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Influence of root exudates on solubilization and speciation of metals in soil solution

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Advances in analytical chemistry over the last 20 years have markedly improved our ability to identify and quantify metal species in the environment. In soils, phytotoxicity, phytoavailability and risk of leaching of metals to the groundwater are controlled by the specific metal species. In particular, the chemical conditions in the rhizosphere soil (soil surrounding the plant roots), can be influenced by root activity. In the last few years, phytoremediation techniques such as phytoextraction using hyperaccumulator plants with exceptional metal accumulating capacities have emerged. To assess the potential of these techniques, we need to get a better understanding of the impact of these green techniques on the speciation and fate of heavy metals in the environment.

The goal of this study is to investigate the role of root exudates on the mobilisation and speciation of heavy metals by hyperaccumulator plants using a 3-step approach.

Firstly, we looked for a system which allows measuring organic acid exudation in the rhizosphere soil solution in situ. For this purpose, we modified the rhizobox system of Göttlein *et al.* [1] which has been used to demonstrate the root influence on the concentration of major inorganic ions, but not the exudation of organic acids. In this system, a flat root system is developed and soil solution in rhizosphere and bulk soil was sampled by means of micro tension lysimeters. The samples were stabilised immediately with formaldehyde and the organic acids were analysed by ion chromatography. As a model plant, we used *Lupinus albus* which is known to exude high amounts of citrate.

The exudation of organic acids was well detected with our system and was significantly higher in the rhizosphere than in the bulk soil (about 600 μM of citrate vs <10 μM). To our best knowledge, this is the first time that the naturally occurring exudation of organic acids was analysed **in situ,** which represents a significant extension in applications of the classical rhizobox system.

Secondly, we tested an ASV (anodic stripping voltammetry) technique with gel integrated microelectrodes for determining labile Cu, Zn and Cd in the small soil solution samples of $<$ 1 ml obtained with our rhizobox system. This technique has been developed and used for in situ measurements in aquatic systems and has been shown to be a unique tool to get quantitative information on metal speciation [2]. So far, this system has not been applied to soil solution. Tests were conducted on samples obtained from the experiment described above and from additional rhizoboxes filled with contaminated soil but without plants. The analyses did not show any interference problems due to the high concentration of organic compounds in soil solution compared to natural waters. In the different soils, we found 34% to 56 % of Cu to be labile.

Thirdly, in an ongoing rhizobox experiment, we are investigating the role of root exudates on the mobilisation and uptake of Zn and Cd by plants and the risk involved with respect to metal mobility in the soil. Three plants are used: *Thlaspi caerulescens* (Cd and Zn hyperaccumulator), *Thlaspi perfoliatum* (non-hyperaccumulator) and *Lupinus albus*. We use metal contaminated and non-contaminated soils. The soil solution samples are obtained at different occasions during the development of the root system. In addition to organic acids and labile metals, we measure total metal concentrations by ICP-MS and pH using an ISFET electrode.

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[2] M.-L. Tercier-Waeber, J. Buffle, M. Koudelka-Hep, F. Graziottin. Ch. 2 in: "*Environmental Electrochemistry: Analysis of Trace Element Biogeochemistry*". M. Taillefert, T.F. Rozan (Eds.), ACS Series No. 811, Washington DC,(2002), pp. 16-39.