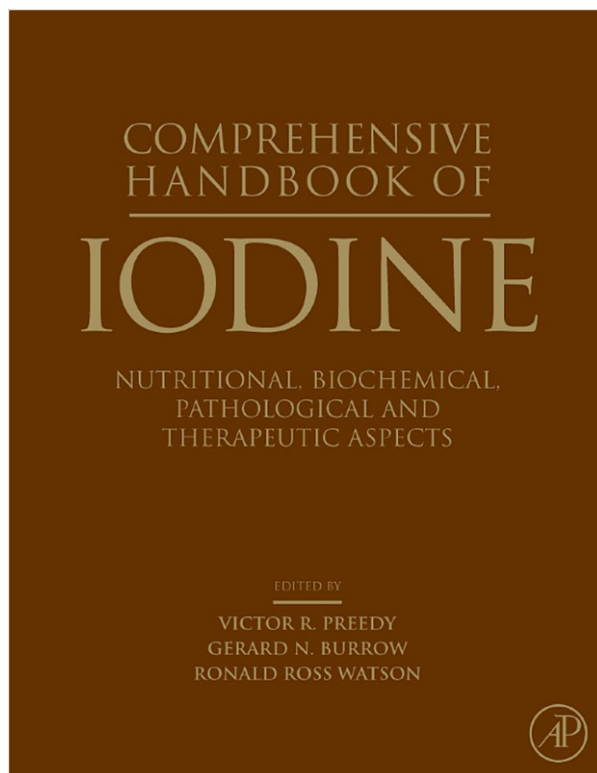


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From Qinhong Hu, Jean E. Moran and Van Blackwood, Geochemical Cycling of Iodine Species in Soils. In: Victor R. Preedy, Gerard N. Burrow and Ronald Watson, editors, *Comprehensive Handbook of Iodine*. Oxford: Academic Press, 2009, pp. 93-105.

ISBN: 978-0-12-374135-6

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Academic Press

## 10

**Geochemical Cycling of Iodine Species in Soils**

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**Abstract**

Iodine is an important element in studies of environmental protection and human health, global-scale hydrologic processes, and nuclear nonproliferation. Biogeochemical cycling of iodine in soils is complex, because iodine occurs in multiple oxidation states and as inorganic and organic species that may be hydrophilic, atmophilic, and biophilic. In this study, we applied new analytical techniques to study the content and speciation of stable iodine in representative surface soils, and sorption and transport behavior of iodine species (iodide, iodate, and 4-iodoaniline) in sediments collected at numerous nuclear facilities in the United States, where anthropogenic  $^{129}\text{I}$  from prior nuclear fuel processing activities poses an environmental risk. The surface soil 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 analyzed by IC and ICP-MS methods to determine iodine concentrations and to examine iodine speciation (iodide, iodate, and organic iodine). In natural soils, iodine is mostly (nearly 90% of total iodine) present as organic species, while inorganic iodine becomes important (up to 50%) only 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. Careful attention must be given to potential interconversion among species when interpreting the biogeochemical behavior of iodine in the environment. In addition to speciation, input concentration and residence time effects will influence the biogeochemical cycling of anthropogenic  $^{129}\text{I}$  deposited on surface soils.

**Abbreviations**

CBD Citrate-bicarbonate-dithionite  
DOE Department of Energy

HPLC High-performance liquid chromatography  
IC Ion chromatography  
ICP-MS Inductively coupled plasma-mass spectrometry  
NIST National Institute of Standards and Technology  
rpm Revolutions per minute  
ORR Oak Ridge Reservation  
SRM Standard Reference Material  
SRS Savannah River Site  
TMAH Tetramethyl ammonium hydroxide

**Introduction**

Iodine is an essential micronutrient in animals and humans, necessary for the production of thyroid hormones and for the proper functioning of the thyroid gland, and deficiencies can lead to severe metabolic disorders. As reported by the World Health Organization in 1999, iodine deficiency is a significant public health problem in 130 countries, with one-third of the world's population estimated to be at risk. Furthermore, because radioactive iodine is concentrated in the human thyroid (VanMiddlesworth *et al.*, 2000), an uncontrolled release of radioactive iodine could constitute a direct threat to human populations.

Iodine has one stable isotope,  $^{127}\text{I}$ , and 25 radioactive isotopes that include 10 fission products with very short half-lives ranging from minutes to a few hours. With a very long half-life ( $1.57 \times 10^7$  years), high-abundance fission yield, and presumably high mobility in the environment,  $^{129}\text{I}$  has been recognized as one of the most important radionuclides in studies of environmental protection and human health, global-scale hydrologic processes, and nuclear nonproliferation. Nuclear fuel reprocessing facilities constitute the major source of  $^{129}\text{I}$  released to the

environment (Table 10.1). Until 1998, a total of 2360 kg of  $^{129}\text{I}$  was discharged in the marine environment by two European facilities at La Hague in France and Sellafield in England, an amount that is 50 times the total release from nuclear weapon tests (Raisbeck and Yiou, 1999; Hou *et al.*, 2000; Fréchet and Calmet, 2003). From 1944 through 1972, the plutonium-production operation at the Hanford Site in Washington released about 266 kg of  $^{129}\text{I}$  into the air (Raisbeck and Yiou, 1999). In comparison, the operation of production reactors from 1953 to about 1990 at the Savannah River Site (SRS) in South Carolina released about 32 kg of  $^{129}\text{I}$  into the air. By comparison, the nuclear accident at Chernobyl released about 1–2 kg  $^{129}\text{I}$  (Raisbeck and Yiou, 1999). The proposed geological repository for storing high-level nuclear waste at Yucca Mountain of Nevada will contain as much as 13,300 kg  $^{129}\text{I}$  based on the storage of 70,000 tons of nuclear waste.

As the only naturally occurring radioactive isotope of iodine,  $^{129}\text{I}$  is produced by cosmic-ray interactions with xenon in the upper atmosphere and by spontaneous fission of uranium-238 in the geosphere (Table 10.1). Anthropogenic inputs of  $^{129}\text{I}$  have overwhelmed the natural inventory, increasing the hydrospheric  $^{129}\text{I}/^{127}\text{I}$  ratio from  $1.5 \times 10^{-12}$  during the pre-nuclear era to up to  $10^{-10}$ – $10^{-4}$  (Moran *et al.*, 1998; Fréchet and Calmet, 2003; Kekli *et al.*, 2003). This marked change in the ratio creates an opportunity for the application of anthropogenic  $^{129}\text{I}$  as an environmental tracer, originally proposed by Edwards (1962), to examine a variety of processes including ocean circulation, biogeochemical cycling, and regional hydrologic (e.g., atmosphere, surface water, and groundwater) processes (Raisbeck *et al.*, 1995; Schink *et al.*, 1995; Moran *et al.*, 1999; Oktay *et al.*, 2001).

However, the biogeochemical behavior of iodine needs to be well understood before  $^{129}\text{I}/^{127}\text{I}$  ratios can be used as an environmental tracer or geochronometer (Santschi and Schwehr, 2004). Iodine “notoriously” exhibits complex biogeochemical behavior, and occurs as various species with their associated hydrophilic, amphiphilic, and biophilic

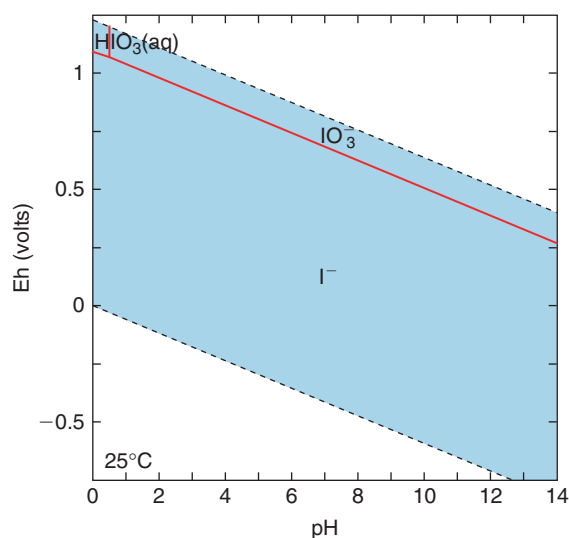
characteristics (Fuge and Johnson, 1986). With oxidation states ranging from  $-1$  to  $+7$ , the predominant states in aqueous systems are  $-1$  (iodide,  $\text{I}^-$ ) and  $+5$  (iodate,  $\text{IO}_3^-$ ) (Figure 10.1). In reducing environments, aqueous iodine usually occurs as the mobile monovalent anion,  $\text{I}^-$ . Under more oxidizing conditions, iodine is present as the more reactive  $\text{IO}_3^-$ , which can lead to retarded transport through interaction with clays and organic matter.

The coexistence of various inorganic and organic iodine species, in different proportions, has been reported in various environments (Liss *et al.*, 1973; Couture and Seitz, 1983; Yuita, 1992, 1994; Yamada *et al.*, 1999; Muramatsu and Ohmono, 1988; Baker *et al.*, 2001). Organically bound iodine can be a significant fraction of total iodine in aqueous systems and in the atmosphere. For example, methyl iodide is an important gaseous form of iodine in the marine atmosphere and in releases from nuclear fuel reprocessing facilities, while dissolved organo-I compounds comprise up to 50% of total iodine in aqueous samples from estuaries, rivers, and rain (Santschi and Schwehr, 2004).

The research objectives of this study are to evaluate the distribution of various iodine species in some soils and sediments in the United States, and to understand the extent and rate of interaction of iodine species (i.e., iodide, iodate, and organoiodine in the form of 4-iodoaniline) with sediment from nuclear facilities in the US Department of Energy (DOE) complex, where major releases of radionuclides, including  $^{129}\text{I}$ , have occurred (NRC, 2000). In this study, we infer important aspects of the environmental behavior of  $^{129}\text{I}$ , based on the similarities and differences between this radionuclide and stable iodine. Salient insights and future work regarding geochemical cycling of iodine in soils are then summarized.

**Table 10.1** Major source of  $^{129}\text{I}$  in the environment

Source	$^{129}\text{I}$	
	kg	TBq
Natural hydrosphere	100	0.65
Natural atmosphere	0.0005	0.000003
Atmospheric testing	50	0.32
Chernobyl	1–2	0.01
Savannah River Site	32	0.21
Hanford Reservation	266	1.7
NTS underground nuclear testing	10	0.065
Yucca Mountain repository	13,300	87
Spent fuel reprocessing (Europe)	2360	15



**Figure 10.1** Eh-pH diagram, drawn at 25°C and activity of  $10^{-11}\text{M}$ , for iodine in a typical  $\text{Na}^+\text{K}^+\text{HCO}_3^-$  type water. Diagram produced using the “thermo.com.V8.R6 +” database in the Geochemist’s Workbench (version 6.0).

## Materials and Methods

### Materials

We obtained a total of 26 soil and sediment samples from across the US (Table 10.2). Among them, 14 surface soils were procured from the North American Proficiency Test Program of the Soil Science Society of America, a repository of various representative US soils used by soil, plant, and water testing laboratories for inter-laboratory sample exchanges and a statistical evaluation of analytical data. These 14 soils were chosen to represent a wide range in texture, physico-chemical properties, and distance from the oceans; factors which may affect the global cycling of iodine. Two standard soil samples from the National Institute of Standards and Technology (NIST), for which total iodine contents have been analyzed by various approaches and research groups, were also obtained for method comparison. In addition, a total of 10 uncontaminated surface and sediment samples were obtained from various nuclear facilities of the US DOE where radionuclide contamination, including from  $^{129}\text{I}$ , could be an environmental problem (Table 10.2). These locations also represent a wide range in geologic and climatologic conditions (NRC, 2000). For example, SRS in South Carolina has a humid subtropical climate with annual rainfall of 91–112 cm, and geology representative of the Atlantic Coastal Plain. In contrast, the Hanford Site in Washington is located in an arid region with an average annual rainfall of only 16 cm and a stratigraphy consisting of bedded alluvial plain sediments with sands and gravels. Three SRS sediment samples were collected at different depths, providing an opportunity to examine the iodine content and speciation, as well as sorption and transport of iodine species, in a vertical sediment core.

All sample properties were measured according to standard procedures (Klute, 1986; Sparks, 1996), and are presented in Table 10.2. The wide range in sample types provide an opportunity to examine the correlation of total iodine content with soil properties (e.g., organic matter, clay mineralogy, soil pH, and texture), and the influence of these properties on the transport behavior of iodine species.

### Extraction of iodine species from solid samples

Chemical extractions using KCl and/or tetramethyl ammonium hydroxide (TMAH; either sequential or single-step) were conducted to investigate iodine speciation (inorganic and organic) in these soil and sediment samples. Extraction of inorganic iodine from soils was performed by adding 10 ml 0.005 M KCl to approximately 2 g of soil sample. The mixture was shaken for 1 h on a table shaker, and centrifuged at 5000 rpm for 30 min to remove particle sizes larger than 0.45  $\mu\text{m}$ . The supernatant was decanted for analysis and an extraction with 0.005 M

KCl was repeated; both supernatants were analyzed by ion chromatography. This extraction scheme was selected based on an evaluation of the extraction efficiency determined by spiking iodine species into a NIST Standard Reference Material (SRM) 2709 soil (San Joaquin), using three different extractants (deionized water, 0.05 M KCl, and 0.5 M KCl) and different iodine species.

Extraction of iodine contained in organic (humic and fulvic) components of the soils was performed by shaking 2 g soil samples in 20 ml of 5% TMAH, using a table shaker, for 4 h. The mixture was then centrifuged, and the supernatant analyzed using ion chromatography and inductively coupled plasma mass spectrometry (ICP-MS). Using the NIST SRM soils with well-known total iodine contents, we also evaluated extraction variables, such as the temperature (TMAH extraction under either room temperature or 80°C), on quantitative iodine extraction.

### Column transport studies of iodine species

Either glass (Kontes in Vineland, NJ; 2.5 cm inner diameter, 15.0 cm long) or stainless steel columns (Alltech in Deerfield, IL; 2.5 cm inner diameter, 7.0 cm long) were incrementally packed with the air-dried soil (<2 mm) to obtain a uniform bulk density. The packed columns were slowly wetted from the bottom with an electrolyte solution of 5 mM  $\text{CaCl}_2$  to establish saturation. Approximately 100 column pore volumes of electrolyte solution were pumped through the column prior to the transport study.

The methods employed for the miscible displacement studies were similar to those used in previous experiments (Hu and Brusseau, 1998). We connected a high-performance liquid chromatography (HPLC) pump (Model 301 from Alltech Associates Inc., Deerfield, IL) to the column, and placed a three-way valve in-line to facilitate switching between treatment solutions. Several iodine species (iodide, iodate, and 4-iodoaniline) were used to study transport behavior. We also examined the transport of tritium and bromide, commonly used conservative tracers, so that we could compare their transport behavior with iodine species. For transport experiments of 4-iodoaniline, which is used as a representative refractory organic iodine species, the solution was allowed contact only with glass or stainless steel, to avoid potential interaction of organoiodine with plastics in the column system. Column effluents were collected with an automated fraction collector (Retriever 500, ISCO Inc., Lincoln, NE) for chemical analysis, as described below.

### Analyses of iodine species

We used a Dionex Corp. (Sunnyvale, CA) ion chromatography (IC) DX-600 system to analyze  $\text{I}^-$  and  $\text{IO}_3^-$ . The system includes a GP50 gradient pump, an ED50A electrochemical detector, and an AS50 autosampler with a thermal compartment for temperature control. To measure low

**Table 10.2** Information and physico-chemical properties of samples used in this study<sup>a</sup>

Note	Sample name	Location	Texture	pH (1:1 0.01 M CaCl <sub>2</sub> )	OM (%)	CEC (meq/ 100g)	Particle size			Carbon (g/kg)		Aluminum (g/kg)	
							Sand (%)	Silt (%)	Clay (%)	CBD ext.	Oxalate ext.	CBD ext.	Oxalate ext.
Surface soil	Ashdos	Washoe County, NV	Sandy loam	6.20	1.78	16.1	61.0	25.4	13.9	3.92	0.60	0.46	0.71
	Bodenburg	Alaska	Silt loam	4.91	5.86	17.6	34.6	59.9	5.5	6.88	3.86	1.16	1.03
	Brazos	Texas	Sand	<u>5.70<sup>h</sup></u>	0.64	1.5	86.7	10.0	4.0	1.00	0.22	0.20	0.10
	Columbia	Columbia Basin, WA	Silt loam	7.43	1.10	12.5	46.0	43.8	11.0	4.66	1.12	0.36	0.58
	Lakeland	Florida	Sand	<u>5.20</u>	1.40	2.7	92.3	3.2	3.6	0.42	0.33	0.83	0.57
	McKinley	Sanger, Fresno County, CA	Sand	<u>7.05</u>	1.80	6.4	85.2	8.9	5.0	3.16	0.76	0.27	0.19
	Michael	Elba, Winona County, MN	Sandy loam	<u>6.20</u>	1.75	8.0	57.7	31.0	11.3	4.50	1.08	0.55	0.36
	Modesto	Modesto, Stanislaus County, CA	Loamy sand	<u>5.02</u>	0.60	2.9	83.0	12.9	4.0	2.58	0.65	0.34	0.21
	Newark	Delaware	Sandy loam	5.00	1.70	5.2	55.0	32.6	12.0	5.56	0.64	1.21	0.55
	San Joaquin soil <sup>a</sup>	San Joaquin				2.04							
	Montana <sup>a</sup>	Montana				3.40							
	Owngate	Santa Fe, NM	Clay loam	7.50	2.30	29.4	35.0	39.2	25.7	3.82	0.21	0.48	0.37
	Pasco	Pasco, Franklin County, WA	Sand	7.78	0.03	4.8	93.2	5.1	1.7	1.94	0.45	0.17	0.21
	Providence	Clinton, East Feliciana Parish, Louisiana	Silt loam	4.61	1.90	7.0	28.0	58.2	13.2	7.06	1.75	1.33	0.55
	Stockton	Holt, San Joaquin County, CA	Loam	4.52	28.10	74.6	44.5	32.0	23.2				
Wisconsin	Plover, Portage County, WI	Sandy loam	5.52	8.70	26.3	67.0	21.0	12.0	10.1	5.86	1.42	1.25	
DOE facility samples	Hanford sediment <sup>b</sup>	Richland, WA	Sand	7.48	0.06	7.37	89.0	7.9	3.1	3.26	0.94	0.28	0.46
	INL basalt <sup>c</sup>	Idaho Falls, ID	Loamy sand	7.46	0.04	1.67	77.4	21.1	1.5	3.12	12.90	0.15	0.39
	LLNL alluvium <sup>d</sup>	Livermore, CA	Sandy clay loam	7.10	0.03	26.3	42.0	25.6	32.4	9.78	0.94	0.14	0.37
	LLNL aquifer <sup>d</sup>	Livermore, CA	Sandy loam	7.75	0.17	21.1	64.8	22.3	12.9	2.04	7.35	0.38	1.40
	NTS alluvium <sup>e</sup>	Mercury, NV	Sandy loam	7.53	0.06	11.8	69.9	19.7	10.3	7.68	0.08	0.36	0.43
	NTS tuff <sup>e</sup>	Mercury, NV	Sand	7.80	0.14	4.54	89.1	8.8	2.1	1.48	0.12	0.20	0.12
	ORR sediment <sup>f</sup>	Oak Ridge, TN	Sandy loam		0.12	9.41	7.7	70.9	21.4	10.8	1.844	4.60	0.80
	SRS aquifer <sup>g</sup>	Aiken, SC	Sand	5.60	0.01	0.064	97.2	0.9	1.9	7.30	0.04	0.42	0.0081
	SRS subsoil <sup>g</sup>	Aiken, SC	Sandy loam	4.20	0.07	1.78	76.7	3.5	19.8	15.9	0.20	2.54	0.37
	SRS surface soil <sup>g</sup>	Aiken, SC	Sand	3.84	2.33	1.29	87.6	2.9	9.5	2.50	0.32	0.97	0.38

<sup>a</sup>San Joaquin soil is the NIST (National Institute of Standards and Technology) SRM (Standard Reference Material) 2709 which was collected 13–46 cm below the surface of an agricultural field, and ground to <74 μm. Montana soil is the NIST SRM 2712 which was collected from the top 15.2 cm of an agricultural field, and ground to <74 μm. NIST SRMs 2709 and 2711 have a NIST-noncertified (yet, verified from many researchers) total iodine value of 5 and 3 μg/g, respectively. OM: organic matter; CEC: cation exchange capacity; CBD: citrate-bicarbonate-dithionite; oxalate: ammonium oxalate.

<sup>b</sup>Composite of core samples 9–12 m below surface in the S-SX tank farm of Hanford Site.

<sup>c</sup>Crushed basalt core from Well S-4 at 0.3 m below surface at Box Canyon near Idaho National Laboratory (INL).

<sup>d</sup>The alluvium and aquifer samples were collected at 0.7 and 14.5 m below surface, respectively, at Site 300 of Lawrence Livermore National Laboratory (LLNL).

<sup>e</sup>The alluvium sample was from ~300 m below surface in the U-1a tunnel complex of Nevada Test Site (NTS), and the tuff sample was a crushed tuff collected at ~300 m below surface of Yucca Mountain at NTS.

<sup>f</sup>Composite of core samples 2–3 m below surface in Y-12 National Security Complex of Oak Ridge Reservation (ORR).

<sup>g</sup>Aquifer, subsurface (composite of sediments collected over 3-m span 12 m below surface), and surface soil of Savannah River Site (SRS).

<sup>h</sup>Underlined pH values were measured from 1:2 (soil:solution) of 0.01 M CaCl<sub>2</sub> solution.

(sub-ppb) concentrations of iodide, we used the ED50A in pulsed amperometric mode, with a silver working electrode and a Ag/AgCl reference electrode, after separation using IonPac AG11 and IonPac AS11 columns. Iodide separation was achieved with 50 mM nitric acid eluent under an isocratic flow of 1.5 ml/min. Under this analytical condition, there is no peak response for iodate. Quantitative conversion of iodate to iodide was achieved by adding 0.1 M NaHSO<sub>3</sub> in a volume ratio of 1:10 to the liquid sample, and the solution was mixed by shaking and standing for several minutes to reduce iodate to iodide; the resulting sample was analyzed for iodide by amperometry. We used a 25 µl injection loop size for sample analyses and Dionex PeakNet 6.2 software for system control, data collection, and processing.

Measurement of total iodine or 4-iodoaniline was carried out using a quadrupole ICP-MS system (Hewlett Packard 4500, Agilent Technologies, Palo Alto, CA or X-7 Series ICP-MS, Thermo Electron Corporation, West Palm Beach, FL). The ICP-MS was operated at a forward power of 1400 W with argon flow rates of 16, 1.0, and 0.9 l/min, respectively for plasma, auxiliary gas, and carrier gas flows. The column effluent sample was spiked with 10 µg/l internal standard elements for iodine-127 analysis. A rinse solution of 10% methanol was used between samples to mitigate potential memory effects. For ICP-MS iodine analysis, we tested several internal standards (Y-89, Rh-103, In-115, Tb-159, and Bi-209) to examine potential matrix effects introduced from soil extractants. Rh-103 stood out as having the most consistent response for all samples types, and was therefore used in the iodine data reduction.

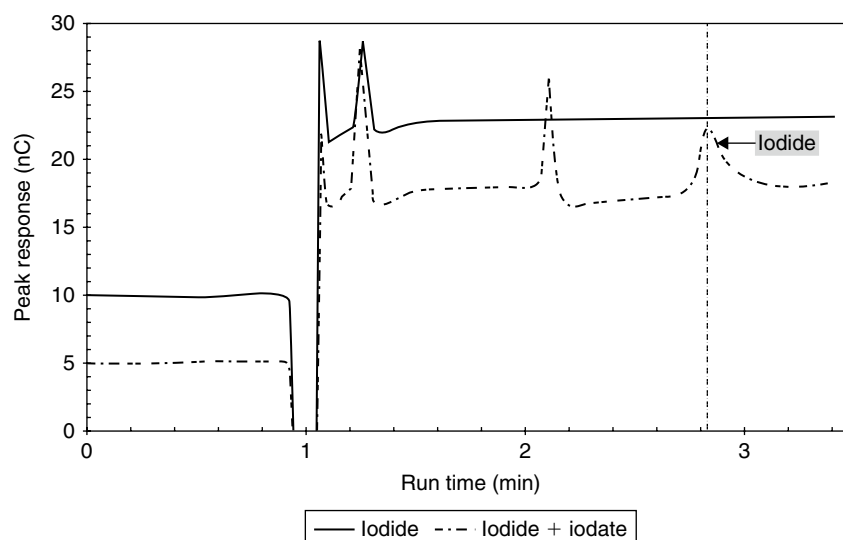
## Results and Discussion

### Analyses of inorganic iodine species by chromatographic amperometry

The method of amperometric detection, after chromatographic separation of ions, provides a fast (with a run time less than 3 min) and sensitive way (with a method detection limit of 0.6 µg/l; comparable to 0.1 µg/l by ICP-MS for total iodine analysis) to determine iodide concentration. Minimal memory effect was observed, as evidenced by a measured apparent iodide concentration of only 0.005% for the first noniodide-containing sample injected immediately after a high-concentration (100 mg/l) iodide standard.

Conversion of iodate to iodide using NaHSO<sub>3</sub> to measure the iodate concentration is shown to be complete (about 100%). Figure 10.2 presents the example chromatogram showing no response of the amperometric method for iodate, and conversion of iodate to be detected as iodide. In this study, this approach is used for detailed studies of quantifying the most common inorganic iodine species (iodate and iodide).

In addition to providing the insights on speciation of inorganic iodine, the amperometric method is also very useful in elucidating iodate–iodide interconversion. Hu *et al.* (2005) found that a portion of iodate, after being in contact with several soils (Hanford and SRS sediments) and clay minerals (kaolinite, illite, and montmorillonite), was converted to iodide, and this abiotic reduction was probably mediated by structural iron (Fe) present in the clay minerals.



**Figure 10.2** Chromatograms for amperometric detection of iodide and/or iodate in a 0.1 ppm iodate sample. We adjusted the position of the baseline in the plot, but the magnitude of the peak signal response in the y-axis has not been altered.

**Iodine content and speciation in US soils and sediments**

We evaluated the efficiency of KCl solution in extracting the iodine species by spiking a known amount of iodide, iodate, or 4-iodoaniline in NIST SRM 2709, which has a reported total iodine content of 5 µg/g. The first test involved using different concentrations of KCl in extracting iodide spiked at 1 ml of 0.91 mg/l into 2 g of SRM 2709. The spiked soils were mixed and left for 3 days. **Table 10.3** presents the results of different ionic strength solutions in extracting iodide. Most (>60%) iodide was extracted in the first pass of the extraction, though the second extraction still contributed to an appreciable (up to 20%) amount of iodide. Among the three ion-strength tests, the lowest one (deionized water) has the best extraction recovery. Therefore, a concentration of 0.005 M KCl solution, with two passes, was selected to extract soil samples; this concentration was suitable for minimizing disaggregation of clay particles and direct sample measurement of extractants using ICP-MS.

We further assessed the extraction recovery of different iodine species in a KCl extractant (**Table 10.4**). Two concentrations (either 0.091 or 0.91 mg/l) of iodine spike species were used. In the mixed iodine treatment, a mixture of iodide, iodate, and 4-iodoaniline (each with a concentration of either 0.091 or 0.91 mg/l) was spiked into SRM 2709. It appears, for iodide and iodate, the lower spike concentration produced a recovery of >100%; this is likely related to the larger analytical uncertainty at lower

concentration and the contribution of extracted inorganic iodine from the soil itself. This interpretation is supported by mass balance calculations, which include the measured inorganic iodine species in SRM 2709 of about 9%. For treatments with 4-iodoaniline, a higher spike level exhibits higher recovery. Overall, iodine species can be extracted with the KCl extractant at a recovery of >70% (**Table 10.4**). This study served to assess whether newly spiked organic iodine can be extracted by the KCl solution, and whether organically bound iodine species are obtained from TMAH extractions.

Finally, we studied the extraction efficiency using 5% TMAH to measure soil iodine contents from two SRM

**Table 10.3** Extraction evaluation of various extractants for iodide in NIST SRM 2709

Extractant	Duplicate	Extraction efficiency (%)			Avg. ± std. dev.
		Extraction pass	Each pass	Total	
Deionized water	A	1st	81.8	97.2	93.4 ± 3.4
		2nd	15.4		
	B	1st	74.4	90.6	
		2nd	16.3		
	C	1st	85.9	92.3	
		2nd	6.34		
0.05 M KCl	A	1st	62.5	77.9	90.9 ± 11.2
		2nd	15.5		
	B	1st	75.1	97.2	
		2nd	22.1		
	C	1st	87.2	97.6	
		2nd	10.4		
0.5 M KCl	A	1st	68.3	80.3	76.2 ± 6.0
		2nd	12.0		
	B	1st	68.1	69.3	
		2nd	1.1		
	C	1st	70.9	79.1	
		2nd	8.27		

**Table 10.4** Extraction evaluation of 0.05M KCl for various iodine species in NIST SRM 2709

Spiked iodine	Duplicate	Extraction pass	Extraction efficiency (%)		
			Each pass	Total	Avg. ± std. dev.
0.091 ppm iodide	A	1st	125	138	108 ± 27.5
		2nd	13.2		
	B	1st	70.6	83.7	
		2nd	73.1		
	C	1st	95.1	104	
		2nd	8.99		
0.91 ppm iodide	A	1st	43.9	63.9	73.0 ± 8.4
		2nd	20.0		
	B	1st	55.3	80.4	
		2nd	25.2		
	C	1st	66.3	74.4	
		2nd	8.14		
0.091 ppm iodate	A	1st	64.2	125	121 ± 5.7
		2nd	60.9		
	B	1st	60.0	117	
		2nd	57.0		
0.91 ppm iodate	A	1st	60.7	89.7	78.9 ± 15.3
		2nd	29.0		
	B	1st	42.9	68.0	
		2nd	25.1		
0.091 ppm 4-iodoaniline	A	1st	63.4	94.4	69.5 ± 10.7
		2nd	30.9		
	B	1st	61.6	94.1	
		2nd	32.5		
0.91 ppm 4-iodoaniline	A	1st	52.4	62.0	78.9 ± 15.3
		2nd	9.56		
	B	1st	64.7	77.1	
		2nd	12.4		
0.091 ppm mixed iodine	A	1st	53.9	61.4	63.0 ± 2.3
		2nd	7.49		
	B	1st	48.1	64.1	
		2nd	16.5		
0.91 ppm mixed iodine	A	1st	69.7	90.8	92.1 ± 1.9
		2nd	21.0		
	B	1st	66.1	93.5	
		2nd	27.3		

soils with much longer contact time and well-known total iodine contents. Iodine extracted with TMAH at room temperature is operationally identified as a labile organic species (after subtracting inorganic iodine), and under elevated temperature (80°C), as total iodine. Tests with SRM soils at elevated temperature produced a complete recovery of  $103.9 \pm 5.1\%$  for SRM 2709 and  $93.8 \pm 9.4\%$  for SRM 2711, respectively. Note that 5% TMAH solution also extracts the inorganic iodine (Table 10.5). TMAH-extractable iodine is nearly identical to the combined iodine content from KCl extraction followed by TMAH extraction. Alkaline TMAH was first reported by Takaku *et al.* (1995) to be a favorable matrix for iodine analysis by ICP-MS. Using TMAH for quantitative iodine extraction of soil samples was first proposed by Yamada *et al.* (1996), and employed in several studies (Rädlinger and Heumann, 1998; Yamada *et al.*, 1999; Tagami *et al.*, 2006).

The measured total iodine contents in 15 (except for Stockton soil, which is a peat sample with an unusually high concentration of organic matter of 28.1%) US surface soils range between 0.46 and 5.42 mg/kg on a dry weight basis for the soils (Table 10.6). For surface soils (usually sampled to 15 cm depth) on a worldwide basis, the average iodine content is about 5 mg/kg (cf. Whitehead, 1984). The iodine contents in 132 surface soils from widely differing soil types in the UK was found to range from 0.5 to 98.2 mg/kg, with a mean of 9.2 mg/kg. The high iodine values are from soils that are close to the coast in the UK where there is relatively high rainfall, and from areas with a substantial proportion of grassland with high soil organic matter. Muramatsu *et al.* (2004) reported a range of 0.2–150 mg/kg iodine in more than 50 soil samples in Japan; the high iodine concentrations are likely caused by the direct influence of the marine atmosphere, high

rainfall (about 2 m per year), and high adsorption capacity for iodine of the Japanese Andosol soils.

In addition to measurement of the total iodine content, assessment of iodine speciation in soils is a major focus of this study. In the natural soil samples that we analyzed, iodine is mostly (nearly 90% of total iodine) present as organic species, among them appreciable amounts (about 50% for most soils) are nonlabile, i.e., extractable with 5% TMAH under elevated temperature (Table 10.6). In contrast, inorganic iodine becomes important (up to 50%) in sediments with low organic matter, however, organic species are still the dominant form of iodine.

Inorganic labile iodine, extractable from a low ion-strength salt, comprised less than 10% of the total iodine in surface soils. This is consistent with the reports that approximately 80% of 183 UK soils contained less than 10% cold-water extractable iodine (cf. Fuge and Johnson, 1986). For some soil samples, we also evaluated the proportion of iodide and iodate in inorganic iodine (Table 10.7), and it seems that either may be dominant. We are not aware of other reports on the distribution of iodide and iodate in soil iodine. Yamada *et al.* (1999) assumed that iodide is more soluble than iodate, and used the first

**Table 10.5** Extraction evaluation of KCl and/or TMAH in NIST SRM 2709

Sample name	TMAH only (mg/kg)	KCl + TMAH (mg/kg)
Ashdos	0.38	0.39
Brazos	0.32	0.30
McKinley	0.18	0.18
Michael	0.74	0.79
Newark	2.17	2.04
Providence	3.84	3.01
NIST SRM 2711	0.65	0.76
NIST SRM 2709	0.96	1.03
Hanford sediment	0.11	0.14
INL basalt	0.02	0.03
LLNL alluvium	0.16	0.12
NTS tuff	0.11	0.13
ORR sediment	1.23	1.15
SRS aquifer	0.08	0.13
SRS subsoil	1.36	1.17
SRS surface soil	0.63	0.74

**Table 10.6** Iodine speciation in soils and sediments

Sample name	Total iodine (g/kg)	Inorganic iodine		Labile organic iodine		Nonlabile organic iodine (%)
	(g/kg)	(g/kg)	(%)	(g/kg)	(%)	(%)
Ashdos	0.898	0.045	5.06	0.344	38.3	56.6
Bodenburg	0.702	0.029	4.20	0.343	48.8	47.0
Brazos	0.449	0.036	7.97	0.269	59.8	32.2
Columbia	1.08	0.079	7.36	0.190	17.6	75.0
Lakeland	2.63	0.210	8.00	1.39	52.9	39.1
McKinley	0.460	0.026	5.59	0.155	33.7	60.7
Michael	1.32	0.080	6.07	0.710	53.8	40.1
Modesto	0.393	0.022	5.60	0.040	10.3	84.1
Newark	2.93	0.132	4.50	1.91	65.2	30.3
Owngate	0.897	0.118	13.2	0.329	36.7	50.1
Pasco	0.477	0.039	8.23	0.439	92.0	-0.20
Providence	5.23	0.166	3.17	2.85	54.5	42.4
Stockton	33.0	0.812	2.46	27.4	83.0	14.5
Wisconsin	1.58	0.027	1.71	1.11	70.3	27.9
San Joaquin soil	5.42	0.478	8.82	0.556	10.3	80.9
Montana	3.01	0.286	9.51	0.473	15.7	74.8
Hanford sediment	0.272	0.031	11.4	0.107	39.3	49.3
INL basalt	0.021	0.012	59.9	0.018	87.0	
LLNL alluvium	0.721	0.006	0.79	0.110	15.2	84.0
NTS tuff	0.029	0.012	42.4	0.016	55.2	2.40
ORR sediment	1.71	0.035	2.04	1.12	65.4	32.6
SRS aquifer	0.172	0.050	29.1	0.077	44.8	26.2
SRS subsoil	2.07	0.088	4.24	1.08	52.0	43.8
SRS surface soil	1.02	0.010	0.98	0.735	71.9	27.1



two repeated extractions with 0.1 M KCl as the iodide content and the subsequent two extractions as the iodate content. They reported that iodide and iodate contributed about equal amounts (about 5 mg/kg) in a red-yellow mountain soil, while iodate (about 6 mg/kg) was the only inorganic iodine found in another Andosol virgin soil.

To assess the correlation of iron and aluminum oxides with iodine content, we used a selective extraction to target the different fractions of Fe and Al in the soil samples. Citrate-bicarbonate-dithionite (CBD) extractable Fe contains crystalline iron oxide minerals, such as hematite, goethite, lepidocrocite, and ferrihydrite, while ammonium oxalate (NH<sub>4</sub>-Ox) extraction targets noncrystalline ("free") Fe oxides, including ferrihydrite and ferrihydrite-like minerals (Loeppert and Inskeep, 1996). The CBD and NH<sub>4</sub>-Ox extractions also remove some crystalline and noncrystalline aluminum oxide phases, respectively.

We performed regression analyses of various iodine components with different physico-chemical properties of surface soils (Table 10.8). The correlation is highest for organic matter and cation exchange capacity, followed by

CBD-extractable Al, clay content, and CBD-extractable Fe. It is commonly reported that the content of organic matter has a dominant influence on total iodine content (Whitehead, 1973; Fuge and Johnson, 1986). As reported in Fuge and Johnson (1986), among a total of 213 soil samples, it was found that soils rich in organic matter were generally enriched in iodine ( $r = 0.57$ ). Surface soil samples (0–20 cm) showed a good correlation between organic matter and total iodine ( $r = 0.70$ ). The good correlation between iodine and organic matter in the surface soils is likely related to the supply (atmospheric input) of iodine and its retainability. However, in 154 samples collected in successive 10-cm increments from 18 soil profiles in the UK, the total iodine content was closely correlated with oxalate-soluble Al, but not with oxalate-soluble Fe or organic matter (Whitehead, 1978). However, in the five most acidic soils, with pH below 4.8, the iodine content was more closely correlated with Fe than with Al. The lack of correlation of iodine content with organic matter in the soil-profile study was ascribed to the short time scale for organic matter turnover, as these soils were either under grass or cultivated annually. Overall, this study confirms the dominant influence of organic matter, clays, and sesquioxides in retaining iodine in soils.

**Table 10.7** Inorganic iodine speciation in some soils

Sample	KCl-extractable iodide		KCl-extractable iodate	
	(mg/kg)	(%)	(mg/kg)	(%)
Bodenburg	0.005	0.71	0.024	3.49
Columbia	0.058	5.4	0.021	1.97
Lakeland	0.103	3.92	0.107	4.07
Modesto	0.022	5.6	0.00	0.00
Owngate	0.030	3.34	0.088	9.8
Pasco	0.014	2.94	0.025	5.29
Wisconsin	0.025	1.58	0.002	0.13
Stockton	0.054	0.16	0.758	2.30

**Physico-chemical properties affecting sorption and transport of iodine species**

We studied the transport of iodine species, along with tracers of bromide and tritium, in various sediments from both DOE nuclear operation facilities and from the Wisconsin soil, which has a high (8.7%) organic matter content. In all of the samples bromide, which is negatively charged like iodide and iodate, exhibited ideal

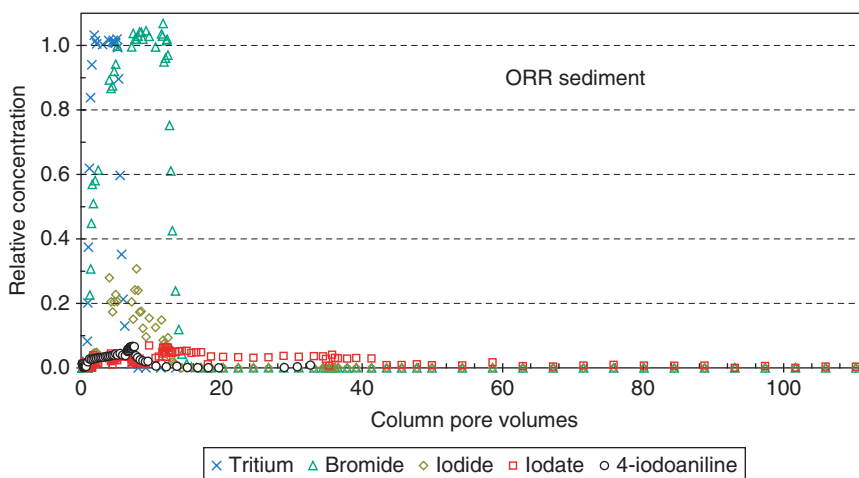
**Table 10.8** Correlation of iodine species with soil properties

Iodine species	Regression	pH (1:1 DI water)	OM (%)	CEC (meq/100 g)	Particle size			Iron (g/kg)		Aluminum (g/kg)	
					Sand (%)	Silt (%)	Clay (%)	CBD ext.	Oxalate ext.	CBD ext.	Oxalate ext.
Inorganic iodine	Slope	-0.072	0.024	0.009	-0.002	0.001	0.016	-0.003	-0.011	0.050	0.001
	Intercept	0.591	0.068	-0.007	0.285	0.094	-0.034	0.090	0.092	0.044	0.077
	Correlation	-0.428	0.762	0.834	-0.278	0.119	0.555	-0.123	-0.294	0.368	0.004
Labile organic iodine	Slope	18.8	-1.3	-2.4	7.7	1.5	-2.7	0.3	0.7	-0.1	0.4
	Intercept	-2.51	0.93	0.33	-0.08	0.04	0.52	0.12	0.08	1.36	0.63
	Correlation	-0.429	0.946	0.878	-0.257	0.108	0.522	0.382	0.155	0.744	0.257
Nonlabile organic iodine	Slope	4.225	0.686	0.136	2.310	0.385	-0.094	0.338	0.601	0.131	0.451
	Intercept	0.228	-0.022	0.016	0.017	-0.021	-0.035	-0.135	-0.038	-0.336	2.935
	Correlation	-0.510	0.615	0.779	-0.416	0.286	0.562	0.304	0.023	0.573	0.187
Total iodine	Slope	23.6	-0.5	-2.2	10.3	2.0	-2.8	0.7	1.4	0.0	1.0
	Intercept	-3.10	1.09	0.39	-0.11	0.06	0.63	0.18	0.07	2.12	0.95
	Correlation	-0.445	0.931	0.870	-0.283	0.135	0.533	0.345	0.089	0.692	0.230

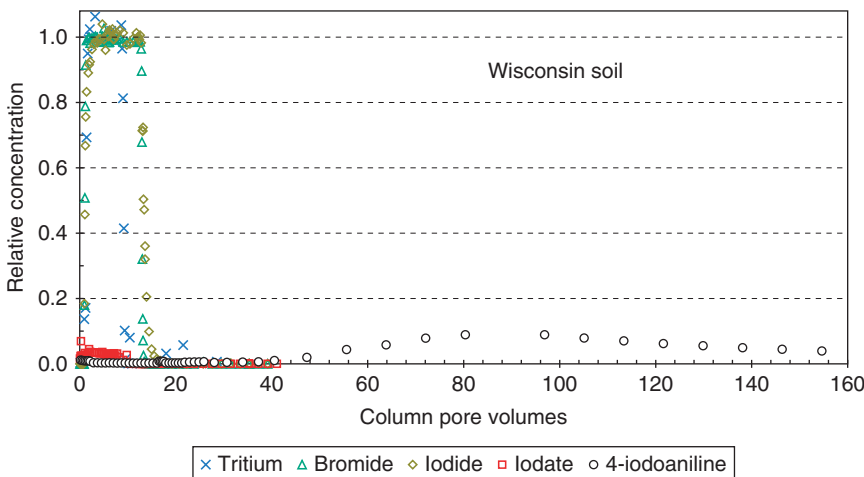
breakthrough with symmetrical behavior and negligible tailing (examples are shown in **Figures 10.3–10.4**) and conservative (not retarded; with the retardation factor of 1) transport (**Table 10.9**). A slight retardation of tritium was observed in the columns packed with Wisconsin soil and Oak Ridge sediment (**Table 10.9**). Tritium sorption of similar magnitude, postulated to occur from the interaction of tritium with clay lattice hydroxyls via hydroxyl exchange (**Stewart and Baker, 1973**), has been reported in numerous publications.

Iodide sorption onto many types of geologic media has been reported to be extremely small (**Whitehead, 1974; Kaplan et al., 2000**). We also observed very limited sorption of  $I^-$  during transport in SRS surface soil, SRS aquifer, and Hanford sediment samples (**Hu et al., 2005**). However,

soil properties play an important role in the sorption of  $I^-$ . There was significantly retarded transport of  $I^-$ , compared to bromide/tritium, in the SRS subsoil sample. This sample contained an appreciable amount of iron and aluminum oxide minerals (**Table 10.2**), which possesses positively charged surfaces that contribute to anionic  $I^-$  sorption. The appreciable number of positively charged surfaces is confirmed by anion exchange capacity (AEC) measurements; the SRS subsoil has a high AEC (4.04 meq/100 g sample) – more than 10 times higher than the other two SRS samples. Similarly, sorption of  $I^-$  has been observed (**Yoshida et al., 1992, 1998**) in Japanese soils that contain substantial amounts of imogolite, ferrihydrite, and allophane, which create a relatively high number of positively charged surfaces.



**Figure 10.3** Breakthrough curves of tritium and iodine species in a column homogeneously packed with Oak Ridge Reservation (ORR) sediment. The input concentration and pulse, which was varied for different solutes, are presented in **Table 10.9**.



**Figure 10.4** Breakthrough curves of tritium and iodine species in a column homogeneously packed with Wisconsin soil. The input concentration and pulse are presented in **Table 10.9**.

**Table 10.9** Experimental parameters and mass recovery for the transport of iodine species

Sample	Solute	Input conc.	Input pulse	Mass recovery	$R_f$
ORR sediment	Tritium	30 kBq/l	4.60	1.01	1.17
	Bromide	$1 \times 10^{-4}$ M	11.2	1.00	2.48
	Iodide	$1 \times 10^{-4}$ M	11.2	0.20	>100 <sup>a</sup>
	Iodate	$1 \times 10^{-4}$ M	11.2	0.16	>100 <sup>a</sup>
	4-iodoaniline	$4 \times 10^{-5}$ M	6.61	0.06	>500 <sup>a</sup>
Wisconsin soil	Tritium	30 kBq/l	7.87	1.06	1.36
	Bromide	$1 \times 10^{-4}$ M	12.3	0.95	1.05
	Iodide	$1 \times 10^{-4}$ M	12.3	1.00	1.19
	Iodate	$1 \times 10^{-4}$ M	12.3	0.02	>50 <sup>a</sup>
	4-iodoaniline	$1 \times 10^{-5}$ M	16.5	0.44	>90 <sup>a</sup>

<sup>a</sup>To obtain the extent of sorption for solutes with large sorption, an alternate approach, such as a batch sorption study, is more appropriate than the column approach.

Iodate commonly exhibits more retarded transport than iodide because it interacts more strongly with both clays and organic matter (Couture and Seitz, 1983; Ticknor and Cho, 1990; Sheppard and Thibault, 1992; Yoshida *et al.*, 1998). As discussed by Kaplan *et al.* (2000), the cause for the difference in  $I^-$  and  $IO_3^-$  sorptive behavior is not known, but is presumably the result of the harder base nature of  $IO_3^-$ , as compared to  $I^-$ , which would favor hard-hard interactions with the hard acid sites on the mineral surfaces. The disparate sorption behavior of  $I^-$  and  $IO_3^-$  was observed in our study, which consistently showed greater sorption for  $IO_3^-$  than for  $I^-$ . Even in the Hanford sediment, which has a very low AEC, noticeable sorption of  $IO_3^-$  took place (Hu *et al.*, 2005). For the Wisconsin soil with high organic matter, sorption of  $IO_3^-$  is much stronger than for  $I^-$  (Figure 10.4 and Table 10.9).

Compared to  $I^-$  and  $IO_3^-$ , studies on the transport of organoiodine compounds are much more scarce, given the challenges associated with the analysis of various organoiodine compounds. In this work, we used 4-iodoaniline as a representative nonvolatile organoiodine species. As expected, we found that transport of 4-iodoaniline is quite different from that of the inorganic forms,  $I^-$  and  $IO_3^-$ , and seems to be related to the amount of organic matter in the sample. This finding is consistent with the hydrophobicity of organoiodine and its affinity for hydrophobic organic matter. In SRS surface soil with 2.33% organic matter, transport of 4-iodoaniline is delayed by more than 20 times that of  $I^-$ . In contrast to SRS surface soil results, 4-iodoaniline migrates without retardation, similar to bromide/tritium, in the SRS subsoil, while  $IO_3^-$  and  $I^-$  are significantly retarded. This is also true for the SRS aquifer material, though the magnitude of sorption for  $IO_3^-$  and  $I^-$  is less than for SRS subsoil. Both SRS subsoil and aquifer samples have extremely low organic matter content, but high amounts of iron and/or aluminum oxides that exhibit anion-sorption capacity. This example, showing disparate transport behavior for the different iodine species

in three types of samples in a vertical cross-section, highlights the need to consider sediment properties when predicting the geochemical behavior and transport of iodine. Furthermore, inorganic iodine could be fixed onto macromolecular humic substances, as reported by Tikhomirov *et al.* (1980) and Rädlinger and Heumann (2000), and this fixation can change the physico-chemical characteristics and associated fate and transport behavior of iodine.

The retardation factor ( $R$ ) and mass recovery, calculated by moment analyses of the breakthrough curves for the transport of iodine species in Oak Ridge Reservation (ORR) sediment and Wisconsin soil, are listed in Table 10.9. The effluent mass recovery for all iodine species in ORR sediment is very low (<20%), with the remainder of the released iodine irreversibly retained in the sample components such as iron/aluminum oxides and organic matter; the ORR sediment has a relatively high amount of both of these components. In the Wisconsin soil with a very high amount of organic matter, mass recovery for iodate and 4-iodoaniline, which is more sorptive than iodide, is also very low. In these cases, geochemical cycling of iodine could be very slow, due to the soil/sediment characteristics and iodine speciation.

### Other factors affecting iodine cycling

In addition to iodine speciation, the input concentration and contact time have an effect on iodine sorption and transport behavior. Because the sorption of both  $I^-$  (especially) and  $IO_3^-$  are related to the presence and magnitude of soil components that possess positively charged surfaces, and since positively charged surface sites are limited, the extent of sorption will probably be affected by the input concentration. Positively charged adsorption sites may exist on the edges of 2:1 clays (such as smectite and illite), on Al- and Fe-oxide surfaces, and on 1:1 clays (such as kaolinite). The number of sorption sites in variable-charge minerals is influenced by ionic strength, solution

pH, and counterion valence (Seaman *et al.*, 1996). Using an input concentration of  $10^{-5}$ – $10^{-4}$  M, Hu *et al.* (2005) studied the sorption and transport of  $I^-$  and  $IO_3^-$  in SRS and Hanford sediments. The trend of  $I^-$  and  $IO_3^-$  sorption with respect to the initial concentration is consistent with the limited number of positively charged sites for sorption. Greater  $I^-$  sorption at a much lower ( $10^{-12}$  M) concentration for three subsurface sediments from the Hanford Site was reported by Kaplan *et al.* (2000).

Ideally, one would use a concentration that is comparable to real-world situations, i.e.,  $10^{-8}$  M for stable iodine in the hydrosphere (Fuge and Johnson, 1986), and a few orders-of-magnitude lower for anthropogenic  $^{129}I$ , as observed at SRS (Beals and Hayes, 1995). However, for trace concentrations of  $I^-$ , usually introduced as radioactive  $^{125}I$  in laboratory experiments, in a system open to air, the  $I^-$  can be oxidized to  $IO_3^-$  (Couture and Seitz, 1983; Fuhrmann *et al.*, 1998), which complicates data interpretation considering the different sorption behavior of  $I^-$  and  $IO_3^-$ . It is not improbable that sorption of iodide, observed in some studies, is actually the result of conversion to  $IO_3^-$  and subsequent sorption.

The effect of residence (contact) time also needs to be considered; this is more critical for anthropogenic  $^{129}I$  which has only been participating in iodine cycling over the past 50 years. Because of the longer interaction times (thousands of years) and the higher concentrations of  $^{127}I$  compared to  $^{129}I$ ,  $^{127}I$  preferentially occupies the thermodynamically favorable sorption sites. Without newly-generated sorption places, which could lead to irreversible  $^{129}I$  adsorption, virtually no irreversible adsorption and immobilization of  $^{129}I$  can take place (Ernst *et al.*, 2003). The relative portion of reversible binding sites is substantially higher for  $^{129}I$  than for  $^{127}I$  on the time scale of anthropogenic  $^{129}I$  fallout. Therefore, trace  $^{129}I$  possesses a higher mobility than stable  $^{127}I$ .

Alvarado-Quiroz *et al.* (2002) measured total iodine and  $^{129}I$  in Ontario, Canada, where low-level radioactive waste has been stored in trenches above a sandy aquifer and drained into an organic-rich swamp. The results indicated that the  $K_d$  distribution coefficients for  $^{127}I$  and  $^{129}I$  were 1.3 and 1.6 l/kg for the sandy aquifer, and 486 and 92.8 l/kg for the swamp sediment. Incremental leaching experiments on the geologic materials produced consistent results showing  $^{127}I$  being more strongly sorbed than  $^{129}I$ . This was postulated to be the result of kinetically controlled sorption mechanisms and the differing residence times for stable vs. radio-iodine in the hydrologic regime.

The input concentration and extent of sorption, as well as sorption kinetics, are seen to be correlated during iodine sorption and transport (Hu *et al.*, 2005). In experiments on iodine transport in SRS surface soils at varying initial concentrations and residence times, iodate sorption was stronger, both at lower concentration and at longer residence time. The first-order desorption rate coefficients

( $T^{-1}$ ),  $k_2$  (which specifies the degree of disequilibrium in systems where disequilibrium increases as  $k_2$  decreases), are much higher for organic than inorganic iodines. For the same iodine species, the value of  $k_2$  decreases as input concentration decreases. Overall, anthropogenic  $^{129}I$ , with its lower concentration and short contact time with soils will likely take a prominent role in the geochemical cycle; the presence of different iodine species further compounds this effect.

## Summary Points

The following can be summarized regarding the current understanding and suggested future work on geochemical cycling of iodine in soils:

- Amperometric detection of iodide after chromatographic separation has proven a sensitive method to study stable iodine, while accelerator mass spectrometry is the method of choice for analyzing  $^{129}I$ . However, further development of sensitive and specific analytical methods for different iodine species in complex matrices is warranted. Multiple and integrated approaches are needed to tackle complex issues surrounding iodine speciation.
- Various iodine species in different proportions exist in soil and sediments. Organically bound iodine, with limited solubility and mobility, commonly comprises the major proportion of total iodine; it is well-correlated with total organic matter, sesquioxides, and clay content.
- Different iodine species exhibit very different sorption and transport behavior in geologic samples. Sorption of iodate is consistently greater than that of iodide, while the transport of organoiodine (exemplified by 4-iodoaniline in this study) is quite limited, and related to the amount of organic matter in the sample. The physical and chemical processes affecting iodine transport include iodate reduction, irreversible retention or mass loss, and rate-limited and nonlinear sorption of iodine.
- Interconversion of iodine species, both abiotically and biologically, may be a very important process and deserves more attention (Councill *et al.*, 1997; Amachi *et al.*, 2003; Hu *et al.*, 2005).
- Examination of iodine speciation, with due attention to potential interconversion among species, is essential when interpreting the environmental behavior of iodine. Conflicting reports of iodine cycling in the environment could be due to the lack of understanding of iodine speciation and their disparate environmental behavior.
- With a shorter contact time than stable iodine, anthropogenic  $^{129}I$  will likely have a higher mobility when in an inorganic form. However,  $^{129}I$  will experience a similar speciation process as stable iodine and will eventually be retained strongly, with organoiodine as the dominant species.

## Acknowledgments

This work was supported by the Laboratory Directed Research and Development program at Lawrence Livermore National Laboratory (LLNL). Van Blackwood thanks the Nuclear Science Internship Program of the Glenn T. Seaborg Institute of LLNL for a summer internship during which he worked on the extraction and analysis of iodine species in soil samples. All surface soils, except for two NIST SRMs, listed in Table 10.2, were procured from the North American Proficiency Testing (NAPT) Program of the Soil Science Society of America. We gratefully acknowledge John Seaman of the University of Georgia, David Watson of Oak Ridge National Laboratory, John Zachara of Pacific Northwest National Laboratory, Boris Faybishenko of Lawrence Berkeley National Laboratory, and Michael Taffet of Lawrence Livermore National Laboratory for providing the sediment samples from DOE facilities. William Austin of Oregon State University provided assistance in analyzing some soil properties. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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