EFFECT OF SOIL pH ON CATION AND ANION SOLUBILITY

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ABSTRACT: The effect of soil pH on the exchangeability and solubility of soil cations (Ca, Mg, Na, K, and NH₄-N) and anions (NO₃-N, Cl, and P) was investigated for 80 soils, spanning a wide range in physical and chemical properties and taxonomic groups. This information is needed from environmental and agronomic standpoints to estimate the effect of changes in soil pH on leachability and plant availability of soil nutrients. Soils were incubated with varying amounts of acid (H₂SO₄) and base (CaCO₃) for up to 30 days. Although acid and base amendments had no consistent effect on cation exchangeability (as determined by neutral NH₄OAc), amounts of water-soluble Ca, Mg, Na, K, NH₄-N, and P decreased, while NO₃-N and Cl increased with an increase in soil pH. The increase in cation solubility was attributed to an increase in the negative charge of the soil surface associated with the base addition. The change in surface electrostatic potential had the opposite effect on amounts of NO₃-N and Cl in solution, with increases in N mineralization with increasing soil pH also contributing to the greater amount of NO₃-N in solution. The decrease in P solubility was attributed to changes in the solubility of Fe-, Al-, and Ca-P complexes. The logarithm of the amount of water-soluble cation or anion was a linear function of soil pH. The slope of this relationship was closely related (R² = 0.90 - 0.96) to clay content, initial soil pH, and size of the cation or anion pool maintaining solution concentration. Although the degree in soil pH buffering...
increased with length of incubation, no effect of time on the relationship between cation or anion solubility and pH was observed except for \( \text{NO}_3^- \)-N, due to N mineralization. A change in soil pH brought about by acid rain, fertilizer, and lime inputs, thus, affects cation and anion solubility. The impact of these changes on cation and anion leachability and plant availability may be assessed using the regression equations developed.

**INTRODUCTION**

The importance of soil pH in determining the dynamics of soil chemical reactions is well recognized (2,22). Changes in soil pH by acid and base additions, such as via ammoniacal fertilizer and lime application, can alter the capacity of soils to retain cations and anions (30,33) and change plant nutrient availability (10).

An increase in soil pH following lime addition has been shown to change soil solution ionic composition. Curtin and Smillie (8) reported that application of lime (\( \text{CaCO}_3 \)) to 3 acid soils from Ireland resulted in an average 1.1-, 1.5-, 1.3-, 5.8-, 1.1-, 50.0-, 6.0-, and 6.9-fold decrease in Mg, Na, K, Al, Fe, Mn, Zn, and Si concentration in solution, respectively, as pH rose an average 2.5 units. At the same time, soil solution organic matter and nitrate-N (\( \text{NO}_3^- \)-N) increased an average 6.3- and 1.2-fold. It was further shown that the logarithms of \( \text{Al}^{3+} \), \( \text{Mn}^{2+} \), and \( \text{Zn}^{2+} \) activities were linearly related to soil pH, and it was concluded that the mechanisms controlling solubilities of these ions were similar in each of the 3 soils (8).

Similarly, Simard et al. (1988) found that lime (\( \text{CaCO}_3 \)) application to a humo-ferric Podzol decreased soil solution concentrations of Mg, Na, K, Al, Zn, Mn, Si, and ammonium-N (\( \text{NH}_4^- \)-N), 3.4-, 1.7-, 1.7-, 159.0-, 5.8-, 1.4-, 1.2-, and 1.4-fold, respectively, with an increase in soil solution pH from 4.1 to 5.0, while the amounts of exchangeable (0.002 \( M \) \( \text{BaCl}_2 \)) forms remained relatively constant. As would be expected, both Curtin and Smillie (8) and Simard et al. (25) observed
an increase in Ca concentration of the soil solution. Although no significant change in phosphorus (P) concentration was found with a lime-induced increase in soil pH by these workers, other studies have reported decreased P solubility with lime application (6,20,21).

Conversely, a decrease in soil pH resulting from acid precipitation can result in an increase in cation solubility and leaching from soil profiles (1,13,29). Limited information is available, however, on the effect of both acid and base amendments to the same soil on the concentration of ions in solution. This information is needed for soils ranging in physical and chemical properties in order to improve the estimation of soil amendment effects on cation and anion solubility from both environmental and agronomic standpoints.

This paper reports an investigation of the content of Ca, Mg, Na, K, NH₄-N, NO₃-N, Cl, and P in soil solution following the incubation of 80 soils with acid or base amendments for 3 and 30 days.

MATERIALS AND METHODS

Eighty soils (Al and Ap horizons) from the continental U.S. and Puerto Rico were obtained from the Soil Conservation Service (SCS), National Soil Survey Laboratory, Lincoln, Nebraska, on the basis of their agricultural importance and availability of samples and adequate laboratory data. Included were 12 Alfisols, 6 Aridisols, 9 Entisols, 2 Histosols, 6 Inceptisols, 29 Mollisols, 2 Oxisols, 2 Spodosols, 9 Ultisols, and 3 Vertisols.

Clay (method 3 Al), organic C (methods 6A1a and 6A1c), cation-exchange capacity (methods 5A6a and 5A8a), and pH (method 8Cle) were determined by SCS according to standard procedures outlined by Soil Survey Investigative Report No. 1 (26,27). Total N content was determined by a semi-micro Kjeldahl procedure (7) and anion-exchange resin P (resin P) was extracted by A-1P anion-exchange resin (bicarbonate form) (24). Phosphorus removed from the resin by 1.5 M NaCl was determined by the method of Murphy and Riley (19).
The effect of soil pH on cation and anion exchangeability and solubility was investigated by incubation (298°K) of 50 g soil with either H₂SO₄ or CaCO₃ at rates of 0 (check), 2, 10, and 20 cmol (H⁺ or 1/2 Ca²⁺) kg⁻¹. Respective additions were as 10 mL of deionized distilled water and H₂SO₄ or CaCO₃ suspensions of 0.05, 0.25, 0.50 M. The soil mixtures were initially brought to approximate field capacity and rewet when dry with deionized distilled water. Subsamples of the soil mixtures were taken after 3- and 30-day incubations and air-dried for pH (1:2 CaCl₂) and exchangeable and water-soluble cation and anion determination. Exchangeable Ca, Mg, Na, and K were extracted by end-over-end shaking of 2 g soil with 20 mL 1.0 M NH₄OAc (pH 7.0) (1:10 soil:solution ratio) for 5 min and water-soluble Ca, Mg, Na, K, NH₄-N, NO₃-N, Cl, and P extracted by end-over-end shaking 4 g soil with 40 mL water for 15 min. Calcium, Mg, Na, and K were measured on filtered (0.45 μm) extracts by atomic absorption. NH₄-N was measured using the Berthelot reaction (32), and NO₃-N by the acidic sulfanilamide method (32). Cl was measured using a Ag/Ag Cl electrode, and P by the colorimetric method of Murphy and Riley (19). In addition, the pH of each water extract was determined with a glass electrode.

Statistical analysis of the data included analysis of variance for paired and unpaired data to determine differences between population means and regression analysis by the SAS STEPWISE and REG procedures (5). Results are presented at the 5.0% level of significance unless noted otherwise.

RESULTS AND DISCUSSION

Physical and chemical properties of the 80 soils varied widely (Table 1) For example, clay ranged from 2 (Lakeland—thermic, coated, Typic Quartzipsament) to 62.4% (Promise—very fine, montmorillonitic, mesic, Vertic Haplustoll), pH from 4.2 (Appling—clayey, kaolinitic, thermic, Typic Hapludult) to 7.9 (Bosque—fine loamy, mixed, thermic, Cumulic Haplustoll), and organic C from 2.0
Table 1. Physical and chemical properties of the 80 soils.

<table>
<thead>
<tr>
<th>Property</th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay, %</td>
<td>21.3</td>
<td>2.0 - 62.4</td>
</tr>
<tr>
<td>pH</td>
<td>6.1</td>
<td>4.2 - 7.9</td>
</tr>
<tr>
<td>Organic C, g/kg</td>
<td>14.6</td>
<td>2.0 - 38.4</td>
</tr>
<tr>
<td>CEC, mmol/kg</td>
<td>45.0</td>
<td>2.0 - 552</td>
</tr>
<tr>
<td>Resin P, mg/kg</td>
<td>17</td>
<td>3.0 - 56</td>
</tr>
<tr>
<td>Total N, mg/kg</td>
<td>1277</td>
<td>100 - 3200</td>
</tr>
<tr>
<td>Exch. Ca, mg/kg</td>
<td>978</td>
<td>66 - 5719</td>
</tr>
<tr>
<td>Exch. Mg, mg/kg</td>
<td>288</td>
<td>7 - 941</td>
</tr>
<tr>
<td>Exch. Na, mg/kg</td>
<td>102</td>
<td>12 - 407</td>
</tr>
<tr>
<td>Exch. K, mg/kg</td>
<td>305</td>
<td>12 - 1341</td>
</tr>
</tbody>
</table>

The soils had differing curves relating pH to amount of acid or base added (Fig. 1). Bagdad (fine silty, mixed, mesic, Calcic Argixeroll) and San Saba (fine, montmorillonite, calcic, Udic Pellustert) are given as examples of soils that have acidic (pH 5.3) and basic (pH 7.6) surface horizons, respectively. The degree of soil pH buffering increased with time of incubation from 3 to 30 days (Fig. 1). In general, all soils were well buffered below pH 4.0 and above pH 7.0, with acid or base amendments greater than 10 cmol (p+) kg\(^{-1}\) having little effect on soil pH (Fig. 1). The increase in pH between 20 cmol kg\(^{-1}\) acid and base amendments decreased with increasing soil organic C content (R\(^2\) = 0.72). Previous studies have also shown the degree of soil pH buffering to be a function of organic matter content (12,18).

Water-soluble Mg, Na, and K content decreased with increasing soil pH, as a result of acid and base amendments (Fig. 2). With acid and base amendments, water-soluble Ca content increased (Fig. 2). No significant (at 5% level) change
Figure 1. Titration curves for Bagdad and San Saba soils incubated with $\text{H}_2\text{SO}_4$ or $\text{CaCO}_3$ amendments for 3 and 30 days.
Figure 2. Effect of soil pH and incubation time on the amount of water soluble Ca, Mg, Na, and K for Bagdad and San Saba soils.
in exchangeable cation content, as measured by neutral NH₄OAc, was observed with acid or base amendments (data not presented). Consequently, cation solubility and not exchangeability is affected by a change in salt pH. The magnitude of change in cation solubility as a function of soil pH, represented by the slope of the linear relationship between the logarithm of the amount of water-soluble cation and soil pH, differed, however, between the exampled soils, Bagdad and San Saba (Fig. 2). Stepwise regression with physical and chemical properties of the 80 soils showed the slope of the relationship between water-soluble cation and pH to be most closely related to clay and exchangeable cation content (R² = 0.90 - 0.96) (Table 2). No individual soil properties accounted for more than 73% of the variation in relationship slope. Relationship slopes for Ca solubility were calculated using acid amendments only.

The effect of changing soil pH on cation solubility increased in the order Na, K, Mg, and Ca, as represented by an increasing average regression slope value of the soil pH-water soluble cation content relationship (0.167, 0.425, 0.664, and 1.024, respectively). Further, it is apparent that the magnitude of change in cation solubility with a change in soil pH increased with an increase in clay content and initial amount of exchangeable cation (Table 2). As incubation time did not affect the relationship between soil pH and cation solubility (Fig. 2), multiple regression equations between relationship slope and soil properties were determined using data combined for the 3- and 30-day incubations (Table 2).

A similar increase in Ca and decrease in Mg, Na, and K concentration of soil solution following lime addition to an acidic humo-ferric podzol from Ontario (initial pH 4.4) and three soils from Ireland (initial pH 5.4 to 5.8) were reported by Simard et al. (25) and Curtin and Smillie (8), respectively. This decrease in cation-water solubility may result from a respective reduction or increase in the number of positive or negative charges on the soil surface as pH is increased via base amendment (30). With a decrease in net positive charge, cations will be held on soil surfaces with greater binding energy.
Table 2. Relationship between cation and anion solubility and soil properties.

<table>
<thead>
<tr>
<th>Ion Solubility</th>
<th>Regression Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.026 Clay + 0.0005 Exch. Ca + 0.003</td>
<td>0.90</td>
</tr>
<tr>
<td>Mg</td>
<td>0.003 Clay + 0.0001 Exch. Mg + 0.581</td>
<td>0.91</td>
</tr>
<tr>
<td>Na</td>
<td>0.003 Clay + 0.0006 Exch. Na + 0.048</td>
<td>0.96</td>
</tr>
<tr>
<td>K</td>
<td>0.004 Clay + 0.0002 Exch. K + 0.0291</td>
<td>0.95</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>0.003 Clay + 0.024 pH + 0.001 Total N - 0.015</td>
<td>0.92</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.006 Clay + 0.114 pH - 0.348</td>
<td>0.93</td>
</tr>
<tr>
<td>P</td>
<td>0.003 Clay + 0.011 pH + 0.026 Resin P - 0.279</td>
<td>0.93</td>
</tr>
</tbody>
</table>

NO₃-N

<table>
<thead>
<tr>
<th>Days</th>
<th>Regression Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 days</td>
<td>0.130 pH + 0.0003 Total N - 0.850</td>
<td>0.90</td>
</tr>
<tr>
<td>30 days</td>
<td>0.190 pH + 0.0004 Total N - 1.155</td>
<td>0.92</td>
</tr>
</tbody>
</table>

+Data for 3- and 30-day incubations combined for all ions except for NO₃-N.

In contrast to cation solubility, Cl and NO₃-N in solution increased with increasing soil pH (Fig. 3). Although soil incubation time had no effect on the amount of Cl in solution, NO₃-N content was greater after the 30-compared to the 3-day incubation for both Bagdad and San Saha soils (Fig. 3). Similar trends were observed for the other soils. The increase in Cl and NO₃-N with increasing soil pH may be attributed to a reduction in the number of positive charges and consequent repulsion of these anions. In addition, enhanced N mineralization with increasing soil pH may also contribute to the observed increase in NO₃-N in solution (Fig. 3). Consistent with this is the release of NO₃-N by mineralization during incubation of the soil mixture. For the 80 soils, slope of the relationship between the logarithm of NO₃-N in solution and pH (Fig. 3) were significantly greater for the 30- (average slope value of 0.551) compared to the 3-day incubation (average slope value of 0.434). This contrasts with the other anions and cations studied, where incubation time had no significant effect on release to solution.
Figure 3. Effect of soil pH and incubation time on the amount of water-soluble P, Cl, NO$_3$-N, and NH$_4$-N for Bagdad and San Saba soils.
The fact that the amount of NH$_4$-N in solution decreased with increasing pH and was not affected by incubation time (Fig. 3), suggests that nitrification was sufficiently rapid in the present soil mixtures to prevent a buildup of NH$_4$-N. It is apparent from the present data that as soil pH is lowered, NH$_4$-N is the dominant N ion in solution compared to NO$_3$-N, as a result of a change in soil surface charge and microbial activity. With the addition of lime and increase in soil pH, NO$_3$-N becomes the dominant N ion in solution.

Slopes of the linear relationship between the logarithm of amount of Cl in solution (Fig. 3), were most closely related to clay content and initial pH of the 80 soils (Table 2). The inclusion of clay content in the stepwise regression of NH$_4$-N solubility is consistent with the role of clay-sized material in NH$_4$-N adsorption/desorption. As was the case for soil cations, individual soil properties accounted for no more than 61% of the variation in the relationship slope.

The amount of water-soluble P decreased with increasing soil pH, in contrast to the other anions Cl and NO$_3$-N studied (Fig. 3). Incubation time had no effect on the change in P solubility with increasing soil pH. Apparently, organic P mineralization in the soil mixture was not great enough to detect any increase in solution P as soil pH increased. The change in soil pH will affect, however, the solubility of Al-, Fe-, and Ca-complexes associated with P adsorption/desorption processes (15,16,28) and thereby P solubility.

Slopes of the linear relationship between the logarithm of P in solution and pH (Fig. 3), were most closely related to clay content and initial pH and resin P content of the 80 soils (Table 2). Clay-sized material and pH have been shown to influence soil P solubility (14,17,31) and resin P to be the source of soil solution P (4,23). A similar decrease in P solubility with increased pH as a result of lime application has been reported by Amarasiri and Olsen (3) for a Columbian Oxisol; by Dunbar and Baker (9) for 7 soils from Pennsylvania, Mississippi, and Jamaica; and by Hartikainen (11) for 2 mineral soils in Finland.
CONCLUSIONS

This study shows that, for soils spanning a wide range of physical and chemical properties, changing soil pH by acid or base amendment changes the concentration of cations and anions in soil solution. A decrease in the number of positive charges and an increase in negative charges on soil surfaces with an increase in soil pH contributed to a decreased solubility of Ca, Mg, Na, K, and NH₄-N. In the case of P, formation of insoluble Ca-P complexes may have also contributed to the decreased P solubility with CaCO₃ amendments. In contrast, NO₃-N and Cl solubility increased with an increase in soil pH. Enhanced N mineralization at higher soil pH may have contributed to the increased content of NO₃-N in solution, in addition to increased repulsion by positive charges.

The overall effect of an increase in soil pH would be a decreased leachability of Ca, Mg, Na, K, NH₄-N, and P in soil, but it could also result in a decreased availability for plant uptake. The opposite would be true for NO₃-N and Cl. A decrease in soil pH, resulting from acid rain input and ammoniacal fertilizer application, for example, would conversely affect cation and anion leaching and plant availability in soil. It may be possible to estimate these changes in cation and anion solubility as a function of soil pH from clay content, initial soil pH, and size of cation or anion pool maintaining the solution concentration. The regression equations relating soil physical and chemical properties and slope of the linear relationship between ion solubility and soil pH may be useful in estimating the effect of soil acid or base amendments on ion leachability and plant uptake availability.

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REFERENCES:


