

# Integrated Approaches to Studying Speciation and Behaviour of Iodine and Technetium

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## INTRODUCTION

Both <sup>129</sup>I (iodine) and <sup>99</sup>Tc (technetium) are important radionuclides in studies of environmental protection and human health, global-scale hydrologic processes and nuclear nonproliferation. They are redox-sensitive elements and exhibit complex geochemical behaviour, with their fate and transport in the environment dictated by chemical speciation. For example, iodine occurs in multiple oxidation states and exists as inorganic and organic species that may be hydrophilic, atmophilic, and biophilic (Fuge and Johnson 1986). In reducing environments, aqueous iodine usually occurs as the mobile anion, I<sup>-</sup>. Under more oxidizing conditions, iodine is present as the more reactive IO<sub>3</sub><sup>-</sup>, which can lead to retarded transport through its interaction with clays and organic matter. In contrast, Tc is sparingly soluble and highly sorptive under reducing conditions, and exists as the soluble and nonsorbing species pertechnetate (TcO<sub>4</sub><sup>-</sup>) in oxidizing environments. This work employs an integrated approach to investigate the occurrence and effect of I and Tc speciation on their biogeochemical cycling and fate and transport in various environments and on different observational scales.

## METHODS

An ion chromatography (IC) method with conductivity detection, under a hydroxide gradient condition, was used to simultaneously analyze I<sup>-</sup> and IO<sub>3</sub><sup>-</sup>, as well as other common anions present in soil/water samples. For low (sub-ppb) concentrations of I<sup>-</sup>, we used another IC method with an electrochemical detector in pulsed amperometric mode. Inductively coupled plasma-mass spectrometry (ICP-MS) was employed to measure total iodine, including organic forms, in aqueous samples.

Sequential chemical extractions using KCl and tetramethyl ammonium hydroxide (TMAH, Yamada et al., 1999) were conducted to investigate iodine speciation (inorganic and organic) in a total of 24 soil and sediment samples from across USA. These samples were chosen for their geographic locations (e.g., near the ocean or nuclear facilities) and for their differing physico-chemical characteristics (organic matter, texture, etc). Extracted solutions were analysed by IC and ICP-MS methods to determine iodine concentrations and to examine iodine speciation (iodide, iodate, and organic iodine).

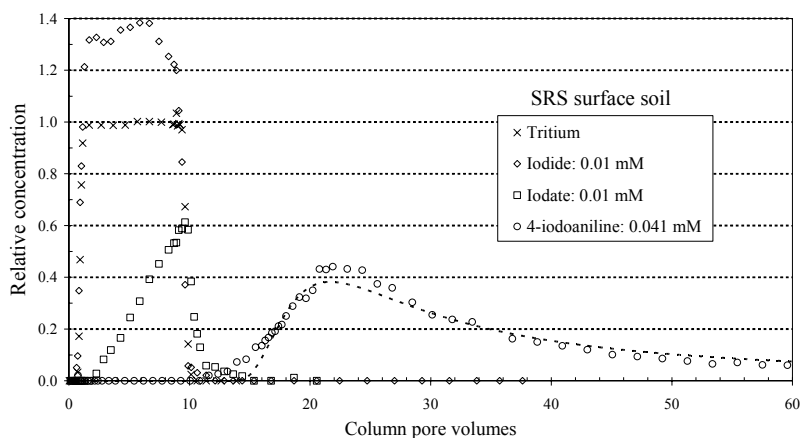
Laboratory column and batch experiments were carried out to better understand the environmental fate and transport of iodine species (i.e., iodide, iodate, and 4-iodoaniline – a representative refractory organic iodine species) in geologic media from two nuclear facilities (Savannah River Site and Hanford Reservation) in the U.S. Department of Energy (DOE) complex, where historical releases of radionuclides, including <sup>129</sup>I and <sup>99</sup>Tc, have occurred.

Groundwater at the Nevada Test Site (NTS) contains many long-lived radionuclides, including <sup>99</sup>Tc and <sup>129</sup>I, as a result of 828 underground nuclear weapons tests conducted between 1951 and 1992. We synthesized a body of data on the distribution of <sup>99</sup>Tc and <sup>129</sup>I in

groundwater in and near test cavities, at field scales over distances of hundreds of meters and for durations of up to forty years.

## RESULTS AND DISCUSSION

In natural soils, iodine is mostly (nearly 90% of total iodine) present as organic species, while inorganic iodine becomes important (up to 50%) in sediments with low organic matter. Results from laboratory column studies aimed at examining transport of different iodine species showed much greater retardation of 4-iodoaniline than iodide or iodate (Figure 1). There was appreciable iodate reduction to iodide (Figure 1), presumably mediated by the structural Fe(II) in some clay minerals; therefore, careful attention must be given to potential interconversion among species when interpreting the biogeochemical behaviour of iodine in the environment. The different iodine species exhibited dramatically different sorption and transport behaviour in three sediment samples from different depths at the Savannah River Site. This indicates that when anthropogenic  $^{129}\text{I}$  is deposited on the surface at this site, different iodine species will have different residence times as they migrate through the various sediment regimes.



**Fig. 1. Breakthrough curves of tritium and iodine species in a column homogeneously packed with Savannah River Site (SRS) surface soil.**

At the field scale, syntheses of NTS results show that Tc does not necessarily exist as the mobile and conservative species  $\text{TcO}_4^-$ , as has been commonly assumed. This conclusion is corroborated by recent in situ redox potential measurements, which show that groundwaters at multiple locations of the NTS are not oxidizing, and that the mobility of reduced Tc species ( $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ) is greatly diminished. Speciation of iodine and its associated reactivity is also complex in the groundwater at the NTS where both oxidising and reducing conditions exist.

## ACKNOWLEDGEMENTS

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