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WHY SHOULD WE CARE ABOUT RADIOIODINE IN THE ENVIRONMENT?

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Why should we care about radioiodine in the environment?

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This editorial article focuses on the pathways, from source to human risk, and opens questions about radioiodine mobility in the environment. While radioiodine is a pollutant, one has to keep in mind some perspective: radioisotope risk to man is obeying to different sets of standards and regulations than other pollutants. This is true even though most of pollutants, including radionuclides, exert toxic effects through similar mechanisms at the cellular level, i.e., most of the damage occurs through the generation of oxygen radicals. While people can have measurable reactions at regulated maximum levels of many pollutants (take ozone), this is not the case for radioactivity, where even at 100 times the permissible levels for chronic exposure it is hard to document any measurable effect. Furthermore, according to an article published in Scientific American (Fischetti, 2011), risk factors (in number of premature deaths, including accidents, per 100 gigawatts power produced per year) for nuclear power are extremely low (0.7), as compared to fossil fuels such as natural gas (719), crude oil (937), and coal (1200). Thus, public perception is an equal or more important factor than relative risks.

With that in mind, radioiodine poses most of the calculated risk of all radionuclides from nuclear waste sites in USA that potentially can reach the natural environment and man. Two of its radioisotopes, ^{131}I ($t_{1/2}$=8 days) and ^{129}I ($t_{1/2}$=16 million years) posing short-term and

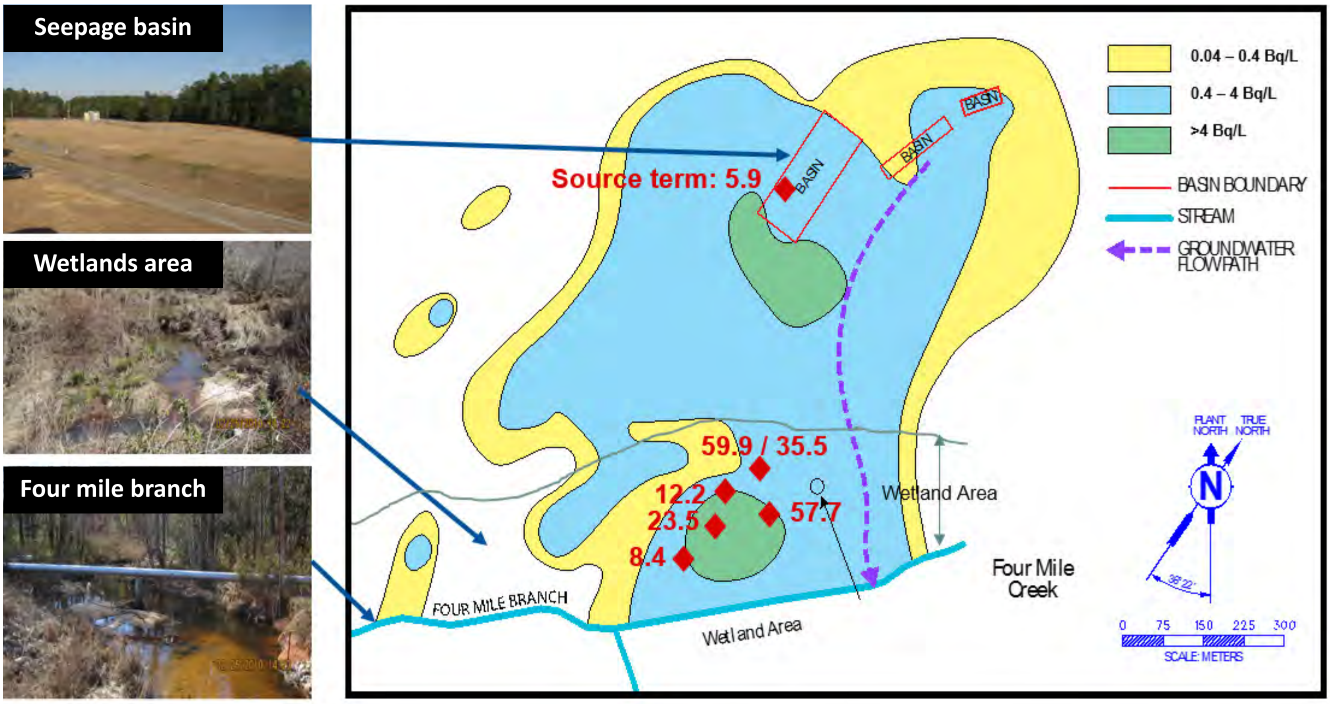

Figure 1. Example of a ^{129}I plume at the F-Area Seepage Basins at the Savannah River Site, near Aiken, South Carolina. The radionuclide seepage basins created as part of a former nuclear material production facility are the source term of the contaminant plume and had an average concentration of 5.9 Bq/L. Today, ^{129}I is concentrated in the down gradient wetland, where natural organic matter is 1000 times greater than in the upland sediment. Note that porewater ^{129}I concentrations (in red font) are as much as 10 times greater in the wetland (units Bq/L) than at the source.

long-terms risks, respectively. ^{129}I is regarded as one of the major risk drivers at radiological waste disposal and contaminated groundwater sites where nuclear material fabrication or reprocessing has occurred. The long-term risk of radioiodine is due to its high toxicity due to incorporation into the thyroid of mammals, a high bioaccumulation factor, a high inventory at source terms (due to its high fission yield) and an extremely long half-life (16M yr) for ^{129}I, a high specific activity of ^{131}I, and rapid mobility of radioiodine in the subsurface environment. To illustrate how the properties of ^{129}I magnify its risk, ^{129}I accounts for only 0.00002% of the radiation released offsite from the Savannah River Site (SRS, but contributes 13% of the population dose, a six orders of magnitude magnification of risk with respect to its radioactivity (Kantelo et al. 1990).

Thus, research and engineering efforts are devoted towards preventing radioiodine reaching the natural environment. Cleanup of stored nuclear waste, long-term geological disposal of waste, development of engineered waste forms to minimize release (e.g., cements, geopolymers, sorbents, vitrification) and natural attenuation of iodine in the environment, especially in wetlands (which act like kidneys of Earth's hydrological system) are important areas of radioiodine research (Fig. 1). Another risk driver, technetium-99 (^{99}Tc), which receives much research attention in the US, is readily converted to a less mobile form by creating an anoxic environments, but there is still no good solution for iodine (Fig. 2). Iodine chemistry is treated as a black box where only one of its chemical species, iodide, is normally considered in transport and risk calculations. It is thus critical that one gets a better understanding of the complex speciation and reactivities of its various chemical species under changing conditions. Waste isolation techniques, transport, interactions with soils need to be considered in more detail than is happening at the moment, with special consideration of the chemical speciation of iodine.

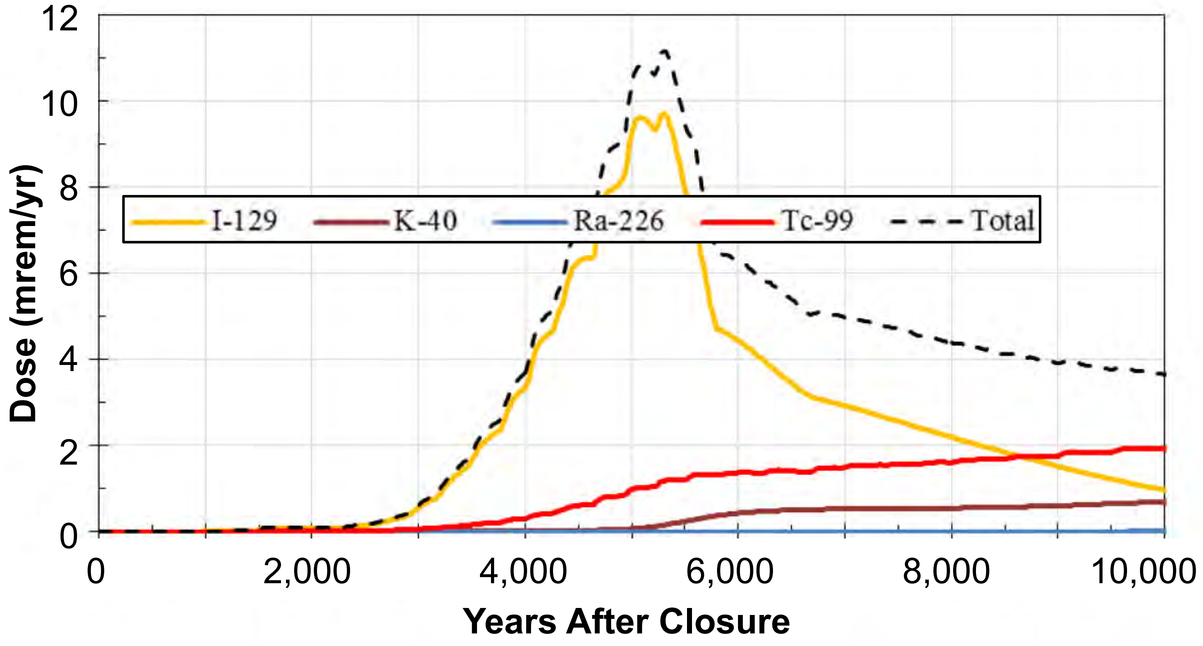

Figure 2. An example of the potential risk posed by low-level waste at the SRS. Note that while ^{99}Tc exists in the waste at much higher concentrations than ^{129}I, it poses minimal risk (red line). ^{99}Tc is immobilized by precipitation within the grout (strongly reducing slag-containing grout). Essentially all the risk (dashed black line) originates from ^{129}I (yellow line) (SRR, 2016)

So, what are the sources of radioiodine in the environment? The Department of Energy (DOE) is concerned about radioiodine because it occurs in the environment at several DOE facilities. It is especially problematic at the Hanford Site and the Savannah River Site (SRS), where ^{129}I groundwater exceeds the drinking water standard (DWS) of 0.04 Bq/L by 40 and 1000 fold, respectively (Kaplan et al., 2014, and references therein). As a by-product of nuclear fission, ^{129}I is abundant in nuclear waste currently being processed and disposed at these sites and in the waste that will be eventually disposed at a national repository (e.g., Department of Energy, 2002, 2003, 2012a).

The increase use of nuclear power in response to greater demand for power presents another concern regarding radioiodine. There have been 10 license applications to the Nuclear Regulatory Commission over the last 10 years to refurbish 18 existing reactors and build another 18 new reactors in the United States, increasing the total number of reactors from 104 to 122. Similarly, India plans to construct another 20–30 reactors by the year 2020 (World Nuclear Association, 2009). China presently has 17 reactors under construction and anticipates building another 13 by the year 2020, increasing their nuclear capacity to at least 50 GW (World Nuclear Association, 2009). Thus, if only a fraction of the proposed nuclear growth from the nuclear renaissance is realized, a significant increase in worldwide radioiodine inventory will be created by the nuclear power industry.

The principle mechanism for radioiodine production is neutron-induced fission. Neutron-induced fission is a nuclear reaction in which the nucleus of an atom (e.g., ^{235}U) splits when bombarded with neutrons into lower atomic-weight isotopes (e.g., ^{129}I), often producing free neutrons and energy. Reactions form a variety of fission products, including 19 iodine isotopes. Typically fission products are by-products and are not the isotopes of interest. At the Hanford Site and SRS, where most ^{129}I exists in the United States, the reactors were fueled with uranium, and part of this uranium was converted into plutonium by the reactor neutron flux.

Once the elements have cooled, the targeted isotopes are recovered through chemical separation or reprocessing. It is at this step that most radioiodine is inadvertently introduced into the environment. It has been estimated that radioiodine emissions to the atmosphere from the Hanford reprocessing operations between 1944 and 1972 were 266 kg. Presently, the two largest commercial reprocessing facilities (facilities that in essence recycle spent nuclear fuel) are at Sellafield (England) and La Hague (France) and they had authorized liquid discharge permits for treated waste to the North East Irish Sea and the English Channel, respectively. The integrated discharges from La Hague (1975–1997) and Sellafield (1961–1997) are estimated to be 1640 kg and 720 kg, respectively. Therefore, the total amount of ^{129}I released over the history of facilities in the United States are much less than that recently released in a single year by these two reprocessing facilities.

Another way radioiodine can enter the environment is through nuclear power plant accidents, such as the Fukushima Daiichi (Japan) and Chernobyl (Ukraine) reactor accidents. The Fukushima Daiichi accident introduced 1.5×10^7 kg ^{131}I (10^{17} Bq ^{131}I) this is about 10% the ^{131}I mass released from the Chernobyl disaster. A relatively small amount of ^{129}I originated from two major nuclear accidents, Chernobyl in 1986 (1.3-6 kg ^{129}I) and Fukushima in 2011 (0.8-1.4 kg ^{129}I) (Kaplan et al., 2014, and references therein).

Nuclear waste is neither more hazardous nor harder to manage relative to other toxic industrial waste. For radioactive waste, isolating or diluting radionuclides to the extent that it the rate or concentration of any radionuclides returned to the biosphere is harmless. To achieve this, practically all radioactive waste is contained and managed, with some clearly needing deep and permanent burial.

Radionuclides with long half-lives tend to be alpha and beta emitters – making their handling easier – while those with short half-lives tend to emit the more penetrating gamma rays. Eventually all radioactive waste decays into non-radioactive elements. The more radioactive an isotope is, the faster it decays. Most radioactive waste in the U.S. is classified as low-level (LLW) or high-level (HLW), dependent, primarily, on its level and type of radioactivity.

In order to prevent the spread of radionuclides in the environment, radionuclides are currently immobilized into solid phases. Radionuclide solubility is one of the factors, along with sorption and inventory, that can determine the source term for potential migration to the far field of a nuclear waste repository.

Several processes can affect the concentration of a radionuclide in porewater, including precipitation as a simple salt; coprecipitation with other phases; lattice incorporation in the major cement hydration products (solid solution); surface sorption at hydrous oxides; complex and colloid formation in the aqueous phase.

The currently favored solid phase for LLW immobilization is cement, while HLW immobilization is the incorporation of waste into glass (vitrification). However, so far, the incorporation into cement and subsequent leaching of only iodide has been seriously investigated. The major problem with this approach is that it ignores the complex speciation of iodine, i.e., it ignores iodate and organo-iodine which have different chemistries. Most of the past research was devoted to the mechanism of iodide uptake in cement hydrate phases that is sorption and/or incorporation. Very few data exist on iodate and organo-iodine incorporation in cement, even though large quantities of liquid waste containing also radioiodine have already been solidified in cement

Even though today most radioactive waste that is produced is well contained, most problems with radioiodine contamination in the environment stem from inadequate disposal approaches in the early days of the nuclear age, and are most pronounced at federal sites at national laboratories in the USA, and at nuclear reprocessing sites worldwide that produce a large volume of liquid waste.

For example, ^{129}I is among the three primary radiological risk drivers at the Hanford site, along with ^{99}Tc and ^{3}H (Department of Energy, 2012b). Mobile radiological and non-radiological contaminants, including ^{129}I, ^{99}Tc, and nitrate, discharged to these facilities have migrated through the vadose zone to the underlying aquifer, some 76-m below grade. Once the contaminants reached the aquifer, they spread relatively rapidly, producing large plumes. Among these plumes are three ^{129}I plumes covering an area >50 km^{2}. The 90th percentile ^{129}I concentration is 3.5 pCi/L, meaning 90% of the groundwater ^{129}I concentration data in the plume is below 3.5 pCi/L. Therefore, major challenges for treating 200 Area groundwater ^{129}I plumes are that the plumes are extremely extensive and the ^{129}I concentrations are extremely dilute (3.5 pCi/L = 0.00002 mg/L = 1.5×10^{-10} M). A technology evaluation for ^{129}I remediation was completed and concluded that there were no current treatment technologies available that can achieve the federal DWS. The present plan for ^{129}I treatment at the site is hydraulic containment that will be performed using withdrawing and injection wells placed at the leading edge of the plume(s) (Department of Energy, 2012b).

The SRS (Aiken, SC) also has extensive ^{129}I environmental contamination. The ^{129}I (and ^{131}I) were produced through similar but not identical operations as existed at the Hanford Site. Targeted radionuclides were extracted from irradiated materials at two locations, F-Area and H-Area, together known as the General Separations Area (Fig. 1). At F-Area and H-Area, low-level radioactive liquid waste was discharged to seepage basins, unlined pits that were about 4 m deep and several hectares in area. Low mobility radionuclides, such as Pu and Cm, have been largely sequestered in the sediments immediately beneath the basins, but more mobile radionuclides such as radioiodine have migrated into the groundwater and discharge into Four Mile Branch wetlands (Fig. 1), a small stream that eventually flows into the Savannah River. The F- and H-Area Seepage Basins received approximately 3 Ci of ^{129}I from 1955 to 1989, over a relatively small area, ≤ 2km^{2}. ^{129}I groundwater concentrations are commonly 30 pCi L^{-1}, and can get as high as 1000 pCi L^{-1} in the wetland area where the ^{129}I plume surfaces, well above the Maximum Contaminant Level (MCL, 1 pCi L^{-1}). The seepage basins have since been closed and capped with a low permeability engineered cover built to The Resource Conservation and Recovery Act (RCRA) specifications and the contaminant plume is being treated with a funnel and gate system that includes a periodic aqueous base injection into the subsurface.

The different iodine species, exhibit different sediment uptake properties. Iodate has Kd values (ratios of iodine concentration in solids vs liquids) that can be 2 orders of magnitude higher than that of iodide. Iodate can be sorbed to sediments by anion exchange or, after reduction, can covalently bound to natural organic matter, while iodide is found to be the most mobile species and can move along with water. However, even iodide at ambient concentrations (8 − 80 nM) can, after oxidation, be covalently bound to aromatic moieties of NOM in sediment and thus retained in the sediment. (Kaplan et al., 2014, and references therein).

Wetlands act as a filter for many contaminants, including radioiodine, and thus, greatly contribute to natural attenuation of contaminants. Subsurface contaminants move with groundwater flow and often pass through wetlands that contain high amounts of natural organic matter, before entering surface aquatic environments. Organic matter tends to enhance iodine uptake by soils; however, low molecular weight NOM can also be remobilized and thus makes soils a source of mobile iodine. The existence of multiple iodine redox states and the susceptibility of various iodine species to inter-conversion make it important to include an analysis of iodine speciation in order to fully understand the environmental and temporal drivers of iodine geochemistry in wetlands. Variability of water saturation in soils at wetlands often follows seasonal patterns, depending on the rise and fall of the water table. Fluctuation of the wetland water level regulates the availability of soil oxygen, microbial activity, and thus the mobility of redox-active radionuclides and essential metals. pH is another important factor affecting iodine speciation and sorption in the subsurface environment at SRS. In piezometers close to the F-Area Seepage Basins, a small pH increase of 0.7 units, from 3.1 to 3.8, over a twenty-year period has caused remobilization of ^{129}I from subsurface sediment resulting in a significant increase in groundwater ^{129}I concentrations. (Zhang et al., 2014, and references therein).

Concluding remarks

While much has been learned in the past decade about radioiodine chemistry and geochemistry, much more has to be learned on how to engineer long-term solutions based on these insights, and implement them into remedial actions at sites that will undergo climatic changes. Radioiodine can only be safely immobilized if we understand better its chemical speciation under changing conditions, e.g., variable pH and redox state. So, why should we care? Continuing to ignore the complexity of environmental interactions of radioiodine, a highly toxic radionuclide, will hamper our efforts to safely dispose of nuclear power waste, deal with accidental releases (such as Chernobyl and Fukushima), and to effectively manage and remediate contaminated environments.

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The Laboratory for Oceanographic and Environmental Research (LOER) was organized in 1989 at the Fort Crockett Campus of Texas A&M University in Galveston as a reasearch arm of the Department of Marine Science. It is supported by funds from the Coastal Zone Laboratory (CZL), the Texas Institute of Oceanography, the Research and Graduate Studies Office, and by research projects of the Principal Investigators. Currently, it serves faculty, postdoctoral research scientists and graduate students from other departments and organizations at TAMUG, including the Departmenst of Marine Sciences and Marine Biology, and the IDP. The laboratory is headed by Peter Santschi and Patrick Louchouarn.

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