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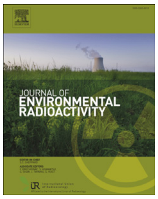

Radioiodine concentrated in a wetland

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ABSTRACT

Most subsurface environmental radioactivity contamination is expected to eventually resurface in riparian zones, or wetlands. There are a number of extremely sharp biogeochemical interfaces in wetlands that could alter radionuclide speciation and promote accumulation. The objective of this study was to determine if a wetland concentrated ^{129}I emanating from a former waste disposal basin located on the Savannah River Site (SRS) in South Carolina, USA. Additionally, studies were conducted to evaluate the role of sediment organic matter in immobilizing the radioiodine. Groundwater samples were collected along a 0.7-km transect away from the seepage basin and in the downstream wetlands. The samples were analyzed for ^{129}I speciation (iodide (I^-), iodate (IO_3^-), and organo-I). Groundwater ^{129}I concentrations in many locations in the wetlands (as high as 59.9 Bq L^{-1} ^{129}I) were greatly elevated with respect to the source term (5.9 Bq L^{-1} ^{129}I). ^{129}I concentration profiles in sediment cores were closely correlated to organic matter concentrations ($r^2 = 0.992$; $n = 5$). While the sediment organic matter promoted the uptake of ^{129}I to the wetland sediment, it also promoted the formation of a soluble organic fraction: 74% of the wetland groundwater ^{129}I could pass through a 1 kDa (<1 nm) membrane and only 26% of the ^{129}I was colloidal. Of that fraction that could pass through a 1 kDa membrane, 39% of the ^{129}I was organo-I. Therefore, while wetlands may be highly effective at immobilizing aqueous ^{129}I, they may also promote the formation of a low-molecular-weight organic species that does not partition to sediments. This study provides a rare example of radioactivity concentrations increasing rather than decreasing as it migrates from a point source and brings into question assumptions in risk models regarding continuous dilution of released contaminants.

1. Introduction

Wetland environments have several extremely efficient biogeochemical processes that promote the concentration of metals and radionuclides from inflowing surface and subsurface water (Feng et al., 2004; Kennish, 2002; Weis and Weis, 2004). This tendency is well recognized in agriculture, where many farmers have purposely left intact riparian zones along the edges of their properties to promote the removal of ecologically damaging fertilizers and agrochemicals from agricultural runoff or subsurface groundwater (Bowden, 1987; Johnston, 1991; Schlesinger, 2009). Similarly, artificial wetlands are widely created to remove surface water contaminants. The artificial ecosystems are designed to promote the decay of plant litter to form soil organic matter (OM). The sediment organic matter has several desirable properties, including increasing microbial activity for chemical degradation, lowering the oxidation state (and formation of sulfides), and creating more contaminant binding sites (Bowden, 1987; Johnston, 1991; Schlesinger, 2009).

^{129}I exists primarily in the environment as iodide (I^-), iodate (IO_3^-), iodine (I_2), and organo iodine (Kaplan et al., 2013). I_2 tends to form under oxidizing acidic conditions with elevated total iodine concentrations and because it is highly reactive, it is not abundant under most environmental conditions. Several studies of sorption in shallow soils that contain OM indicate that the OM is the primary control on iodine sorption (Assemi and Erten, 1994; Bird and Schwartz, 1997; Fukui et al., 1996; Hu et al., 2009; Kaplan, 2003; Neal and Truesdale, 1976; Sheppard and Thibault, 1991; Whitehead, 1974; Yoshida et al., 1992; Yu et al., 1996). In a survey of 26 soils and sediments samples from across the U.S., with natural OM concentrations ranging from 0.01 to 8.70 wt % (except for one organic soil that was 28.1 wt-%), Hu et al. (2009) reported that

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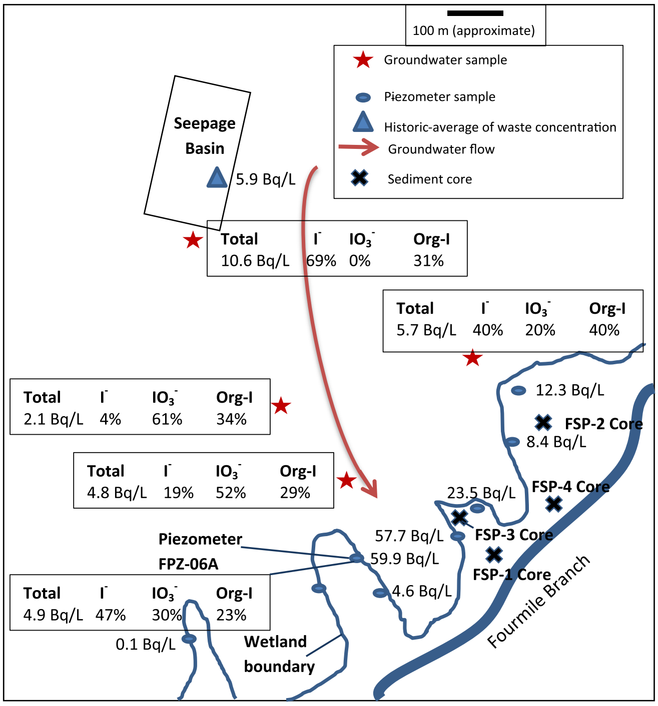

Fig. 1. Map of Savannah River Site's F-Area showing: 1) the historic average of ^{129}I concentrations in the Seepage Basin waste, 2) ^{129}I concentrations and speciation in groundwater (stars – Otosaka et al., 2011), 3) groundwater ^{129}I concentrations in wetland adjacent to FourMile Branch, 4) sediment core locations, and 5) ^{129}I concentration and speciation in a sample FPZ-6A.

~90% of the total iodine in soils was present as organic iodine. They also noted in the survey that inorganic iodine species became important in sediments with very low OM contents. Similarly, Whitehead (1973) demonstrated that iodine sorption in untreated soils was greater than in soils that were treated to destroy the OM. There was some sorption of iodine in the treated soils, primarily by iron and aluminum oxides (Whitehead, 1973). In a single soil profile studied (Bors et al., 1988), sorption of iodide correlated with organic carbon content of samples that ranged from 0.06 to 6.2 wt % organic carbon.

The SRS F-Area is a nuclear processing facility that disposed of millions of cubic meters of aqueous nuclear waste in unlined seepage basins between the years 1955 and 1988 (WSRC, 2006) (Fig. 1). In addition to several radionuclides, the waste also included various heavy metals (As, Cd, Cr, Hg, and Pb) and enormous quantities of HNO_3 and NaOH. The influent waste had an average pH of 2.9, and a range of 1.5–13. To remediate the seepage basins, a large amount of the contaminated soils were removed, limestone and slag were added, and finally a low permeable cap was placed over the top. There are several other former radiological disposal sites in the United States that were remediated/dispositioned in a similar manner as the SRS Seepage Basins, such as the S-3 Ponds in Oak Ridge Reservation (Tennessee) and the 200-West cribs at the Hanford Site (Washington state). These sites are in similar states as the SRS F-Area seepage basin, namely they continue to slowly leach low concentrations of radioactivity into the underlying vadose zone and aquifer.

Approximately 2 Ci of ^{129}I was disposed in the F-Area Seepage Basins (WSRC, 2006). Iodine-129 groundwater concentrations near the basin continue to increase to >37 Bq L^{-1}, which is >1000 times drinking water limits (MCL = 0.037 Bq L^{-1}) (Kaplan et al., 2011). The increase in ^{129}I concentrations was attributed to increasing pH levels in the lime-treated basins. The ^{129}I speciation near the basins tend to be primarily iodide, but as the ^{129}I moves away from the Seepage Basin, and concomitantly the pH and Eh increase in the plume, the ^{129}I species distributions tends to include more iodate and organo-iodine (Otosaka et al., 2011) (Fig. 1). ^{129}I mobility in this aquifer is greatly dependent on ^{129}I species and its concentration (Schwehr et al., 2009; Zhang et al., 2011), pH (Xu et al., 2011a) sediment redox state, and sediment equilibration times (Xu et al., 2011a). For example, at ambient concentrations (~10^{-7} M), I^- and IO_3^- were significantly retarded by sorption to mineral surfaces and covalent binding to natural organic matter, while at concentrations traditionally examined in sorption studies (i.e., 10^{-4} M or higher), I^- mobility is similar to that of tritium (Zhang et al., 2011). Iodide and iodate interactions with OM recovered from wetland sediments in F-Area, lead to covalent binding of iodine to a limited number of aromatic carbon moieties on the particle surface (Xu et al., 2013, 2011b, 2012). Iodine association with OM is important in sediments, even when OM concentrations are very low (e.g., <0.2% at Hanford Site) (Zhang et al., 2013). Removal of iodine from the groundwater through interaction with OM is complicated by the release of mobile organo-I species (Xu et al., 2013, 2011b, 2012). A fraction of OM may behave as a mobile organo-I source (Xu et al., 2011a). Bacteria from the ^{129}I-contaminated aerobic aquifer at the F-area accumulated I^-, but account for only a minor fraction of the total iodide (0.2–2.0%) (Li et al., 2011), indicating that bacterial I^- accumulation likely does not account for the high fraction of measured organo-I in groundwater (Li et al., 2011; Schwehr et al., 2009). However, exo-enzymatic iodide oxidizing activity of bacteria and organic acid produced by bacteria significantly contribute to organo-iodine formation (Li et al., 2012a, 2012b).

The objective of this study was to compare F-Area groundwater ^{129}I concentrations previously reported by Otosaka et al. (2011) to groundwater ^{129}I concentrations in wetlands where the ^{129}I-plume resurfaces. Particular attention was directed at understanding the role of sediment OM and dissolved groundwater OM on ^{129}I partitioning in wetland systems.

2. Materials and methods

2.1. Site description and aqueous and sediment sample collection

The study site was F-Area on the Savannah River Site (Fig. 1). Seven piezometers (FPZ-2A, -6A, -6B, -7B, -8A, and -8B) located in the F-Area wetland were used in this study. These piezometers are part of the existing SRS groundwater monitoring program and are 5 cm in diameter and made of PVC pipe; the distance between the ground surface and top of the 60-cm screened zone varies from 60 to 1016 cm. A peristaltic pump set to ~200 mL min^{-1} was used to first purge stagnant groundwater for two pour volumes and then collect the sample needed for the study. The following parameters were measured in the field during groundwater sampling: pH, temperature, turbidity, electrical conductivity, Eh, dissolved oxygen, and depth to water. Piezometer FSP-6A was resampled to permit additional speciation and filtration studies to be conducted. No preservatives (acids) were added to the groundwater samples. The samples were stored under ice until they arrived at the lab, where they were stored in a 4 °C refrigerator.

Four soil cores were collected with a 5-cm diameter auger (Fig. 1). Prior to collecting the core, the surface leaf litter was removed and therefore the first sample, rather than starting a depth of 0 cm, started at about 2.5 cm. Continuous cores were collected until the water table was reached, which was at a depth of between 20 and 36 cm depth. These soil samples were collected in locations that were found in an earlier survey to have elevated ^{129}I concentrations, and as such represent hotspots and not necessarily typical ^{129}I concentrations at the study site. Because this area of the