



Manure and inorganic fertilizer effects on speciation of metals and trace elements in soil solution

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The distribution and speciation of dissolved ($<0.45 \mu\text{m}$) trace elements (TEs) in soils have implications for their availability, accessibility, and toxicity due to the distinct behavior of each species. The application of manure and inorganic fertilizer play a key role in the speciation of TE in soil solutions, which also depends on the chemical properties of the elements and soil factors (e.g. moisture content, pH, redox potential, ionic strength, organic matter concentrations and soil texture). In this study we characterized the distribution of TE species in soil solutions using asymmetrical flow field-flow fractionation (AF4) coupled to UV-Visible absorption (UV) and ICP-MS, and examined the impacts of manure, inorganic fertilizer and soil properties on TE speciation. AF4-UV-ICPMS is a powerful method for measuring the distribution of TE among primarily ionic and small species $< 1 \text{ nm}$, organic-dominated colloids, and primarily inorganic colloids on the basis of molecular size. Eight soil treatments were chosen from the University of Alberta Breton Plots and associated Bentley Forest Reserve, including the control, NPKS inorganic fertilizer, and manure treatments, applied under different crop rotations (2-year of wheat-fallow rotation and 5-year of cereal-forage rotation), and the pristine forest (never cultivated). Soil solutions were collected under vacuum using surgical (316) stainless steel lysimeters (5 micron pore size), after irrigating with high purity water (deionized, type II Milli-Q). Analyses were performed in the metal-free, ultraclean SWAMP lab. The acid-cleaned lysimeters yielded excellent blank values for most of trace elements of environmental interest (Li, Al, Mn, Co, Ni, Cu, As, Mo, Cd, Ba, Tl, Pb, Th and U). Using the new lysimeter combined with AF4-UV-ICPMS, we provide a new perspective on TE speciation in soil solutions, with a view towards understanding the effect of long-term fertilization on the bioavailability of micronutrients and potentially toxic trace elements.