Co-transport of dissolved organic matter and heavy metals in soils induced by excessive phosphorus applications

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Abstract

To evaluate the effects of long-term applications of phosphorus fertilizers on mobility of dissolved organic matter (DOM) and heavy metals in agricultural soils, a sandy soil and a loamy soil were spiked with ammonium phosphate at application rates of 0, 25, 50, 100, 250, and 500 mg P per kilogram of soil. A series of 15-cm long soil columns were constructed by packing incubated soils of varying concentrations of P. The soil columns were consecutively leached by simulated rainfalls for six cycles. The contents of water extractable organic carbon in both sandy and loamy soils increased significantly with increasing rates of P applications. Relatively high rates of P applications could induce a marked increase in DOM concentrations in the leachates, the effects were larger with the sandy soil rather than with the loamy soil. Applications of P changed the partitioning of trace metals in the soil solids and the soil solutions. The increased P application rates also seemed to elevate the leaching of Cu, Cd, and Zn from soils. The concentrations of Cu, Cd, and Zn in the leachates were positively correlated with DOM, probably due to the formation of metal-DOM complexes. In contrast, Pb concentrations in the leachates were negatively correlated with DOM, and decreased with increasing rates of P applications. The boosted leaching of DOM induced by high rates of P applications was probably due to the added phosphate ions competing for adsorption sites in the soil solids with the indigenous DOM.

Key words: dissolved organic matter; heavy metals; phosphorus fertilizer; leaching

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Introduction

Dissolved organic matter (DOM) is composed of an array of molecules generally reflecting the composition of total soil organic matter (Zsolnay, 2003). It accounts for only a small proportion of the total organic matter in soils. Nevertheless, it is now recognized that those molecules are active materials in terrestrial and aquatic systems, and play a crucial role in substance transport through soils and influence soil biological activity. They can act as a carrier for a variety of elements, ranging from nutrients to toxics such as heavy metals and pesticides (Lehman and Mills, 1994; Kalbitz and Wennrich, 1998; Zhou and Thompson, 1999; Akerblom et al., 2008; Ashworth and Alloway, 2008). Heavy metals in soils are capable of strong and specific binding to the common functional groups of DOM molecules. The most important of such functional groups are carboxylic acid and phenolic OH groups. Binding of heavy metals with DOM can influence their mobility in soils. The DOM-heavy metal complexes can easily move to streams and ground waters through surface transport and leaching.

Numerous biotic and abiotic factors can control the temporal and spatial dynamics of DOM in soils (Clay et al., 1995; Michalzik and Matzner, 1999; Andersson et al., 2000; Prechtel et al., 2000; Chantigny, 2003; Kone and Borges, 2008; Vestin et al., 2008). Soil pH and ionic strength determine organic matter solubility, whereas Al and Fe oxides and clay minerals determine the sorption/desorption equilibrium between the dissolved phase and the solid phase of soil organic matter (Benke et al., 1999). The adsorption intensity of the DOM on soils depended on solid components, solution properties and environmental conditions. Adsorption mechanisms of the DOM on soils include anion exchange, ligand exchange, cation bridging, van der Waals attraction or static adsorption (Salvestrini et al., 2004; Wagai and Mayer, 2007). Land use and application of limestone, organic amendments, and mineral fertilizers affect soil properties, and thereby are likely to influence the concentration of DOM. Several studies reported significant fluctuations in DOM following a change in land use or management practices (Qualls and Haines, 1991; Kone and Borges, 2008; Vestin et al., 2008). However, the processes and the driving forces behind the effects are largely unknown. Some anions in soil solutions can compete with DOM

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and thus influences adsorption capacity of soils to the DOM (Jara et al., 2006; Akerblom et al., 2008; Ashworth and Alloway, 2008; Sokolova and Alekseeva, 2008). High concentrations of anions such as phosphate could be introduced into anthropogenic soils by the applications of fertilizers. Long-term applications of fertilizers may result in phosphorus accumulation. In addition, large amounts of phosphorus are generally applied as soil amendments to chemically stabilize toxic metal contaminants like lead in Pb-contaminated soils (Cao et al., 2003; Brown et al., 2004). Therefore, an increase in anions in soils could result in a keen competition between anions and DOM for adsorption sites on soil solids, leading to the enhanced desorption of DOM from soils, and thus increasing the mobility of heavy metals in the soils (Lehman and Mills, 1994; Kalbitz and Wennrich, 1998; Zhou and Thompson, 1999; Akerblom et al., 2008; Ashworth and Alloway, 2008).

The objectives of this study were to verify a possible effect of long-term P applications on the mobility of DOM in soils under experimental conditions, and to estimate the mobilization of DOM-mediated heavy metals through the soils.

1 Materials and methods

1.1 Soils

One sandy soil and one loamy soil were selected for this study and they were sampled up to a depth of 0–15 cm from cultivated citrus soils in Quzhou and vegetable soils in Hangzhou, respectively, in Zhejiang Province, China. Parent materials of the sandy soil were river alluvium, and marine alluvium for the loamy soil. The sandy soil and loamy soil can be classified as fluvaquents and endoaqualfs, respectively, according to the Soil Taxonomy of the U.S. Department of Agriculture. The soil samples were allowed to air-dry, and then the same individual layer samples were mixed. All samples passed through a 2-mm sieve. The basic properties of the soils are presented in Table 1. It is obvious that both soils showed weak acid reaction. Table 1 also reveals the fact that the contents of clay, organic carbon, total P, total Pb, total Cu, total Zn and total Cd in the loamy soil were greater in comparison with the sandy soil. However, concentrations of available and water soluble metals were greater in the sandy soil than that in loamy soil (Table 1). Both soils were slightly contaminated by heavy metals possibly as a result of long-term applications of chemical fertilizers, organic manures, pesticides, and industrial pollution.

1.2 Phosphorus treatment

Soil samples were treated by adding P solution in the form of (NH₄)₂HPO₄ at six rates (0, 25, 50, 100, 250, and 500 mg P/kg soil). All treated soil samples were set a same NH₄⁺ concentration (844 mg/kg) by adding different amounts of (NH₄)₂SO₄, a control treatment was prepared in which only (NH₄)₂SO₄ was applied. After complete mixing, the soil samples were moistened with deionized water to 70% of field capacity and then transferred to polyethylene bags and incubated at 25°C for 30 days. During the period of incubation, field moisture capacity was maintained by weighing each soil sample and adding water weekly. After incubation, each soil sample was air-dried.

1.3 Experimental design

The leaching study was conducted in laboratory using PVC leaching columns with an inner diameter of 30 cm and a length of 20 cm. The bottom of the column was a PVC plate containing several 5-mm-diameter holes. The top of the plate was covered with nylon mesh and glued to the bottom of the column. Each of surface soils treated with P were packed in the top of the columns. Soil columns were packed with air-dried soil on the basis of original depth layer (15 cm) and bulk density (1.30 g/cm³) in the field. Triplicate columns were used for each treatment. Several filter papers were placed on the top of soil columns to prevent the disturbance by water droplets during leaching.

The experiment, including the simulation of six rainfall events, was carried out under greenhouse conditions for 100 days. Altogether, ca. 300 mm (50 mm each rainfall event) water was applied to each soil column during the 100 days. Before start the leaching experiment, deionized water was added to the columns up to free drainage of the soil material. The columns were leached by six rainfall events with one irrigation day per event. A dry period of 19 days was kept between each rainfall event. The experiment was carried out at room temperature (20–25°C), and the influent flow was controlled at 10 mL/min. The water was drawn through the column by gravity, and leachates were collected in glass bottles.

Column leachate was analyzed for pH, electrical conductivity (EC), DOC and heavy metals (Cd, Cu, Pb and Zn). Metals and DOC were determined on filtered samples (0.45 μm membrane filter), whereas EC and pH were

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sandy soil</th>
<th>Loamy soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Organic C (g/kg)</td>
<td>14.6</td>
<td>18.3</td>
</tr>
<tr>
<td>Sand (g/kg)</td>
<td>873</td>
<td>656</td>
</tr>
<tr>
<td>Silt (g/kg)</td>
<td>92</td>
<td>263</td>
</tr>
<tr>
<td>Clay (g/kg)</td>
<td>35</td>
<td>121</td>
</tr>
<tr>
<td>CEC (cmol/kg)</td>
<td>3.24</td>
<td>6.34</td>
</tr>
<tr>
<td>Total P (g/kg)</td>
<td>0.27</td>
<td>0.69</td>
</tr>
<tr>
<td>Olsen P (mg/kg)</td>
<td>14</td>
<td>21</td>
</tr>
<tr>
<td>Total Cu (mg/kg)</td>
<td>64</td>
<td>106</td>
</tr>
<tr>
<td>Total Zn (mg/kg)</td>
<td>56</td>
<td>90</td>
</tr>
<tr>
<td>Total Pb (mg/kg)</td>
<td>30</td>
<td>66</td>
</tr>
<tr>
<td>Total Cd (mg/kg)</td>
<td>0.28</td>
<td>0.64</td>
</tr>
<tr>
<td>Available Cu (mg/kg)</td>
<td>5.48</td>
<td>3.43</td>
</tr>
<tr>
<td>Available Zn (mg/kg)</td>
<td>6.34</td>
<td>2.28</td>
</tr>
<tr>
<td>Available Pb (mg/kg)</td>
<td>1.12</td>
<td>0.57</td>
</tr>
<tr>
<td>Available Cd (mg/kg)</td>
<td>0.074</td>
<td>0.046</td>
</tr>
<tr>
<td>Water soluble Cu (mg/kg)</td>
<td>0.39</td>
<td>0.18</td>
</tr>
<tr>
<td>Water soluble Zn (mg/kg)</td>
<td>0.85</td>
<td>0.44</td>
</tr>
<tr>
<td>Water soluble Pb (mg/kg)</td>
<td>0.12</td>
<td>0.046</td>
</tr>
<tr>
<td>Water soluble Cd (mg/kg)</td>
<td>0.0031</td>
<td>0.0017</td>
</tr>
</tbody>
</table>

CEC: cation exchange capacity.
measured on unfiltered samples. The leachates were filtered through 0.45 µm, divided in two aliquots and stored at 4°C until analysis. One aliquot for heavy metals determination was stabilized with HNO₃. The other aliquot was analyzed for DOC within 4 days using a Shimadzu TOC 5000A analyzer (Japan). Within 1 week, the concentration of Cd and Pb were determined by a graphite furnace atomic absorption spectrophotometer (GFAAS, Model SIMAA 6000, Perkin-Elmer, Germany), and those of Cu and Zn were determined by a flame atomic absorption spectrometry (FAAS, Perkin-Elmer, USA). Some of leachates with low concentrations of heavy metals were pre-concentrated to reduce their volumes by electrothermal vaporization before the measurement. The method detection limits were 0.12, 0.65, 14, and 12 µg/L, respectively for Cd, Pb, Cu and Zn.

1.4 Measurement of soil properties

Soil pH was measured in the supernatant at water:soil ratio of 2.5:1 (W/W). Sand, silt and clay contents in the soil samples were evaluated by the micropipette method (Miller and Miller, 1987). For heavy metal analysis, each of 1 g soil samples was digested with nitric acid and hydrochloric acid on a hot plate (Reed and Martens, 1996). The resulting solutions were diluted to 50 mL with ultrapure water. Available and water soluble heavy metals in the soil samples were extracted, respectively, by 1 mol/L NH₄OAc and 0.01 mol/L CaCl₂ (Reed and Martens, 1996). Cadmium and Pb concentrations in digestates and extracted solutions were measured using the GFAAS, and Cu, and Zn concentrations were measured using the FAAS. Analysis of the internal standards was repeated every 10 samples. All the reagents used were of trace pure grade. The samples were analyzed in three replicates.

Soil organic carbon was analyzed by the Walkley and Black dichromate oxidation method (Walkley and Black, 1934). Water soluble organic carbon was extracted with 20 mL distilled water from soil samples (10 g oven-dried equivalent). The resulting suspension was shaken for 16 hr, centrifuged at 10,000 r/min for 30 min and filtrated using a 0.45-µm membrane filter. Filtrates were stored at −10°C until analysis.

All chemicals used in the experiments were of analytical grade. All glassware was acid and water rinsed prior to use to avoid metal contamination. Statistical differences in measured variables among the treatments were analyzed with the SAS procedures (SAS Institute, 1998).

2 Results

2.1 Effect of P application on soil pH and water soluble organic carbon

Application of P fertilizer did not significantly caused the change of soils pH (Fig. 1a). Mean pH values of the treated soil samples ranged from 5.81 to 6.13 for sandy soil, and 6.11 to 6.37 for loamy soil. However, application of P fertilizer increased significantly concentrations of water extractable organic carbon in soils (Fig. 1b). For sandy soil, the concentrations of water extractable organic carbon in soils treated with P application rate of > 50 mg P/kg were significantly higher than that of the control treatment. While a significant increase in water extractable organic carbon was found in soils treated with P application rates of > 250 mg P/kg for loamy soil. In sandy soil, concentrations of water soluble organic carbon in soil samples treated with P application rates of 50, 100, 250, and 500 mg P/kg were 23%, 47%, 89%, and 145% more than the control, respectively. In loamy soil, concentrations of water soluble organic carbon in soil samples treated with P application rates of 250 and 500 mg P/kg were 52% and 72% more than the control, respectively.

2.2 pH and EC of leachates

For both soils, leachate pH increased slightly with increasing sequence of leaching, from 5.11–5.25 to 5.34–5.48 for sandy soil, and from 5.03–5.21 to 5.32–5.44 for loamy soil (Fig. 2). The lower pH values measured in first two leachates could be explained by a release of exchange acidity from the soils due to the addition of salts ((NH₄)₃PO₄ and (NH₄)₂SO₄). For both soils, however, no significant difference in pH values of leachates was found among the different P treatments through the whole experiment (Fig. 2).

EC was largest in the first leachate and decreased thereafter during the experiment due to the removal of the most
2.3 Leaching of DOM

Figure 4 shows the temporal changes in the DOC concentration in the leachates after application of P. For all P treatments, the DOC concentration was the largest in the first leachate and decreased gradually thereafter during the experiment due to the removal of the most soluble DOC fractions. The DOC concentration in the leachates increased in both soils as the rate of P application increased, it did not reflect the initial content of soil organic matter, rather it was a result of the different treatments. At same rate of P application, the concentrations of DOC in leachates from sandy soil were generally greater than those from loamy soil. The concentrations of DOC in leachates from the sandy soil ranged from 8.4 to 92.6 mg/L, with a mean of 34.4 mg/L. The concentrations of DOC in leachates from loamy soil ranged from 9.6 to 42.4 mg/L, with a mean of 20.4 mg/L. The results indicated that effect of P application on leaching of DOC in sandy soil was greater than loamy soil, since loamy soil had a higher amount of clay and stronger capacity to fix the DOC than sandy soil.

2.4 Leaching of heavy metals

Metal concentrations measured on individual leachate generally varied with leaching sequence and were highly variable among the different P treatments (Fig. 5). Application of P had an effect on amounts of cumulative dissolved heavy metals leached from soils (Table 2). However, the four metals exhibited different treatment-specific effects. Leaching of Cu and Cd increased significantly with increasing rate of P application. The Cu and Cd concentration were consistently higher in the leachates from the P treatment columns than those of control column (Fig. 5). The application of 500 mg P/kg to soil produced the
Fig. 4  DOC concentrations in leachates. P0, P25, P50, P100, P250, and P500 are the same as that in Fig. 1.

Fig. 5  Effects of P application on leaching of heavy metals in sandy and loamy soils. P0, P25, P50, P100, P250, and P500 are the same as that in Fig. 1.

Table 2  Amounts of cumulative DOM, Cu, Zn, Cd, and Pb leached from each soil column

<table>
<thead>
<tr>
<th>Element</th>
<th>P application rate (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Sandy soil</td>
<td>DOM-C (mg)</td>
</tr>
<tr>
<td></td>
<td>Cu (mg)</td>
</tr>
<tr>
<td></td>
<td>Zn (mg)</td>
</tr>
<tr>
<td></td>
<td>Cd (µg)</td>
</tr>
<tr>
<td></td>
<td>Pb (µg)</td>
</tr>
<tr>
<td>Loamy soil</td>
<td>DOM-C (mg)</td>
</tr>
<tr>
<td></td>
<td>Cu (mg)</td>
</tr>
<tr>
<td></td>
<td>Zn (mg)</td>
</tr>
<tr>
<td></td>
<td>Cd (µg)</td>
</tr>
<tr>
<td></td>
<td>Pb (µg)</td>
</tr>
</tbody>
</table>

Data within a row with same letter(s) are not significantly different at p = 0.05 probability.
highest leachate concentrations of Cu and Cd, whereas the lowest concentrations were seen in the control treatment. Leaching of Zn increased with increasing rate of P application only in sandy soil, but not significant in loamy soil. Zinc were mainly mobilised in the P treatment for sandy soil, whereas small effect of P treatments was observed for loamy soil. Leaching of Pb decreased with increasing rate of P application. The highest Pb concentration was observed in the control treatment. The total amount of Pb leached in six cycles of leaching was only 27%–60% for sandy soil and 18%–43% for loamy soil treated with P at rates of 50–500 mg/kg, as compared with the control treatment.

Despite that total concentrations of heavy metals in loamy soil were higher than those in sandy soil, the leaching of the metals was consistently larger from sandy soil than from loamy soil, reflecting a higher availability and mobility of the metals in the sandy soil (Table 1). Concentrations of Cu, Zn, Cd, and Pb in leachates from sandy soil ranged from 13 to 78, 14 to 57, 0 to 1.3, and 0.13 to 0.87 µg/L, respectively, and averaged 35, 29, 0.48, and 0.31 µg/L, respectively (Fig. 5). Those of Cu, Zn, Cd, and Pb in leachates from loamy soil ranged from 14 to 58, 21 to 55, 0 to 2.90, and 0 to 0.34 µg/L, respectively, and averaged 29, 33, 0.96, and 0.098 µg/L.

In order to get a better understanding of the leaching behaviour of each single metal, we analyzed the relationships between the measured metal concentrations and DOC for all leachate samples. For both soils, there was a strong positive correlation between the DOC concentration and the Cu, Zn, and Cd concentrations. Clearly, the decrease in the Cu, Zn, and Cd concentrations were coincided with the decrease in the DOC concentrations (Figs. 4 and 5). This was not surprising given that all these metals are known to form strong complexes with organic substances (Tipping, 2002). Since these trends in the DOC and the metal concentrations are clearly coupled, DOC seemed to control the mobility of Cu, Zn and Cd in soil columns. However, it is not true for Pb and there is a negative correlation between the DOC concentration and the Pb concentrations (Table 3). A possible explanation is that high P application rate increased the formation of pyromorphites (Schwab et al., 2006).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy soil</td>
<td>0.941**</td>
<td>0.777**</td>
<td>−0.537**</td>
<td>0.903**</td>
</tr>
<tr>
<td>Loamy soil</td>
<td>0.768**</td>
<td>0.313*</td>
<td>−0.370*</td>
<td>0.821**</td>
</tr>
</tbody>
</table>

* *, ** mean significance at p < 0.05 and p < 0.01, respectively.

3 Discussion

3.1 Effect of P application on the release of DOM in soils

Both P and DOM are multiprotic anions. Similar to the sorption of DOM sorption, the reactions of P anions in soils are closely linked to soil sesquioxides, and their relative affinity for mineral surfaces is similar to that of DOM (Kaiser and Zech, 1998). When more than two anions are present in solution, competition is expressed either through direct physical competition for sorption sites or through electrostatic competition arising in the “plane of adsorption” following adsorption of the respective anions. The electrostatic competition is a consequence of increased negative surface charging following adsorption, and can occur where concentrations are not high enough for physical competition for sites to become significant and will be higher where anions sorb to soil surfaces in the same “plane of adsorption”.

Organic matter (OM) interacts with P in soils in a variety of ways that potentially influence P and dissolved organic matter adsorption reactions (Shenker et al., 2005; Satti et al., 2007). As applied OM decomposes in the soil, carbon compounds are produced through microbial action that may react directly with P sorption sites on soil, potentially increasing the solution P concentration (Hue, 1991; Bar-Yosef, 1996; Kaiser and Zech, 1997; Borovec and Hejzlar, 2001). Many studies have been undertaken to assess the competitive effects of DOM on P sorption on soils and synthetic surfaces (Cai et al., 2007; Hunt et al., 2007; Chen et al., 2008). Afif et al. (1995) examined the ability of P to competitively displace adsorbed DOM from a brazilian Oxisol over time. Addition of P released 1–9 µmol low molecular weight organic acids (LOA) per gram (predominantly oxalate and malate), increasing both with the amount of P applied and with time. Slow P sorption displaced approximately 2 mol LOA for each mole of P adsorbed and was correlated with the ratio of soil OM to specific surface area. Competitive sorption between humic and fulvic acids or low molecular weight aliphatic acids and P for soil sorption sites results in the increase in DOM concentration. Sorption of P may increase the negative charge on the soil surface, or decrease the point of zero charge, thus making it more difficult for DOM sorption to occur. Jones and Brassington (1998) demonstrated that the ligand exchange reactions of DOM are weak, rapidly saturation the anion sorption capacity of the soils examined. The amount sorbed followed the series of phosphate > oxalate > citrate > malate > acetate. Therefore, the elevated leaching of DOM induced by high rate of P application was probably due the competition adsorption between phosphate and DOM on the soils.

3.2 Effect of P application on release of heavy metals in soils

Changes of soil conditions could influence the mobility of trace metals in contaminated soils (Kabata-Pendias, 2001). The solubility of heavy metals is sensitive to the changes in pH (Kabata-Pendias, 2001). The lowering of pH after sulfur application has been demonstrated to increase significantly the solubility and uptake of soil Zn and Cd by sunflower and maize (Kayser et al., 2000). Increased concentrations of soluble salts may displace weakly sorbed metals such as Cd and Zn from soil sorption sites, which may also increase the dissolution of these metals. It was
reported that increased susceptibility to leaching of trace metals was increased when exposure to high NaCl concentrations (Norrström and Jacks, 1998; Bäckström et al., 2004). However, our results showed that leachate pH, or EC did not significantly differ among different P treatments over the course of this study. It is likely that such a small change in soil pH and EC by P treatments were not strong enough to significantly affect metal adsorption and ion exchange processes to result in elevated leaching of soluble metals. Therefore, pH and EC may be of minor importance on the mobilization of heavy metals in soils under the studied experimental conditions.

The soil organic matter and organic amendments can release soluble organic acids, which can increase the mobility of heavy metals (Berggren, 1990; Ross, 1994; Wu et al., 2002). Many authors had reported that soluble organic complexes may increase metal mobility and leaching potential in soils (del Castillo et al., 1993; Li and Shuman, 1996). Our results showed that there was a strong positive correlation between the DOC concentration and the Cu, Zn, and Cd concentrations. Therefore, the increased concentrations of Cu, Cd, and Zn in leachates from soils with high rate of P application were probably due to the formation of metal-DOM complexes.

Decreases in leachate Pb concentration in soils with high P application rate were due to the formation of pyromorphites, and insoluble Pb-phosphate complex (Schwab et al., 2006). Pyromorphite is an insoluble lead phosphate (Pb₅(PO₄)₃(OH, Cl, F,...)), and it is chemically and biologically stable under the surface soil conditions. Application of phosphate-based amendments, including synthetic hydroxyapatite, phosphate rocks, triple superphosphates, has been shown to effectively remove Pb from aqueous and soil solution (Ma et al., 1995), and to minimize leachable Pb in industrial wastes (Crannell et al., 2000). The leachability of Pb has been reported to decrease with increasing soluble P in soil (Yang et al., 2001, 2002). The decrease of Pb in the leachates may also be caused by the presence of phosphate adsorbed to ferrhydrite, which increased Pb sorption through surface charge adjustment or surface precipitation (Weesner and Bleam, 1998).

4 Conclusions

This study has demonstrated that excessive phosphorus application could accelerate vertical migration of DOM and heavy metals in soils. The results confirm the central role of DOC for the mobilization of Cu, Cd and Zn in soils. Content of water extractable organic matter in both sandy and loamy soils increased significantly with increasing rate of P application. The effect of P application on DOM leaching in sandy soil was greater than that in loamy soil. The increased P application rate also elevated the leaching of Cu, Cd, and Zn from soils. The concentrations of Cu, Cd, and Zn in the leachates were positively correlated with DOM. In contrast, Pb concentration in leachates was negatively correlated with DOM, and decreased with increasing rate of P application. The elevated leaching of DOM induced by high rate of P application was probably due to the competition adsorption between phosphate and DOM on the soils. The increased concentrations of Cu, Cd, and Zn in leachates from soils with high rate of P application were probably correlated to the formation of metal-DOM complexes. Decline in leachate Pb concentration in soils at high P rate may be due to the formation of pyromorphites, an insoluble Pb-phosphate complex.

However, above phenomena were observed in laboratory with constructed soil columns. It may be not complete representative of fields. For example, the production of DOC in the field will also be controlled by plant and microbial activity. Microbial activity is probably playing some important role. There is likely a stimulation of a microbial community in the P fertilized soils that may also result in the increase in DOC. Factors influencing the leaching of metals in soils under the field conditions were more complex than that in laboratory conditions. Further studies were needed to verify these possibilities.

Acknowledgments

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