2+} = NaX$	0.33
$CaX_2 + Mg^+ \Leftrightarrow Ca^{2+} + MgX_2$	1.20
$1/2\,CaX_2 + H^+ \Leftrightarrow 1/2\,Ca^{2+} + HX$	0.50
$1/2\,CaX_2 + K^+ \Leftrightarrow 1/2\,Ca^{2+} + KX$	0.33

5. Applications of Geochemical Modeling

To obtain the theoretical *ANC* curves and to determine the potential impacts on soil pH due to air emissions, EPA's geochemical speciation model MINTEQA2 (Allison *et al.*, 1990) described in the previous section was used. The analysis is based on calculations of changes in the equilibrium chemical composition, in turn, pH of the soil solution due to acid deposition. Ultimately, the purpose was to compare the experimental and theoretical ANC curves to evaluate the performance of the geochemical modeling approach in assessing soil acidification impacts due to air emissions.

MINTEQA2 simulations were performed using the measured soil chemistry data. Geochemical processes that are considered important for the analysis are aqueous speciation, ion exchange and precipitation-dissolution reactions. The soil chemistry data required for the geochemical modeling are soil pH, CEC and total dissolved concentrations of anions and cations present in the soil solution. Measured values of these parameters for a calcareous and a noncalcareous soil samples are shown in Tables I, II and III. Ion exchange reactions between Ca^{2+}, Mg^{2+}, Na^+, K^+ and H^+ ions and pertinent selectivity coefficients provided by Bolt (1982) and Stosh (1986) are specified as given in Table IV. Initially, exchange sites can safely be assumed to be Ca^{2+} saturated as the sum of exchangeable Ca^{2+} and Mg^{2+} comprises nearly 80% or more of the CEC for soils with pH $\geq$ 5 (Bohn *et al.*, 1985). Simulations were performed for soils with and without free solid $CaCO_3$. This situation represents insensitive and sensitive soil cases, respectively since the presence or absence of solid $CaCO_3$ plays a significant role on the *ANC* of soils.

For the construction of *ANC* curves using the geochemical modeling approach, addition of H^+ in soil is mimicked by progessively increasing the input H^+ concentration while keeping the rest of the input constant. Allowing the soil solution to equilibrate with each increment of H^+ concentration, simulations are continued until the soil pH reaches near 5.0. The *ANC* curves constructed in this manner for calcareous and noncalcareous soil cases are shown in Figures 1 and 2, re-
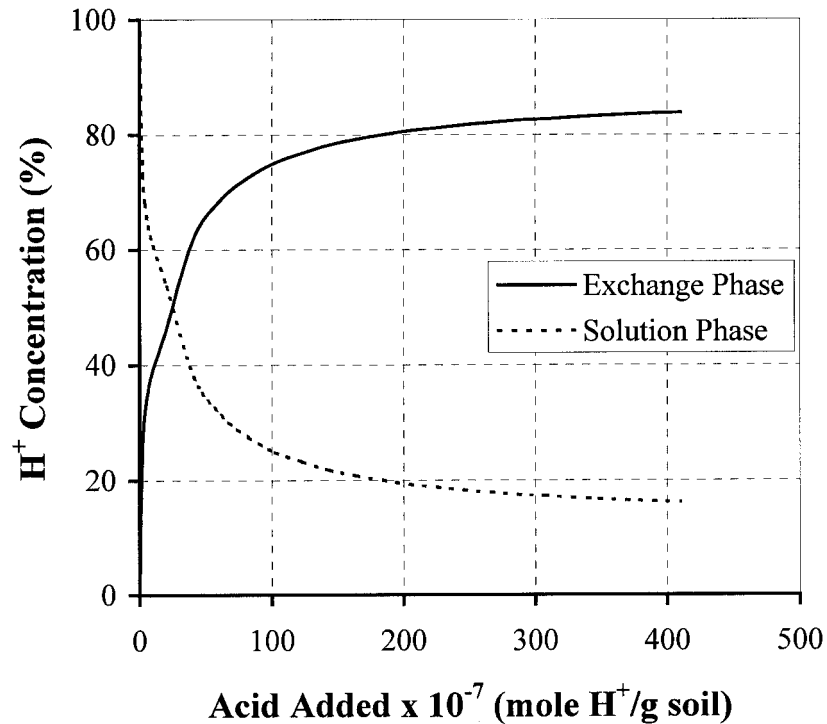
Figure 3. Percent distributions of H^+ concentration in the solution and exchange phases as a function of acid addition into the noncalcareous soil.

spectively along with the experimentally measured *ANC* curves. For calcareous soil, the *ANC* curve obtained by the geochemical modeling approach matches well with the experimental *ANC* curve obtained based on pH measurements in the saturation extract. For noncalcareous soils, however, the *ANC* curve obtained by the geochemical modeling approach falls between the *ANC* curves of saturation paste and saturation extract. At the low range of acid additions, modeled *ANC* curve approaches the *ANC* curve of saturation paste whereas at the high range of acid additions it tends to approach the *ANC* curve of saturation extraxt. Somewhat poor performance of the geochemical modeling approach can be due to inadequate input data used in modeling of the ion exchange reactions. Especially, values of selectivity coefficients reported in the literature are highly dependent on the experimental conditions at which they were measured and thus subject to large uncertainties (Bolt, 1982).

Overall, in terms of producing the ANC curve for the soil solution, the geochemical modeling approach seems to work better for calcareous soils than for noncalcareous soil. In other words, geochemical modeling approach appears to be more reliable within the carbonate buffer range compared with the exchange buffer

TABLE V

Comparison of the results of geochemical modeling and experimental *ANC* curves

	β_H (mole H$^+$ g^{-1} soil pH)			Time to pH = 5 (yr)		ΔpH yr^{-1}	
	Paste	Extract	Model	Extract	Model	Extract	Model
Calcareous soil	3.5×10^{-4}	5.1×10^{-4}	5.1×10^{-4}	49622	46252	6.55×10^{-5}	6.5×10^{-5}
Noncalcareous soils	1.5×10^{-5}	1.6×10^{-5}	2.3×10^{-5}	1490	2008	2.10×10^{-3}	1.5×10^{-3}

range. This situation can be further explained by examining the percent distributions of H$^+$ concentrations in the solution and exchange phases as a function of acid addition into the soil. Figure 3 shows plots of such distributions for the noncalcareous soil. As seen from the figure, the percent concentration of the H$^+$ in the exchange phase increase with the addition of acid while the percent concentration in the solution phase decreases. Initially, H$^+$ in the solution primarily occurs as free H$^+$, HCO$_3^-$, CaHCO$_3^+$ and H$_2$CO$_3$(aq) species. Upon addition of 4×10^{-5} mole of H$^+$ g^{-1} of soil, 84% of the H$^+$ was neutralized by the exchange sites. The remaining 16% of H$^+$ was in the soil solution as free H$^+$ and H$_2$CO$_3$(aq) species. Similar distributions for calcareous soils revealed that within the overall range of acid addition nearly 100% of the H$^+$ remained in the solution primarily tied up with the species of HCO$_3^-$. CaHCO$_3^+$ and H$_2$CO$_3$(aq). Only 1% of H$^+$ concentration was observed in the exchange phase upon addition of very high amounts of acid (10^{-3} mole H$^+$ g^{-1} soil) indicating that free H$^+$ was completely neutralized by CaCO$_3$ dissolution.

For the comparison of the geochemical modeling and experimental *ANC* curve approaches in terms of soil acidification impacts due to air emissions, calculated approximate values of buffer intensity (β_H), number of years to reach the critical pH value of 5 in the saturation extract (T) and the expected annual change in soil pH (ΔpH y^{-1}) for calcareous and noncalcareous soils are presented in Table V. The rate of acid deposition due to air emissions is calculated based on the maximum total NO$_x$ deposition rate as obtained from the modeling studies conducted for deposition and air quality impact assessment due to air emissions of a proposed natural gas fired power plant project (Yurteri *et al.*, 1994). This study revealed negligible SO$_2$ emissions compared to NO$_x$ emissions for the proposed natural gas fired power plant and a maximum NO$_x$ deposition rate of 450 mg m^{-2}. yr^{-1}, yielding an H$^+$-equivalent maximum deposition rate of 10 mg m^{-2} yr^{-1}. In converting H$^+$-equivalent acid deposition rates from mg m^{-2} yr^{-1} to mg g^{-1} soil yr^{-1}, a soil depth value of 0.2 m and an average bulk density value of 1.5 gm cm^{-3} were used.

Results presented in Table V indicate that in general the geochemical modeling approach agrees well with the experimental *ANC* curve approach for calcareous soils. In order to have a final soil pH value of 5 in the saturation extract of calcareous soil, the total number of moles of H^+ required to be added to per gram of soil is approximately 2×10^{-5} moles, yielding nearly the same β_H value (5.1 $\times 10^{-5}$ mol g^{-1} pH) for both the geochemical modeling and experimental *ANC* approaches. Based on this β_H value, for the annual maximum acid deposition rate considered, the expected annual change in soil pH is nearly 7×10^{-3} pH unit. Thus, maintaining the acid deposition rate at its maximum, the number of years required to lower the soil pH to 5 will be in the order of thousands of years (49000 yr) for the calcareous soil. This time frame implies that no imminent threat to soil pH quality exists within the lifetime of the proposed power plant. Despite somewhat poor agreement between the geochemical modeling and experimental *ANC* approaches for noncalcareous soil, a similar discussion for noncalcareous soil reveal that the values of all these parameters describing the soil acidification impacts due to air emission differ from those of calcareous soil at least an order of magnitude. These results indicate that the pH of the two soils will be quite insensitive to the acid depositions under the expected deposition rates due to air emissions of the proposed power plant. However, if the air emission rate of the proposed power plant were allowed to be 1000 mg m^{-2}. yr^{-1}, i.e., increased by nearly two orders of magnitude, the soil pH of the noncalcareous soil would be quite sensitive to the acid depositions and lowered to 5 within 15 yr. This situation indicates the existence of a reasonable threat to soil pH quality within the lifetime of the proposed power plant. Since the results indicate that the geochemical modeling approach does not seem to work well for the noncalcareous soil, the approach may not be used reliably for noncalcareous soils when the air emission rates are high.

6. Summary and Conclusions

Soil acidification impacts arising from depositions of industrial air emissions may become a serious environmental concern. Currently, three different approaches have been identified in the literature to assess the long-term soil acidification impacts of industrial air emissions. Among these, mechanistic modeling and the experimental acid neutralizing capacity (*ANC*) approaches are quantitative while the third one is a qualitative evaluation approach classifying soils into various levels of sensitivity to acid additions based on soil chemical properties. A recent comparison of the three approaches in the literature indicated that results of the quantitative approaches agreed well with those of the qualitative approach. However, the two quantitative approaches produced significantly different estimates of the time required for soil pH to drop to a critical level.

Another alternative quantitative approach proposed by this study is the geochemical modeling approach that can be used to simulate an *ANC* curve based on

relevant soil chemistry data by calculating the equilibrium distributions of chemical species in the soil solution according to the specified geochemical processes. The purpose of this study was essentially to present the application and utility of the proposed geichemical modeling approach to assessing soil acidification impacts due to industrial air emissions. The application of the geochemical modeling approach was illustrated by comparisons of the experimental and simulated *ANC* curves for a calcareous and a noncalcareous soil representing insensite and sensitive soil cases, respectively.

To measure the *ANC* curves experimentally for calcareous and noncalcareous soils, seventeen (17) and twenty two (22) soil samples, respectively, each weighing 100 g, were subjected to additions of H_2SO_4 solutions at various concentrations within a specified range and at amounts sufficient to saturate the 100 g soil sample. This way, the change in soil pH in response to additions of H^+ was observed. The pH of each soil sample was measured on both saturation paste and saturation extract using a digital pH meter. Experimental results showed that neutralization of free H^+ additions in calcareous soil were consecutively neutralized by the carbonate and exchange buffers while in noncalcareous soil this is accomplished only by the exchange buffer.

To obtain the simulated *ANC* curves and to determine the potential impacts on soil pH due to industrial air emissions a geochemical speciation model MINTEQA2 was used. MINTEQA2 simulations were performed using the measured soil chemistry data. For the construction of *ANC* curves for both calcareous and noncalcareous soils using the geochemical modeling approach, addition of H^+ in soil is mimicked by progressively increasing the input H^+ concentration while keeping the rest of the input parameters constant. Results obtained from the comparisons of the experimental *ANC* curves for the soil solution reveal that the geochemical modeling approach seems to perform well and produce reliable results for calcareous soil than for noncalcareous soil. In other words, geochemical modeling approach appears to be more reliable within the carbonate buffer range compared with the exchange buffer range. Somewhat poor performance of the geochemical modeling approach for noncalcareous soil can be due to inadequate modeling of the ion exchange reactions, especially due to large uncertainty in the values of selectivity coefficients. However, the approach can also be used for noncalcareous soils when the air emission rates are low. Although these results demonstrates the applicability of the proposed geochemical modeling approach to assessing soil acidification impacts due to air emissions, for the generality of the results the approach may need further testing with additional measured data for a wide range soils other than those two (calcareous and noncalcareous) soils presented in this study.

Acknowledgments

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