





Review

The crucial and versatile roles of bacteria in global biogeochemical cycling of iodine

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Abstract

Iodine (I) is a trace element with health and environmental significance. Iodate (IO_3^-), iodide (I^-) and organic iodine (org-I) are the major species of iodine that exist in the environment. Dissimilatory IO_3^- -reducing bacteria reduce IO_3^- to I^- directly under anoxic conditions via their IO_3^- reductases that include periplasmic iodate reductase IdrABP_{1P2}, extracellular DMSO reductase DmsEFAB and metal reductase MtrCAB. IdrAB and DmsEFAB reduce IO_3^- to hypoiodous acid (HIO) and H_2O_2 . The reaction intermediate HIO is proposed to be disproportionated abiotically into I^- and IO_3^- at a ratio of 2:1. The H_2O_2 is reduced to H_2O by IdrP_{1P2} and MtrCAB as a detoxification mechanism. Additionally, dissimilatory Fe(III)- and sulfate-reducing bacteria reduce IO_3^- to I^- directly via their IO_3^- reductases and indirectly via the reduction products Fe(II) and sulfide in the presence of Fe(III) and sulfate, respectively. I^- -oxidizing bacteria oxidize I^- to molecular iodine (I_2) directly under oxic conditions via their extracellular multicopper iodide oxidases IoxAC. In addition to I_2 , a variety of org-I compounds are also produced by the I^- -oxidizing bacteria during I^- oxidation. Furthermore, ammonia-oxidizing bacteria oxidize I^- to IO_3^- directly under oxic conditions, probably via their intracellular ammonia-oxidizing enzymes. Many bacteria produce extracellular reactive oxygen species that can oxidize I^- to triiodide (I_3^-). Bacteria also accumulate I^- during which I^- is oxidized to HIO by their extracellular vanadium iodoperoxidases. The HIO is then transported into the bacterial cells. Finally, bacteria methylate I^- to org-I CH_3I , probably via their methyltransferases. Thus, bacteria play crucial and versatile roles in the global biogeochemical cycling of iodine via IO_3^- reduction, I^- oxidation and accumulation and org-I formation.

Keywords: bacteria; iodate reduction; iodide oxidation; iodide accumulation; organic iodine formation

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Introduction

As a trace element, iodine (I) plays a crucial role in human health as well as is of environmental significance. Iodine is a major component of the human thyroid hormones thyroxine (T4) and triiodothyronine (T3). Thus, iodine is an integrated part of the thyroid functions of humans and other vertebrates (Zimmermann, 2009). It has been estimated that iodine-deficient disorder (IDD) affects ~1.9 billion people worldwide, whose symptoms included thyroid enlargement (goiter) and cretinism (Santos et al., 2019). Salt iodization and the fortification of foods, beverages and seasoning with iodine could efficiently prevent and control human IDD (Santos et al., 2019; Zimmermann, 2009). Iodine supplementation in the human diet, however, could result in hyperthyroidism and hypothyroidism (Farebrother et al., 2019; Leung and Braverman, 2014; Zimmermann, 2009). Subclinical hypothyroidism was also suggested to be attributed to excess intake of iodine via drinking groundwater with high iodide (I^-) in China (Ma et al., 2022). Thus,

both deficient and excess intakes of iodine have negative impacts on human health.

Radioactive isotopes of iodine also negatively impact human health. Iodine has a stable isotope ^{127}I and a variety of radioactive isotopes. The latter was produced mainly by neutron-induced fission during the production of nuclear weapons and energy (Kaplan et al., 2014). Among the radioactive isotopes produced, ^{131}I and ^{129}I were the main radionuclides that could negatively affect human health. For example, a large quantity of ^{131}I released from the explosion of the Chernobyl nuclear power plant caused thyroid cancer among the children who lived in the Chernobyl area when the incident occurred (Robbins and Schneider, 1998). ^{131}I has a half-life of 8.02 days and high specific activity ($4.59 \times 10^3 \text{ TBq g}^{-1}$). Thus, ^{131}I was only a short-lived radioiodine (Hu and Moran, 2010; Kaplan et al., 2014; Yeager et al., 2017). Another example is the ^{129}I contamination in the Hanford Site at Washington State, USA, where subsurface ^{129}I plumes were $> 50 \text{ km}^2$ and the ^{129}I level in the groundwater was higher than the standard for ^{129}I ($< 1 \text{ pCi/L}$) listed in the US Federal Registry. The discharge of radioactive liquid during nuclear weapon production contributed to ^{129}I contamination in the groundwater at the Hanford site. Currently, there is no existing method to remediate ^{129}I levels below 1 pCi/L in the

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groundwater (Zhang et al., 2013). Compared to ^{131}I , ^{129}I has a half-life of 1.57×10^7 years and low specific activity (6.6 MBqg^{-1}) (Hu and Moran, 2010; Kaplan et al., 2014; Yeager et al., 2017). Given its very long half-life, high toxicity to humans, highly specific accumulation in the human thyroid gland, high inventory in the Hanford Site, high mobility in groundwater and the uncertainty of its biogeochemical fate and transport in the environment, ^{129}I is a primary risk driver at the Hanford Site (Kaplan et al., 2014).

The Earth's oceans contain ~70% of the iodine on the Earth's surface (Carpenter et al., 2021; Fuge and Johnson, 2015). At the interface between surface air and surface water of oceans, ozone (O_3) in the air interacts with I^- in the oceans to produce molecular iodine (I_2) and hypiodous acid (HIO) (Carpenter et al., 2013; Read et al., 2008). The produced I_2 and HIO in the oceans are then volatilized into the atmosphere. Up to 80% of atmospheric iodine is from volatilization of the I_2 and HIO produced from the air-ocean interface (Carpenter et al., 2021; Carpenter et al., 2013). This interfacial reaction between O_3 and I^- functions as a negative feedback mechanism for regulating atmospheric levels of O_3 (Carpenter et al., 2021; Prados-Roman et al., 2015). Furthermore, atmospheric iodine also contributes to ozone depletion (Fig. 1) (Koenig et al., 2021; Sherwen et al., 2017a; Sherwen et al., 2017b; Sherwen et al., 2016b; Yeager et al., 2017). Thus, atmospheric iodine impacts air quality and human health (Carpenter et al., 2021; Chance et al., 2014; Koenig et al., 2021). Given that it is the major source of aerosols (Fig. 1) (Gomez Martin et al., 2020), atmospheric iodine may also have an impact on the climate (Carpenter et al., 2021; Chance et al., 2014; Yeager et al., 2017).

Bacteria play crucial and versatile roles in the global biogeochemical cycling of iodine (Amachi, 2008; Carpenter, 2015; Luther III, 2023; Yeager et al., 2017). The Gram-negative bacteria *Denitromonas* sp. IR-12, *Pseudomonas* sp. SCT and *Shewanella oneidensis* MR-1 can use small organic acids, such as acetate and lactate, to reduce iodate (IO_3^-) to I^- directly via their IO_3^- -reducing enzymes under anoxic conditions (Amachi et al., 2007a; Guo et al., 2022b;

Reyes-Umana et al., 2022; Shin et al., 2022; Yamazaki et al., 2020). In addition to the direct reduction of IO_3^- , bacteria can also reduce IO_3^- indirectly via the reactive chemical species produced by the bacteria (Jiang et al., 2023c; Jiang et al., 2023d). For example, sulfate-reducing bacteria used lactate to reduce sulfate to sulfide biotically under anoxic conditions. The latter reduces IO_3^- to I^- abiotically (Jiang et al., 2023d). Furthermore, bacteria can also oxidize I^- to I_2 under oxic conditions (Amachi, 2008; Luther III, 2023). For example, IO_3^- was the predominant ^{129}I species in the groundwater at the Hanford Site. Four bacterial isolates from the groundwater of the Hanford Site were able to oxidize I^- to I_2 (Lee et al., 2020). Given that I_2 could be oxidized to IO_3^- abiotically (Amachi, 2008), the I^- -oxidizing activity of these bacterial isolates might contribute to the IO_3^- accumulation in the groundwater at the Hanford Site (Lee et al., 2020). Bacteria also accumulated and methylated I^- (Amachi et al., 2001; Amachi et al., 2005b).

This review focuses on recent advances in the bacterial impacts on the global geochemical cycling of iodine, especially the molecular mechanisms by which bacteria mediate the biogeochemical transformation of iodine. These include recently discovered bacterial genes and enzymes directly involved in iodine biotransformation. Readers are encouraged to read other excellent reviews related to different aspects of biological contributions to the global cycling of iodine (Amachi, 2008; Carpenter, 2015; Duborska et al., 2021; Duborska et al., 2023; Luther III, 2023; Yeager et al., 2017).

The global geochemical cycle of iodine

Geochemical cycling of iodine occurs mainly in the oceans, which contain ~70% of the iodine on the Earth's surface (Amachi, 2008; Carpenter, 2015; Carpenter et al., 2021; Fuge and Johnson, 2015; Luther III, 2023; Yeager et al., 2017). Inorganic IO_3^- and I^- are the two dominant species of iodine in the oceans, where their combined concentration is $0.45 - 0.50 \mu\text{molL}^{-1}$ (Chance et al., 2014). Organic iodine (org-I) also exists in the oceans. IO_3^- , I^- and org-I

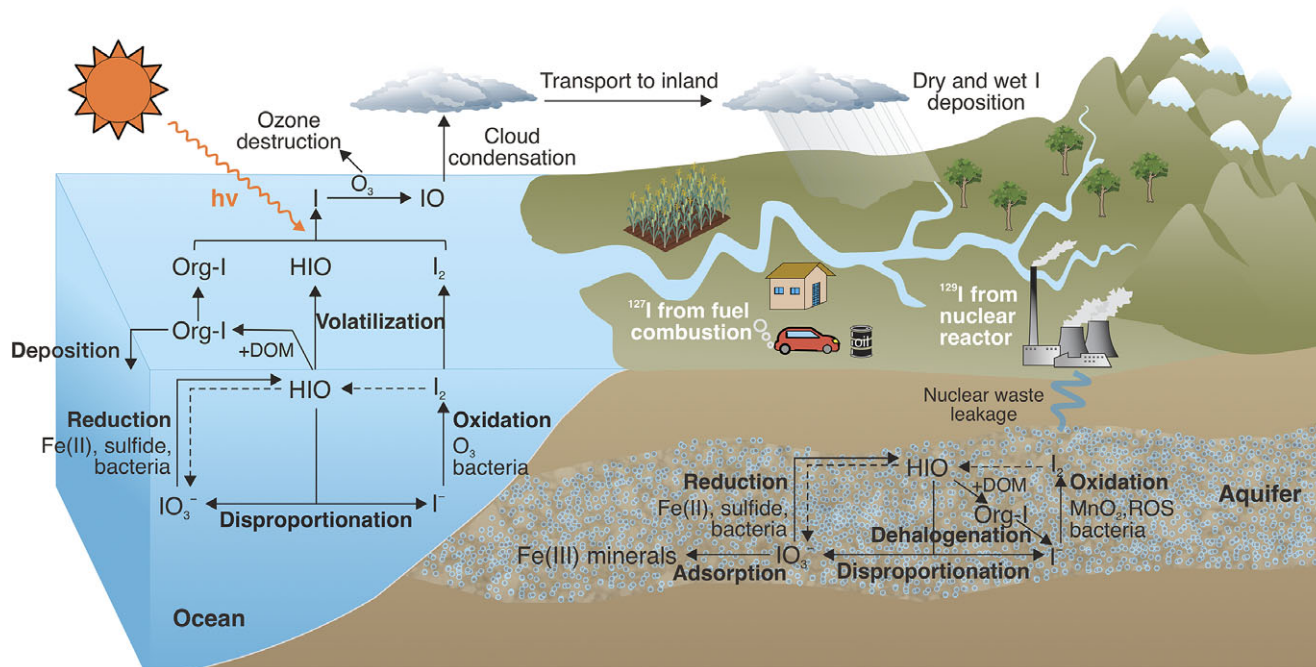


Figure 1. Bacterial roles in global biogeochemical cycling of iodine.

concentrations in the oceans vary substantially (Amachi, 2008; Carpenter, 2015; Carpenter et al., 2021; Yeager et al., 2017). In the surface layer of oceans, the concentrations of IO_3^- and I^- are similar and higher than that of org-I. In the deep oceans, the concentrations decrease in the order of $\text{IO}_3^- > \text{I}^- > \text{org-I}$ (Fig. 1) (Carpenter, 2015; Carpenter et al., 2021; Yeager et al., 2017). As mentioned previously, O_3 oxidizes I^- to I_2 and HIO abiotically at the air-ocean interface. The produced I_2 and HIO in the oceans are then volatilized into the air (Fig. 1) (Carpenter et al., 2021; Carpenter et al., 2013; Prados-Roman et al., 2015). HIO could be converted to IO_3^- and I^- abiotically (Fig. 1) (Carpenter et al., 2021). Importantly, bacteria reduced IO_3^- to I^- with HIO as a reaction intermediate under anoxic conditions (Guo et al., 2022a; Guo et al., 2022b; Reyes-Umana et al., 2022; Yamazaki et al., 2020) and oxidized I^- to I_2 in the oceans under oxic conditions, during which org-I is formed (Amachi et al., 2005c). Microorganisms in the oceans also play key roles in org-I volatilization and can accumulate iodine (Fig. 1) (Amachi et al., 2005a; Amachi et al., 2001; Amachi et al., 2004; Amachi et al., 2007b; Amachi et al., 2005b).

Once volatilized into the air, I_2 , HIO and volatile org-I are photolyzed to atom iodine (I), which reacts with O_3 to form iodine oxide radicals (IO). The latter reaction also results in O_3 decay. IO further react with nitrogen and hydrogen oxides to form iodine-containing aerosols, which contribute to cloud formation (Fig. 1) (Carpenter et al., 2021; Prados-Roman et al., 2015; Sherwen et al., 2017a; Sherwen et al., 2017b; Sherwen et al., 2016a; Sherwen et al., 2016b; Sipila et al., 2016). The iodine-containing chemicals in the clouds cycle back to the oceans and land surface via dry and wet depositions (Fig. 1) (Carpenter et al., 2021; Sherwen et al., 2016a). All of these reactions are abiotic. Thus, iodine in terrestrial environments originates mainly from oceans.

In addition to ocean-originated iodine, the human use of coal and fossil fuels also contributes to the inventory of terrestrial and atmospheric iodine (Fig. 1) (Fan et al., 2023). Iodine is a biophilic element so becomes enriched in organic matter, which is the cause of iodine in coal and petroleum. Contact with shallow coal seams or the uplift from formation waters contributes to iodine enrichment in coal and crude oil (Chen et al., 2016; Fehn et al., 1987; Wu et al., 2008; Wu et al., 2014). Org-I is the dominant species of iodine detected in terrestrial environments (Amachi et al., 2003; Biester et al., 2006; Fuge and Johnson, 1986; Gilfedder et al., 2009; Keppler et al., 2004; Sheppard and Thibault, 1992; Shetaya et al., 2012;

Yamada et al., 1999). Similar to that in oceans, terrestrial bacteria also plays a crucial role in org-I formation; and some of the org-I is volatilized into the atmosphere (Amachi et al., 2003).

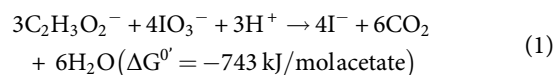
High concentrations of iodine in groundwater have been reported in Algeria, Argentina, Canada, Chile, China, Denmark and Japan, which is a major health concern to millions of people (Wang et al., 2021; Wang et al., 2018). The iodine in the groundwater originated from a variety of sources, such as Quaternary lacustrine sediments, ancient marine transgressions, salt water and soil deposition (Alvarez et al., 2015; Li et al., 2013; Muramatsu et al., 2001; Voutchkova et al., 2014; Wang et al., 2021). The iodine was released to groundwater via burial dissolution and compaction-release (Wang et al., 2021). IO_3^- , I^- and org-I all exist in groundwater and their concentrations vary considerably (Bagwell et al., 2019; Ma et al., 2022; Neeway et al., 2019; Wang et al., 2021; Zhang et al., 2013). For example, I^- is the dominant species of iodine in the deep groundwater of the North China Plain, in which org-I is a minor species and no IO_3^- was detected (Jiang et al., 2023c). However, IO_3^- is the dominant species of iodine in groundwater at the Hanford site (Zhang et al., 2013). Bacteria are directly involved in IO_3^- reduction, I^- oxidation and org-I formation in groundwater (Fig. 1) (Bagwell et al., 2019; Jiang et al., 2023c; Lee et al., 2020).

Bacterial reduction of IO_3^-

Thermodynamically, IO_3^- is much more stable than I^- in the environment (Luther III, 2023). Bacterial reduction of IO_3^- contributes to the environmental formation of I^- .

Direct reduction by IO_3^- -respiring bacteria

Isolated from marine sediment, the Gram-negative bacterium *Pseudomonas* sp. SCT was the first microorganism experimentally demonstrated to be capable of respiring on IO_3^- for anaerobic growth in which acetate served as an electron donor (Yamazaki et al., 2020):



Given that the reduced iodine species was not incorporated into any bacterial molecule, respiration of IO_3^- by *Pseudomonas* sp. SCT was also referred to as the dissimilatory reduction of IO_3^- (Fig. 2a)

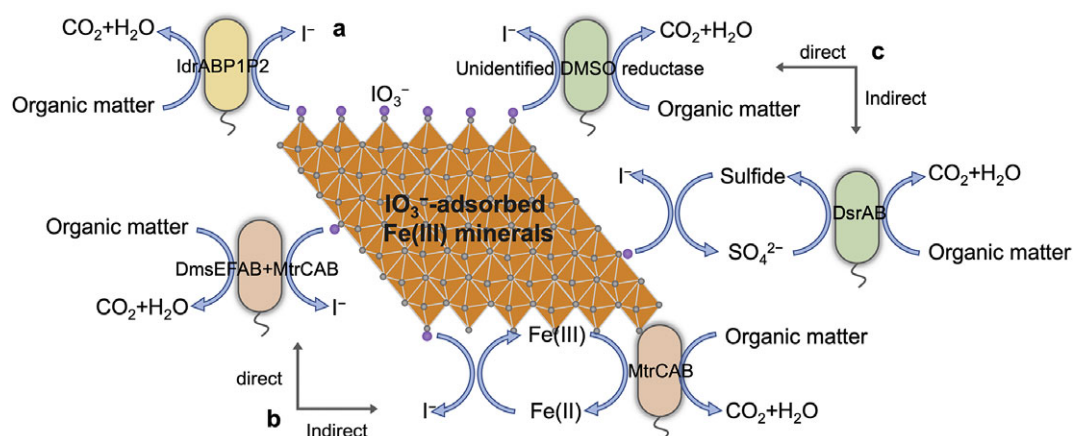


Figure 2. Bacteria-mediated direct and indirect reduction of IO_3^- : (a) IO_3^- -respiring bacteria; (b) the Fe(III)-reducing bacterium *Shewanella oneidensis* MR-1, (c) the sulfate-reducing bacterium *Desulfovibrio* sp. B304, modified with permission from Jiang et al. (2023c) ©(2023) American Chemical Society.

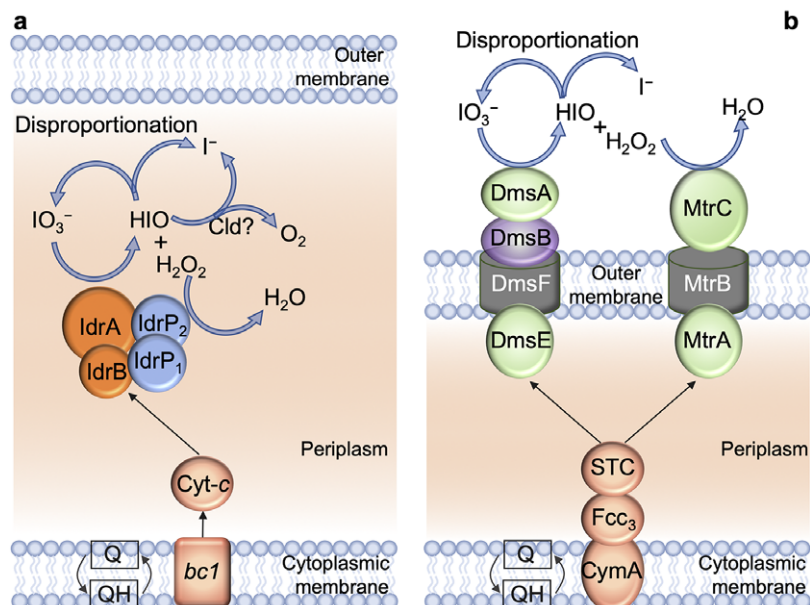


Figure 3. The molecular mechanisms for the bacterial reduction of IO_3^- : (a) periplasmic reduction by IdrAB₁P₂, modified with permission from Reyes-Umana et al. (2022) ©(2022) Oxford University Press and (b) extracellular reduction by DmsEFAB and MtrCAB, modified with permission from Guo et al. (2022b) ©(2022) Blackwell Publishing LTD.

(Amachi et al., 2007a; Yamazaki et al., 2020). Subsequently, biochemical characterization identified a periplasmic iodate reductase (Idr) in *Pseudomonas* sp. SCT, which consisted of subunits of IdrA, IdrB, IdrP₁ and IdrP₂. The genes for these subunits, *idrABP₁P₂*, were clustered together. Phylogenetic analyses revealed that IdrAB belonged to the superfamily of dimethyl sulfoxide (DMSO) reductases that required molybdenum as a cofactor, while IdrP₁P₂ were the *c*-type cytochromes (*c*-Cyt) (Yamazaki et al., 2020). Compared to that under the nitrate- or O_2 -respiring conditions, the mRNA levels of *idrA*, *idrP₁* and *idrP₂* were all elevated substantially under the IO_3^- -respiring conditions (Yamazaki et al., 2020). Further analyses detected H_2O_2 as a byproduct under the IO_3^- -respiring conditions (Yamazaki et al., 2020). Based on these results, Yamazaki et al. proposed that during IO_3^- -respiration, *Pseudomonas* sp. SCT used IdrAB to reduce IO_3^- to HIO and H_2O_2 , and IdrP₁P₂ to reduce H_2O_2 to H_2O as a detoxification mechanism (Fig. 3a). The reduction intermediate HIO was proposed to be reduced to I^- , probably by the Cld protein (Yamazaki et al., 2020).

The *idrABP₁P₂* gene cluster was also found in the genome of the IO_3^- -respiring bacterium *Denitromonas* sp. IR-12 that was isolated from an estuarine sediment. The deletion of the *idrA* gene abolished the bacterial ability to reduce IO_3^- , which provided genetic evidence for the direct involvement of IdrA in IO_3^- reduction (Reyes-Umana et al., 2022). Similar to that in *Pseudomonas*, sp. SCT, IdrAB of *Denitromonas* sp. IR-12 was proposed to reduce IO_3^- to HIO and H_2O_2 . The latter was further detoxified to H_2O by IdrP₁P₂. Given that no Cld homolog was identified in *Denitromonas* sp. IR-12, the HIO was proposed to be disproportionated abiotically into I^- and IO_3^- at a ratio of 2:1 (Fig. 3a) (Reyes-Umana et al., 2022). The *idrABP₁P₂* gene cluster existed in phylogenetically diverse groups of bacterial genomes, which was probably attributed to the horizontal gene transfer of the *idrABP₁P₂* gene cluster in different bacterial genomes (Reyes-Umana et al., 2022; Sasamura et al., 2023). The bacteria with the *idrABP₁P₂* gene cluster were predicted to be enriched in marine anoxic environments rich in nitrate and phosphate (Reyes-Umana et al., 2022).

Comparative metagenomic analyses also identified the *idrABP₁P₂* gene clusters in the groundwater of North China Plain, where iodine concentration was high; I^- constituted up to 98% of iodine detected and IO_3^- was below the detectable level. Biochemical

characterization of an identified *idrABP₁P₂* gene cluster confirmed its IO_3^- -reducing activity. Thus, the microorganisms with the *idrABP₁P₂* gene clusters contributed at least in part to the I^- formation in the groundwater of North China Plain (Jiang et al., 2023c).

Direct reduction by *S. oneidensis* MR-1

The dissimilatory Fe(III)- and DMSO-reducing bacterium *S. oneidensis* MR-1 respire on Fe(III)-containing minerals and DMSO extracellularly under anoxic conditions (Gralnick et al., 2006; Myers and Neelson, 1988; Neelson et al., 2002). Crucial to the ability of *S. oneidensis* MR-1 to reduce Fe(III)-containing minerals and DMSO extracellularly are the MtrCAB and DmsEFAB protein complexes, respectively (Gralnick et al., 2006; Shi et al., 2016; White et al., 2016). The MtrAB are the homologs of DmsEF and their function is to transfer electrons across the bacterial outer membrane. The extracellular MtrC is a terminal reductase of Fe(III)-containing minerals, while DmsAB is the extracellular terminal reductase of DMSO (Edwards et al., 2020; Gralnick et al., 2006; Hartshorne et al., 2009; White et al., 2013; Xiong et al., 2006). The *mtrCAB* and *dmsEFAB* genes are clustered together (Beliaev and Saffarini, 1998; Gralnick et al., 2006).

Under the anoxic condition, *S. oneidensis* MR-1 also reduced IO_3^- in a dissimilatory way with lactate as an electron donor. The deletion of the gene involved in nitrate reduction did not impact the ability of *S. oneidensis* MR-1 to reduce IO_3^- (Mok et al., 2018). However, deletions of the genes in the *mtrCAB* or *dmsEFAB* gene clusters all diminished the bacterial ability to reduce IO_3^- (Guo et al., 2022b; Shin et al., 2022; Toporek et al., 2019). Further analyses showed that the *dmsEFAB* gene cluster was more dominant than the *mtrCAB* gene cluster in IO_3^- reduction. Neither HIO nor H_2O_2 were detected after the deletion of the *dmsEFAB* gene cluster, while HIO was still detectable, and H_2O_2 was accumulated after the deletion of the *mtrCAB* gene cluster (Guo et al., 2022b). Protein purification and characterization revealed that the purified MtrC was a *c*-Cyt with intrinsic peroxidase activity (Shi et al., 2006). Collectively, all these results showed that on the bacterial surface, DmsAB reduced IO_3^- to HIO and H_2O_2 . MtrC then reduced H_2O_2 to H_2O (Fig. 3b) (Guo et al., 2022b). Similar to that produced with IdrAB₁P₂ (Fig. 3a) (Reyes-Umana et al., 2022), the reduction

intermediate HIO was probably disproportionated abiotically into I^- and IO_3^- (Fig. 3b) (Guo et al., 2022b). DmsEF and MtrAB transferred electrons from the periplasm and across the outer membrane to the DmsAB and MtrC, respectively (Fig. 3b) (Guo et al., 2022b). The Mtr extracellular electron transfer pathway supplied electrons to DmsEFAB and MtrCAB for extracellular reduction of IO_3^- (Fig. 3b) (Guo et al., 2022b; Shi et al., 2016).

Many bacterial genomes contained both *dmsEFAB* and *mtrCAB* gene clusters, suggesting that they had the capability for extracellular reduction of IO_3^- (Guo et al., 2022a). Indeed, other *Shewanella* species also reduced IO_3^- (Councell et al., 1997; Farrenkopf et al., 1997). These bacteria were found in a variety of ecosystems, such as oceans, lakes, rivers and subsurface rocks. Global distribution of the bacteria with the capability for extracellular reduction of IO_3^- , especially their widespread occurrence in oceans, suggested the importance of these bacteria in the global geochemical cycling of iodine (Guo et al., 2022a).

Notably, DmsAB of *S. oneidensis* MR-1 and IdrAB of *Pseudomonas* sp. SCT and *Denitromonas* sp. IR-12 are members of the DMSO reductase superfamily, whose diverse functions range from sulfur and nitrate reductions to sulfite and arsenite oxidations. How the DmsAB and IdrAB reduce IO_3^- is currently unknown (Wells et al., 2023). Furthermore, DmsEF and Mtr CAB of *S. oneidensis* MR-1 share no sequence similarity to IdrP₁P₂ of *Pseudomonas* sp. SCT and *Denitromonas* sp. IR-12. Thus, IO_3^- reduction by IdrABP₁P₂ and DmsEFAB/MtrCAB are the results of convergent evolution. Moreover, DmsEFAB and MtrCAB of *S. oneidensis* MR-1 functioned primarily for the extracellular respiration of DMSO and Fe(III)-containing minerals, respectively (Gralnick et al., 2006; Shi et al., 2016; White et al., 2016). No cell growth was observed for *S. oneidensis* MR-1 during dissimilatory reduction of IO_3^- (Guo et al., 2022b; Toporek et al., 2019). Thus, the extracellular reduction of IO_3^- by *S. oneidensis* MR-1 was considered a fortuitous reaction (Guo et al., 2022b). Nevertheless, this fortuitous reaction may help bacterial survival in environments where IO_3^- is available but DMSO and Fe(III) are absent.

Indirect reduction by *S. oneidensis* MR-1 in the presence of Fe(III)-containing minerals

In soils, sediments and subsurfaces rich in Fe(III)-containing minerals, IO_3^- and org-I adsorb to the surface of minerals (Dai et al., 2004; Fuge and Johnson, 1986; Guido-Garcia et al., 2015; Li et al., 2022; Li et al., 2020; Shetaya et al., 2012; Wang et al., 2021). Reductive dissolution of Fe(III)-minerals by the Fe(III)-reducing microorganisms results in the release of IO_3^- and org-I from the mineral surface to the solution (Guido-Garcia et al., 2015; Jiang et al., 2023b; Jiang et al., 2023c; Li et al., 2022; Li et al., 2020). Furthermore, Fe(II), the product of Fe(III) reduction, also reduces IO_3^- abiotically (Councell et al., 1997). The high concentration of iodine in the groundwater of North China Plain was believed to have originated from the iodine adsorbed on Fe(III)-containing minerals (Li et al., 2022; Xue et al., 2022). Comparative metagenomic analyses of groundwater with a high concentration of I^- from the North China Plain identified MtrCAB and OmcS homologs (Jiang et al., 2023c). Similar to MtrCAB of *S. oneidensis* MR-1, OmcS of the dissimilatory Fe(III)-reducing bacterium *Geobacter sulfurreducens* was directly involved in the extracellular reduction of Fe(III)-containing minerals (Jiang et al., 2023a; Mehta et al., 2005). Thus, Fe(III)-reducing bacteria may also contribute to the formation of high I^- -containing groundwater in the North China Plain (Fig. 2b) (Jiang et al., 2023c).

Further investigation showed that Fe(II) abiotically reduced IO_3^- to HIO and I^- at a ratio of 1:2. The produced HIO was then disproportionated into I^- and IO_3^- at a ratio of 2:1 (Jiang et al., 2023b). IO_3^- reductions in the presence of water-soluble Fe(III)-citrate or different forms of Fe(III)-containing minerals by *S. oneidensis* MR-1, its mutants without *dmsEFAB* or *mtrCAB* and *Shewanella* sp. ANA-3, which contained only a *mtrCAB* homolog, was also comparatively analysed. The results consistently demonstrated that IO_3^- was abiotically reduced by the Fe(II) produced from bacteria-mediated Fe(III) reduction. The indirect reduction of IO_3^- by *S. oneidensis* MR-1 via biogenic Fe(II) was more predominant than the direct reduction of IO_3^- by *S. oneidensis* MR-1 under the conditions rich in Fe(III). Direct reduction of IO_3^- by *S. oneidensis* MR-1 via DmsEFAB and MtrCAB occurred mainly when the Fe(III) level was low. Compared to that with Fe(III)-citrate, the Fe(II) produced with Fe(III)-containing minerals reduced IO_3^- more efficiently. Collectively, these results demonstrated that Fe(III)-reducing bacteria, such as *S. oneidensis* MR-1, *Shewanella* sp. ANA-3 and probably *G. sulfurreducens* reduced IO_3^- indirectly via the Fe(II) from Fe(III) reduction (Fig. 2b) (Jiang et al., 2023b).

Direct and indirect reduction by sulfate-reducing bacteria

The dissimilatory sulfate-reducing bacterium *Desulfovibrio desulfuricans* was among the first microorganisms experimentally demonstrated to be capable of reducing IO_3^- to I^- directly under anoxic conditions (Councell et al., 1997). Similar to Fe(II), the sulfide, which was a byproduct of sulfate reduction, abiotically reduced IO_3^- to I^- (Councell et al., 1997). Sulfur isotope and chemical analyses reveal that the $\delta^{34}S_{SO_4}$ value of groundwater was positively correlated with the concentrations of iodine, I^- and sulfide in the aquifer of the North China Plain (Jiang et al., 2023c; Jiang et al., 2023d). Metagenomic and qPCR analyses also revealed that the concentrations of iodine and I^- in these groundwaters were positively correlated with the abundance of microbial genes directly involved in sulfate reduction, such as *dsrA* and *dsrB*, and sulfate-reducing bacteria (Jiang et al., 2023c; Jiang et al., 2023d). Further analyses showed that the dissimilatory sulfate-reducing bacterium *Desulfovibrio* sp. B304, which was isolated from the groundwater of high iodine in Northern China, reduced IO_3^- to I^- in the absence of sulfate. The addition of molybdenum also improved the IO_3^- reduction by *Desulfovibrio* sp. B304, suggesting that the direct reduction of IO_3^- by *Desulfovibrio* sp. B304 was probably mediated by the molybdenum-dependent DMSO reductase. In the presence of sulfate, the rate and extent of reducing IO_3^- by *Desulfovibrio* sp. B304 increased substantially. This enhanced reduction was attributed to the abiotic reduction of IO_3^- by the sulfide produced from the sulfate reduction (Jiang et al., 2023d). Thus, sulfate-reducing bacteria reduced IO_3^- directly, probably via their molybdenum-dependent DMSO reductases, as well as indirectly via the sulfide from sulfate reduction, which all contributed to the I^- enrichment in the groundwater of the North China Plain and probably other sites rich in I^- (Fig. 2c) (Jiang et al., 2023c; Jiang et al., 2023d).

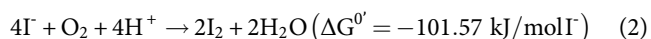
In addition to IO_3^- reduction, sulfate-reducing bacteria might also mediate org-I dehalogenation directly via their dehalogenases and the reductive dissolution of the Fe(III)-containing minerals adsorbed with iodine indirectly via sulfide from sulfate reduction in the groundwater of high I^- from the North China Plain, which could contribute to the I^- enrichment in the groundwater (Jiang et al., 2023c; Jiang et al., 2023d).

Bacterial oxidation of I⁻

The first I⁻-oxidizing bacterium was isolated from a marine aquarium where fish death was associated with the elevated I₂ level in the aquarium water (Gozlan, 1968; Gozlan and Margalith, 1973, 1974). Subsequently, I⁻-oxidizing bacteria were isolated from the brine waters and biofilms of natural gas plants, seawaters, marine sediments, soils, groundwater from the Hanford Site and subsurface sediments of contaminated ¹²⁹I in the Savanna River Site, South Carolina, USA (Amachi et al., 2005a; Amachi et al., 2003; Amachi et al., 2005c; Arakawa et al., 2012; Fuse et al., 2003; Hughes et al., 2021; Iino et al., 2016; Lee et al., 2020; Li et al., 2012a; Zhao et al., 2013).

Direct oxidation by bacterial multicopper oxidases

The I⁻-oxidizing bacteria strain *Iodidimonas* sp. Q-1 and *Roseovarius* sp. strain A-2 oxidized I⁻ extracellularly to I₂ via their multicopper iodide oxidases with O₂ as the electron acceptor (Fig. 4a) (Amachi and Iino, 2022; Amachi et al., 2005c; Shiroyama et al., 2015; Suzuki et al., 2012). Once I₂ was formed, following its hydrolysis to HIO and I⁻, the disproportionation reaction of HIO to form IO₃⁻ and I⁻ might spontaneously occur (Amachi and Iino, 2022). The proposed sum of this reaction is:

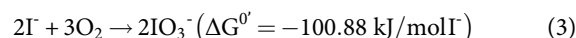


The multicopper iodide oxidases of these bacteria consisted of at least two subunits—IoxA and IoxC, whose genes were clustered together with other genes, such as *ioxB* and *ioxDEF* (Shiroyama et al., 2015; Suzuki et al., 2012). IoxA and IoxC homologs were found in other I⁻-oxidizing bacteria, and multicopper iodide oxidase activity was also detected in the I⁻-oxidizing bacteria isolated from the Hanford Site (Lee et al., 2020; Shiroyama et al., 2015; Suzuki et al., 2012). In addition to I₂, volatile org-I compounds such as diiodomethane (CH₂I₂) and chloroiodomethane (CH₂ClI) were also produced by I⁻-oxidizing bacteria during I⁻ oxidation (Amachi et al., 2005a; Amachi et al., 2003; Amachi et al., 2005c; Fuse et al., 2003). Notably, microbial multicopper iodide oxidase activity was detected in soils. The addition of bacterial multicopper oxidase to the soil samples with I⁻ and organic matter oxidized I⁻ to I₂ and HIO that were eventually incorporated into the organic matter of soil to form org-I, some of which are immobilized (Seki et al., 2013; Xu et al., 2011a; Xu et al., 2011b; Zhang et al., 2013).

As a bactericide, iodine kills bacteria. Although the exact killing mechanism remains uncertain, I₂, HIO and probably I₃⁻ have all been proposed to contribute to bacterial killing (Gottardi, 1999; Hickey et al., 1997). Compared to non-I⁻-oxidizing bacteria, I⁻-oxidizing bacteria were more tolerant to I₂ (Arakawa et al., 2012; Zhao et al., 2013). The I⁻-oxidizing bacteria with multicopper oxidases killed other non-I⁻-oxidizing bacteria in the presence of I⁻, probably via the I₂ produced from I⁻ oxidation (Yuliana et al., 2015; Zhao et al., 2013). This antibacterial capability might improve the ability of I⁻-oxidizing bacteria to compete with other bacteria in the presence of I⁻ (Yuliana et al., 2015).

Direct oxidation by ammonia-oxidizing bacteria

Global modeling of iodine has suggested that I⁻ oxidation to IO₃⁻ was probably linked to bacterial nitrification in oceans (Truesdale et al., 2001; Wadley et al., 2020). Bacterial nitrification is mediated by two different groups of bacteria: ammonia-oxidizing bacteria and nitrite-oxidizing bacteria. The former oxidizes ammonia to nitrite, while the latter oxidizes nitrite to nitrate (Kowalchuk and Stephen, 2001). Indeed, the marine ammonia-oxidizing bacteria *Nitrosomonas* sp. (Nm51) and *Nitrosococcus oceani* (Nc10) oxidizes I⁻ to IO₃⁻ (Fig. 4b). However, no I⁻ oxidation activity has been detected in the nitrite-oxidizing bacteria *Nitrospira marina*, *Nitrospina gracilis* or *Nitrococcus mobilis*. Hence it was proposed that *Nitrosomonas* sp. (Nm51) and *Nitrosococcus oceani* (Nc10) used ammonia-oxidizing enzymes to oxidize I⁻ (Hughes et al., 2021). The proposed electron acceptor for this reaction is O₂:



Moreover, a low iodide level has been found in the ocean depths where the nitrite level is high, which is consistent with the I⁻ oxidation driven by ammonia-oxidizing bacteria in the oceans (Moriyasu et al., 2023).

Indirect oxidation by the extracellular reactive species produced by bacteria

Many bacteria produce extracellular reactive oxygen species, such as superoxide and H₂O₂, under oxic conditions (Bond et al., 2020; Diaz et al., 2013; Hansel and Diaz, 2021). In the presence of H₂O₂, the bacterial isolates from the Savanna River Site oxidized I⁻ to triiodide (I₃⁻). This H₂O₂-dependent oxidation of I⁻ was facilitated by the organic acids produced by bacterial isolates. The organic

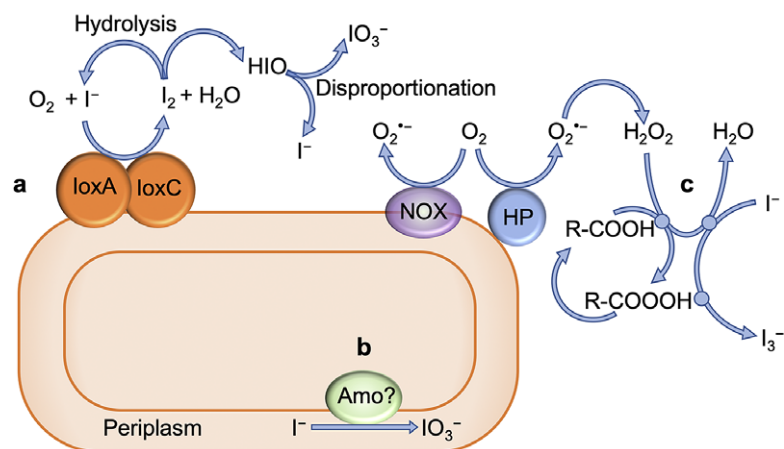


Figure 4. Bacterial oxidation of I⁻: (a) extracellular multicopper iodide oxidase; (b) ammonia-oxidizing bacteria; (c) extracellular reactive oxygen species. Abbreviations: Amo: ammonia monooxygenase; HP, heme peroxidase; Iox: iodide oxidase; NOX, NADPH oxidase.

acids produced lowered the pH of the reaction solution and reacted with H_2O_2 to form peroxy-carboxylic acids that were stronger oxidants than H_2O_2 , which all contributed to I^- oxidation to I_3^- (Fig. 4c) (Li et al., 2012b). Similarly, the marine bacterium *Roseobacter* sp. AzwK-3b produced extracellular superoxide that oxidized I^- (Li et al., 2014).

Bacterial accumulation of I^-

As a biophilic element, iodine accumulates in the cells of different organisms (Amachi, 2008). For example, humans and other mammals accumulate iodine in the thyroid gland. Accumulation occurs in the thyroid follicular cells that use the Na^+ and I^- co-transporter located at the basolateral membrane to transport I^- into the cells. Once inside thyroid follicular cells, I^- is oxidized to I_2 by the thyroid peroxidase in the presence of H_2O_2 . The I_2 is finally incorporated into thyroid hormones T3 and T4 (Smyth and Dwyer, 2002). Brown algae also accumulate a significant amount of iodine, and the iodine content of brown algae *Laminaria digitata* could be as great as 5% of its dry weight (Gall et al., 2004). In the presence of H_2O_2 , the extracellular vanadium iodoperoxidase of *L. digitata* oxidized I^- to I_2 , HIO and I_3^- that were then transported into algal cells (Kupper and Carrano, 2019; Kupper et al., 1998; Verhaeghe et al., 2008). Inside the cells of *L. digitata*, I^- was the major species of iodine, while org-I was the minor species (Gall et al., 2004). Brown algae accumulated I^- as a defense mechanism against infection of microbial pathogens, as well as an antioxidant in response to oxidative stress (Kupper and Carrano, 2019).

Arenibacter sp. strain C-21, which was isolated from the surface of marine sediments, was the first I^- -accumulating bacterium reported (Amachi et al., 2005b; Ito et al., 2016). The uptake of I^- by *Arenibacter* sp. strain C-21 is dependent on glucose, O_2 and H_2O_2 (Amachi et al., 2007b; Amachi et al., 2005b). It was proposed that the oxidation of glucose by *Arenibacter* sp. strain C-21 produced extracellular H_2O_2 . The extracellular vanadium iodoperoxidase of *Arenibacter* sp. strain C-21 used H_2O_2 to oxidize I^- to HIO, which was then transported into bacterial cells (Amachi et al., 2007b). Indeed, the genome of *Arenibacter* sp. strain C-21 contains at least five putative genes for vanadium-dependent iodoperoxidase (Ito et al., 2016). The I^- -accumulating bacteria have also been isolated from subsurface sediments of the Savanna River Site and the Lastensuo Bog, Finland (Li et al., 2011; Lusa et al., 2016). Some cyanobacteria, such as *Nostoc commune*, *Scytonema javanicum* and *Stigonema ocellatum*, display a high ability to accumulate I^- (Fukuda et al., 2014).

Bacterial formation of org-I

A variety of terrestrial and aquatic bacteria produce volatile org-I (Amachi et al., 2001; Amachi et al., 2004; Brownell et al., 2010; Fujimori et al., 2012; Fuse et al., 2003; Gomez-Consarnau et al., 2021; Hirata et al., 2017; Smythe-Wright et al., 2006). As mentioned above, the I^- -oxidizing bacteria also produce org-I during I^- oxidation in addition to I_2 (Amachi et al., 2005a; Amachi et al., 2003; Amachi et al., 2005c; Fuse et al., 2003). Once accumulated inside bacterial cells, some of the HIO was believed to be transformed into org-I (Amachi et al., 2007b). Thus, HIO and I_2 produced during IO_3^- reduction and I^- oxidation contributed to org-I formation (Luther III, 2023)

In the *Arabidopsis* plant, the deletion of a gene for methyltransferase increased the iodine content in the plant cells, demonstrating the crucial role of methyltransferase in iodine metabolism in plant cells (Landini et al., 2012). Methyltransferases were proposed to use S-adenosyl-L-methionine as a methyl donor for methylating I^- (Duborska et al., 2021; Itoh et al., 2009). Indeed, the cell extracts of the I^- -methylating bacterium *Rhizobium* sp. strain MRCD 19 possesses the enzymatic activity that catalyzes I^- methylation in the presence of S-adenosyl-L-methionine, which suggests a similar role of bacterial methyltransferases in I^- methylation (Amachi et al., 2001). In the presence of H_2O_2 , the vanadium-dependent iodoperoxidases were also involved in methylating I^- by brown algae *L. digitata* (Colin et al., 2003). The molecular mechanisms underlying bacterial formation of org-I are, however, currently unknown.

Perspectives

Bacteria play crucial and versatile roles in the global geochemical cycling of iodine via IO_3^- reduction, I^- oxidation and accumulation as well as org-I formation. Recently, substantial advances have been made in the understanding of the molecular mechanisms used by bacteria for reducing IO_3^- , as well as the importance of ammonia-oxidizing bacteria in I^- oxidation, which provide new insights into the bacterial roles in the global geochemical cycling of iodine.

Despite these progresses, key knowledge gaps still remain regarding bacterial roles in the biogeochemical cycling of iodine. For example, the ecological importance of IO_3^- -reducing, Fe(III)-reducing or sulfate-reducing bacteria in the biogeochemical cycling of iodine is currently unknown. Whether the I^- -oxidizing bacteria can conserve energy for chemolithoautotrophic growth remains to be demonstrated. Additionally, further investigation should also focus on whether bacterial iodine-transforming activity is fortuitous, mixotrophic or syntrophic.

Bridging these knowledge gaps will not only shed new light on bacterial roles in the global geochemical cycling of iodine but also help develop the models for predicting the biogeochemical fate and transport of ^{129}I in the contaminated sites and iodine cycling in oceans.

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