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Iodine-129 and Iodine-127 Speciation in Groundwater at the Hanford Site, U.S.: Iodate Incorporation into Calcite

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S *Supporting Information*

ABSTRACT: The geochemical transport and fate of radioiodine depends largely on its chemical speciation that is greatly affected by environmental factors. This study reports, for the first time, the speciation of stable and radioactive iodine in the groundwater from the Hanford Site. Iodate was the dominant species and accounted for up to 84% of the total iodine present. The alkaline pH (pH $\sim$ 8) and predominantly oxidizing environment may have prevented reduction of the iodate. In addition, groundwater samples were found to have large amounts of calcite precipitate which were likely formed as a result of CO_2 degassing during removal from the deep subsurface (>70m depth). Further analyses indicated that between 7 and 40% of the dissolved ^{127}I and ^{129}I that was originally in the groundwater had coprecipitated in the calcite. Iodate was the main species incorporated into calcite and this incorporation process could be impeded by elevating the pH and decreasing ionic strength in groundwater. This study provides critical information for predicting the long-term fate and transport of ^{129}I. Furthermore, the common sampling artifact resulting in the precipitation of calcite by degassing CO_2, had the unintended consequence of providing insight into a potential solution for the in situ remediation of groundwater ^{129}I.
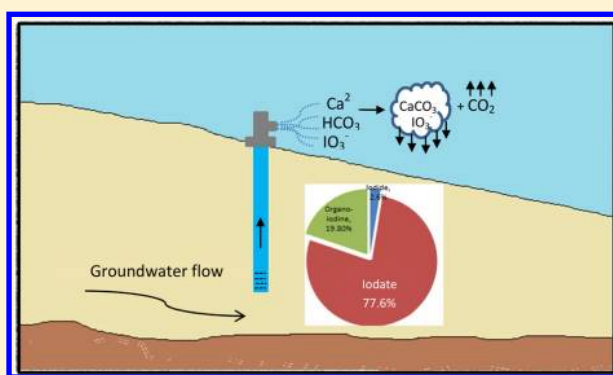
■ INTRODUCTION

^{129}I has been identified as a major risk in groundwater near nuclear waste disposal sites.[1−3] In the past few years, significant advancements in radioiodine biogeochemistry were made possible after the development of analytical methods for detecting iodine species at ambient concentrations.[4,5] These studies demonstrated the importance of organo-iodine as a major species in groundwater[5−7] and revealed that soil organic matter[8−10] and microbial processes[11,12] play important roles in speciation, and fate and transport of subsurface iodine. For example, at the Savannah River Site (SRS), iodate and organo-iodine accounted for 50% of the total iodine, with the balance as iodide. These results are consistent with studies examining ^{127}I in a variety of natural waters. The coexistence of inorganic and organic iodine species is not uncommon in surface waters. As summarized in Truesdale et al. (2013),[13] 50% inorganic iodine exists as iodide in tropical and subtropical oceans, while iodate is the dominant species in oxic deep water and polar surface water. Organo-I is also prevalent in riverine, coastal and estuarine systems.[4,5,14,15] Yang et al. (2007)[16] reported three classes of iodine speciation in groundwater from Shan-xi, China: classes dominated by (1) coexistence of iodide and iodate, (2) coexistence of iodide and organo-iodine, and (3)

enriched iodate. Studies on iodine speciation in groundwater have demonstrated that pH, salinity, natural organic matter (NOM) and microorganisms are involved in regulating iodine biogeochemical processes. It has been proposed that iodide is the major species in saline groundwater due to the presence of diatoms which reportedly reduce iodate to iodide.[17−19]

The Hanford Site in Washington U.S., a former plutonium production site, is the most contaminated nuclear site in the United States. High-level nuclear waste is stored underground in 177 tanks, 67 of which were single-shell, carbon-steel tanks that have leaked into the underlying vadose zone sediments and surface aquifer water.[20,21] Radioactive liquid discharges from former disposal cribs (unlined surface pits) in the 200 West Areas of Hanford Site (Figure 1) contributed a majority of the ^{129}I groundwater contamination in this area, forming three ^{129}I plumes covering an area >50 km². Presently, no treatment technology exists for these ^{129}I plumes to achieve the federal DWS (Drinking Water Standard, <1pCi/L). The interim
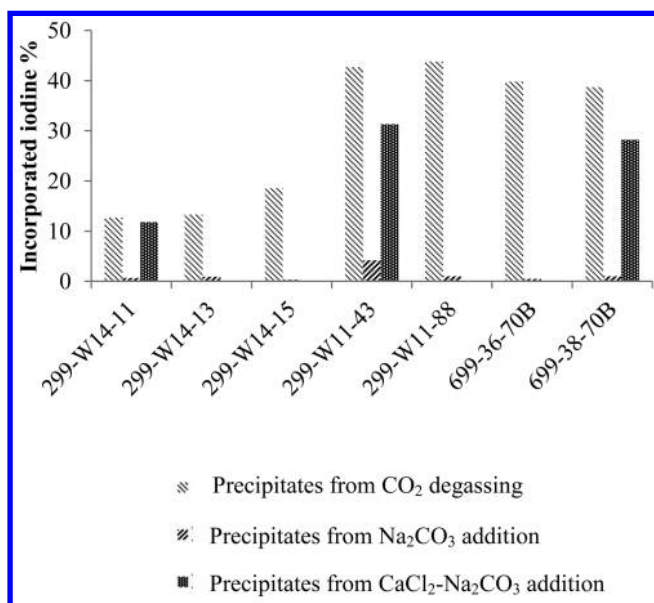
Figure 1. Iodine precipitation in Hanford Site groundwater by the three processes: CO_2-degassing, addition of Na_2CO_3 and addition of 4 mL $CaCl_2$ and 0.4 mL Na_2CO_3 (precipitation of $CaCl_2-Na_2CO_3$ addition was only performed for three wells 299-W14-11, 299-W14-43, and 699-38-70B).

record of decision is to use hydraulic containment. Very few studies have been carried out at Hanford Site to understand radioiodine biogeochemistry and iodine speciation. Iodide was assumed to be the main species present based on considerations of thermodynamic stability of iodine in natural waters.[22]

The 200 West Area within the Hanford Site represents a typical subsurface environment of arid regions where subsurface sediments contain relatively young, largely unweathered minerals and the aqueous chemistry is dominated by high concentrations of carbonate, hydroxide, and calcium ions in equilibrium with calcite. These geochemical characteristics distinguish the Hanford Site from other subsurface systems presently being studied in depth for radioiodine geochemistry, such as the Savannah River Site (SRS). The objectives of this study was to (1) determine the speciation of ^{129}I and ^{127}I in Hanford Site groundwater and (2) understand how specific geochemical conditions at Hanford Site (e.g., high pH, low DOC concentration, high carbonate or high ionic strength) control iodine speciation, fate and transport. During the study, it became apparent that calcite had precipitated from the groundwater samples recovered from the deep (>70m) subsurface. This discovery prompted a third research objective to determine whether this precipitation influenced otherwise-dissolved radioiodine, ^{129}I, and stable iodine, ^{127}I.

■ MATERIALS AND METHODS

Groundwater Sampling and Characterization. Groundwater from boreholes, 299-W14-11, 299-W14-13, 299-W14-15, 299-W11-43, 299-W11-88, 699-36-70B, and 699-38-70B in the ^{129}I plumes of the Hanford Site 200 West Area (Supporting Information (SI) Figure S1) were collected and provided by the Pacific Northwest National Laboratory (PNNL). The likely source of ^{129}I for the first five groundwater samples is from the crib T-26 characterized by ferrocyanide sludge from in-plant scavenging of T-Plant 1C waste (without coating waste). ^{129}I in

wells 699-36-70B and 699-38-70B probably originated from cribs U1, U2, and S-9 which received waste from a high temperature, nitric acid process, and as such is an oxidizing environment.

Groundwater was stored frozen and analyzed within two months. Groundwater samples were filtered through 0.22 μm membrane (Millipore, HTTP) and filtrates were collected for iodine speciation (iodide, iodate and organo-iodine) analysis as described below. In addition, DOC, pH, Ca, Si, and suspended particle concentrations in groundwater were determined. Total carbon, organic carbon, Ca, Si, and total iodine in the suspended particles were measured.

Determination of Iodine Speciation. Iodine speciation was determined according to procedures reported in Zhang et al. (2010).[5] Briefly, iodide concentrations were quantified using gas chromatography-mass spectrometry (GC-MS) after derivatization to 4-iodo-N,N-dimethylaniline. Iodate concentrations were quantified by measuring the difference of iodide concentrations in the solution before and after reduction by $Na_2S_2O_5$. Total iodine, including inorganic and organic iodine, was measured after conversion to iodate by combustion at 900 °C, followed by reduction to iodide as described above. Organo-iodine then was calculated as the difference between the total iodine and total inorganic iodine (iodide and iodate).

Precipitating Calcite in the Laboratory. By the time the groundwater samples were analyzed, it was observed there were white uniform precipitates that had formed in suspension. Additional analyses were conducted to characterize and understand the formation mechanism of the precipitates and evaluate whether their presence influenced the dissolved iodine speciation distribution and concentration. To this end, two laboratory methods of synthesizing calcite crystals were applied to compare their capacity of immobilizing iodine (SI Figure S2). The intent of these experiments was to create calcite precipitates under varying conditions, but not necessarily to replicate varying groundwater pressure and CO_2 degassing conditions.

Precipitating Calcite by Sodium Carbonate Addition to Filtered Groundwater. Sodium carbonate (70 mL, 27g/L, pH 11) was added to 350 mL of filtered groundwater to facilitate the precipitation of Ca^{2+} in groundwater. Precipitates were formed gradually and suspended in the aqueous phase. After stirring the solution overnight, the precipitates were filtered through 0.22 μm filters (Millipore, HTTP). The filtrates were collected for analysis of iodine speciation (^{127}I and ^{129}I), Ca, and pH. The precipitates were analyzed for Ca, Si, total carbon, organic carbon, and total iodine analyses.

Precipitating Calcite by the Addition of Calcium Chloride Followed by Sodium Carbonate. In order to maintain groundwater ~pH 8 during laboratory calcite formation, 4 mL 0.1 M $CaCl_2$ was added to 80 mL groundwater, and then Na_2CO_3 (0.4 mL, 1M) was gradually added in increments of 10 μL every 10 min for 2 h and then 10 μL every 4 min thereafter. The pH in the system was closely monitored. pH of the system increased to 9.2 during the initial 50 μL Na_2CO_3 addition, but decreased to 8.2−8.3 as precipitates formed. After addition of 0.4 mL of the 1 M Na_2CO_3, the solution was stirred overnight at room temperature. Groundwater from three wells (299-W14-11, 299-W11-43, 699-38-70B) representing different iodate levels was used for this experiment. In addition, groundwater from 299-W11-43 was further used to test if incorporated iodate would proportionally increase with increasing production of calcite

Table 1. Chemistry and ^{127}I Speciation of Hanford Site Groundwater[a]

well	pH	TOC μM	Ca mg/L	Si mg/L	iodide μg/L	iodate μg/L	OI μg/L	TI μg/L	iodide %	iodate %	OI %
299-W14-11	7.7	50.2	59.4	7.5	0.35	59.50	15.18	75.03	0.5	79.3	20.2
299-W14-13	7.7	63.0	81.9	7.4	0.33	42.72	17.01	60.05	0.6	71.1	28.3
299-W14-15	7.9	25.5	35.4	5.6	0.43	32.63	5.66	38.72	1.1	84.3	14.6
299-W11-43	7.6	37.2	78.8	7.0	0.36	6.66	2.76	9.78	3.7	68.1	28.3
299-W11-88	7.8	15.6	22.1	15.0	0.17	7.08	2.08	9.33	1.8	75.9	22.3
699-36-70B	7.8	35.3	19.4	10.7	0.23	5.87	2.28	8.38	2.8	70.0	27.2
699-38-70B	7.8	21.5	29. 7	8.9	1.38	4.18	3.68	9.24	15.0	45.2	39.8
average	7.8	35.5	49.5	8.9	0.46	22.66	6.95	30.08	3.6	70.6	25.8

^{127}I speciation of Hanford Site groundwater after CaCO$_3$ precipitation by Na$_2$CO$_3$								
well	pH	Ca mg/L	iodide μg/L	iodate μg/L	OI μg/L	TI μg/L	iodide %	iodate %	OI %
299-W14-11	10.7	0.05	0.94	42.90	32.34	76.17	1.2	56.3	42.5
299-W14-13	10.7	1.21	1.05	30.39	24.57	56.01	1.9	54.3	43.9
299-W14-15	10.7	0.96	0.78	27.60	7.99	36.37	2.1	75.9	22.0
299-W11-43	10.6	0.95	0.56	4.03	4.15	8.75	6.4	46.1	47.5
299-W11-88	10.6	0.52	0.06	5.71	2.52	8.29	0.7	68.9	30.4
699-36-70B	10.6	0.76	0.08	5.00	3.36	8.44	0.9	59.3	39.8
699-38-70B	10.7	0.93	0.57	4.26	3.31	8.14	7.0	52.3	40.7
average	10.7	0.77	0.58	17.13	11.18	28.88	2. 9	59.0	38.1

[a]OI represents organo-iodine, TI is total iodine.

by using different combinations and amounts of CaCl$_2$ and Na$_2$CO$_3$ (i.e., 2 mL CaCl$_2$/ 0.2 mLNa$_2$CO$_3$, 4 mL CaCl$_2$/ 0.4 mLNa$_2$CO$_3$, 6 mL CaCl$_2$/ 0.6 mL Na$_2$CO$_3$). The precipitated calcite and filtered groundwater were subjected to the analyses as described in section above.

Determination of Total Carbon and Organic Carbon in Particles. Total carbon in particles was measured by a Perkin-Elmer CHNS 2400 analyzer after air drying at 50 °C for 24 h. Acetanilide (71.09% C, 6.71% H, and 10.36% N) was used as an analytical standard. To measure organic carbon, 2 mg of particles were acidified by adding 200 μL of 1 M HCl and then dried at 50 °C for 24 h. This process was repeated once to effectively remove inorganic carbon and acid residue. Carbon remaining in the acidified particles (measured with the CHNS 2400 analyzer) was considered as organic carbon.

Determination of Calcium in Groundwater Samples and Particles. Calcium in groundwater was determined by inductively coupled plasma mass spectroscopy (ICP-MS, Thermo Scientific Xseries 2, Waltham, MA). Measurements were performed using the internal standard scandium and a five-level calibration (0, 25, 50, 75, 100 μg/L). Calcium in particles was analyzed after digestion in 8 M nitric acid at 90 °C overnight.

Determination of Si in Groundwater Samples and Particles. Silicate in groundwater was determined according to the procedure of Strickland and Parsons (1968)[23] after a 5× dilution. Particles and reference material NIST SRM 2709 (Si: 29.7%) were digested in 25% tetramethylammoniumhydroxide (TMAH) as described by Hauptkorn et al.[24] Briefly, 2 mg of precipitates were added to Teflon tubes containing 2 mL 25% TMAH and 2.5 mL Milli-Q dH$_2$O. These mixtures were pretreated for 30 min in an ultrasonic bath and then digested on a heating block at 90 °C overnight. The digestion solutions were then centrifuged at 3220g for 10 min. The supernatants were diluted 10× and analyzed as described above for groundwater silicate.

■ RESULTS

Geochemistry and Iodine Speciation of Hanford Site Groundwater. The primary geochemistry of Hanford Site groundwater is shown in Table 1. The groundwater is slightly basic with an average pH of 7.8. Dissolved organic carbon (DOC) ranged from 16 to 63 μM with an average of 35 μM. These DOC concentrations are similar to those recently reported in the humid region of the SRS in Aiken, SC: 10−60 μM.[6] Groundwater from the two wells, 299-W14-11 and 299-W14-13, closest to the disposal source had the highest DOC values and relatively high calcium concentrations. Si, an abundant trace element in groundwater, ranged in concentration from 6−15 mg/L.

For stable iodine (Table 1), iodate was the dominant species in all the groundwater samples, accounting for 45−84% of total iodine. Organo-iodine ranked second in abundance, comprising 15−40% of the total iodine. Iodide was generally the least abundant in the groundwater, accounting for <4% of the total iodine, except for well 699-38-70B, where iodide accounted for 15%. On average, iodate accounted for 70.6%, organo-iodine accounted for 25.8%, and iodide accounted for 3.6% of the total iodine (Table 1, SI Figure S3a). Even though groundwater from the two wells that were enriched in DOC, 299-W14-11 and 299-W14-13, exhibited the highest organo-iodine concentrations, the relative percentage of organo-iodine was not elevated compared to groundwater from other wells.

For radioactive ^{129}I (Table 2), only iodate could be detected. Iodates concentration decreased with distance from the source, from 42.5 pCi/L to 4 pCi/L. Organo-iodine and iodide were below the detection limit of 0.2 nM ^{129}I. The atomic ratio of ^{129}IO$_3$/^{127}IO$_3$ was calculated to range from 0.003 to 0.008, with an average of 0.004, which is 10 times lower than those for SRS.[5]

Characterization of Suspended Particles Formed during Groundwater Sampling (CO$_2$ Degassing). The water table within the Hanford Site's 200 West Area is more than 76 m below the grounds surface. When groundwater is pumped to the surface, the dramatic decrease in barometric pressure can result in degassing of CO$_2$ and, in turn,

C

Table 2. ^{129}I Speciation in Hanford Site Groundwater^a

well	iodide μg/L	iodate μg/L	iodate pCi/L	OI μg/L	$^{129}IO_3/^{127}IO_3^-$
299-W14-11	<DL	0.22	42.5	<DL	0.004
299-W14-13	<DL	0.21	40.6	<DL	0.005
299-W14-15	<DL	0.13	25.9	<DL	0.004
299-W11-43	<DL	0.02	3.6	<DL	0.003
299-W11-88	<DL	0.02	4.1	<DL	0.003
699−36−70B	<DL	0.05	9.3	<DL	0.008
699−38−70B	<DL	0.02	3.0	<DL	0.004

iodine-129 speciation in HANFORD SITE groundwater after $CaCO_3$ precipitation by Na_2CO_3					
well	iodide μg/L	iodate μg/L	iodate pCi/L	OI μg/L	$^{129}IO_3/^{127}IO_3^-$
299-W14-11	<DL	0.10	19.1	<DL	0.002
299-W14-13	<DL	0.11	21.6	<DL	0.004
299-W14-15	<DL	<DL	<DL	<DL	
299-W11-43	<DL	0.02	3.4	<DL	0.004
299-W11-88	<DL	0.01	2.2	<DL	0.002
699−36−70B	<DL	0.02	4.1	<DL	0.004
699−38−70B	<DL	<DL	<DL	<DL	

^{a}DL, detection limits: 0.08 nM or 2 pCi/L for $^{129}I^-$ and $^{129}IO_3^-$; 0.2 nM or 5 pCi/L for OI-129.

precipitation of $CaCO_3$.[25] Indeed, characterization of Hanford Site groundwater revealed that high concentrations of precipitates (86−133 mg/L) had formed (Table 3). Calcium and silicon comprised, on average, 21.5% and 11.3% of the particulate matter, suggesting that 54% of the suspended particles was composed of $CaCO_3$ and 24% as SiO_2. Low organic carbon (0.12%) and total carbon (7.5%) measurements

indicated that organic carbon was a minor component of the suspended particles.

The concentration of total stable ^{127}I in the suspended particles from the seven groundwater samples varied (Table 3). The lowest concentration of particulate total iodine was measured in groundwater from well 699-38-70B (48.6 μg/g), whereas groundwater from well 299-W14-11 had the highest concentration of particulate total iodine (96.7 μg/g). The average ratio $^{129}I/^{127}I$ in the suspended particles was 0.002.

The particulate iodine percentages shown in Table 3 were defined as iodine in particles versus that in the bulk groundwater (particulate and dissolved) and is expressed as

%, particulate iodine

$$= [\text{particle conc.}][\text{particulate I conc.}]$$
$$/([\text{particle conc.}][\text{particulate I conc.}]$$
$$+ [\text{filtrate I conc.}]) \times 100\% \quad (1)$$

Thus, particulate iodine (%) was used as an indication of the incorporation capacity of iodine through the precipitation process. For both stable and radioactive iodine, groundwater from wells adjacent to the ^{129}I source demonstrated lower incorporation rates, less than 20% iodine was incorporated into the particles. Groundwater from wells 299-W11-43 and 299-W11-88, which are further away from the ^{129}I source, had highest incorporation rates, with up to 40% iodine.

Calcite Precipitation through the Addition of Na_2CO_3. Addition of Na_2CO_3 successfully precipitated Ca ions resulting in reduced concentrations of Ca (<1.3 mg/L) remaining in the aqueous phase, and increased groundwater pH values from 7.8 to 10.7 (Table 1). Upon Na_2CO_3-induced precipitation, iodate concentrations in the aqueous phase decreased by 15−40% for each of the groundwater samples, except groundwater from well 699-38-70B which increased 1.9%. Additionally, the percentage of organo-iodine with respect to the total iodine increased by 10−113%. An average iodine speciation calculation (Table 1 and SI Figure S3b) indicated the same trends. t-Test analysis demonstrated that aqueous phase iodate ($p = 0.03$) and organo-iodine ($p = 0.005$) concentrations exhibited significant changes upon Na_2CO_3-induced precipitation, whereas iodide concentrations were unaffected ($p > 0.05$). For radioiodine only

Table 3. Chemistry of Suspended Particles Formed by CO_2 Degassing

well	particle concentration mg/L	total carbon %	organic carbon %	Ca %	Si %	TI-127 μg/g	TI-129 μg/g	$^{129}TI/^{127}TI$	I/Ca μmol/mol	Particulate ^{127}I %^{a}	Particulate ^{129}I %^{a}
299-W14-11	113.0	7.62	0.11	22.6	11.7	96.67	0.14	0.001	134.7	12.7	6.8
299-W14-13	114.3	6.69	0.14	22.9	9.4	80.68	0.20	0.003	111.0	13.3	10.0
299-W14-15	99.5	6.5	0.13	19.9	14.0	88.84	0.18	0.002	140.6	18.6	11.8
299-W11-43	133.5	7.99	0.09	26.7	9.7	54.64	0.08	0.002	64.5	42.7	37.5
299-W11-88	85.7	8.56	0.15	17.1	-	84.97	0.17	0.002	156.5	43.8	41.2
699−36−70B	87.1	7.44	0.09	17.4	13.8	63.57	0.18	0.003	115.1	39.8	24.9
699−38−70B	120.2	7.81	0.11	24.0	9.0	48.59	0.07	0.001	63.8	38.7	35.4
average	107.6	7.5	0.12	21.5	11.3	74.0	0.15	0.002	108.4	29.9	23.9

^{a}Particulate iodine percentage is defined as the percentage of iodine in particles vs that of bulk groundwater (particulate and dissolved), expressed as: [particle conc.][particulate I conc.]/([particle conc.][particulate I conc.] + [filtrate I conc.]) × 100.

Table 4. Chemistry of Suspended Particles Formed by Addition of Na_2CO_3

well	particle concentration mg/L	Ca %	total carbon %	organic carbon %	TI-127 μg/g	I/Ca μ mol/mol	particulate [127]I %
299-W14-11	128.0	39.8	12.0	0.9	2.80	2.3	0.7
299-W14-13	136.9	36.2	12.1	1.0	2.52	2.2	0.9
299-W14-15	62.3	37.3	12.8	2.1	1.55	1.3	0.3
299-W11-43	149.1	39.8	12.5	2.1	1.64	1.3	2.7
299-W11−88	44.0		12.3	2.3	1.92		1.0
699−36−70B	27.4		20.4		1.67		0.5
699−38−70B	80.0	31.9	17.3	7.0	0.99	1.0	1.0

Table 5. [127]I Speciation of Hanford Site Groundwater and Chemistry of Suspended Particles upon $CaCO_3$ Precipitation by $CaCl_2$ and Na_2CO_3,[a]

	well	iodide μg/L	iodate μg/L	OI μg/L	TI μg/L	iodide %	iodate %	OI %
groundwater	299-W14-11	1.07	51.04	17.54	69.65	1.5	73.3	25.2
	299-W11-43	0.24	4.15	3.17	7.56	3.2	54.8	41.9
	699−38−70B	0.33	3.11	4.26	7.70	4.3	40.4	55.3
	average	0.55	19.43	8.32	28.30	3.0	56.2	40.8
	well	precipitate mg	Ca %	total carbon %	organic carbon %	TI-127 μg/g	[127]I/Ca μ mol/mol	particulate [127]I %
suspended particles	299-W14-11	21.0	36.8	12.0	0.9	28.7	24.5	11.8
	299-W11-43	22.2	32.4	12.5	2.1	12.4	12.0	31.3
	699−38−70B	21.7	40.2	17.3	7.0	9.1	7.1	28.2

[a]Precipitation using this method was only performed on groundwater from wells 299-W14-11, 299-W14-43, and 699-38-70B. They represent the range of iodine concentration of Hanford Site groundwater.

[129]IO_3^- was detected in the Na_2CO_3-precipitated groundwater. The ratio of [129]IO_3/[127]IO_3 was in the range of 0.002 - 0.003, with an average value of 0.003 (Table 2).

The precipitates formed in the groundwater from wells 299-W14-11, 299-W14-13, 299-W14-15, 299-W11-43, and 299-W11-88 were composed of ∼36−40% Ca, 12% total carbon and <2.3% organic carbon (Table 4), suggesting that the precipitates were mainly $CaCO_3$, with minimal organic matter. In contrast, precipitates from wells 699-36-70B and 699-38-70B had relatively higher organic carbon (7%), indicating that these precipitates accumulated much more organic matter during the artificial precipitation process. However, all the Na_2CO_3-induced precipitates did not incorporate iodine to the extent expected, with total iodine contents of 1−2.8 μg/g, in the same range of those in natural Hanford Site sediments (0.4−4.8 μg/g),[26] but much lower than those recovered from the original groundwater samples (CO_2 degassing-produced precipitates; Table 3, 4). As a result, using Na_2CO_3 to induce calcite precipitation removed only 0.3−2.7% of the aqueous iodine.

Calcite Precipitation through the Addition of $CaCl_2$ Followed by Na_2CO_3. Considering that elevated pH might have restricted iodine incorporation into calcite crystals, calcite precipitation was performed under near-constant pH (8.2) by the addition of $CaCl_2$ followed by gradual addition of Na_2CO_3. The yield of this calcite precipitation process was 54%, that is, 21.6 mg of calcite was collected in the systems where 4 mL $CaCl_2$ (0.1 M) and 0.4 mL Na_2CO_3 (1 M) were added.

Similar to the Na_2CO_3 calcite precipitation treatment, precipitation via $CaCl_2$ followed by Na_2CO_3 caused a decrease in the aqueous iodate concentration (14 −38%; 3 groundwater samples were tested), accompanied by an increase in the concentration of organo-iodine (Table 5 and SI Figure S3c). Significant amounts of aqueous iodine were incorporated into calcite during this process, with particulate iodine concentrations ranging from 9−28.7 μg/g, accounting for the removal of 11.8−31.3% iodine from the aqueous phase. The incorporation capacity was comparable to that observed during the formation of precipitates by CO_2 degassing (Figure 1) and varied with the location of [129]I plume. Groundwater from wells 299-W14-11 and 299-W14-13, which are very close to the cribs, demonstrated a lower incorporation capacity than other wells. Iodine incorporation increased when higher amounts of $CaCl_2$ and Na_2CO_3 were used to produce more calcite precipitates, that is, 17% aqueous iodine was incorporated when 2 mL $CaCl_2$ and 0.2 mL Na_2CO_3 were used, while 51% aqueous iodine was incorporated when 6 mL $CaCl_2$ and 0.6 mL Na_2CO_3 were used. The atomic ratio (μmol/mol) of [127]I/Ca, however, remained constant at 12.0 regardless of the amount of calcite produced.

■ DISCUSSION

Geochemistry and Iodine Speciation in Hanford Site Groundwater. In contrast to the subsurface environment at SRS, where sediments are greatly weathered and rarely contain carbonate phases and the groundwater has an extremely low ionic strength (0.5 mM) and a pH between 3.1 and 5,[2] the Hanford Site subsurface sediments contain relatively young minerals and large amounts (∼2%) of carbonate minerals, very low soil organic matter[22,26,27] and the pH is appreciably more alkaline, pH 7 to 9.5. In addition, highly alkaline and high ionic strength waste solutions have caused the dissolution and transformation of silicate minerals in Hanford Site plumes, resulting in changes in the geochemistry of groundwater, for example, high salinity and decreasing porosity and permeability.[28] These unique environmental conditions regulate iodine speciation in Hanford Site groundwater. Iodate dominated stable and radioactive iodine species in Hanford Site groundwater regardless of the distance from the contamination source, suggesting that iodate was likely the dominant species in the waste solutions introduced into the cribs and then released into the groundwater due to leakage. Furthermore, a relatively nonreducing environment might have contributed to maintaining the abundance of iodate, considering that the relatively high pH (∼7.8) could hinder the abiotic reduction of iodate. Steinberg et al. (2008)[29] demonstrated a

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Table 6. Corrected ^{127}I and ^{129}I Speciation in Hanford Site Groundwater When Taking into Account the Amount of Iodate Incorporated into the Calcite Formed upon CO_2-Degassing[a]

well	^{127}I$^-$ µg/L	^{127}IO$_3^-$ µg/L	^{129}IO$_3^-$ pCi/L	O^{127}I µg/L	T^{127}I µg/L	^{127}I$^-$ %	^{127}IO$_3^-$ %	OI %
299-W14-11	0.35	69.03	45.4	15.18	84.56	0.4	81.6	18.0
299-W14-13	0.33	50.71	44.7	17.01	68.05	0.5	74.5	25.0
299-W14-15	0.43	39.83	29.0	5.66	45.92	0.9	86.7	12.3
299-W11-43	0.36	10.84	5.0	2.76	13.96	2.6	77.6	19.8
299-W11-88	0.17	11.17	5.8	2.08	13.42	1.3	83.2	15.5
699−36−70B	0.23	9.21	11.6	2.28	11.72	2.0	78.6	19.5
699−38−70B	1.38	7.76	4.1	3.68	12.82	10.8	60.5	28.7

[a]O^{127}I represents stable organo-iodine, T^{127}I is total stable iodine.

pH-dependent iodate reduction by sphagnum peat. The rate of reaction of IO_3^- with sphagnum peat significantly decreased when pH was >8. Even though Hanford Site sediments have low soil organic matter, the DOC and organo-iodine percentages measured in Hanford Site groundwater (25.8%, Table 1 and SI Figure S3a) were comparable to values reported for SRS.[5] This may be due to the fact that humic acids are more soluble in alkaline solutions and thus can remobilize iodine from soils. Xu et al.[30] observed the remobilization of soil organo-iodine at SRS, and the released organo-iodine was categorized in the colloidal form, which is consistent with the observations in the groundwater at SRS that the colloidal fraction was composed of dissolved organo-iodine.[5]

Researchers have reported a very low sorption of iodide on Hanford Site sediments with K_d values of <0.23 mL/g; a large fraction of the iodide in these tests were reversibly sorbed.[21,24] In contrast, iodate and organo-iodine commonly are more retarded than iodide because of their relatively strong interaction with clays and organic matter.[30−32] Santschi et al. (2012)[26] have shown that the iodate K_d value was 89% greater than that of iodide in Hanford Site sediments. The abundance of iodate and organo-iodine in Hanford Site groundwater is thus consistent with the observed phenomenon that total ^{127}I and ^{129}I concentrations decreased significantly with increasing distance from the disposal cribs (Tables 1, 2, and SI Figure S1), leaving more diluted stable and radioactive iodine in the water column away from the source. Appreciable absorption and/or dilution must have taken place as the groundwater moved along the flow path. Importantly, these results indicate that the present site-wide ^{129}I K_d values derived from the iodide-dominating assumption might overestimate ^{129}I transport at Hanford Site.

Incorporation of Iodate by Calcite Formation. The mineralogy of Hanford Site groundwater is dominated by Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, $SO_4^{2−}$, and supersaturated with $CO_2(g)$ ($pCO_2(g) \sim -2.6$ to -3.1 atm) in equilibrium with calcite.[25] Because the groundwater is supersaturated with CO_2 (g), samples degassed after retrieval from the subsurface would be strongly prone to formation of calcite. This is the mechanism by which speleothems (stalactites etc.) grow within caves, as groundwater equilibrates with atmospheric conditions. Characterization of the precipitates from Hanford Site groundwater demonstrated the incorporation of stable and radioactive iodine, which were originally in the aqueous phase, into the particles, (Table 3). The concentration of total iodine in the suspended particles ranged from 48.6 to 96.7 µg/g. These values are very high compared to the iodine concentration in the Callovian−Oxfordian clay formation in the region of Bure French, which is 1−5 µg/g,[33] and total iodine in natural Hanford Site sediments (0.4−4.8 µg/g).[26] Thus, laboratory

analysis of iodine concentrations in groundwater filtrate can underestimate the true in situ iodine concentration in deep groundwater samples retrieved from the Hanford Site subsurface. Low organic carbon and high iodine concentration in these precipitates indicate that minerals are responsible for the removal of iodine from the aqueous phase rather than organic matter. Claret et al., (2010)[33] also found that iodine in the Callovian-Oxfordian clay formation exists in an inorganic form associated with carbonate minerals. Lu et al.[34] precipitated calcite in the laboratory to demonstrate that iodate, rather than iodide, is the iodine species that is incorporated into marine carbonates. Iodate was postulated to be the iodine species incorporated into carbonate by substituting for the carbonate ion in the calcite structure due to the fact that the Ca−O distance in $Ca(IO_3)_2$ is similar to that in calcite.[35] Here, we present the speciation and concentration of both ^{127}I and ^{129}I in Hanford Site groundwater—after correcting for iodate incorporation into calcite particulates formed upon the CO_2 degassing that occurs during groundwater withdrawal from the subsurface (Table 6).

Lu et al. reported that the atomic ratio of I/Ca linearly increased with iodate concentration in the solution and was appropriately 4 µmol/mol for a solution with 0.4 µmol/L iodate.[34] In the present study, high amounts of iodine, approximately 48−100 mg/kg (Table 3), were preserved in the CO_2 degassing-induced precipitates (comprised of 50% $CaCO_3$) resulting in much higher I/Ca ratios (average, 108.4 µmol/mol). In addition, there was no correlation between aqueous iodate concentration and I/Ca ratio ($r^2 = 0.2$, Figure 2). Therefore, a simple substitution of CO_3^- with IO_3^- would not adequately interpret this phenomenon, which could be complicated by the presence of other cation species and
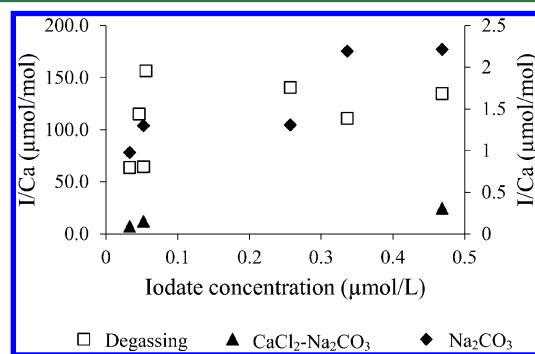
Figure 2. I/Ca ratios of CO_2 degassing-induced precipitates (primary axis), Na_2CO_3-induced precipitates (secondary axis), and precipitates induced by the addition of $CaCl_2$ and Na_2CO_3 (primary axis) as a factor of iodate concentration in HANFORD SITE groundwater.

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coprecipitation of Fe, Mg, and Si. Iodate has been observed to strongly sorb to the minerals allophane and ferric and aluminum,[36,37] and iodate sorption to hematite was shown to increase with increasing concentrations of total dissolved solids.[38]

Precipitates formed upon the addition of Na_2CO_3 to the filtered Hanford Site groundwater consisted largely of $CaCO_3$, except for the precipitates generated in groundwater from wells 699-36-70B and 699-38-70B, which were also enriched with organic matter. The decreases in aqueous iodate, but not iodide or organo-iodine, confirmed that iodate was the primary species incorporated into the precipitates (Table 1 and SI Figure S3). The precipitated calcite had iodine concentrations ranging from 1 to 3 μg/g, which is comparable to the amount of natural iodine found in the Callovian−Oxfordian clay formation (1−5 μg/g).[33] Unlike the CO_2 degassing-induced precipitates, a positive correlation was observed between iodate concentration in groundwater and I/Ca ratios in the precipitates produced by Na_2CO_3 addition ($r^2 = 0.8$, $p = 0.003$, Figure 2). However, the I/Ca ratio (~2 μmol/mol for groundwater containing 0.4 μmol/L IO_3^-) was lower than that obtained by Lu et al. who synthesized calcite in a neutral solution.[34] Thus, elevated pH values (10.7) might have accounted for the relatively low iodine incorporation into calcite when we added Na_2CO_3, to Hanford Site groundwater. The zero point of charge (ZPC) of calcite lies in the range of 8−9.5.[39] When the solution pH is higher than the ZPC, calcite becomes negatively charged and tends to repulse the similarly charged IO_3^- ion from the calcite surface and hinder the subsequent sorption and incorporation. In addition, the high content of organic carbon of precipitates from wells 699-36-70B and 699-38-70B (impacted by a different contamination source than the other wells examined here) did not appear to facilitate iodate incorporation, suggesting that organics have little influence on iodate incorporation into the precipitates.

By controlling the pH during calcite precipitation, through the addition of $CaCl_2$ followed by Na_2CO_3, iodate incorporation into the precipitates was increased significantly. Even though iodine concentrations in these precipitates were lower than those in the degassed Hanford Site groundwater precipitates (Table 3 and 5), incorporation capacity (particulate iodine %) could be compensated by precipitating more calcite. Iodine incorporation was comparable for these two processes, that is, CO_2 degassing and the addition of $CaCl_2$ followed by Na_2CO_3, when 4 mL $CaCl_2$ and 0.4 mL Na_2CO_3 were used for calcite precipitation (Figure 1). It is notable that pH-controlled calcite precipitation was carried out using filtered Hanford Site groundwater that, to some extent, had been desalted due to CO_2 degassing. Lower concentrations of dissolved ions might partly account for the lower iodine incorporation observed when Hanford Site was treated with $CaCl_2$−Na_2CO_3 than with CO_2 degassing. As a result, it is reasonable to anticipate comparable iodine concentrations in precipitates for these two processes when applied to groundwater samples with similar chemistry. In addition, for calcite precipitated at pH ~8, I/Ca ratios correlated with iodate concentrations in groundwater ($r^2 = 0.9$, Figure 2), but were considerably higher than precipitates from $NaCO_3$ addition (pH ~10.7) as discussed above, further confirming that pH plays an important role in mediating iodate sorption and incorporation. Such a retention process, where iodine incorporation into calcite precipitates was weak when pH values were elevated (pH > ZPC of calcite) and ionic concentrations (e.g., Mg^{2+}, Ca^{2+}, Na^+ SO_4^{2-}, etc.) were low, has

important implications for laboratory experiments, indicating that control of pH, $_pCO_2$ and the concentration of calcium and other major ions are required to realistically evaluate sorption/ diffusion of iodine in carbonate-dominated groundwater samples. The results presented here also reveal a possible remediation strategy for [129]I whereby pH manipulation of contaminated aquifers that promote calcite precipitation would result in iodate immobilization.

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Notes
The authors declare no competing financial interest.

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