

Freeze–Thaw Cycle-Enhanced Transformation of Iodide to Organoiodine Compounds in the Presence of Natural Organic Matter and Fe(III)

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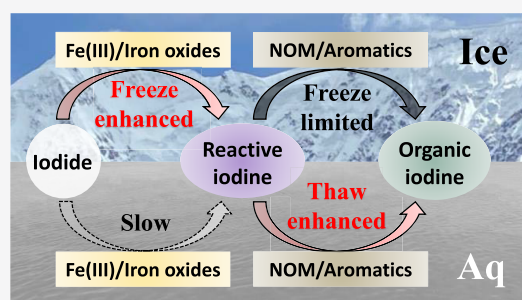
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ABSTRACT: The formation of organoiodine compounds (OICs) is of great interest in the natural iodine cycle as well as water treatment processes. Herein, we report a pathway of OIC formation that reactive iodine (RI) and OICs are produced from iodide oxidation in the presence of Fe(III) and natural organic matter (NOM) in frozen solution, whereas their production is insignificant in aqueous solution. Moreover, thawing the frozen solution induces the further production of OICs. A total of 352 OICs are detected by Fourier transform ion cyclotron resonance mass spectrometry in the freeze–thaw cycled reactions of Fe(III)/I[−]/humic acid solution, which are five times as many as OICs in aqueous reactions. Using model organic compounds instead of NOM, aromatic compounds (e.g., phenol, aniline, *o*-cresol, and guaiacol) induce higher OIC formation yields (10.4–18.6%) in the freeze–thaw Fe(III)/I[−] system than those in aqueous (1.1–2.1%) or frozen (2.7–7.6%) solutions. In the frozen solution, the formation of RI is enhanced, but its further reaction with NOM is hindered. Therefore, the freeze–thaw cycle in which RI is formed in the frozen media and the resulting RI is consumed by reaction with NOM in the subsequently thawed solution is more efficient in producing OICs than the continuous reaction in frozen solution.

KEYWORDS: iodination, reactions in ice, freeze-concentration effect, humic substances, reactive iodine formation



INTRODUCTION

Iodide (I[−]) extensively exists in river water, groundwater, and soil.¹ The concentration of iodide in typical river waters is lower than 100 μg/L² but may reach the mg/L level in some aquifers,^{3,4} hydraulic fracturing processes,⁵ and conventional oil or gas wells.⁶ Iodide can be gradually transformed to other inorganic iodine species (I₂, HOI, or IO₃[−]) during biotic and chemical oxidation or disinfection processes.^{7–10} Natural metal oxides such as manganese dioxides,^{11,12} lead oxides,^{13,14} and Fe(III)/ferrihydrite^{15–19} may play the role of abiotic oxidants of iodide in aqueous solutions. Furthermore, the presence of ubiquitous natural organic matter (NOM) in water and soil can induce the formation of organoiodine compounds (OICs) during the iodide oxidation processes.^{13,17–22} Among OICs, iodinated disinfection byproducts (I-DBPs) generated in water treatment processes are generally more cytotoxic and genotoxic to mammalian cells than their brominated and chlorinated analogues.^{2,23} Thus, the formation of OICs via iodination of NOM during the oxidative treatment of iodide-containing water or in natural processes has aroused research interest.^{8,10,24–27} In addition, volatile OICs (e.g., CH₃I, CH₂I₂, and C₂H₅I) and molecular iodine (I₂) produced during the oxidation of iodide may introduce iodine species into the atmosphere.^{28–30} Therefore, any unknown abiotic transformation mechanisms of iodide in water and soil environments may contribute to the global iodine cycle.

Most of the global freshwater is stored in ice sheets and glaciers as the frozen state.³¹ In addition, surface water in the mid- and high-latitudes is frequently frozen in winter. It has been reported that many environmental redox^{14,29,32–39} and photochemical^{40,41} reactions can be markedly accelerated in the frozen solution, compared with those in aqueous solution. It is commonly believed that the accelerated chemical reactions in ice are ascribed to the freeze-concentration effects: the solutes are highly concentrated in the unfrozen grain boundary regions of ice crystals.^{42,43} However, a variety of environmental chemical reactions in frozen water still remain unknown. Abiotic oxidation processes of iodide, which have been frequently studied in aqueous solution, were rarely investigated in ice. We have previously shown that the oxidation of iodide to triiodide by dioxygen³⁰ and iron oxides^{36,37} can be significantly accelerated in ice. It is well known that triiodide, the reactive electrophilic species,⁴⁴ can further react with NOM to generate OICs. However, the mechanism of OIC

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formation in ice (or frozen environmental media) coupled with iodide oxidation in the presence of NOM has not been recognized yet.

This work aims to understand the abiotic transformation of iodide ions and the subsequent formation of OICs in the presence of Fe(III) (or iron oxides) and NOM (or model aromatics) in aqueous, frozen, and freeze–thaw cycled solutions. Based on the experimental results, we propose a previously unrecognized mechanism for the formation of OICs which result from the iodination of NOM by the in situ formed reactive iodine (RI) in ice. This freezing-induced formation of OICs is even more enhanced when the freeze–thaw process is repeated, which has a high environmental relevance considering the cycling nature of the freeze–thaw process in the natural environments.

MATERIALS AND METHODS

Materials. Chemicals used in this work include KI, $\text{Fe}_2(\text{SO}_4)_3$, phenol, aniline, catechol, hydroquinone, resorcinol, *o*-cresol, guaiacol, formic acid, acetic acid, propionic acid, $\text{Na}_2\text{S}_2\text{O}_8$, and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonate) (ABTS), which were purchased from Sigma-Aldrich; 4-methoxyphenol, 2-iodo-phenol, and 4-iodo-phenol from TCI; and ethyl alcohol from Samchun. Suwannee River humic acid (HA) and fulvic acid (FA) were purchased from the International Humic Substances Society (<https://ihss.humicsubstances.org/>). Commercial humic acid (AHA) and humic acid sodium salt (AHA-Na) were obtained from Sigma-Aldrich. Chemicals were used without further purification, and all solutions were prepared with ultrapure water (18.2 M Ω ·cm). Raw water samples (see Supporting Information (SI) Table S1) were taken from the Geumho River (RW_{GH}) in Yeongcheon and the Hyeongsan River (RW_{HS}) in Pohang, South Korea. Commercial samples of hematite (α - Fe_2O_3 , Aldrich, Brunauer–Emmett–Teller (BET) surface area 8 m 2 /g),⁴⁵ maghemite (γ - Fe_2O_3 , Aldrich, BET surface area 36 m 2 /g),⁴⁵ goethite (α - FeOOH , Alfa Aesar, BET surface area 12 m 2 /g), and magnetite (Fe_3O_4 , Aldrich, BET surface area 8 m 2 /g) were used as iron oxides in this study.

Experimental Procedure. Five milliliters of the aqueous solution or river water with fixed concentrations of different reactants (50–100 μM Fe(III), 1–100 μM I^- , and 3.2–10 mg C/L NOM or 100 μM model organic compound) was transferred into a conical tube (15 mL). For experiments with iron oxides, 20 mL of 1 g/L suspension containing iron oxides was freshly prepared in ultrapure water and then sonicated for dispersion (~ 5 min). Five milliliter suspension containing 0.1 g/L iron oxide, 10 μM I^- , and 5 mg C/L HA was placed in the conical tube.^{36,46} The solution pH was adjusted using H_2SO_4 and NaOH before the reaction. Freezing experiments were initiated by transferring the conical tube into a precooled thermostatic bath of ethanol (-20 ± 1 °C) (reaction time $t = 0$). At different time intervals, the frozen sample was taken out and immediately thawed in another thermostatic bath (20 ± 1 °C) before the sample analysis. When needed, the thawed sample was kept in the thermostatic bath (20 ± 1 °C) to monitor the subsequent aqueous-phase reactions. The freezing or thawing process in all experiments could be completed within 15 min without controlling freezing or thawing speeds. The suspension samples with iron oxide were passed through a 0.45 μm filter (PTFE) to remove the particles.

Chemical Analysis. The solution pH was measured using an Orion Star A211 pH meter (Thermo Scientific). The total

organic carbon (TOC) was measured using a TOC-L analyzer (Shimadzu). The reactive iodine (RI: I_2 , I_3^- , and HOI) was detected as the sum of 2-iodo- and 4-iodo-phenols in the sample quenched by excessive phenol.^{21,47} The 2-iodo- and 4-iodo-phenols were analyzed by high-performance liquid chromatography (HPLC) (1260 Infinity, Agilent) equipped with an XTerra MS C18 column (5 μm , 4.6 $\times$ 250 mm, Waters) and a UV detector at 231 nm, and the mobile phase was 45%/55% (v/v) acetonitrile/ H_3PO_4 solution (0.1%) (1 mL/min). Concentrations of model aromatics were also measured by HPLC. In some experiments' testing of the iodination of phenol as a model substrate, ascorbic acid was used as an additional quencher for RI. Iodide in phenol-quenched samples was determined by HPLC equipped with an Acclaim Trinity P2 column (3 μm , 3 $\times$ 100 mm, Thermo Scientific) and a UV detector at 226 nm, and the mobile phase was 50%/50% (v/v) acetonitrile/ KH_2PO_4 solution (50 mM) (0.3 mL/min). OICs were calculated from the difference between total iodine (Tot-I) and total inorganic iodide (the sum of detected iodide and RI). Tot-I could be completely oxidized to iodate by the basic peroxydisulfate at 105 °C.⁴⁸ 100 μL $\text{Na}_2\text{S}_2\text{O}_8$ (45 g/L) and 75 μL KOH (1 M) were added into a 2.5 mL sample, and then the mixture was heated in an HS-R200 water analyzer for 1 h. When heated, 15 μL NaHSO_3 (1 M) and 50 μL ascorbic acid (1 g/L) were added into a 1 mL sample to reduce iodate to iodide completely,^{49,50} and then Tot-I was detected by HPLC in the form of iodide.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR/MS) Analysis. Fifty milliliters of water sample (added with 50 μM EDTA to complex iron species after reactions) was acidified with 1 M H_2SO_4 to around pH 2 and loaded on a 6 mL solid-phase extraction (SPE) tube (Supelclean ENVI-18, 500 mg, SUPELCO). Then 10 mL ultrapure water (0.1% formic acid) was passed through the SPE tube to remove salts, and the SPE tube was further dried by centrifugation (1500 rpm for 5 min). Finally, absorbed OICs were eluted with methanol (10 mL) from the SPE tube. The eluate was collected and dried out with argon gas and then stored in a refrigerator (-20 °C) before analysis. When analyzed, the dried samples were redissolved with 2 mL solution (50% acetonitrile/50% water (v/v)). The blank sample was obtained from 50 mL ultrapure water by following the above SPE processes.

The OICs were identified using a solarix FT-ICR/MS (Bruker Daltonics, 15 T) within the range of 150–1200 m/z with the negative ion electrospray ionization mode (ESI^-), which could better ionize NOM compounds mainly composed of phenolic and acidic carboxyl groups.^{51,52} Here, 4 M words data size, 200 acquired scans, and 0.1 s accumulation time were summed for one mass spectrum. The capillary voltage was set to 4500 V, and the injection of the sample into the ion source was performed using a syringe pump (120 $\mu\text{L}/\text{h}$). The flow rate and temperature of dry gas were 4 L/min and 210 °C, respectively. A skimmer voltage of -15.0 V, a collision voltage of -3.0 V, a transient length of 1.3981 s, and a time-of-flight window of 0.75 ms were applied for the ICR transfer.

Formula assignments were processed by the Composer (Sierra Analytics). Peaks with a signal-to-noise ratio >10 were assigned to elemental compositions of $\text{C}_{1-100}\text{H}_{1-200}\text{O}_{1-60}\text{N}_{0-4}\text{S}_{0-2}\text{I}_{1-3}$ with the mass accuracy <0.5 ppm. In addition, assigned formulas should meet the chemical criteria,⁵³ and iodine atoms were treated like H atoms. The

additional constraints of O/C (0–1.0) and H/C (0.3–2.2) were applied for assigning OIC formulas.⁵⁴

RESULTS AND DISCUSSION

Effects of the Freeze–Thaw Cycle on Iodide Oxidation by Fe(III) in the Presence of HA. Iodide could be oxidized to iodine by Fe(III)^{15,16} (or iron oxides³⁷) under ambient conditions (see eqs 1 and 2), but the formation rate of elemental iodine is very slow in aqueous solution. In contrast, the direct oxidation of iodide to hypoiodite or iodate by Fe(III) is thermochemically nonspontaneous (eqs 1, 3, and 4).⁵⁵ However, hypoiodite might be produced from the hydrolyzation of iodine (I₂) (eq 5),⁵⁶ and the detected RI is mainly present in the form of I₂ in the acid solution. The time profiles of iodine species transformation in aqueous and frozen solutions containing Fe(III), iodide, and HA are shown in Figure 1. Iodate was not detected in this study in agreement

the transformation of iodide to OICs in the Fe(III)/I[−]/HA system compared to the frozen reaction alone.

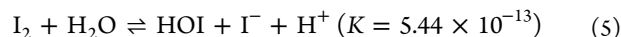
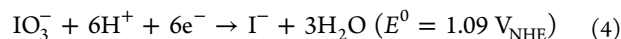
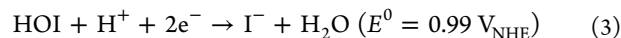
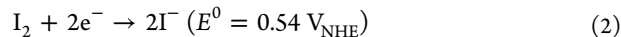
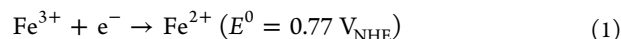


Figure 2 illustrates the freeze–thaw cycling effects on the transformation of iodine species in Fe(III)/I[−]/HA system during a long-term experiment of 120 h. The variation of iodine species exhibits a similar trend under different concentrations of reactants. The final concentrations of RI

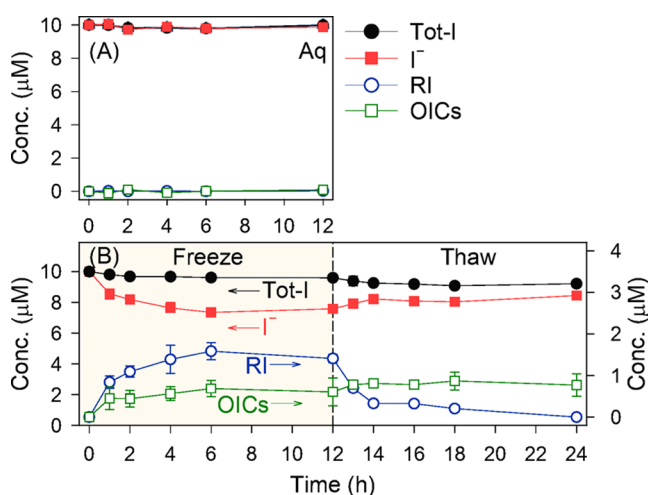


Figure 1. Time profiles of iodine species transformation in the Fe(III)/I[−]/HA system in (A) aqueous solution and (B) frozen and the subsequent thawed solution. Experimental conditions: [I[−]]₀ = 10 μM, [Fe(III)]₀ = 50 μM, [HA]₀ = 5 mg C/L, and pH_i = 3.0.

with the previous work.³⁷ Iodide remains unreacted in aqueous solution (see Figure 1A) but is slowly oxidized to RI in frozen solution with accompanying the formation of OICs (see Figure 1B). After thawing the ice, the in situ formed RI is gradually transformed to OICs and iodide in the aqueous solution via reactions with HA (iodine substitution and reductive conversion of RI, respectively).^{21,47,57–59} The control reaction between I₂ and HA in 24 h aqueous solution shows the production of both I[−] and OICs ([I[−]] being three times higher than [OICs]), which indicates that the RI reaction with HA proceeds via both iodine substitution and reduction pathways (see SI Figure S1). Note that RI is completely consumed via reaction with HA in aqueous solution but remains even after 24 h in the frozen solution. This indicates that the reaction of RI with HA is fast in aqueous solution but hindered in frozen solution. This is consistent with the observation that in situ generated RI reached the plateau region and maintained the concentration up to 12 h in the frozen solution but was gradually depleted after the frozen solution was thawed (see Figure 1B). As a result, the depletion of RI was accompanied by additional production of OICs in the thawed solution. Overall, the combined freeze–thaw process further enhances

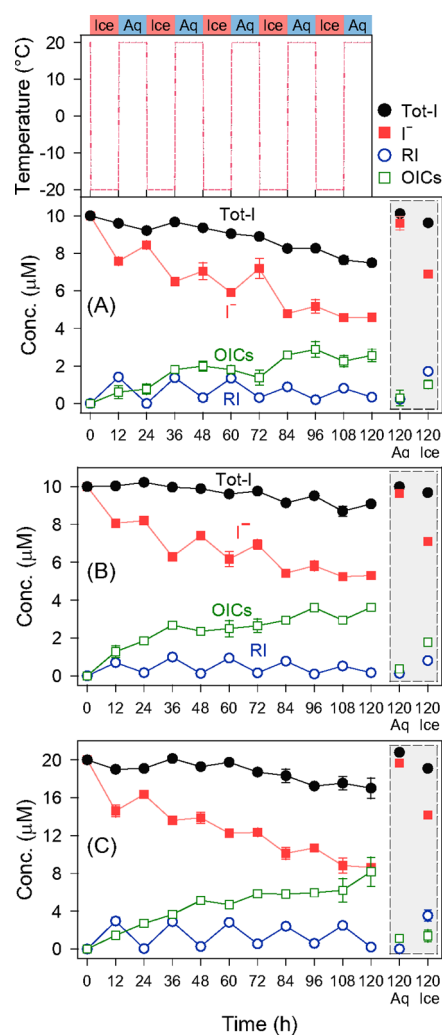


Figure 2. Time profiles of iodine species transformation in the Fe(III)/I[−]/HA system during five freeze–thaw cycles. The iodine species concentrations in the dashed line box indicate the final concentration of each species after continuous 120 h reactions in aqueous and frozen solution. Experimental conditions: (A) [I[−]]₀ = 10 μM, [Fe(III)]₀ = 50 μM, [HA]₀ = 5 mg C/L, and pH_i = 3.0; (B) [I[−]]₀ = 10 μM, [Fe(III)]₀ = 50 μM, [HA]₀ = 10 mg C/L, and pH_i = 3.0; (C) [I[−]]₀ = 20 μM, [Fe(III)]₀ = 100 μM, [HA]₀ = 10 mg C/L, and pH_i = 3.0.

and OICs in 120 h reactions in frozen solution are higher than those in aqueous solution, which reconfirms that the frozen solution enhances the oxidation of iodide and the iodination of HA. Increasing the concentration of HA or I^- does not enhance the OIC formation in ice significantly but repeating the freeze–thaw cycle effectively increases it. While only 6.9–17.8% of initial iodide was transformed to OICs in the continuous (120 h) frozen-phase reaction, about 25.7–40.9% of initial iodide was converted to OICs after five cycles of freeze–thaw processes. Repeating the freezing and thawing process allows more time for in situ generated RI to react with HA. Although the formation of RI is accelerated in the frozen solution, its further reaction with HA to generate OICs or iodide is faster in aqueous solution. Consequently, as the freeze–thaw cycle continues, [OICs] gradually increases and $[I^-]$ decreases with consuming itself for iodination of HA. The slight decrease of Tot-I with time might be ascribed to the volatile loss of OICs and I_2 when the frozen solution is thawed.^{18,19,29,30,60,61} Alternatively, specific OICs (e.g., iodoacetic acids and iodinated alkanes) are resistant to thermally activated persulfate oxidation,^{62,63} which may underestimate Tot-I. Therefore, the freeze–thaw cycled reaction for 120 h (five cycles repeated) is significantly more efficient in iodide transformation than in a continuous aqueous- or frozen-phase reaction. Takenaka et al.⁶⁴ and Kim et al.³⁴ also reported the effect of enhancement of freeze–thaw cycles on chemical reactions. We also investigated the pH dependence of iodine species transformation in Fe(III)/ I^- /HA systems (see Figure S2). The formation of RI decreases with increasing pH and is negligible above pH 4.0 in aqueous, frozen, and freeze–thaw cycled solutions, which is similar to the pH-dependent RI generation in iron oxides/ I^- systems.³⁷ This can be ascribed to the fact that higher pH drives the hydrolysis of aqueous Fe(III) ions to $FeOH^{2+}$, which is inactive toward iodide oxidation.¹⁶ The variation of OICs also shows the same pH-dependent behavior as that of RI. The low OIC formation yields (<2%) obtained in a neutral pH region are similar to the results of Xu et al.²²

Oxidation of Iodide by Fe(III) in the Presence of Different NOM. Figure 3 compares the transformation of iodine species by Fe(III)/ I^- with different kinds of NOM in aqueous, frozen, and freeze–thaw cycled solutions. Compared to aqueous solution, the frozen solution significantly enhanced the formation of RI and OICs regardless of the kind of NOM; moreover, the production of OICs was further enhanced after five freeze–thaw cycles. It is noted that the formation yields of OICs in frozen or freeze–thaw cycled solutions were much higher in the presence of natural HA or FA than commercial HA (AHA or AHA-Na). The reactivity of NOM toward electrophilic reagents such as RI can be represented by electron-donating capabilities (EDCs) of NOM.^{65,66} The ABTS method can be employed to measure the EDC of NOM as recently reported by Walpen et al.⁶⁶ In this study, a long chromogenic time was required because of the slow reaction rate between ABTS radical cations and NOM at pH 3.0. The estimated EDC value of HA ($1.75 \text{ mmol}_{e^-} (\text{g}_{\text{NOM}})^{-1}$) was very close to that of FA ($1.7 \text{ mmol}_{e^-} (\text{g}_{\text{NOM}})^{-1}$) after 23 h reaction, which was much higher than those of AHA ($0.3 \text{ mmol}_{e^-} (\text{g}_{\text{NOM}})^{-1}$) and AHA-Na ($0.82 \text{ mmol}_{e^-} (\text{g}_{\text{NOM}})^{-1}$). Aeschbacher et al.^{65,67} also concluded that natural NOM has always a higher EDC than AHA at pH 7.0. Natural NOM should be more favorable to the formation of OICs via electrophilic iodination reactions. NOM in raw water samples

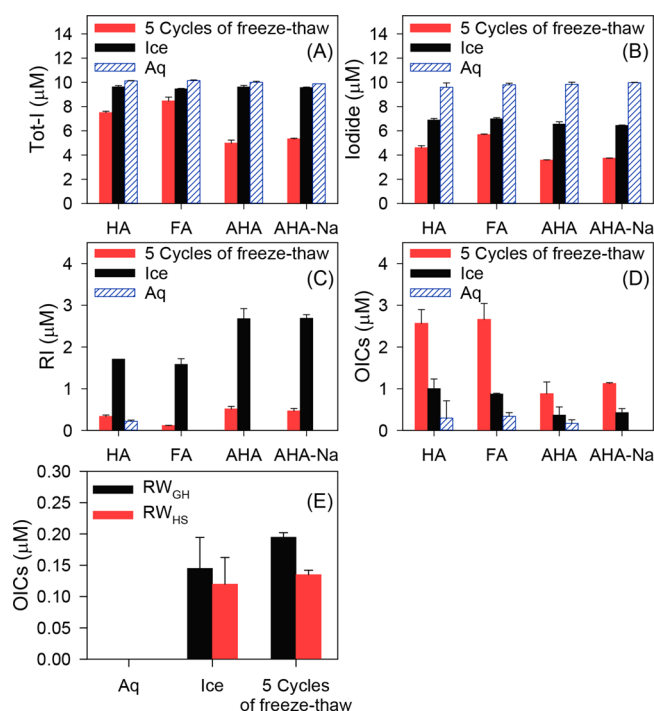


Figure 3. Concentrations of iodine species ((A) Tot-I, (B) iodide, (C) RI, and (D) OICs) in the presence of HA, FA, AHA, and AHA-Na, and (E) OICs in iodide-added river water after 120 h in aqueous, frozen, and freeze–thaw cycled Fe(III)/ I^- systems. Experimental conditions: (A–D) $[I^-]_0 = 10 \mu\text{M}$, $[Fe(III)]_0 = 50 \mu\text{M}$, $[NOM]_0 = 10 \text{ ppm}$ ($[HA] = 5 \text{ mg C L}^{-1}$, $[FA] = 4.3 \text{ mg C L}^{-1}$, $[AHA] = 4.1 \text{ mg C L}^{-1}$, and $[AHA-Na] = 3.2 \text{ mg C L}^{-1}$), $pH_i = 3.0$, and (E) add $1 \mu\text{M}$ iodide and $50 \mu\text{M}$ Fe(III), and then adjust pH to 3.0.

was also tested to evaluate the potential of OIC formation in Fe(III)/ I^- systems. Some background matrix constituents in natural water such as chloride and bromide may affect the formation potential of halogenated DBPs during disinfection.^{68,69} As shown in Figure 3E, the formation of OICs in iodide-added river water can be ignored. However, freezing or freeze–thaw cycles can induce 12–19.6% of iodide to form OICs in the RW_{GH} and RW_{HS} samples. Thus, natural NOM can also be considered as the potential source of OICs in the acidic Fe(III)/ I^- system.

Oxidation of Iodide by Iron Oxides in the Presence of HA. Previous studies have reported that Fe(III) ions are rapidly dissolved from iron oxides in frozen solutions,^{45,46} and the formation of triiodide was remarkably enhanced in the frozen solution of I^- /iron oxides.³⁷ Hereon, we used different heterogeneous iron oxides as a source of iron to replace aqueous Fe(III) ions for the oxidation of I^- in the presence of HA in ice, which may be helpful to understand the iodide transformation in natural environments. Iron oxide is one of the most abundant minerals on Earth surface and the most important source of dissolved iron in natural environments. Figure 4 illustrates the transformation of iodine species in aqueous, frozen, and freeze–thaw cycled HA/ I^- solutions with different iron oxides. The formation of OICs and RI was simultaneously enhanced in frozen solution. With the increase of BET surface areas of iron oxides, the concentration of RI increased in ice, which agrees with the previous reports that the dissolution rates of iron oxides in ice are positively correlated with the surface area.^{36,45} However, RI was not detected after five freeze–thaw cycles. This indicates that the in situ formed

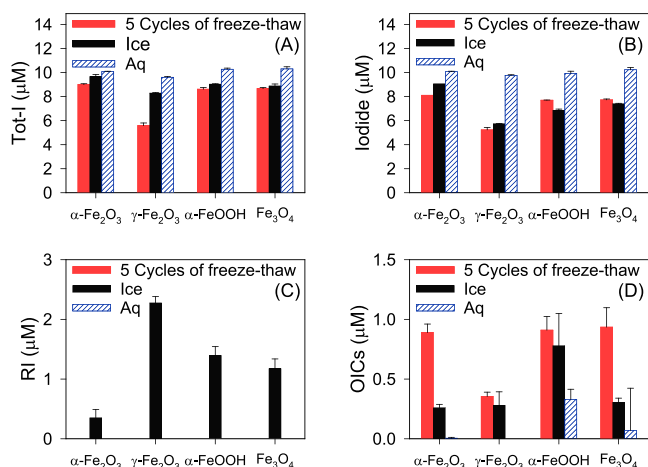


Figure 4. Concentrations of (A) Tot-I, (B) iodide, (C) RI, and (D) OICs after 120 h in aqueous, frozen, and freeze-thaw cycled solutions of HA/I[−] in the presence of different types of iron oxides. The BET surface area of iron oxide samples: α-Fe₂O₃ (8 m²/g); γ-Fe₂O₃ (36 m²/g); α-FeOOH (12 m²/g); Fe₃O₄ (8 m²/g). Experimental conditions: [I[−]]₀ = 10 μM, [Iron oxides] = 0.1 g/L, [HA]₀ = 5 mg C/L, and pH_i = 3.0.

RI was quickly consumed by HA in thawed solution, which is consistent with the observed phenomenon in Fe(III)/I[−]/HA systems. On the other hand, the production of OICs was not the highest with the iron oxide (γ-Fe₂O₃) with the largest surface area, which might be ascribed to the potential absorption of NOM on iron oxides.^{70–73} Overall, frozen or

freeze–thaw cycled processes can enhance the formation of OICs as well in (iron oxides)/I[−]/HA systems.

Characterization of OICs Formed in Fe(III)/I[−]/HA Systems. FT-ICR/MS was employed to identify newly formed OICs in aqueous and freeze–thaw cycled Fe(III)/I[−]/HA solutions. Figures S3–S6 show the ultrahigh-resolution mass spectra at the selected nominal mass (*m/z* = 351, 363, 391, and 403) of samples obtained from the aqueous and freeze–thaw cycled reactions. OIC peaks in these mass regions were clearly observed in the sample from the freeze–thaw cycled reaction whereas those were negligible in the aqueous reaction. Figures 5A,B shows the van Krevelen diagrams of all the assigned OICs formed in aqueous and freeze–thaw cycled reactions, respectively. A total of 352 OICs were detected in freeze–thaw cycled reactions, while only 69 OICs were found in aqueous reactions. One-iodine-containing compounds (OICs-I) accounted for 87.0 and 92.9% of total OICs in aqueous and freeze–thaw cycled reactions, respectively. OICs-I are commonly identified as the absolute majority of total OICs during other iodination processes of NOM.^{74,75} The formation of two-iodine-containing (OICs-2I) and three-iodine-containing compounds (OICs-3I) was relatively unfavorable to RI species.

In addition, the proportions of newly formed OICs and OICs-I with the same elements are shown in Figure 5C. Iodine-containing CHO compounds were the majority of OICs in aqueous or freeze–thaw cycled reactions, indicating that CHO compounds are more readily iodinated than CHON, CHOS, and CHONS compounds. Furthermore, the van Krevelen diagram can be divided into different regions

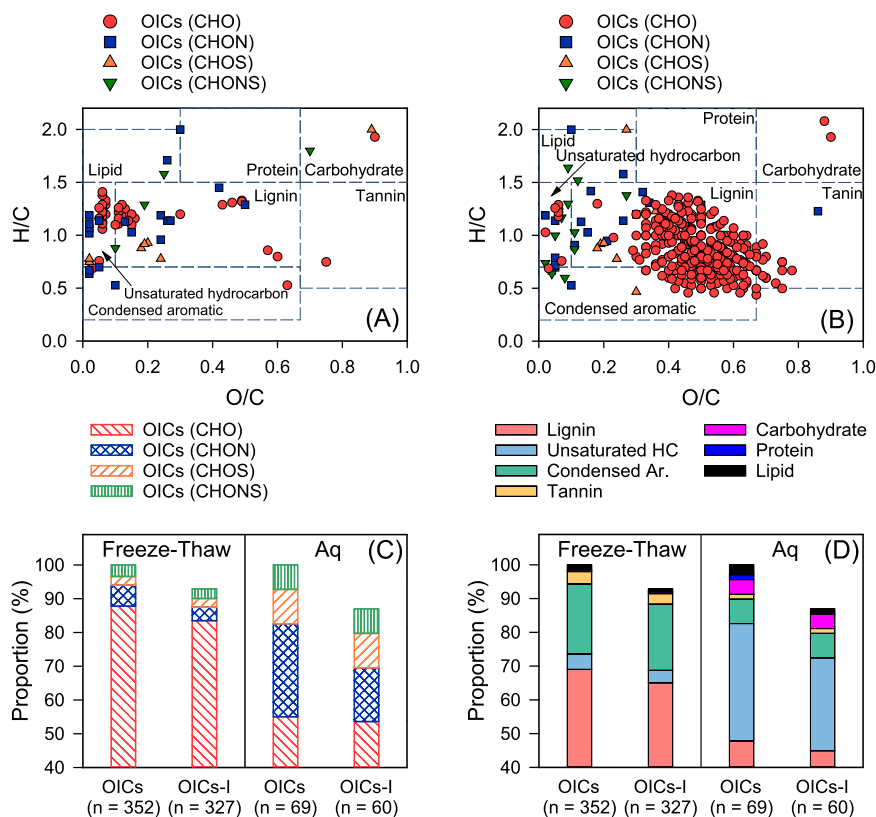


Figure 5. van Krevelen diagrams of OICs generated in (A) aqueous and (B) freeze–thaw cycled Fe(III)/I[−]/HA solutions. Stacked bar diagrams illustrate the contribution of different (C) chemical compositions and (D) classes to total OICs and OICs-I. Experimental conditions: [I[−]]₀ = 10 μM, [Fe(III)] = 50 μM, [HA]₀ = 5 mg C/L, pH_i = 3.0, total reaction time is 120 h (aqueous reaction or five freeze–thaw cycles).

Table 1. Iodination of Model Compounds in the Fe(III)/I[−] System^a

model compound	Aq (24 h)			ice (24 h)			freeze–thaw solution (12–12 h)		
	removal of compounds (%) ^b	RI (μM)	OICs (μM)	removal of compounds (%) ^b	RI (μM)	OICs (μM)	removal of compounds (%) ^b	RI (μM)	OICs (μM)
ethyl alcohol		0.0	0.0 ± 0.3		20.2 ± 5.8	1.8 ± 1.0		11.9	0.7 ± 0.5
acetic acid		0.1	0.1 ± 0.2		23.8 ± 0.8	2.1 ± 0.1		12.7 ± 0.2	1.0 ± 0.6
propionic acid		0.1	0.0 ± 0.3		20.5 ± 5.4	1.4 ± 1.8		13.1 ± 1.2	1.6 ± 0.3
phenol	1.8 ± 1.3	0.4	1.9	1.4 ± 2.0	22.8 ± 0.1	2.7	19.4 ± 1.7	2.7 ± 0.7	18.6 ± 0.8
aniline	3.4 ± 0.1	0.1	2.1 ± 1.1	3.5 ± 0.1	18.1 ± 0.5	4.2 ± 1.7	22.1 ± 6.0	1.4 ± 0.2	18.5 ± 0.2
<i>o</i> -cresol	11.5 ± 0.2	0.3 ± 0.1	1.1 ± 0.1	8.2 ± 0.5	15.8 ± 1.4	7.6 ± 0.6	28.3 ± 0.7	0.5 ± 0.3	14.8 ± 0.4
guaiacol	22.7 ± 0.6	0.0	1.7 ± 1.8	4.4 ± 0.1	14.6 ± 0.2	2.9 ± 0.6	30.0 ± 0.5	0.0	10.4 ± 1.9
resorcinol	7.5 ± 0.4	0.0	1.3 ± 0.1	30.5 ± 6.9	0.0	31.6 ± 0.3	28.3 ± 6.2	0.0	27.9 ± 0.7
catechol	17.2 ± 1.3	0.1	1.6 ± 0.8	6.1 ± 3.1	0.0	0.3 ± 0.3	18.8 ± 1.6	0.0	2.7 ± 2.0
hydroquinone	46.3 ± 0.2	0.1	0.8 ± 0.1	44.9 ± 0.1	0.2	0.0 ± 0.6	47.5 ± 1.0	0.1	1.1 ± 0.2
4-methoxyphenol	47.2 ± 0.2	0.0	0.9 ± 0.5	33.4 ± 0.3	0.7 ± 0.1	0.4 ± 0.5	53.6 ± 0.5	0.1 ± 0.2	1.5 ± 1.7

^aExperimental conditions: [I[−]]₀ = 100 μM, [Fe(III)]₀ = 100 μM, [Model compounds]₀ = 100 μM, pH_i = 3.0, and reaction time 24 h. ^bRemoval of ethyl alcohol, acetic acid, and propionic acid was not monitored.

representing different biochemical classes.^{76–78} The proportions of OICs and OICs-I with biochemical class categories are shown in Figure 5D. About 47.8 and 34.8% of OICs formed in aqueous reactions could be classified as lignin-like structures and unsaturated hydrocarbons, respectively. Similar structures of OICs (O/C < 0.4) are also observed in the enzymatic iodination of FA from I[−], and their low O/C ratios may retard their mobility in water environments.⁵¹ Furthermore, lignin-like and condensed aromatic compounds accounted for 69.0 and 20.7% of OICs in freeze–thaw cycled reactions, respectively. Lignin-like compounds with high phenolic units, which are important precursors of aquatic or terrestrial NOM, generally exhibit very high EDC values⁶⁷ that facilitate the formation of iodinated products. Thus, freeze–thaw cycled Fe(III)/I[−]/HA reactions significantly enhanced the formation of OICs, which are mainly classified as lignin-like compounds with C, H, and O elements.

Formation of OICs from Model Organic Compounds in Fe(III)/I[−] Systems. Table 1 illustrates the formation of OICs and RI in the presence of different model organic compounds after 24 h aqueous, 24 h frozen, and 12–12 h freeze–thaw reactions. The production of RI was significantly enhanced in ice and freeze–thaw solutions via the freeze-enhanced oxidation of I[−] by Fe(III) in the presence of alcohol, acetic acid, or propionic acid. However, the formation yields of OICs were negligible, indicating that RI was difficult to iodinate alcohol or carboxylic acids. The low production yield of OICs (0.4–4.1%) in the presence of carboxylic acids was also observed in MnO₂/I[−] systems.²¹ The relatively low RI production in the freeze–thaw solution might be ascribed to the volatilization of I₂. As shown in SI Figure S7, RI in the frozen Fe(III)/I[−] system without any organics decreases after melting, and this phenomenon has also been reported by Kim et al.²⁹

Generally, RI favorably reacts with the aromatic rings of NOM to form an iodine-carbon covalent bond,^{7,79} and a positive correlation between the aromaticity of NOM and OIC formation was found.^{22,80} The iodination efficiencies of model aromatics with electron-donating groups which may facilitate the iodination⁸¹ in the Fe(III)/I[−] system are shown in Table 1. The formation yields of OICs (<3%) and RI (<1%) were relatively low in aqueous solution in the presence of model aromatics, which is similar to aqueous Fe(III)/I[−]/NOM

systems. In the presence of catechol, hydroquinone, and 4-methoxyphenol, the production of OICs and RI was also relatively low in frozen and freeze–thaw reactions. As catechol, hydroquinone, and 4-methoxyphenol are the reducing agents of Fe(III),^{82,83} these phenols can be removed rapidly by Fe(III) in aqueous, ice (except catechol), or freeze–thaw solution. The low removal of catechol (6.1%) by Fe(III) in ice can be ascribed to the fact that the formation of monodentate catechol–Fe complexes under acidic conditions⁸⁴ may limit the oxidation of I[−] by free Fe(III). As a result, catechol, hydroquinone, or 4-methoxyphenol hinders the formation of RI and OICs by complexing or reducing Fe(III). On the other hand, OICs generated from the iodination of phenol, aniline, guaiacol, and *o*-cresol were much enhanced (2.7–7.6 μM) in ice, where high concentrations of RI were produced. The production of OICs was further enhanced in the freeze–thaw solution where the concentration of RI remained low. This indicates that iodide is efficiently converted to RI in ice (containing phenol, aniline, guaiacol, and *o*-cresol), and the resulting RI further reacts to generate OICs in the subsequent thawed solution. This result is in accordance with that in the presence of NOM. Among the tested aromatics, resorcinol exhibited the highest iodination rate in ice (31.6%) and the freeze–thaw solution (27.9%). However, RI was not even detected in frozen Fe(III)/I[−]/resorcinol solution, which implies that RI is highly reactive with resorcinol. The iodination rate of resorcinol by I₂ was three orders of magnitude higher than that of phenol,⁴⁴ and therefore, the in situ formed RI in ice can be rapidly transformed to OICs.

Mechanism of Freeze–Thaw Cycle-Enhanced OIC Formation in Fe(III)/I[−]/NOM Systems. Keppler et al.^{18,19} proposed a synchronous reaction scheme for the formation of volatile OICs: the abiotic oxidation of phenolics by Fe(III) and the nucleophilic substitution of oxidized phenolics by I[−]. They explained the formation of volatile OICs through this mechanism but did not consider the possible role of RI involvement. However, OIC formation in aqueous solution was insignificant in the present work because we used much lower reactant concentrations than theirs (e.g., [I[−]]: 10 mM, [Fe(III)]: 10 mM, [AHA-Na]: 100 g/L).¹⁸ Experiments with model aromatic compounds in aqueous solution indicate that the rapid removal of aromatics does not induce the high production yields of OICs (see Table 1), which is not

consistent with the Keppeler's mechanism. Therefore, the direct substitution of oxidized phenols by I^- should not be primarily responsible for the production of OICs in this case. Furthermore, Jeong et al.⁴⁵ also reported that the reduction of iron oxides by NOM under dark frozen conditions is negligible. Overall, the formation of OICs via the direct iodide substitution of oxidized NOM by Fe(III) in ice is highly unlikely.

Here, we propose that OICs are produced in a two-step process. The first step is the enhanced formation of RI via the oxidation of iodide by Fe(III) in ice (eqs 1 and 2). The freeze-concentration effects should be responsible for the acceleration mechanism of iodide oxidation as previously reported.³⁷ One possible concern is the involvement of the Fenton-like reaction in iodide oxidation. H_2O_2 can be generated during the reduction of Fe(III) by hydroquinone under acidic conditions.⁸⁵ The production of H_2O_2 may lead to subsequent generation of radical oxygen species, which should oxidize iodide. However, Table 1 shows that the production of RI and OICs in the Fe(III)/hydroquinone/ I^- is very low under all the tested conditions, which implies that the role of the Fenton-like reaction in iodide oxidation in this studied system should be insignificant. Therefore, the following step (second step) should play a critical role in OIC formation, which involves the reaction between in situ formed RI and NOM. The direct iodination of NOM by RI has been frequently reported in other aqueous abiotic systems.^{13,17,21} However, the observation that the OIC formation is low and the in situ formed RI is long-lived (up to 12 h) in the frozen solution (see Figure 1B) indicates that the reaction between RI and NOM is hindered in the frozen medium. Similarly, RI can be well preserved in ice in the presence of phenol or aniline instead of NOM, and OIC formation is significantly enhanced in the freeze-thawed solution (see Figure S8). On the other hand, it should be noted that the concentration of I_2 (main species of RI) in the ice grain boundary should be decreased because of its low solubility at low temperature⁸⁶ whereas iodide is highly concentrated in ice grain boundaries.³⁶ A high concentration of iodide should retard the iodination rate of phenols (or NOM) by I_2 according to a previously proposed kinetic model of the organic iodination reaction (iodination rate for phenols $\propto [I^-]^{-2}$).⁴⁴ Thus, freeze-concentration effects do not enhance the direct reactions between RI and NOM (or aromatics) to form OICs compared to aqueous reactions. Overall, the freeze-enhanced formation of RI in the frozen solution and the subsequent iodination of NOM by RI in the frozen or thawed solution explain the freeze-thaw cycle effects on the formation of OICs in the Fe(III)/ I^- /NOM system.

Environmental Implications. Generally, iodide is considered as an important iodine source of OICs. The oxidation of iodide-containing water by chemical oxidants (e.g., chlorine, ferrate, permanganate, and persulfate) can generate RI, which iodinated NOM to form OICs.^{62,69,87,88} Because of the lack of strong oxidants in natural environments, the abiotic transformation of iodide to RI or OICs may be not readily achieved under environmental concentrations of reactants. In this study, OICs ($\mu\text{g/L}$ level of I) can be generated in the coexistence of I^- (1–20 μM), Fe(III) or iron oxides (mg/L level), and NOM (up to 10 mg C/L) in frozen or freeze-thaw cycled solution under acidic conditions (pH < 5.0). Highly acidic waters (pH < 3.5) (e.g., acidic mine drainage and natural iron-rich drainages),^{89,90} acidic soil (pH < 4.5),⁹¹ and acidic atmospheric water⁹² are often reported. In addition, the acidic

drainages (pH 3.2–4.5) containing dissolved iron (up to 1.7 mM)⁹³ and the strong enrichment of iodine are also found in Antarctic regions,⁹⁴ where the proposed mechanism may provide a pathway to generate OICs. The spontaneous formation of OICs in the absence of disinfectants may reveal a new formation pathway of OICs in the natural environment (ice, snow, or frozen soils). In midlatitude regions, natural water and soil frequently experience freeze-thaw cycled processes. Although freezing-enhanced chemical reactions have been often studied, the subsequent reactions in the thawed solution have been largely ignored. This study reveals the freeze-thaw cycle-enhanced effects on OIC formation in Fe(III)/ I^- /NOM systems. Furthermore, the freeze-thaw cycle effects may also be extended to other freezing-induced chemical reactions, which would improve the understanding of environmental reaction mechanisms in cold environments that undergo periodic freeze-thaw cycles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c06747>.

The iodination of HA by elemental iodine in aqueous solutions and ice, effects of pH on iodine species transformation, negative ion ESI FT-ICR/MS at selected nominal mass values, formation of RI in Fe(III)/ I^- systems without organics, and formation of RI and OICs in Fe(III)/ I^- systems with phenol and aniline in ice and after a 12–12 h freeze-thaw process (PDF)

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Notes

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REFERENCES

- (1) Shetaya, W. H.; Young, S. D.; Watts, M. J.; Ander, E. L.; Bailey, E. H. Iodine dynamics in soils. *Geochim. Cosmochim. Acta* **2012**, *77*, 457–473.
- (2) Richardson, S. D.; Fasano, F.; Ellington, J. J.; Crumley, F. G.; Buettner, K. M.; Evans, J. J.; Blount, B. C.; Silva, L. K.; Waite, T. J.; Luther, G. W.; McKague, A. B.; Miltner, R. J.; Wagner, E. D.; Plewa, M. J. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environ. Sci. Technol.* **2008**, *42*, 8330–8338.
- (3) Fabryka-Martin, J.; Whittemore, D. O.; Davis, S. N.; Kubik, P. W.; Sharma, P. Geochemistry of halogens in the Milk River aquifer, Alberta, Canada. *Appl. Geochem.* **1991**, *6*, 447–464.
- (4) Fuge, R.; Johnson, C. C. The geochemistry of iodine—a review. *Environ. Geochem. Health* **1986**, *8*, 31–54.
- (5) Harkness, J. S.; Dwyer, G. S.; Warner, N. R.; Parker, K. M.; Mitch, W. A.; Vengosh, A. Iodide, bromide, and ammonium in hydraulic fracturing and oil and gas wastewaters: Environmental implications. *Environ. Sci. Technol.* **2015**, *49*, 1955–1963.
- (6) Parker, K. M.; Zeng, T.; Harkness, J.; Vengosh, A.; Mitch, W. A. Enhanced formation of disinfection byproducts in shale gas wastewater-impacted drinking water supplies. *Environ. Sci. Technol.* **2014**, *48*, 11161–11169.
- (7) Seki, M.; Oikawa, J.; Taguchi, T.; Ohnuki, T.; Muramatsu, Y.; Sakamoto, K.; Amachi, S. Laccase-catalyzed oxidation of iodide and formation of organically bound iodine in soils. *Environ. Sci. Technol.* **2013**, *47*, 390–397.
- (8) Shimamoto, Y. S.; Takahashi, Y.; Terada, Y. Formation of organic iodine supplied as iodide in a soil-water system in Chiba, Japan. *Environ. Sci. Technol.* **2011**, *45*, 2086–2092.
- (9) Amachi, S.; Muramatsu, Y.; Akiyama, Y.; Miyazaki, K.; Yoshiki, S.; Hanada, S.; Kamagata, Y.; Ban-nai, T.; Shinoyama, H.; Fujii, T. Isolation of iodide-oxidizing bacteria from iodide-rich natural gas brines and seawaters. *Microb. Ecol.* **2005**, *49*, 547–557.
- (10) Dong, H. Y.; Qiang, Z. M.; Richardson, S. D. Formation of iodinated disinfection byproducts (I-DBPs) in drinking water: Emerging concerns and current issues. *Acc. Chem. Res.* **2019**, *52*, 896–905.
- (11) Allard, S.; von Gunten, U.; Sahli, E.; Nicolau, R.; Gallard, H. Oxidation of iodide and iodine on birnessite ($\delta\text{-MnO}_2$) in the pH range 4–8. *Water Res.* **2009**, *43*, 3417–3426.
- (12) Fox, P. M.; Davis, J. A.; Luther, G. W. The kinetics of iodide oxidation by the manganese oxide mineral birnessite. *Geochim. Cosmochim. Acta* **2009**, *73*, 2850–2861.
- (13) Lin, Y. P.; Washburn, M. P.; Valentine, R. L. Reduction of lead oxide (PbO_2) by iodide and formation of iodoform in the $\text{PbO}_2/\text{I}^-/\text{NOM}$ system. *Environ. Sci. Technol.* **2008**, *42*, 2919–2924.
- (14) Menacherry, S. P. M.; Min, D. W.; Jeong, D.; Aravindakumar, C. T.; Lee, W.; Choi, W. Halide-induced dissolution of lead(IV) oxide in frozen solution. *J. Hazard. Mater.* **2020**, *384*, 121298–121305.
- (15) Fudge, A. J.; Sykes, K. W. 25. The reaction between ferric and iodide ions. Part I. Kinetics and mechanism. *J. Chem. Soc.* **1952**, 119–124.
- (16) Sykes, K. W. 26. The reaction between ferric and iodide ions. Part II. The influence of ionic association. *J. Chem. Soc.* **1952**, 124–129.
- (17) Ding, S. K.; Deng, Y.; Li, H. W.; Fang, C.; Gao, N. Y.; Chu, W. H. Coagulation of iodide-containing resorcinol solution or natural waters with ferric chloride can produce iodinated coagulation byproducts. *Environ. Sci. Technol.* **2019**, *53*, 12407–12415.
- (18) Keppler, F.; Borchers, R.; Elsner, P.; Fahimi, I.; Pracht, J.; Schöler, H. F. Formation of volatile iodinated alkanes in soil: Results from laboratory studies. *Chemosphere* **2003**, *52*, 477–483.
- (19) Keppler, F.; Eiden, R.; Niedan, V.; Pracht, J.; Schöler, H. F. Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature* **2000**, *403*, 298–301.
- (20) Allard, S.; Gallard, H.; Fontaine, C.; Croue, J. P. Formation of methyl iodide on a natural manganese oxide. *Water Res.* **2010**, *44*, 4623–4629.
- (21) Gallard, H.; Allard, S.; Nicolau, R.; von Gunten, U.; Croue, J. P. Formation of iodinated organic compounds by oxidation of iodide-containing waters with manganese dioxide. *Environ. Sci. Technol.* **2009**, *43*, 7003–7009.
- (22) Xu, C.; Miller, E. J.; Zhang, S.; Li, H. P.; Ho, Y. F.; Schwehr, K. A.; Kaplan, D. I.; Otsuka, S.; Roberts, K. A.; Brinkmeyer, R.; Yeager, C. M.; Santschi, P. H. Sequestration and remobilization of radioiodine (^{129}I) by soil organic matter and possible consequences of the remedial action at Savannah River Site. *Environ. Sci. Technol.* **2011**, *45*, 9975–9983.
- (23) Wagner, E. D.; Plewa, M. J. CHO cell cytotoxicity and genotoxicity analyses of disinfection by-products: An updated review. *J. Environ. Sci.* **2017**, *58*, 64–76.
- (24) Humphrey, O. S.; Young, S. D.; Crout, N. M. J.; Bailey, E. H.; Ander, E. L.; Watts, M. J. Short-term iodine dynamics in soil solution. *Environ. Sci. Technol.* **2020**, *54*, 1443–1450.
- (25) Hao, Z. N.; Yin, Y. G.; Cao, D.; Liu, J. F. Probing and comparing the photobromination and photoiodination of dissolved organic matter by using ultra-high-resolution mass spectrometry. *Environ. Sci. Technol.* **2017**, *51*, 5464–5472.
- (26) Choung, S.; Um, W.; Kim, M.; Kim, M. G. Uptake mechanism for iodine species to black carbon. *Environ. Sci. Technol.* **2013**, *47*, 10349–10355.
- (27) Bowley, H. E.; Young, S. D.; Ander, E. L.; Crout, N. M.; Watts, M. J.; Bailey, E. H. Iodine binding to humic acid. *Chemosphere* **2016**, *157*, 208–214.
- (28) Chameides, W. L.; Davis, D. D. Iodine: Its possible role in tropospheric photochemistry. *J. Geophys. Res.: Oceans* **1980**, *85*, 7383–7398.
- (29) Kim, K.; Ju, J.; Kim, B.; Chung, H. Y.; Vetráková, L.; Heger, D.; Saiz-Lopez, A.; Choi, W.; Kim, J. Nitrite-induced activation of iodate into molecular iodine in frozen solution. *Environ. Sci. Technol.* **2019**, *53*, 4892–4900.
- (30) Kim, K.; Yabushita, A.; Okumura, M.; Saiz-Lopez, A.; Cuevas, C. A.; Blaszcak-Boxe, C. S.; Min, D. W.; Yoon, H. I.; Choi, W. Production of molecular iodine and tri-iodide in the frozen solution of iodide: Implication for polar atmosphere. *Environ. Sci. Technol.* **2016**, *50*, 1280–1287.
- (31) Bell, R. E.; Seroussi, H. History, mass loss, structure, and dynamic behavior of the Antarctic Ice Sheet. *Science* **2020**, *367*, 1321–1325.
- (32) Kim, K.; Choi, W. Enhanced redox conversion of chromate and arsenite in ice. *Environ. Sci. Technol.* **2011**, *45*, 2202–2208.
- (33) Kim, K.; Kim, J.; Bokare, A. D.; Choi, W.; Yoon, H. I.; Kim, J. Enhanced removal of hexavalent chromium in the presence of H_2O_2 in frozen aqueous solutions. *Environ. Sci. Technol.* **2015**, *49*, 10937–10944.
- (34) Kim, K.; Chung, H. Y.; Ju, J.; Kim, J. Freezing-enhanced reduction of chromate by nitrite. *Sci. Total Environ.* **2017**, *590*–591, 107–113.
- (35) Min, D. W.; Choi, W. Accelerated reduction of bromate in frozen solution. *Environ. Sci. Technol.* **2017**, *51*, 8368–8375.
- (36) Menacherry, S. P. M.; Kim, K.; Lee, W.; Choi, C. H.; Choi, W. Ligand-specific dissolution of iron oxides in frozen solutions. *Environ. Sci. Technol.* **2018**, *52*, 13766–13773.
- (37) Kim, K.; Menacherry, S. P. M.; Kim, J.; Chung, H. Y.; Jeong, D.; Saiz-Lopez, A.; Choi, W. Simultaneous and synergic production of bioavailable iron and reactive iodine species in ice. *Environ. Sci. Technol.* **2019**, *53*, 7355–7362.
- (38) Min, D. W.; Kim, K.; Lui, K. H.; Kim, B.; Kim, S.; Cho, J.; Choi, W. Abiotic formation of humic-like substances through freezing-accelerated reaction of phenolic compounds and nitrite. *Environ. Sci. Technol.* **2019**, *53*, 7410–7418.
- (39) Min, D. W.; Kim, K.; Kim, B.; Lee, G.; Choi, W. Cr(VI) formation via oxyhalide-induced oxidative dissolution of chromium oxide/hydroxide in aqueous and frozen solution. *Environ. Sci. Technol.* **2020**, *54*, 14413–14421.
- (40) Kim, K.; Choi, W.; Hoffmann, M. R.; Yoon, H. I.; Park, B. K. Photoreductive dissolution of iron oxides trapped in ice and its

environmental implications. *Environ. Sci. Technol.* **2010**, *44*, 4142–4148.

(41) Kim, K.; Yoon, H. I.; Choi, W. Enhanced dissolution of manganese oxide in ice compared to aqueous phase under illuminated and dark conditions. *Environ. Sci. Technol.* **2012**, *46*, 13160–13166.

(42) Pincock, R. E. Reactions in frozen systems. *Acc. Chem. Res.* **1969**, *2*, 97–103.

(43) Takenaka, N.; Bandow, H. Chemical kinetics of reactions in the unfrozen solution of ice. *J. Phys. Chem. A* **2007**, *111*, 8780–8786.

(44) Warner, J. A.; Casey, W. H.; Dahlgren, R. A. Interaction kinetics of $I_2(aq)$ with substituted phenols and humic substances. *Environ. Sci. Technol.* **2000**, *34*, 3180–3185.

(45) Jeong, D.; Kim, K.; Choi, W. Accelerated dissolution of iron oxides in ice. *Atmos. Chem. Phys.* **2012**, *12*, 11125–11133.

(46) Jeong, D.; Kim, K.; Min, D. W.; Choi, W. Freezing-enhanced dissolution of iron oxides: Effects of inorganic acid anions. *Environ. Sci. Technol.* **2015**, *49*, 12816–12822.

(47) Bichsel, Y.; von Gunten, U. Formation of iodo-trihalomethanes during disinfection and oxidation of iodide-containing waters. *Environ. Sci. Technol.* **2000**, *34*, 2784–2791.

(48) Gu, F.; Marchetti, A. A.; Straume, T. Determination of iodine in milk and oyster tissue samples using combustion and peroxydisulfate oxidation. *Analyst* **1997**, *122*, 535–537.

(49) Hou, X. L.; Dahlgaard, H.; Rietz, B.; Jacobsen, U.; Nielsen, S. P.; Aarkrog, A. Determination of chemical species of iodine in seawater by radiochemical neutron activation analysis combined with ion-exchange pre-separation. *Anal. Chem.* **1999**, *71*, 2745–2750.

(50) Gong, T. T.; Zhang, X. R. Determination of iodide, iodate and organo-iodine in waters with a new total organic iodine measurement approach. *Water Res.* **2013**, *47*, 6660–6669.

(51) Xu, C.; Chen, H. M.; Sugiyama, Y.; Zhang, S. J.; Li, H. P.; Ho, Y. F.; Chuang, C. Y.; Schwehr, K. A.; Kaplan, D. I.; Yeager, C.; Roberts, K. A.; Hatcher, P. G.; Santschi, P. H. Novel molecular-level evidence of iodine binding to natural organic matter from Fourier transform ion cyclotron resonance mass spectrometry. *Sci. Total Environ.* **2013**, *449*, 244–252.

(52) Pfeifer, T.; Klaus, U.; Hoffmann, R.; Spiteller, M. Characterisation of humic substances using atmospheric pressure chemical ionisation and electrospray ionisation mass spectrometry combined with size-exclusion chromatography. *J. Chromatogr. A* **2001**, *926*, 151–159.

(53) Kujawinski, E. B.; Behn, M. D. Automated analysis of electrospray ionization fourier transform ion cyclotron resonance mass spectra of natural organic matter. *Anal. Chem.* **2006**, *78*, 4363–4373.

(54) Hawkes, J. A.; D'Andrilli, J.; Agar, J. N.; Barrow, M. P.; Berg, S. M.; Catalán, N.; Chen, H. M.; Chu, R. K.; Cole, R. B.; Dittmar, T.; Gavard, R.; Gleixner, G.; Hatcher, P. G.; He, C.; Hess, N. J.; Hutchins, R. H. S.; Ijaz, A.; Jones, H. E.; Kew, W.; Khaksari, M.; Palacio Lozano, D. C.; Lv, J. T.; Mazzoleni, L. R.; Noriega-Ortega, B. E.; Osterholz, H.; Radoman, N.; Remucal, C. K.; Schmitt, N. D.; Schum, S. K.; Shi, Q.; Simon, C.; Singer, G.; Sleighter, R. L.; Stubbins, A.; Thomas, M. J.; Tolic, N.; Zhang, S. Z.; Zito, P.; Podgorski, D. C. An international laboratory comparison of dissolved organic matter composition by high resolution mass spectrometry: Are we getting the same answer? *Limnol. Oceanogr.: Methods* **2020**, *18*, 235–258.

(55) Lide, D. R., Ed.; *CRC handbook of chemistry and physics*, 84th ed.; CRC press: Boca Raton, Florida, 2004.

(56) Burger, J. D.; Liebafsky, H. A. Thermodynamic data for aqueous iodine solutions at various temperatures. Exercise in analytical chemistry. *Anal. Chem.* **2002**, *45*, 600–602.

(57) Steinberg, S. M.; Schmetz, G. T.; Kimble, G.; Emerson, D. W.; Turner, M. F.; Rudin, M. Immobilization of fission iodine by reaction with insoluble natural organic matter. *J. Radioanal. Nucl. Chem.* **2008**, *277*, 175–183.

(58) Struyk, Z.; Sposito, G. Redox properties of standard humic acids. *Geoderma* **2001**, *102*, 329–346.

(59) Skogerboe, R. K.; Wilson, S. A. Reduction of ionic species by fulvic acid. *Anal. Chem.* **1981**, *53*, 228–232.

(60) Atkinson, H. M.; Huang, R. J.; Chance, R.; Roscoe, H. K.; Hughes, C.; Davison, B.; Schönhardt, A.; Mahajan, A. S.; Saiz-Lopez, A.; Hoffmann, T.; Liss, P. S. Iodine emissions from the sea ice of the Weddell Sea. *Atmos. Chem. Phys.* **2012**, *12*, 11229–11244.

(61) Saiz-Lopez, A.; Blaszcak-Boxe, C. S.; Carpenter, L. J. A mechanism for biologically induced iodine emissions from sea ice. *Atmos. Chem. Phys.* **2015**, *15*, 9731–9746.

(62) Wang, L.; Kong, D. Y.; Ji, Y. F.; Lu, J. H.; Yin, X. M.; Zhou, Q. S. Transformation of iodide and formation of iodinated by-products in heat activated persulfate oxidation process. *Chemosphere* **2017**, *181*, 400–408.

(63) Huang, K. C.; Zhao, Z.; Hoag, G. E.; Dahmani, A.; Block, P. A. Degradation of volatile organic compounds with thermally activated persulfate oxidation. *Chemosphere* **2005**, *61*, 551–560.

(64) Takenaka, N.; Tanaka, M.; Okitsu, K.; Bandow, H. Rise in the pH of an unfrozen solution in ice due to the presence of NaCl and promotion of decomposition of gallic acids owing to a change in the pH. *J. Phys. Chem. A* **2006**, *110*, 10628–10632.

(65) Aeschbacher, M.; Graf, C.; Schwarzenbach, R. P.; Sander, M. Antioxidant properties of humic substances. *Environ. Sci. Technol.* **2012**, *46*, 4916–4925.

(66) Walpen, N.; Houska, J.; Salhi, E.; Sander, M.; von Gunten, U. Quantification of the electron donating capacity and UV absorbance of dissolved organic matter during ozonation of secondary wastewater effluent by an assay and an automated analyzer. *Water Res.* **2020**, *185*, 116235–116246.

(67) Aeschbacher, M.; Sander, M.; Schwarzenbach, R. P. Novel electrochemical approach to assess the redox properties of humic substances. *Environ. Sci. Technol.* **2010**, *44*, 87–93.

(68) Rose, M. R.; Roberts, A. L. Iodination of dimethenamid in chloraminated water: Active iodinating agents and distinctions between chlorination, bromination, and iodination. *Environ. Sci. Technol.* **2019**, *53*, 11764–11773.

(69) Crique, J.; Allard, S.; Salhi, E.; Joll, C. A.; Heitz, A.; von Gunten, U. Iodate and iodo-trihalomethane formation during chlorination of iodide-containing waters: Role of bromide. *Environ. Sci. Technol.* **2012**, *46*, 7350–7357.

(70) Au, K. K.; Penisson, A. C.; Yang, S.; O'Melia, C. R. Natural organic matter at oxide/water interfaces: Complexation and conformation. *Geochim. Cosmochim. Acta* **1999**, *63*, 2903–2917.

(71) Weng, L. P.; van Riemsdijk, W. H.; Koopal, L. K.; Hiemstra, T. Adsorption of humic substances on goethite: Comparison between humic acids and fulvic acids. *Environ. Sci. Technol.* **2006**, *40*, 7494–7500.

(72) Tang, Z.; Zhao, X. L.; Zhao, T. H.; Wang, H.; Wang, P. F.; Wu, F. C.; Giesy, J. P. Magnetic nanoparticles interaction with humic acid: In the presence of surfactants. *Environ. Sci. Technol.* **2016**, *50*, 8640–8648.

(73) Goldt, A. E.; Polyakov, A. Y.; Sorkina, T. A.; Dubov, A. L.; Davidova, G. A.; Selezneva, I. I.; Maximov, Y. V.; Presnyakov, I. A.; Polyakova, N. Y.; Goodilin, E. A.; Perminova, I. V. Humic acid-stabilized superparamagnetic maghemite nanoparticles: Surface charge and embryotoxicity evaluation. *Nanosyst.: Phys., Chem., Math.* **2019**, *10*, 184–189.

(74) Hao, Z. N.; Yin, Y. G.; Wang, J.; Cao, D.; Liu, J. F. Formation of organobromine and organoiodine compounds by engineered TiO_2 nanoparticle-induced photohalogenation of dissolved organic matter in environmental waters. *Sci. Total Environ.* **2018**, *631–632*, 158–168.

(75) Hao, Z. N.; Wang, J.; Yin, Y. G.; Cao, D.; Liu, J. F. Abiotic formation of organoiodine compounds by manganese dioxide induced iodination of dissolved organic matter. *Environ. Pollut.* **2018**, *236*, 672–679.

(76) Kim, S.; Kramer, R. W.; Hatcher, P. G. Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram. *Anal. Chem.* **2003**, *75*, 5336–5344.

(77) Hockaday, W. C.; Purcell, J. M.; Marshall, A. G.; Baldock, J. A.; Hatcher, P. G. Electrospray and photoionization mass spectrometry

for the characterization of organic matter in natural waters: A qualitative assessment. *Limnol. Oceanogr. Methods* **2009**, *7*, 81–95.

(78) Ohno, T.; Parr, T. B.; Gruselle, M. C.; Fernandez, I. J.; Sleighter, R. L.; Hatcher, P. G. Molecular composition and biodegradability of soil organic matter: A case study comparing two new England forest types. *Environ. Sci. Technol.* **2014**, *48*, 7229–7236.

(79) Schlegel, M. L.; Reiller, P.; Mercier-Bion, F.; Barré, N.; Moulin, V. Molecular environment of iodine in naturally iodinated humic substances: Insight from X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **2006**, *70*, 5536–5551.

(80) Xu, C.; Zhang, S. J.; Ho, Y. F.; Miller, E. J.; Roberts, K. A.; Li, H. P.; Schwehr, K. A.; Ohtsuka, S.; Kaplan, D. I.; Brinkmeyer, R.; Yeager, C. M.; Santschi, P. H. Is soil natural organic matter a sink or source for mobile radioiodine (^{129}I) at the Savannah River Site? *Geochim. Cosmochim. Acta* **2011**, *75*, 5716–5735.

(81) Xu, C.; Zhong, J. Y.; Hatcher, P. G.; Zhang, S. J.; Li, H. P.; Ho, Y. F.; Schwehr, K. A.; Kaplan, D. I.; Roberts, K. A.; Brinkmeyer, R.; Yeager, C. M.; Santschi, P. H. Molecular environment of stable iodine and radioiodine (^{129}I) in natural organic matter: Evidence inferred from NMR and binding experiments at environmentally relevant concentrations. *Geochim. Cosmochim. Acta* **2012**, *97*, 166–182.

(82) Chen, F.; Ma, W. H.; He, J. J.; Zhao, J. C. Fenton degradation of malachite green catalyzed by aromatic additives. *J. Phys. Chem. A* **2002**, *106*, 9485–9490.

(83) Wildmann Ramos, P.; Gouveia de Amorim, A. F.; Dorigan Moya, H. A comparative study of spectrophotometric assays based on the formation of iron(II)-complexes to determine the reduction capacity of phenol derivatives. *Int. J. Environ. Anal. Chem.* **2021**, 1–14.

(84) Tofan-Lazar, J.; Situm, A.; Al-Abadleh, H. A. DRIFTS studies on the role of surface water in stabilizing catechol-iron(III) complexes at the gas/solid interface. *J. Phys. Chem. A* **2013**, *117*, 10368–10380.

(85) Jiang, C.; Garg, S.; Waite, T. D. Hydroquinone-mediated redox cycling of iron and concomitant oxidation of hydroquinone in oxic waters under acidic conditions: Comparison with iron-natural organic matter interactions. *Environ. Sci. Technol.* **2015**, *49*, 14076–14084.

(86) Kiovsky, T. E.; Pincock, R. E. Demonstration of a reaction in frozen aqueous solutions. *J. Chem. Educ.* **1966**, *43*, 361–362.

(87) Shin, J.; von Gunten, U.; Reckhow, D. A.; Allard, S.; Lee, Y. Reactions of ferrate(VI) with iodide and hypoiodous acid: Kinetics, pathways, and implications for the fate of iodine during water treatment. *Environ. Sci. Technol.* **2018**, *52*, 7458–7467.

(88) Zhao, X. D.; Salhi, E.; Liu, H. L.; Ma, J.; von Gunten, U. Kinetic and mechanistic aspects of the reactions of iodide and hypoiodous acid with permanganate: Oxidation and disproportionation. *Environ. Sci. Technol.* **2016**, *50*, 4358–4365.

(89) Geller, W.; Klapper, H.; Salomons, W., Eds. *Acidic Mining Lakes*, 1st ed.; Springer: Berlin, Heidelberg, 1998.

(90) Nixdorf, B.; Fyson, A.; Krumbeck, H. Review: Plant life in extremely acidic waters. *Environ. Exp. Bot.* **2001**, *46*, 203–211.

(91) Rengel, Z., Ed. *Handbook of Soil Acidity*, 1st ed.; CRC Press: New York, 2003.

(92) Fu, H.; Cwiertny, D. M.; Carmichael, G. R.; Scherer, M. M.; Grassian, V. H. Photoreductive dissolution of Fe-containing mineral dust particles in acidic media. *J. Geophys. Res.* **2010**, *115*, D11304.

(93) Dold, B.; Gonzalez-Toril, E.; Aguilera, A.; Lopez-Pamo, E.; Cisternas, M. E.; Bucchi, F.; Amils, R. Acid rock drainage and rock weathering in Antarctica: important sources for iron cycling in the Southern Ocean. *Environ. Sci. Technol.* **2013**, *47*, 6129–6136.

(94) Saiz-Lopez, A.; Plane, J. M.; Baker, A. R.; Carpenter, L. J.; von Glasow, R.; Martin, J. C.; McFiggans, G.; Saunders, R. W. Atmospheric chemistry of iodine. *Chem. Rev.* **2012**, *112*, 1773–1804.

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