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Leaching Behavior of Copper (II) in a Soil Column Experiment

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Leaching of heavy metals into groundwater has received increasing attention. The environmental impact of heavy metal contaminants strongly depends on the metals speciation, mobility, and bioavailability in soil (Morton et al. 2000). The chemical behavior of heavy metals in soils is affected by a number of processes, including sorption onto surface of soils (Allen et al. 1995; Zhou and Wong 2001), complexed with inorganic and organic ligands (DiToro et al. 2000), and so on.

There are two sources for heavy metals to leach from soil to groundwater. One is the disposal of industrial sludge or dredged sediment, which will cause the groundwater contamination by solution elution. Many researchers have studied the leaching behavior of heavy metals from contaminated soils, industrial sludges, dredged sediments, and municipal solid wastes (Meima and Comans 1997; Voegelin et al. 2003; Dijkstra et al. 2004; Dubey and Townsend 2004). The potential risk of heavy metals in soils, with respect to their mobility and ecotoxicological significance, is determined by their solid-solution partitioning rather than the total heavy metal content (Dijkstra et al. 2004). The release of heavy metal cations to the water phase depends on their affinity to bind to reactive surfaces in the soil matrix and pore water. The other source is the process of irrigation with wastewater which contains high concentrations of heavy metals. Downward migration of heavy metals in wastewater is much easier because of their being in soluble phase. But the migration process is mainly controlled by adsorption in soil (Zhou and Wong 2001). Many factors can influence the migration process as well, such as pH, dissolved organic matter, and soil characteristics (Zhou and Wong 2001; Zomeren and Comans 2004). But little has been studied on the copper migration under different leaching solvents. The objective of this study was to evaluate the transport of copper (II) in a soil column experiment and to investigate the influence of different leaching solvents on the downward migration of copper.

MATERIALS AND METHODS

Soils (pH 7.11, 2.48% organic matter) used in the column experiments were taken from the garden in Nankai University, Tianjin, China. The soils were air dried and passed through a 60 mesh sieve. Three plexiglass columns 2.5 cm in diameter by

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30 cm in length were packed identically with the soil to a bulk density of 1.38 kg/L. The soil was packed into each of the plexiglass columns while gently tapping the sides of the column until the soil height was 25 cm. Glass wool was placed on the base of each column, minimizing the dead end volume.

On the top of each soil column an aliquot of 10 mL of 1000 mg/L $Cu(NO_3)_2$ was added. A multichannel peristaltic pump was used to apply solutions to elute the columns. Solutions for elution include DIW (deionized water, Millipore Ultra-pure Water System), leaching solvents for TCLP (toxicity characteristic leaching procedure) and SPLP (synthetic precipitation leaching procedure), solution with DOC (disolved organic carbon, Humic acid, Fluka, Switzerland) content of 10 mgC/L. The leaching solvent used for the pH experiment consisted of DIW, to which 1 N nitric acid or 1 N sodium hydroxide was added to obtain the desired pH. The leaching solvent for the SPLP (pH 4.20±0.05) (USEPA Method 1312) consisted of a mixture of DIW to which a solution of sulfuric acid/ nitric acid (60/40 wt%) was added. For the TCLP (USEPA Method 1311), the leaching solvent was buffered acetic acid (pH 4.93±0.05) (USEPA 1996).

Flow rate of leaching solutions was 1.0 mL/min, and leachate was collected in 50 mL portions. After the elution experiment the columns were sectioned into 5 cm depth layers. Each layer of soil was lyophilized with a freeze dryer (CHRIST ALPHA 1-2 LD, Germany). In each layer exchangeable copper was determined using the method by Tessier (1979). In brief, 1 g of soil was extracted at room temperature for 1 h with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) with continuous agitation. After centrifugation, the supernatant copper concentration was determined. All samples were passed through 0.45 μm filter membrane before analysis. Copper was analyzed using ICP-AES (IRIS Intrepid II XSP, Thermo Electron Corporation).

RESULTS AND DISCUSSION

The leaching rate of copper was affected by eluted solutions. Figure 1 showed the cumulative leachates concentrations of four leaching solutions. The data were the average of three duplicates in this study. All the four solutions could leach large amounts of copper in the first 50 mL of leaching solution. From Figure 1 we can conclude that leaching solvent for SPLP can make copper move downward faster than the other three solutions. In the first 50 mL of leachates, copper concentration in SPLP leachate was about twice amount or more than in the other three leachates, indicating its high ability to leach copper. SPLP is the standardized procedure designed by USEPA to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes(USEPA 1996). The SPLP simulates conditions where infiltrating rainfall can result in the leaching of chemicals from recycled waste that is intended for land application and is used to assess if leaching poses a threat to groundwater contamination. Because leaching solvent for SPLP is prepared by sulfuric acid/nitric acid, the result also indicates acid rain which occurs frequently in many places can enhance the copper downward movement to groundwater. This trend also can be seen by exchangeable copper

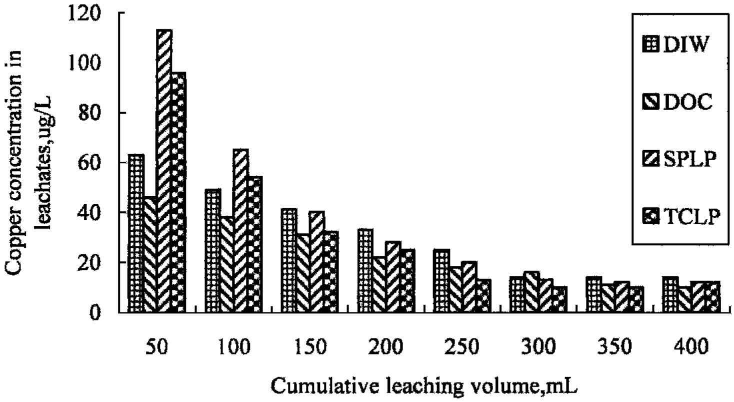

Figure 1. Concentration of copper in column leachates at a flow rate of 1.0 mL/min.

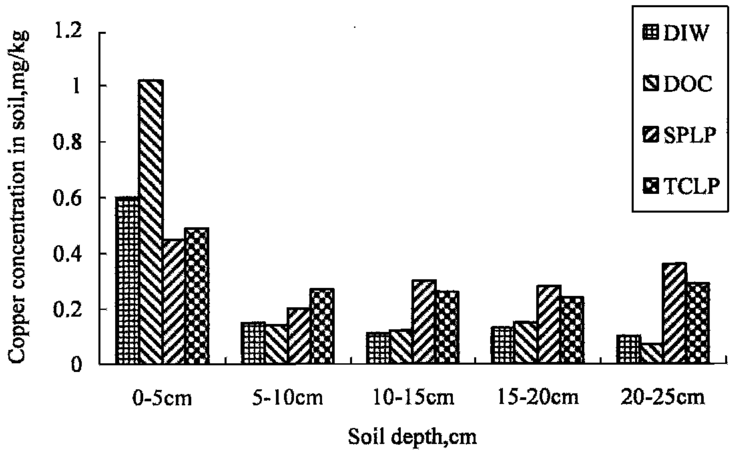

Figure 2. Vertical distribution of copper concentrations in soil columns

concentrations in different soil layers of the soil columns as shown in Figure 2. Copper concentrations in soil layers eluted by SPLP leaching solvents were higher in depth 10-25 cm than the other three soil columns. In column soil layers TCLP leaching solvents has the same leaching ability as SPLP.

Dissolved organic matter (DOM) is a very important component which plays an important role in facilitating the leaching of contaminants in soil (Haberhauer et al. 2002; Zomeren and Comans 2004). Dissolved organic matter can facilitate metal transport in soil and groundwater by acting as a carrier through formation of soluble metal-organic complexes (McCarthy and Zachara 1989). Zhou and Wong (2001) found in presence of DOM, Cu sorption capacity decreased markedly for the calcareous soil. The results in this study showed DOC increased the copper retention in soil columns. DOC solution could take less copper from the soil

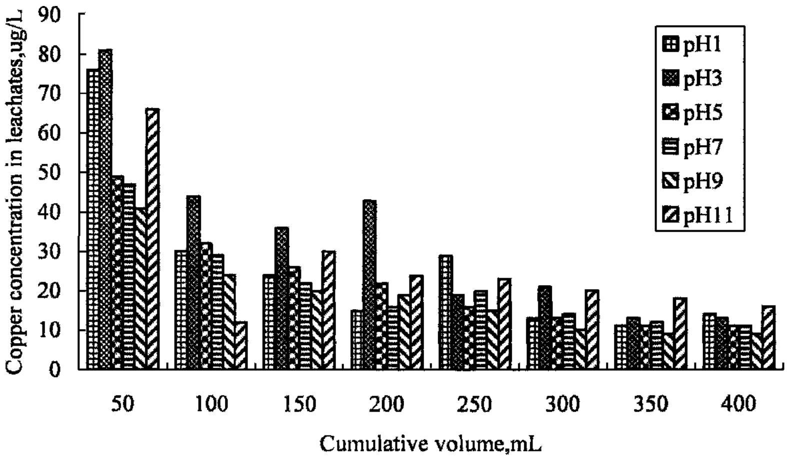

Figure 3. Concentration of copper in column leachates at a flow rate of 1.0 mL/min.

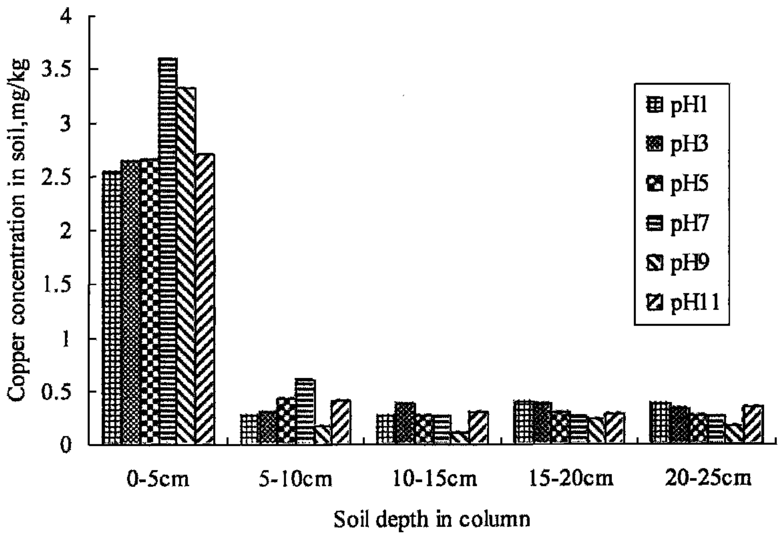

Figure 4. Vertical distribution of copper concentrations in soil columns.

columns compared with DIW and SPLP leaching solutions, as shown in Figure 1. In Figure 2 the same trend can also be seen. In the soil layers of 0-5 cm for the four soil columns, the highest copper concentration appeared in the column eluted by DOC solution, and in the layer of 20-25 cm, its concentration was the lowest, indicating the increased retention of copper by DOC solution. Dissovled organic matter may transfer into solid organic matter and therefore increase the binding capacity of the soil. Temminghoff et al. (1997) found that when DOC was added to the feed solution, the solid organic matter became larger in the first two sampled layers of the columns due to coagulation. Copper may be complexed with DOC in the soil so that the mobility decreased.

The concentrations of copper leached from soil columns eluted by different pH-value solutions were in Figure 3. In Figure 3, leachates of elution solutions at pH 1, 3 and 11 had high copper concentrations, suggesting their high abilities to mobilize copper in soil columns. Leaching solutions at pH 5, 7 and 9 gave relatively poor copper concentrations in leachates.

In this study, the added stock copper solution was 10 mL of 1000 mg/L Cu^{2+}. In the first 50 mL of portion for pH 3 leachate, leached copper only occupied 0.04% of the total added copper in the soil column. Even for the leaching solvents for SPLP, the proportion was only 0.06%. Generally, heavy metals in the soil are rapidly retained as insoluble compounds and adsorbed to soil surface (Loganathan and Hedley 1997). Therefore, downward movement of soluble heavy metals to groundwater has seldom occurred, even over several decades (Barbarick et al. 1998).

The vertical distributions of copper concentration in the soil columns affected by pH were presented in Figure 4. Solutions at pH 7 and 9 leached out less copper from the columns (Figure 3), so the copper concentrations at 0-5 cm layer were higher than the other soils. At other layers, the copper concentrations had no significantly difference. The results also showed that, most copper existed in the top layers (0-5 cm) of the soil columns. Concentrations of exchangeable copper decreased drastically from the top layer to the bottom layer, suggesting soluble copper was adsorbed to soil significantly when it entered into the soil.

The study on the leaching behaviors of copper in soil columns showed that copper leaching differed under different conditions. Leaching solvents for SPLP and TCLP could enhance the downward movement of copper in the soil column, while DOC solution increased the copper retention. At pH 1, 3 and 11, copper mobility was enhance as well. However, although the concentration of copper in some leachates was high, most of their concentrations were lower than the limitation value of Quality Standard for Ground Water of China (1.0 mg/L for agricultural use) (Chinese National Standard: GB/T 14848-93). Copper can be more strongly adsorbed in soils than other heavy metals such as zinc, manganese, and cadmium (Tam and Wong 1996). Most of added copper existed in the top layer of the soil.

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