

Bioavailability of metals and organic contaminants in soils

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Abstract

Recent advances in the understanding and prediction of the risk of metal toxicity in different soils which explicitly include the concept of bioavailability are reviewed, along with development of terrestrial biotic ligand models for metals. Both of these are aimed at assessing the “safe” concentrations of metals that can accumulate in soils without negative biological effects. For organic contaminants, the recent emphasis appears to be on the area of their partial extraction from soils, and the search for extraction regimes that mimic either their bioavailability or bioaccessibility in soils. This appears to be due to the focus in the organic arena not on toxicity *per se* but on the assessment and remediation of already contaminated sites.

Key Words

Zinc, copper, nickel, cobalt, polycyclic aromatic hydrocarbons.

Introduction

Concerns regarding the potential risks of existing chemicals in the environment gave rise to the European Union Directive (793/93/EEC) for the evaluation and control of risks posed by existing substances including metals and organic contaminants. New research has been carried out to include bioavailability in the assessment of potential toxic effects of metals and metalloids in different environmental compartments, including soils, by an international research group. These assessments do not use extractants in an attempt to describe bioavailability in different soils, but instead take an empirical approach of relating soil properties themselves to the degree of toxicity expressed in bioassays. A further development for metals has been the more mechanistic concept of the terrestrial biotic ligand model (tBLM), which seeks to explain the interactions that lead to toxicity in organisms. Toxicity risk assessments for a number of organic contaminants have been performed, but usually on the basis of desk studies, and often, because of a lack of data, large assessment factors are imposed. For organics, the emphasis has been on defining and attempting to characterize their bioavailability and bioaccessibility. Bioavailability is defined as the contaminant fraction “which is freely available to cross an organism’s (cellular) membrane from the medium the organism inhabits at a given point in time”. Whereas bioaccessibility encompasses what is actually bioavailable now plus what is “potentially bioavailable” (Semple *et al.* 2004). Extraction procedures that mimic or parallel bioavailability/bioaccessibility have been sought in order to assess exposure and bioremediation potential. Such procedures are often referred to as biomimetic techniques (Semple *et al.* 2007). It is likely that the dichotomy described above between metals and organic comes from an emphasis in the latter case not on toxicity, but on the degradation and remediation of contaminants over time.

Objectives and results

Risk assessments in the EU are done according to the Technical Guidance Document of the European Commission (2003), comparing the predicted environmental concentration (PEC) and predicted no-effect concentration on representative organisms (PNEC). Risk decisions are made if the PEC:PNEC ratio for a particular metal is >1. Assessment factors are also applied if few organisms have been tested for toxicity data for a particular substance. The main organisms considered for toxicity evaluation within the terrestrial ecosystem are soil microbes, invertebrates and plants; usually with three examples in each trophic level. However, gaps in knowledge and inconsistency in published data sets due to their frequent use of non-systematic and non-standard tests necessitated new research. The objectives for the metals Zn, Cu, Ni and Co were: 1) to account for the huge differences in toxicity between soils given the same doses of metals, using the same standard bioassays, and 2) to account or the differences in toxicity between laboratory and field experiments (“ageing”). Comprehensive testing can also reduce the size of assessment factors.

For organics, considerable effort has been directed towards developing non-exhaustive chemical techniques for the measurement of putative contaminant bioavailability (Semple *et al.* 2003). Non-exhaustive techniques are mostly based on the principle that bioavailability, in particular to microorganisms, is governed by

contaminant mass transfer mechanisms such as desorption from solid to aqueous soil phases (Bosma *et al.* 1997). Several disadvantages or limitations of utilising mild solvent extraction have been outlined, such as (i) the type of solvent used (i.e. polar or non-polar solvent, e.g. methanol or hexane, respectively), ii) the nature of the extraction (e.g. soxhlet, shake, supercritical fluid) and iii) the impact of the extraction procedure on the physico-chemical properties of the soil (Semple *et al.* 2003). Subsequently, a range of non-exhaustive extraction techniques that are not dependent on organic solvents have been considered for bioavailability prediction such as solid phase extraction (Tenax beads (Cornelissen *et al.* 1997) and XAD resin (Cuypers *et al.* 2001)), supercritical fluid extraction (Hawthorne *et al.* 2000), cyclodextrin extraction (Reid *et al.* 2000) and persulphate oxidation (Cuypers *et al.* 2000).

Metals

Up to nineteen relatively uncontaminated soils were collected (depending on the metal studied) from Europe (and North America in the case of Ni) that ranged widely in soil pH, clay, organic C and content of amorphous oxides (Smolders *et al.* 2009). These were amended with soluble metal salts at sufficient doses to measure a dose-response to each metal individually. In a further series of tests on aged soils, known established metal gradients or long term field experiments were selected and sampled to be used either for direct toxicity tests or in parallel toxicity studies where the control (low metal) soils were amended and short term toxicity tested for direct comparison with the long-term contaminated soils. The tests used were usually OECD or ISO standard tests, or for some endpoints where standardized test did not exist, well documented published methodologies were used. Data were fitted to log-logistic curves for the dose-response to metals whether possible, and these were used to derive 10 or 50% effect concentrations (EC10 or EC50) expressed as added metals. No observed effect concentrations (NOEC) were determined using analysis of variance. Relationships between the degree of toxicity and soil properties were investigated using single and multiple regression techniques.

The following total numbers of chronic toxicity test data for the 4 metals were produced: plants (189), invertebrates (211), and microbial processes (270). Toxicity thresholds based on the free metal ion activity in soil solution were generally more variable than those expressed on total soil metal (Figure 1). Soil pH was generally a good predictor of metal solubility, but a poor predictor of metal toxicity across soils. The toxicity thresholds based on total soil metal concentrations were found to rise almost proportionally to a soil's effective cation exchange capacity. In general total metal as a percentage of soil eCEC was the best fit for many metals and biological endpoints. Total soil metal concentrations yielding 10% biological inhibition in *freshly amended* soils were up to 100 fold smaller (median 3.4 fold, n=110) than in corresponding *aged* soils or field-contaminated soils. The PNEC values for specific soil types were calculated using this information. Allowing for the modifying effects of soil properties and for ageing was shown to result in PNEC values that are above the natural background concentration range for soils.

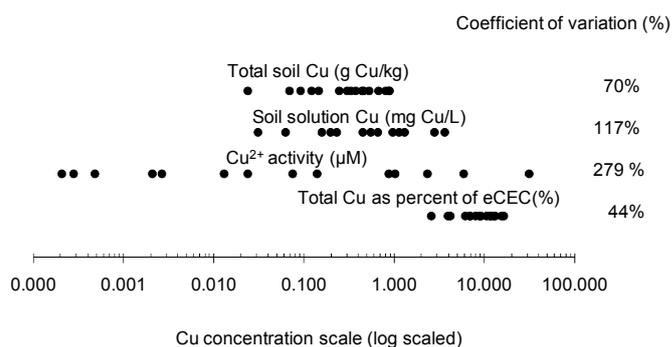


Figure 1. Four different expressions of the toxic EC50 concentrations to shoot growth of tomato in 19 freshly Cu amended soils (after Smolders *et al.* 2009).

A tBLM which accounts for the effects of competition from protons, Ca and Mg on toxicity of the metals Cu and Ni was tested using the data (Thakali *et al.* 2006a,b).

Organics

Cyclodextrins are cyclic oligosaccharides, formed from enzymatic degradation of starch by bacteria, comprising a torus of α 1,4-linked glucose units. Cyclodextrin molecules have high aqueous solubilities, due to the array of hydroxyl functional groups on the exterior, but also possess a hydrophobic organic cavity to the interior which is approximately 6.5 Å in diameter for β -cyclodextrin. Unlike the portion of contaminants extracted by the use of organic solvents, cyclodextrins have been shown to correlate closely with key biological fractions, such as the portion of the contaminant that is mineralisable. Owing to their molecular structure they also contain a hydrophobic cavity. It is possible to form an inclusion complex between the cyclodextrin macrocycle and a hydrophobic organic molecule i.e. the cyclodextrin acts as a 'molecular bucket' (Reid *et al.* 2000).

Numerous studies have shown investigated the use of cyclodextrin extraction as a predictor for microbial degradation of PAHs in single contaminant-spiked soils, multiple PAH spiked soils and field contaminated soils. In each case, the cyclodextrin extraction directly predicted the extent to which the PAHs would be degraded. Two sediment samples were sequentially extracted with HPCD, Tenax and Triton-X and PAH removal during extraction was then compared with PAH removal during biodegradation. It was demonstrated that HPCD and the Tenax extractions closely followed biodegradation and removed primarily readily available PAHs, while the Triton X-100 over-predicted biodegradation endpoints (Cuypers *et al.* 2002).

The principle aim of developing a method that quantifies bioavailability/bioaccessibility is to provide practitioners with a tool that accurately predicts the rates and end points of bioremediation strategies that employ microbial degradation. Bioavailability/bioaccessibility is considered to be the primary factor affecting the success of any such clean up approach. Fractions removed using non-exhaustive extraction techniques have been successfully correlated with the extent of degradation after the application of bioremediation practices (Semple *et al.* 2003; 2007).

Conclusions

This series of metals projects resulted in calibrated bioavailability models that can be used to normalize toxicity across different soil types, and allow for the effects of ageing, which had previously resulted in many previous soil risk assessments producing PNEC values below those of typical background soils. The bioavailability and ageing factors have been accepted by EU regulators and have already been used as a first screening tier in the Ecological Risk Assessment Framework in the UK, and in the Flemish regulation on soil remediation and soil protection in Belgium. We used our data to calibrate tBLM models for Cu and Ni toxicity to plants, invertebrates and microbes and although these explain the expression of toxicity they are not predictive. More work is needed to develop robust predictive tBLM models for use with soils. In terms of organic contaminants, it is clear that chemical techniques routinely used and described in the literature, estimate the bioaccessible rather than the bioavailable fraction. Remediation scientists are more concerned with what is bioaccessible over time at a given site than what is bioavailable. But question: "can the bioavailable portion of substance X to species Y actually be measured?" remains to be answered (Semple *et al.* 2004).

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