



Recent advances in the detection of specific natural organic compounds as carriers for radionuclides in soil and water environments, with examples of radioiodine and plutonium



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ABSTRACT

Among the key environmental factors influencing the fate and transport of radionuclides in the environment is natural organic matter (NOM). While this has been known for decades, there still remains great uncertainty in predicting NOM-radionuclide interactions because of lack of understanding of radionuclide interactions with the specific organic moieties within NOM. Furthermore, radionuclide-NOM studies conducted using modelled organic compounds or elevated radionuclide concentrations provide compromised information related to true environmental conditions. Thus, sensitive techniques are required not only for the detection of radionuclides, and their different species, at ambient and/or far-field concentrations, but also for potential trace organic compounds that are chemically binding these radionuclides. GC-MS and AMS techniques developed in our lab are reviewed here that aim to assess how two radionuclides, iodine and plutonium, form strong bonds with NOM by entirely different mechanisms; iodine tends to bind to aromatic functionalities, whereas plutonium binds to N-containing hydroxamate siderophores at ambient concentrations.

While low-level measurements are a prerequisite for assessing iodine and plutonium migration at nuclear waste sites and as environmental tracers, it is necessary to determine their in-situ speciation, which ultimately controls their mobility and transport in natural environments. More importantly, advanced molecular-level instrumentation (e.g., nuclear magnetic resonance (NMR) and Fourier-transform ion cyclotron resonance coupled with electrospray ionization (ESI-FTICRMS)) were applied to resolve either directly or indirectly the molecular environments in which the radionuclides are associated with the NOM.

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1. Introduction

Radionuclides that reach the environments from natural or anthropogenic sources equilibrate with different phases over time through redox, complexation, sorption, precipitation and microbial reactions with inorganic and organic phases, e.g., specific natural organic matter (NOM) compounds with clustered chelating sites. While there is evidence for natural organic matter bound radionuclides from sequential extraction experiments (e.g., Livens and Baxter, 1988; Qiao et al., 2012), such evidence is often fraught with ambiguity since the results are not very specific and can depend on the nature and order of sequential leaching agents, and prevalence for re-adsorption artefacts to different fractions (Martin et al., 1987; Nirel and Morel, 1990; Hou et al., 2007; Okoro et al., 2012). Thus, it is highly desirable to combine radioanalytical techniques with molecular level organic matter identification techniques in order to pinpoint the organic carrier molecules for specific radionuclides in the environment.

The objective of this review is to assess the recent advances in measuring natural organic matter associated radionuclides, ^{129}I and Pu, as well as molecular characteristics of these carriers. Two radionuclides that bond strongly to natural organic matter, plutonium and iodine, are used as examples to demonstrate that radionuclide binding mechanisms to organic matter can differ greatly. Furthermore, the intent of this review is to also demonstrate that it is not adequate or in some cases even important to consider total organic carbon or organic matter when attempting to understand radionuclide–NOM interactions. Instead, advances need to be made to identify the specific reactive moieties within organic matter that are involved in the bonding. Such information is important because it helps prediction of bonding scenarios when system chemistry changes spatially or temporally. Sensitive techniques are required not only for the detection of radionuclides and their different species at low ambient concentrations prevalent in the far-field, but also for the detection of potential trace organic compounds that chemically bind to these radionuclides. Examples are discussed of studies conducted at radionuclide contaminated field sites. Particular attention is directed at measurements of organically bound radionuclides where specific organic compounds affect iodine (e.g., ^{129}I) and plutonium (e.g., $^{239,240}\text{Pu}$) speciation and environmental transport. This review does not include an exhaustive description of our understanding of radionuclide interactions with NOM, instead it focuses on recent findings related to Pu and I. Previous reviews of Pu–NOM interaction have been provided by Neu. (2000) and I–NOM interaction have been provided by Kaplan et al. (2014a).

2. Iodine

2.1. Analytical methods to determine ^{129}I and ^{127}I concentration and speciation

Iodine (I) exists in multiple oxidation states in the form of organic (org-I) and inorganic species (iodide, I^- , and iodate, IO_3^-) in aquatic systems, leading to complex biogeochemical cycling of stable iodine, ^{127}I , and its long-lived isotope, ^{129}I , a major by-

product of nuclear fission (reviewed by Kaplan et al., 2014b). In order to assess the distribution of ^{129}I and stable ^{127}I in environmental systems on a regular basis, a sensitive and rapid method was developed, enabling us to simultaneously determine isotopic ratios ($^{129}\text{I}/^{127}\text{I}$) and I speciation via inexpensive GC–MS (Fig. 1, also see Zhang et al., 2010). Basically, iodide concentrations are quantified after being derivatized to 4-iodo-N,N-dimethylaniline. Total inorganic iodine (the sum of iodide and iodate for most environmental samples) are determined by a two-step chemical process: first iodate is reduced to iodide and followed by oxidation and derivatization steps of iodide. Thus iodate is calculated as the difference of total inorganic iodine and iodide. Total iodine, including the sum of iodide, iodate and organo-iodine, is determined by converting organo-iodine into inorganic-iodine via combustion with V_2O_5 under O_2 stream and following the way of measuring total inorganic iodine. Organo-iodine is then calculated by the difference between total iodine and total inorganic iodine. Differentiating ^{129}I from ^{127}I in each species ($^{129}\text{I}^-$, $^{129}\text{IO}_3^-$ and $^{129}\text{organo-iodine}$) is obtained by applying mass-to-charge ratio of 247 and 249 filters, and integrating the appropriate peaks in the chromatogram, for the derivative products of ^{127}I and ^{129}I iodinated N,N-dimethylaniline, respectively. This method has a detection limit of 0.04 $\mu\text{g/L}$, 0.14 $\mu\text{g/L}$ and 0.35 $\mu\text{g/L}$ for $^{127}\text{I}^-$, $^{127}\text{IO}_3^-$ and organo- ^{127}I , respectively. The detection limit of total ^{129}I is 73 mBq/L, which is far below the ^{129}I far-field concentration in many DOE sites (e.g., Hanford Site and Savannah River Site (SRS)).

In addition to the GC–MS method, a pH-dependent solvent extraction along with combustion paired with accelerator mass spectrometry (AMS) was developed to measure ambient levels of $^{129}\text{I}/^{127}\text{I}$ isotope ratios and the speciation of ^{129}I (I^- , IO_3^- , and organo-I) (Schwehr et al., 2014). AMS enables ^{129}I speciation measurement at much lower concentrations ($<10^{-12}\text{M}$) than GC–MS (10^{-9} – 10^{-10}M). ^{129}I concentration and speciation in the contaminated groundwater collected from SRS were determined via both approaches (GC–MS vs. AMS) with consistent results.

2.2. Iodine speciation in the natural environment

Results using a novel GC–MS method demonstrated that the mobility of ^{129}I depends greatly on speciation and its concentration, pH, and sediment redox state, with equilibration times of up to 12 weeks (e.g., Xu et al., 2011a, 2015a; Zhang et al., 2011, 2014; Emerson et al., 2014; Schwehr et al., 2014). For instance, at ambient concentrations ($\sim 10^{-7}\text{M}$), I^- and IO_3^- are significantly retarded by sorption onto mineral surfaces and covalent binding to NOM, while at concentrations traditionally examined in laboratory sorption studies (i.e., 10^{-4}M or higher), I^- appears to have negligible sorption to soils and to travel along with the groundwater (Zhang et al., 2011) (Fig. 2). Iodate removal from the mobile aqueous phase can also occur through incorporation into CaCO_3 crystal lattice, which was demonstrated under field conditions at the Hanford Site, in eastern Washington, USA (Xu et al., 2015a; Zhang et al., 2013a, 2013b). Iodide and iodate interactions with NOM can lead to covalent binding of I to active sites of aromatic carbon moieties on the particle surface (Xu et al., 2011b, 2012, 2013). Iodine

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