



Production of Methyl-Iodide in the Environment

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Iodine is an essential micronutrient for most of the living beings, including humans. Besides its indispensable role in animals, it also plays an important role in the environment. It undergoes several chemical and biological transformations resulting in the production of volatile methylated iodides, which play a key role in the iodine's global geochemical cycle. Since it can also mitigate the process of climate change, it is reasonable to study its biogeochemistry. Therefore, the aim of this review is to provide information on its origin, global fluxes and mechanisms of production in the environment.

Keywords: biomethylation, iodine, biogenic methyl-iodide, volatilization, iodide

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INTRODUCTION

Atmospheric iodine species, such as methyl-iodides, are distributed to terrestrial and aquatic environments *via* wet and dry depositions. The primary processes that affect iodine's allocation and speciation in the atmosphere are photochemical reactions (Moore and Zafriou, 1994), and the production of volatile iodide's transformants by marine phytoplankton, cyanobacteria and algae, which are the main sources of biogenic alkyl-iodides in the atmosphere (Carpenter, 2003).

The environmental relevance of the methyl-iodide is highlighted by the estimates which suggest that in the regions between 40 N° and 40 S° up to 174 Gg of methyl-iodide is produced annually *via* biological and photochemical processes (Stemmler et al., 2014). Furthermore, according to Bell et al. (2002), almost 70% of the annual flux of methyl-iodide originates from the open oceanic waters. These accrued volatile organo-iodine species participate in the formation of cloud condensation nuclei (Saunders and Saiz-Lopez, 2009), which can cause albedo and regional cooling with a negative effect on climate. Furthermore, the reactive methyl-iodide species also take part in the depletion of ozone layer (Chameides and Davis, 1980; Solomon et al., 1994; Davis et al., 1996).

MECHANISMS OF METHYL-IODIDES' GENESIS

Methyl-iodide compounds are produced in seawater *via* the reaction between photochemically produced methyl and iodine radicals, typically in temperate and tropical waters (Moore and Zafriou, 1994). Nevertheless, the illumination, as well as the acidic pH, and the dissolved organic carbon presence accelerate the production of methyl-iodide in sea water (Chen et al., 2020).

Besides photochemical reaction, iodide methylation can be mediated biologically. Thayer (2002) noted that there are three pathways of iodine methylation. The first pathway is the reaction of iodide with β -dimethylsulphonioacetate (DMSP), an algal osmoprotectant. However, the production of methyl-halides through this reaction is not favored, because of its endothermic character. Thus,

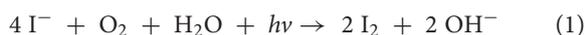
it was estimated that only less than 1% of methyl-halides in the atmosphere are produced by this reaction (Hu and Moore, 1996).

The second mechanism suggests the direct transformation of iodide into methylated species *via* enzymatic transformation originally proposed for arsenic methylation (Challenger, 1951). *Via* this methylation pathway, the transformation of inorganic iodide into methylated compounds involves the nucleophilic attack of iodide at the electrophilic CH_3^+S site of the S-adenosyl-L-methionine methyl donor mediated by the methyltransferases (Itoh et al., 2009). This pathway is proved to be favored by various microorganism. Amachi et al. (2001) demonstrated that methyl-iodide producing ability is widespread among marine and terrestrial bacteria (e.g., *Variovorax* sp., *Photobacterium leiognathi*), while anaerobic microorganisms (e.g., methanogens) produce methyl-iodide less likely. In plants, Hol-1 protein was identified as a methyltransferase that catalyzes the S-adenosyl-L-methionine dependent methylation of halides (Landini et al., 2012).

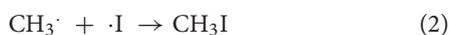
The third mechanism suggests the formation of methyl-iodide by vanadium-dependent haloperoxidases (Punitha et al., 2018) in the presence of hydrogen peroxide (Leblanc et al., 2006). Iodine specific iodoperoxidase was identified in various marine diatoms and macrophytes (Colin et al., 2003). Such peroxidase is also considered to be responsible for iodine methylation in plants (Neidleman and Geigert, 1987).

PRODUCTION OF METHYL-IODIDE IN SEAWATER

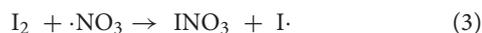
Elemental iodine is also released into the atmosphere by photochemical oxidation of iodide by UV radiation in the presence of O_2 (Saunders and Saiz-Lopez, 2009):



Methylated iodine compounds are produced photochemically in seawater *via* the reaction between photochemically produced methyl radicals and iodine atoms (Moore and Zafriou, 1994) *via* the reaction:



While iodine radicals can be produced *via* the reaction of I_2 with NO_3 radicals while sunlight is not needed for this reaction (Saiz-Lopez et al., 2006):



Other possible pathways are suggested too by Moore and Zafriou (1994) but they are unlikely to occur in natural non-contaminated waters.

PRODUCTION OF METHYL-IODIDE BY MARINE ALGAE

Küpper et al. (2018) studied iodine metabolism in the filamentous brown alga *Ectocarpus siliculosus*, whose predominant emission was methyl-iodide among various other volatile halogenated compounds. Elevated methyl-iodide concentrations were also found in the algal beds of *Laminaria digitata* at the coasts of Scotland (Nightingale et al., 1995) and California (Manley et al., 1992). Excessive amounts of methyl-iodide levels are also common in the beds of giant kelp (*Macrocystis pyrifera*), but it is not considered a significant source of iodine (Manley and Dastoor, 1987). Large amounts of iodine were observed also above the sea ice in the Weddell sea at Antarctic coast presumably originating from diatoms found in the sea ice (Atkinson et al., 2012).

Since algal activity is sensitive to light, it should also affect the production of methyl-iodide. However, the results are contradicting. While Nightingale et al. (1995) indicated that the methyl-iodide production by *L. digitata* was enhanced in the dark, Carpenter et al. (2000) noted that the organoiodine production by macroalgae is stimulated by light.

PRODUCTION OF METHYL-IODIDE BY BACTERIA

Aerobic incubation of seawater showed that the iodine is volatilized from the seawater biologically. Further investigation showed that the production of methyl-iodide is due to bacterial activity, thus, the addition of antibiotics caused a significant decrease in iodine's volatilization (Amachi et al., 2004). Fuse et al. (2003) isolated two strains of iodine-producing bacteria, identified as *Roseovarius* spp., which were capable of producing not only methyl-iodide but also other methyl-iodide derivatives from the iodide supplemented media. Members of the *Proteobacteria*, *Cytophaga-Flexibacter-Bacteroides* group (Amachi et al., 2004), and also the strains of *Alteromonas macleodii* and *Vibrio splendidus* (Amachi et al., 2001) can also facilitate organo-iodide release from the seawater. Smythe-Wright et al. (2006) estimated that the methyl-iodide production by cyanobacteria *Prochlorococcus* at 5.3×10^{11} g year⁻¹. However, Brownell et al. (2010) suggested, that methyl iodide production of this species accounts only about 0.3% of the global marine production, in future it may represent a remarkable source of volatile iodine species in low latitude waters of the Atlantic and Indian oceans, since the recent models showed an increase in the abundance of this bacterial species by up to 15% due to global warming (Smythe-Wright et al., 2006) while the production rate is dependent on the physiological state of cells and culture conditions (Hughes et al., 2011). Under optimal conditions, some bacterial strains belonging to *Erythrobacter* are capable of producing as much as 49 pmol L⁻¹ h⁻¹ of methyl-iodide

(Fujimori et al., 2012). Nevertheless, Gómez-Consarnau et al. (2021) noted that the methyl-iodide synthesis is a generalized process in representatives of the major marine heterotrophic bacterial groups.

PRODUCTION OF METHYL-IODIDE IN TERRESTRIAL ENVIRONMENTS

In soils, the presence of manganese oxides can contribute to the formation of methyl-iodide abiotically. Under conditions that the iodide and the natural organic matter is present, Allard et al. (2010) showed that the manganese sand can initiate the formation of methyl-iodide. However, the speciation of the final product depends on the properties of the present organic matter. While the methyl-iodide was produced in the presence of humic acids, the abiotic synthesis of high-molecular alkyl-iodides, such as propyl- and butyl-iodides, was enhanced when the other major fractions of soil organic matter were also present and exposed to iodine.

The iodine volatilization from soils is stimulated by plants, especially in flooded soils, partially due to the action of enzymes produced by the roots (Muramatsu and Yoshida, 1995). Furthermore, in flooded soils where redox potential is low, thus, under such conditions, iodine is reductively desorbed from the soil particles to soil solution as iodide and transformed into reactive volatile species (Yuita, 1992). Some soil organic compounds with large carbonyl moieties, or alkyl-chlorides can enhance the formation of volatile iodine compounds, while aromatic compounds can stabilize the iodine in soil (Taghipour and Evans, 2001). Biotic transformation of iodine into the methyl-iodides plays also prominent role in the oligotrophic sediments at nuclear waste sites where the isolated microcosm possessed iodine methylation abilities (Bagwell et al., 2019).

Production of Methyl-iodide by Plants

Methyl-halides do not play a fundamental role in the plant development (Rhew et al., 2003), although iodine has reportedly adverse effects on plant's growth at high concentrations (Duborská et al., 2018). Therefore, the accumulated iodine is preferentially volatilized as methyl-iodide through the activity of specific methyl transferase encoded by *HOL* (*HARMLESS TO OZONE LAYER*) genes (Carlessi et al., 2021). There are two types of *HOL* genes from which the *HOL-1* is responsible for iodine methylation (Landini et al., 2012).

Contribution of methyl-iodide production by higher plants on total flux of iodine to atmosphere from soils is minor on global scale, however, it was estimated that the total annual amount of volatilized iodine from rice fields approximates 2×10^{10} g (Muramatsu and Yoshida, 1995). Furthermore, the emission of methyl-iodide from the shoots of rice plant are more significant in comparison to the contribution of flooded soil surface (Muramatsu and Yoshida, 1995).

The enzyme responsible for iodide methylation in leaves of cabbage (*Brassica oleracea*) was classified as a halide/bisulfide

TABLE 1 | Global production, loss, emission, and inventory of methyl-iodide (Stemmler et al., 2014).

Production pathway	
Production (Gg.year ⁻¹)	348.27
Biological (%)	0.2
Photochemical ^a (%)	28
Photochemical ^b (%)	72
Net emission (Gg.year ⁻¹)	170.61
Loss (Gg.year ⁻¹)	164.97
Inventory (Gg)	14.10

^aProduction from semi-labile dissolved organic carbon. ^bProduction from refractory dissolved organic carbon.

methyltransferase with pH optimum for iodide methylation in the range of 5.5–7. It catalyzes the S-adenosyl-L-methionine-dependent methylation of the halides (iodide, bromide, and chloride) to monohalogenated methanes (Attieh et al., 1995).

Various other species of *Brassicaceae* family (e.g., *B. rapa* and *Raphanus sativus*) and species of the *Poaceae* family, such as *Triticum aestivum*, were also reported to be able of releasing of volatile iodine species (Rhew et al., 2003); and it is generally accepted that the iodide methylation is widespread among higher plants (Saini et al., 1995).

Production of Methyl-iodide by Fungi

Generally, fungi are not considered relevant producers of methylated iodine species on global scale. However, considering their abundance in the environment, more attention should be taken toward their investigation. So far, the methyl-iodide was the only reported volatile organic transformant of iodine produced by fungi (Ban-Nai et al., 2006). The release of environmentally significant amount of methyl-iodide was reported from wood-rotting fungus *Phellinus pomaceus* (Harper, 1985). Various Basidiomycota species, including *Lentinula edodes*, *Hebeloma vinosophyllum*, *Pleurotus ostreatus* and *Agaricus bisporus* (Ban-Nai et al., 2006), as well as the ectomycorrhizal fungal species *Cenococcum geophilum*, *Hebeloma crustuliniforme*, *Inocybe maculata*, and *Laccaria laccata* (Redeker et al., 2004) were also reported to produce methyl-iodide under laboratory conditions. However, the exact mechanism of iodine biovolatilization by fungi is not yet sufficiently explained; and, thus, it was hypothesized that both intracellular and extracellular transformations into methyl-iodides may occur (Urík et al., 2007; Duborská et al., 2017). It is also very likely that the filamentous fungi can facilitate iodine methylation indirectly *via* production of extracellular metabolites, e.g., the strains of *Alternaria alternata*, *Fusarium oxysporum*, *Penicillium roqueforti*, *P. chrysogenum*, *Cladosporium cladosporioides*, *Aspergillus niger* and *A. oryzae*, which possess the abilities of methyl-iodide production. While the precursor for such transformation by fungi in aquatic environments was reportedly almost exclusively iodide, the preferable source in terrestrial systems seems to be iodate (Duborská et al., 2017).

GLOBAL EFFLUXES OF METHYL-IODIDES

While the global annual ocean-atmosphere flux of methyl-iodide is estimated at 219 Gg, its local estimations vary significantly depending on the region or season. In seawater, the photochemical and biological processes are co-occurring, thus, both biological and photochemical production pathways (**Table 1**) need to be taken into account to approximate the global production of methyl-iodide (Stemmler et al., 2014).

While the biological production of methyl-iodide is observable during the whole year in the tropical eastern Atlantic and equatorial Pacific zones, the fluxes in regions with boreal winter occur predominantly from the atmosphere to the ocean (Stemmler et al., 2014). In the southern ocean, the biological production is limited to the period of austral spring (Stemmler et al., 2014). On the other hand, a large number of macroalgae isolated from the Antarctic are capable of methyl-iodide production (Laternus et al., 1998). Smythe-Wright et al. (2006) estimated that the annual flux of methyl-iodide produced by cyanobacterium *Prochlorococcus* alone is 4.3×10^9 mol. However, Manley and de la Cuesta (1997) stated that methyl-iodide produced by the marine phytoplankton is not significant on global scale. Butler et al. (1981) suggested that the methyl-iodide produced by the phytoplankton is only a short-lived intermediate which is converted to methyl-chloride.

Nevertheless, the terrestrial sources are not as significant as the marine sources. However, the rice plants possessing the ability to methylate iodide are considered a significant source with 5% contribution to the global flux of methyl-iodide (Redeker et al., 2000). Furthermore, Dimmer et al. (2001) reported annual flux of 1.4 Gg from peatland ecosystems and 7.3 Gg from wetlands. Burning of biomass can also contribute to the annual flux of methyl-iodide by up to 3.5 Gg (Blake et al., 1996).

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CONCLUSION

Since methyl-iodides play an important role in the depletion of ozone layer and the formation of cloud condensation nuclei which can result in regional cooling with a negative climate feedback, the release of organoiodine compounds can mitigate global warming, causing a further increase in number of iodide-methylating bacteria and algae. This short review provides a biogeochemical context for such a scenario since it notes the mechanisms that are behind the formation and propagation of methyl-iodide into the environment. It also highlights that process of transforming iodine into methyl-iodine is regulated and accelerated biotically, and this ability is almost universal across the genera of various organisms, including phytoplankton, fungi and plants as well. To conclude, the research to improve understanding of the contribution of biogenic sources on methyl-iodide distribution and their impact on the environment is much needed.

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ED and MU: writing—original draft preparation. MM, OZ, KB, and BF: writing—review and editing. PL: supervision. MU: funding acquisition. All authors have read and agreed to the published version of the manuscript.

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