The fate of organic pollutants in soil – Emerging views on the relevance of non-extractable residues

ANJA MILTNER¹*, KAROLINA NOWAK¹, CRISTOBAL GIRARDI¹, ANDREAS SCHÄFFER² AND MATTHIAS KÄSTNER¹

¹UFZ - Centre for Environmental Research, Department of Environmental Biotechnology, Leipzig, Germany (*correspondence: anja.miltner@ufz.de)

²RWTH Aachen, Department of Environmental Biology and Chemodynamics, Aachen, Germany

C from soil pollutants partitions into parent compound, metabolites, non-extractable residues (NER), CO2 and microbial biomass. This distribution must be known to assess the fate of a compound in soil, but simulation tests in soils are rarely performed because they are expensive and complex. Data from aqueous systems are much more abundant, and using them for fate assessment in soils would increase the database enormously. The main obstacle for this is that NER formation cannot be simulated in aqueous systems. In the past, NER were considered to mainly consist of adsorbed and sequestered parent compound or metabolites and thus hazardous. However, they may partly derive from bacterial biomass, resulting in harmless biogenic residues. We compared the biodegradation of isotope labeled 2, 4-D, ibuprofen and ciprofloxacin in aqueous systems and soil and quantified the contribution of microbial residues to NER in soil. Both 2, 4-D and ibuprofen were mineralized fast in aqueous systems. In soil, mineralization was lower, and significant amounts of NER were formed. The amount of label found in biomolecules indicated that virtually all of the NER derived from microbial biomass. We found no mineralization of ciprofloxacin in aqueous systems, but a low mineralization in soil. NER formation from ciprofloxacin was fast and independent of microbial activity. Ciprofloxacin reduced microbial activity more in aqueous systems than in soil, because sorption and spatial inaccessibility reduced the toxicity in soil. In conclusion, for readily degradable compounds, mineralization is lower in soil than in water, and a significant part of the carbon is channeled to microbial biomass, which later is stabilized in soil organic matter, resulting in biogenic residues. Toxic compounds are mineralized more easily in soil than in water, because NER formation, spatial heterogeneity, and microbial biodiversity in soil reduce the toxicity of the compounds. NER formation without corresponding mineralization indicates formation of potentially hazardous NER derived from the parent compounds or (toxic) metabolites. In contrast, NER formed along with significant mineralization are biogenic and thus non-hazardous.

Boron isotopes by laser ablation MC-ICPMS

J. ANDY MILTON*, FRANCES DEMUTH, GAVIN L. FOSTER AND MARTIN R. PALMER

School of Ocean and Earth Science, National Oceanography Centre, Southampton, Southampton, UK (*correspondence: jam2@soton.ac.uk)

The invention of multicollector inductively coupled plasma mass spectrometers (MC-ICPMS) has revolutionised the way in which a number of isotope systems are measured. Not least the light dual-isotope systems such as boron where the large, but stable, mass fractionation of the plasma ion source allows accurate correction using bracketing standards of known isotope composition [1]. An additional advantage of these instruments is the ability use a laser ablation introduction system that allows relatively precise isotopic analysis, without prior chemical purification, on the scale of 10-100's of microns (e.g. [2]). The few studies that report boron isotopes by LA-MCICPMS [3, 4] are very encouraging, especially given the obvious advantages offered by rapid sample throughput and high spatial precision by LA and the difficulties associated with boron isotope analysis by solution MC-ICPMS (e.g. poor washout, low sensitivity, and the difficulties associated with silicate dissolution).

Here we present our recent efforts investigating the accuracy and precision of boron isotope analysis by LA-MCICPMS of a variety of samples and reference materials (glass, tourmaline, carbonates). Our initial results suggest accurate and precise data, rivalling the most precise solution analyses [1], can be generated *in situ* on samples amounting to <0.5 ng of boron.

[1] Foster (2008) *EPSL*, **271**, 254–266. [2] Foster & Vance (2006) *Nature*, **444**, 918–921. [3] le Roux *et al*. (2004) *Chem. Geol.* **203**, 123–138. [4] Fietzke *et al*. (2010) *JAAS* doi, 10.1039/c0ja00036a.

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