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Environmental Pollution 133 (2005) 103–116

ENVIRONMENTAL POLLUTION

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Comparison of the method of diffusive gels in thin films with conventional extraction techniques for evaluating zinc accumulation in plants and isopods

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Received 9 January 2004; accepted 21 May 2004

"Capsule": *The newly developed method of diffusive gels in thin films (DGT) does not have an added value over conventional extraction techniques in predicting zinc uptake by plants and isopods.*

Abstract

The measurement of diffusive gels in thin films (DGT) has recently been developed to assess metal bioavailability in soils. The DGT-method is based on diffusion in a porous matrix. To test the predictive capabilities of the method with regard to metal bioavailability, a study was set up with 28 soils having a variety of textures and amounts of zinc salts added. Correlation and regression analyses were performed to compare DGT-extracted zinc levels to zinc concentrations obtained by extraction with 0.01 M $CaCl_2$ and 0.43 M HNO_3, digestion with *aqua regia* and the zinc concentration in pore water. The amount of zinc extracted with $CaCl_2$ correlated well with DGT-extracted zinc levels in all soils spiked with different amounts of $ZnCl_2$. A similar correlation was not found for zinc concentrations in soil samples collected in the field. Experiments were performed to compare zinc content in organisms and in soils. The organisms tested were plants (grass, lettuce and lupine) and the hard bodied soil dwelling isopod *Oniscus asellus*. Good correlations were found between zinc accumulation in grass and lettuce and the C_E (effective concentration) measured by a DGT-device, $CaCl_2$ extracted zinc and the zinc content in the pore water of all soils. The correlation with C_E was not significant for lupine, neither for spiked soils, nor for field soils ($p \leq 0.001$). Zinc levels in the isopods were not significantly related to any set of zinc measurements. From a synthesis of all results obtained it is concluded that the DGT-methodology does not have an additional value in predicting bioavailability of zinc in terrestrial ecosystems as compared to conventional extraction methods.

Keywords: DGT; Bioavailability; Zinc; Plants; Soil

1. Introduction

Risks of heavy metals in terrestrial ecosystems are currently evaluated on the basis of the total metal content in the solid phase of a soil. It is realised that the metal content in the solid phase often does not well predict toxic effects in soil dwelling organisms and plants (Crommentuijn et al., 1997). Reasons for this discrepancy may be found in the fact that the bioavailability of metals in natural soils amongst others depends on differences in soil texture, such as concentrations of clay, sand and organic matter. Also the

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0269-7491/$ - see front matter
doi:10.1016/j.envpol.2004.05.022

properties of the soils used in laboratory experiments to assess toxicity of metals differ significantly from the properties of field soils, and hence the bioavailability of metals in both types of soils differs significantly. This difference of bioavailability is especially evident in laboratory experiments in which typically a fixed amount of a metal salt is added to a soil.

Bioavailability can initially be considered to consist of two processes taking place in the soil: a physicochemically driven desorption process by which metals equilibrate between the solid phase and the pore water, and a physiologically driven uptake process from the solid or liquid phase by the organism that is studied (Posthuma et al., 1998). Soil characteristics play a profound role in the physicochemical processes that determine possible toxicity for biota associated with soil pollution. This involves especially their impact on the partition of the metal between the solid phase and the pore water (Peijnenburg et al., 2000a). A third process that completes the concept of bioavailability concerns the internal distribution processes in the organism, transport to specific targets for toxicity and detoxification mechanisms like inert storage in specific organs. It is assumed that toxic effects only manifest themselves after exceeding a critical internal value in organs or organelles of an organism. In aquatic invertebrates for instance, trace metals present in organisms can be divided into two categories, metal that is in a metabolically available form and metal that has been detoxified and is no longer available to play any role in metabolism. Only the metal amount in the first category will be toxic when a threshold concentration is passed (Rainbow, 2002).

According to this concept of bioavailability, the soil texture, pH, DOC, the metal concentration, the organism living in contact with the soil and even the presence of competing ions like Na and Ca are the major factors in assessing the impact of soil pollution on terrestrial ecosystems. To estimate the actual risk of polluted soil it will be necessary to take account of these three factors. However this seems a complicated approach, and research to find new ways to establish the risks in a relatively simple way is needed. In the past years all sorts of soil extraction methods were developed to be able to predict metal bioavailability. Depending on the chemical effect that is expected, several groups of extraction solutions can be distinguished. For a weak extraction of metal from a soil, water, salt solutions like 0.1 M $NaNO_3$ or 0.01 M $CaCl_2$ might be used (Houba et al., 1996). Other methods include extraction with a dilute strong acid, like HNO_3 or concentrated strong acids like HCl or *aqua regia* (HNO_3 + HCl).

Generally, in studies for plant uptake, a weak extraction method is used to mimic the bioavailable fraction because the results correspond better to the interaction of plants and soil than the action of more aggressive agents. A solution of 0.01 M $CaCl_2$ is often preferred, because its concentration approaches that of the average soil solution. Ca^{2+} is a dominant cation in the adsorption complex of soil and various elements can be measured simultaneously (Novozamsky et al., 1992). Houba et al. (1996) even suggested using $CaCl_2$ as a universal extraction solution. In a bioavailability study the uptake of copper by maize in vineyard soils was studied by Brun et al. (2001). Four single extraction solutions, EDTA, DTPA, ammonium acetate and 0.01 M $CaCl_2$ were tested. The results showed that copper content in the roots correlated best with the amount of metal extracted with EDTA, DTPA and ammonium chloride but that the $CaCl_2$-extractable copper correlated best with the copper content in the shoot. These results make it difficult to decide which extracted copper content reflects bioavailability best. Singh and Narwal (1984) performed a study in which *aqua regia* was used to extract zinc from sludge-amended soils and to determine the correlation with zinc uptake by fodder rape (*Brassica napus*). Their results showed no correlation between the zinc extracted from the soil and the zinc content in the rape.

Recently a new approach to assess the bioavailability of metal in soils has been developed. The approach is based on a chemical measurement of the metal content in soils by use of a gel technique, the DGT (Diffusion Gradients in Thin Films) method (Zhang and Davison, 1995; Harper et al., 1998; Hooda et al., 1999). A measurement device is used that consists of a layer of an ion exchange resin (Chelex 100) embedded in a hydro gel. The interesting feature of the DGT-method is that it is based upon quantification of diffusion in a porous matrix, which is basically the same process as organisms use to extract liquid from soil. When this DGT-unit is placed into a soil, metal will accumulate in the resin gel layer. The result will be a diffusive flux to the DGT-unit of metal ions present in the pore water and the ions that become available by desorption from the solid phase. With the more "classical" methods, like pore water collection or extraction with 0.01 M $CaCl_2$, to establish the metal content of a soil, a physical separation of solid phase and water takes place thus irreversibly disturbing the delicate partition equilibrium of metal between the solid phase and the pore water. When using a DGT-device, the natural situation is marginally disturbed. Currently this method is being tested to see if metal levels determined with DGT-devices correlate with the uptake of metals by certain organisms. Zhang et al. (2001) for instance showed that the copper availability to the plant *Lepididium heterophyllum* as measured with the DGT-method was highly correlated to the copper concentrations in the plants.

To test the hypothesis that the DGT-method is predictive for uptake of zinc by a range of soil organisms and plants, a study was performed in which Dutch field soils with different concentrations of zinc were