



## Investigating soluble iodine dynamics in soil using microdialysis and SEC-UV-ICP-MS

Olivier S Humphrey (1,2), Scott D Young (2), Elizabeth H Bailey (2), Neil M J Crout (2), E Louise Ander (1), and Michael J Watts (1)

(1) British Geological Survey, Inorganic Geochemistry, Centre for Environmental Geochemistry, Nottingham, United Kingdom (olivier.humphrey@nottingham.ac.uk), (2) University of Nottingham, School of Biosciences, Sutton Bonington Campus, Leicestershire, LE12 5RD, UK

Iodine is an essential micronutrient for human health required for the production of thyroid hormones, which are critical for vital physiological processes including energy metabolism, growth and brain function. The biogeochemical cycling of iodine is governed by many complex processes. Soil properties, such as pH and the concentration of organic matter and Fe/Al/Mn hydrous oxides, influence the speciation of iodine and its availability to plants, which can then impact human consumption. Our current understanding of iodine bioavailability to plants and iodine geodynamics following inputs (e.g. rainfall, fertilisation) would be significantly improved with a greater understanding of soluble iodine interactions with soil. In this study we report the first use of microdialysis to extract native ( $^{127}\text{I}$ ) and isotopically labelled ( $^{129}\text{I}$ ) iodine from soils in order to observe short-term sorption and fixation processes without disturbing the system dynamics.

We validated the use of microdialysis to extract inorganic soluble iodine species in solution before applying the technique to soils. To investigate the speciation of native iodine in the soil solution extracted with microdialysis we coupled (i) size exclusion chromatography (SEC), which separates chemical species in aqueous samples according to molecular size, with (ii) online UV-Vis molecular absorption analysis measuring at 254 nm to detect dissolved organic carbon, and (iii) inductively coupled plasma mass spectrometry (ICP-MS) to measure iodine isotope concentrations. In addition, to investigate short-term soil iodine dynamics we spiked three soils with  $^{129}\text{I}^-$  or  $^{129}\text{IO}_3^-$  prior to a continuous 40-hour extraction in which we passively extracted the soluble soil phase using microdialysis. We then employed ICP-MS equipped with a triple quadrupole (QQQ) facility and oxygen cell gas to separate interfering isobaric and polyatomic species from the target analyte ( $m/z=129$ ).

We successfully demonstrated the use to microdialysis to passively monitor short-term sorption and fixation processes without disturbing the soil microcosms under test. Native soil iodine was found to be present as organically-bound iodine  $> \text{I}^- > \text{IO}_3^-$ . The isotopically spiked soils showed a rapid decline of iodine present in the soil solution due to sorption by soil components. We also witnessed the conversion of inorganic iodine species to organically-bound iodine within the 40-hour experimental period. The newly formed soluble organically-bound iodine was primarily associated with dissolved organic matter with low molecular weights ( $<5$  kDa), identified using SEC-UV-ICP(QQQ)-MS. In conclusion, microdialysis was proven to be an effective extraction method for soluble soil iodine species and the use of online SEC combined with UV and MS detection enabled greater understanding of short-term iodine dynamics in soils. The results from this study have the potential to influence future agricultural practices for iodine phytofortification and understanding the fate and transport of anthropogenic  $^{129}\text{I}$ .