



In-situ observation of the mobilization of heavy metals in soil columns in the presence of plants

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The aim of this study was to gain high-resolution data on mobilization and transport of heavy metals during percolation of water through unsaturated soil columns in the absence and presence of plants. Soil solution sampling has been performed by the use of suction cups installed along the length of the column. The columns were irrigated with artificial rainwater at different flow rates. *Lupinus albus* was chosen as a model plant known for its high exudation of organic acids. Total metals (Zn and Cu) as well as their speciation (free Cu^{2+} and labile Zn) were measured in addition to general chemical parameters. This experimental set-up was able to give a direct view of the processes in the soil with a spatial resolution of a few centimeters without disturbance of the soil.

Dissolved Zn and Cu increased with depth in the topsoil. Rapid immobilization of Cu and Zn occurred within few centimeters of the polluted topsoil- clean subsoil boundary. The mobilization of Cu and Zn along the column was strongly coupled to the slow mobilization of DOC. The mobilization of DOC was promoted when the flow rate was increased. Labile Zn was always around 60% of dissolved Zn, free Cu^{2+} was decreased when the DOC was increased at the higher flow rate.

Lupine had no significant influence on dissolved Zn and Cu in the column. Citrate was never detected in soil solution and oxalate only in a few samples at very low concentration (less than $2 \mu\text{M}$). The effect of the plants (exudation or water and solute uptake) on heavy metal mobilization was therefore not significant under the experimental conditions.

Our results show that small-scale and temporal changes in pH and DOC mobilization were the main factors that determined Cu and Zn mobilization and transport in the polluted soil that we have used. Understanding the changes of pH and DOC caused by different irrigation regimes are a key to interpret the mobilization and transport of heavy metals. Exudation or water uptake by plants did not significantly contribute to metal mobilization in the column.