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## The production of volatile iodocarbons by biogenic marine aggregates

*Abstract*—We present the first reported measurements of volatile iodocarbon production by biogenic marine aggregates. Iodomethane ( $\text{CH}_3\text{I}$ ), iodoethane ( $\text{C}_2\text{H}_5\text{I}$ ), 2-iodopropane ( $\text{CH}_3\text{CHICH}_3$ ), and 1-iodopropane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ ) concentrations were determined in incubations of aggregates formed by concentrating the  $>53 \mu\text{m}$  fraction of the plankton during a field campaign in the Celtic Sea. All four iodocarbons increased significantly in concentration in the aggregate incubations relative to filtered seawater controls. Maximum production rates ranged from  $0.01 \text{ pmol L}^{-1} \text{ h}^{-1}$  for  $\text{CH}_3\text{CHICH}_3$  to  $0.31 \text{ pmol L}^{-1} \text{ h}^{-1}$  for  $\text{C}_2\text{H}_5\text{I}$ . Accompanying pheopigment and bacterial heterotrophic production suggest that the processes taking place on the aggregates studied were a good representation of those known to occur on natural marine particles. We also report iodocarbon production rates observed in natural marine aggregates, including a diatom mucilage collected in the Celtic Sea and phytodetritus sampled from Kongsfjord in the Arctic. Detrital particles could be hotspots of iodocarbon production in the marine environment.

Over 50 years ago, the enrichment of iodine relative to chlorine in air masses of marine origin was recognized (Rankama and Sahama 1949) and this led to conjecture that sea-to-air transfer is an important pathway in the global cycling of this element. Subsequent research suggested that the sea-to-air flux of iodine might be mediated by molecular iodine ( $\text{I}_2$ ) formed at the sea surface (Garland and Curtis 1981). However, the discovery of

iodomethane ( $\text{CH}_3\text{I}$ ) in seawater from a kelp bed (Lovelock 1975) brought about a change in focus by introducing another potential vector for sea-to-air iodine transfer. It is now known that a whole suite of iodocarbons in addition to  $\text{CH}_3\text{I}$  are produced naturally in seawater, including iodoethane ( $\text{C}_2\text{H}_5\text{I}$ ), the iodopropanes ( $\text{C}_3\text{H}_7\text{I}$ ), diiodomethane ( $\text{CH}_2\text{I}_2$ ), and mixed chloro- and bromiodomethanes ( $\text{CH}_2\text{ClI}$ ,  $\text{CH}_2\text{BrI}$ ) (Carpenter et al. 2000). All of these compounds are volatile and so have the potential to evade to the atmosphere and contribute to the sea-to-air flux of iodine.

In parallel with increasing knowledge of the range of volatile iodocarbons in seawater has been growing awareness of the environmental consequences of sea-air iodine flux. Balancing the global iodine cycle is dependent on rain-out and dry deposition from the air to land. In addition, the flux of iodocarbons from the oceans to the atmosphere has significant implications for human health and the prevalence of iodine deficiency disorders such as goiter and cretinism. The driving force for most current iodocarbon research is the influence that atmospheric iodine has on air quality and climate. Iodocarbons are readily photolyzed in the atmosphere and release reactive iodine, which reacts with ozone to form the iodine oxides (IO and OIO); these, in turn, can react with themselves,  $\text{NO}_2$ , or  $\text{HO}_2$  (Allan et al. 2000). As a consequence, atmospheric iodine can influence (1) ozone concentrations in the marine boundary layer (McFiggans et al. 2000), (2) the capacity of the atmosphere to process emissions of greenhouse gases such

as methane, and (3) the formation of new particles, and hence production of potential cloud condensation nuclei (O'Dowd and Hoffman 2005).

Traditionally, estimating the size of the oceanic source of the iodocarbons has been performed by extrapolating from concentration distributions determined during ship-based field campaigns to the global scale. This approach provided a first estimate of the annual rate of flux of  $\text{CH}_3\text{I}$  on the order of  $10^8 \text{ Kg yr}^{-1}$  (Moore and Groszko 1999), which is enough to satisfy the predicted sea-air flux of iodine of  $5 \times 10^8 \text{ Kg yr}^{-1}$  needed to balance the geochemical budget of iodine (Miyake and Tsunogai 1963). More recently, greater emphasis has been placed on gaining the knowledge required to predict iodocarbon distributions by determining marine iodocarbon production and loss processes. Incubations of coastal macroalgae have provided direct evidence of a biogenic iodocarbon source in coastal regions (Carpenter et al. 2000). Laboratory culture studies have revealed that selected strains of marine microalgae (Manley and de la Cuesta 1997) and bacteria (Amachi et al. 2001) are capable of iodocarbon production. However, annual iodocarbon production rates (i.e.,  $10^3$ – $10^6 \text{ Kg yr}^{-1}$ ) calculated by the global extrapolation of data collected in experimental incubations (e.g., Manley and de la Cuesta 1997) are much lower than the estimated sea-air flux of these compounds (Moore and Groszko 1999).

Here, we report results from the first study of iodocarbon production by biogenic marine aggregates formed by plankton concentration (Ploug and Grossart 2000). We also report the results of our preliminary investigations examining iodocarbon production by natural marine particles, including a diatom mucilage aggregation and phytodetritus.

## Materials and methods

**Plankton concentrate**—The plankton concentrate was collected from the Celtic Sea during a field campaign on RRS *Discovery*. The concentrate was formed by concentrating the  $>53\text{-}\mu\text{m}$  fraction of the plankton from 1,000 liters of seawater with a nylon mesh and resuspending the resulting accumulation in 1 liter of  $0.7\text{-}\mu\text{m}$  GF/F (Whatman) filtered seawater. Care was taken during concentration and filtration to avoid excessive damage to the plankton cells. Seawater was supplied from the ship's pumped supply (from 6 m). Microscopic observation of the concentrate revealed that it was dominated by the diatom *Rhizosolenia* sp. but also contained *Chaetoceros* sp. and dinoflagellates. The chlorophyll *a* concentration in the concentrate was  $82.2 \text{ mg m}^{-3}$ . After collection, the concentrate was homogenized by gently shaking and divided between 10, 100-mL glass syringes. The concentrate rapidly flocculated after collection and formed small aggregates. The syringes were placed in the dark at a constant temperature of  $12^\circ\text{C}$  (ambient seawater temperature) and incubated for 66 h. One syringe was removed at 0, 6, 12, 18, 24, 30, 36, 42, 54, and 66 h, and duplicate subsamples were taken for iodocarbon analysis. Samples were also taken for bacterial heterotrophic production (BHP) and phytoplankton pigment analyses at each time

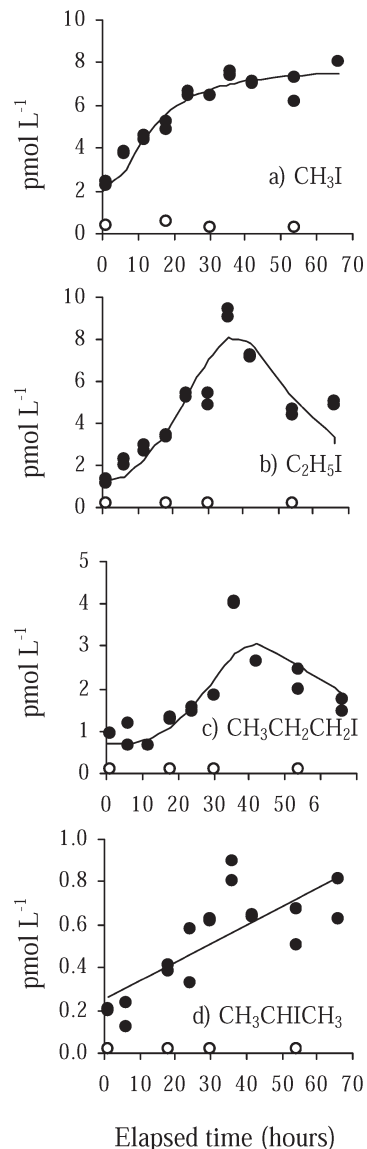


Fig. 1. Observed changes in (a)  $\text{CH}_3\text{I}$ , (b)  $\text{C}_2\text{H}_5\text{I}$ , (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and (d)  $\text{CH}_3\text{CHICH}_3$  concentrations during the incubation of marine aggregates formed by plankton concentration. Closed symbols show data collected for the aggregates, and open symbols show data for associated filtered seawater controls. Solid lines show trend lines fitted to the iodocarbon concentration data ( $R^2 > 0.70$ ,  $p < 0.001$ ). Trend lines fitted to the plankton concentrate  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ , and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  data are of the form  $y = (ax^2)/(b + x^n)$ , where  $x$  is the time in hours and  $y$  is the iodocarbon concentration. A linear regression line was the best fit to the  $\text{CH}_3\text{CHICH}_3$  data. Note the different  $y$ -axis scales.

point. Filtered ( $0.7 \mu\text{m}$  GF/F) seawater controls with no additions of biological material were incubated alongside the concentrate incubations.

**Analytical techniques**—All iodocarbon analyses were carried out with a purge-and-cryogenic trap sample preparation system with a Hewlett-Packard 6890A gas chromatograph and 5973 mass selective detector (GC-MSD) fitted with a 60-m DB-VRX capillary column (J&W;

Table 1. Iodocarbon production rates ( $\text{pmol L}^{-1} \text{h}^{-1}$ ) observed in experimental incubations of a flocculated plankton concentrate, diatom mucilage aggregation, and phytodetritus. The ocean region from which each aggregate was sampled is given in parentheses.

	$\text{CH}_3\text{I}$	$\text{C}_2\text{H}_5\text{I}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	$\text{CH}_3\text{CHICH}_3$
Plankton concentrate (Celtic Sea)*	0.27	0.31	0.12	0.01
Diatom mucilage aggregation (Celtic Sea)†	0.43	3.74	1.04	1.69
Phytodetritus (Kongsfjord, Arctic)†	0.03	0.14	0.07	0.40

\* Maximum production rates predicted from derivatives of trend lines applied to the concentration data by least squares regression ( $R^2 > 0.7$ ;  $n = 20$ ). Units represent production per liter of concentrated plankton.

† Production rates predicted from trend lines applied to the concentration data by linear regression ( $R^2 > 0.7$ ;  $n = 4$ ). Units represent production in a solution with a mucilage or phytodetritus to seawater volume ratio of 1:50.

film thickness  $0.32 \mu\text{m}$ ). All samples were  $0.7\text{-}\mu\text{m}$  GF/F filtered before trace gas extraction by purging and preconcentration. Filtration was performed gently by hand to avoid cell rupture with a 47-mm filtration unit placed between the incubation syringe and a second 100-mL glass syringe. Care was taken to not introduce any headspace or bubbles into the syringes during filtration. Sample preparation and analytical techniques are described in detail in Hughes et al. (2006). Deuterated surrogate analytes ( $\text{CD}_3\text{I}$  and  $\text{CD}_3\text{CDICD}_3$ ) were added to each sample analyzed to monitor and correct for system sensitivity drift. Detection limits, determined by examining the signal-to-noise ratio and external calibration with the use of liquid standards injected into previously purged seawater samples, were on the order of  $0.01 \text{ pmol L}^{-1}$  for  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$  and  $0.1 \text{ pmol L}^{-1}$  for 1-iodopropane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ ), 2-iodopropane ( $\text{CH}_3\text{CHICH}_3$ ),  $\text{CH}_2\text{ClI}$ ,  $\text{CH}_2\text{BrI}$ , and  $\text{CH}_2\text{I}_2$ . Exact values are subject to system sensitivity drift. Average analytical precision for this experiment, determined by carrying out replicate analyses of each sample, was 2% for  $\text{CH}_3\text{I}$ , 2% for  $\text{C}_2\text{H}_5\text{I}$ , 12% for  $\text{CH}_3\text{CHICH}_3$ , and 3% for  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ .

BHP was estimated from L-[4,5- $^3\text{H}$ ]-leucine (Amersham Pharmacia Biotech) incorporation into bacterial protein (Dixon et al. 2006) with the theoretical conversion factor of  $1.55 \text{ kg C mol}^{-1}$  leucine (Ducklow et al. 2002). For BHP, four replicates and two control samples were incubated in the dark at in situ temperature ( $12^\circ\text{C}$ ) for 45–60 min.

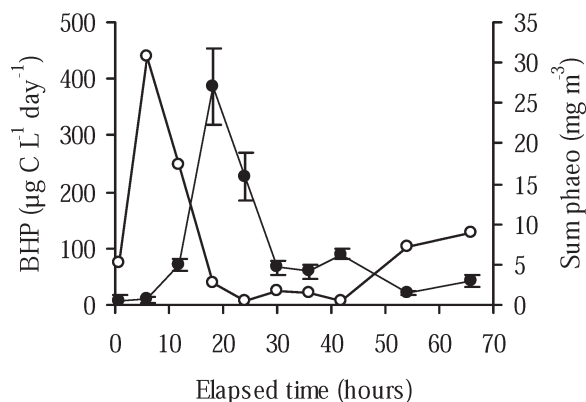


Fig. 2. Changes in bacterial heterotrophic production (BHP, closed symbols) and the sum of the pheopigments (phaeo, open symbols) observed during the incubation of the plankton concentrate collected in the Celtic Sea. Error bars on BHP data are standard deviations of four replicates.

Pheopigment concentrations were determined by high-performance liquid chromatography as described in Walker and Keely (2004).

## Results

The concentrations of  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  increased in incubations of marine aggregates formed by concentrating Celtic Sea plankton (Fig. 1). Maximum iodocarbon concentrations reached in the incubation were  $8.02\text{--}8.07 \text{ pmol L}^{-1}$  for  $\text{CH}_3\text{I}$ ,  $9.03\text{--}9.38 \text{ pmol L}^{-1}$  for  $\text{C}_2\text{H}_5\text{I}$ ,  $0.81\text{--}0.89 \text{ pmol L}^{-1}$  for  $\text{CH}_3\text{CHICH}_3$ , and  $4.01\text{--}4.07$  for  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  in replicates A and B. Initial starting concentrations in the incubation were  $2.23$  and  $2.47 \text{ pmol CH}_3\text{I L}^{-1}$ ,  $1.16$  and  $1.36 \text{ pmol C}_2\text{H}_5\text{I L}^{-1}$ ,  $0.20$  and  $0.21 \text{ pmol CH}_3\text{CHICH}_3 \text{ L}^{-1}$ , and  $0.96$  and  $0.96 \text{ pmol CH}_3\text{CH}_2\text{CH}_2\text{I L}^{-1}$ . The slightly elevated iodocarbon concentrations in the concentrate incubation relative to the controls at  $T = 0$  indicate that the concentrate contained a background level of these compounds. Maximum production rates predicted from derivatives of trend lines applied to the concentration data are presented in Table 1 and range from  $0.01 \text{ pmol L}^{-1} \text{ h}^{-1}$  for  $\text{CH}_3\text{CHICH}_3$  to  $0.31 \text{ pmol L}^{-1} \text{ h}^{-1}$  for  $\text{C}_2\text{H}_5\text{I}$ . The concentrations of the dihalogenated iodocarbons, such as  $\text{CH}_2\text{ClI}$ ,  $\text{CH}_2\text{BrI}$ , and  $\text{CH}_2\text{I}_2$ , were below detection or remained constant throughout the incubation. The concentrations of all iodocarbons remained very low throughout the incubation period in the filtered seawater controls containing no aggregates. BHP and pheopigment analyses carried out alongside the iodocarbon measurements in the aggregate incubations suggested a succession of biological processes (Fig. 2) typical of natural detrital particles (Ploug and Grossart 2000). A peak in pheopigment concentrations ( $30.9 \text{ mg m}^{-3}$ ) at 6 h, indicating microalgal senescence, was followed by a peak in BHP ( $386 \mu\text{g C L}^{-1} \text{ d}^{-1}$ ) at 18 h.

## Discussion

The presence of the detrital material and particles resulting from the concentration process induced enhanced formation of the monoiodinated iodocarbons. Because no production of dihalogenated iodocarbons was observed, it is unlikely that haloperoxidase enzymes mediated the observed increases in  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  concentrations (Butler and Walker 1993). Additionally, because the aggregates were incubated in the

dark, photochemical iodocarbon production observed by Richter and Wallace (2004) can be ruled out. The likely mechanisms for iodocarbon production in the aggregate incubations are alkylation of inorganic iodine (Urhahn and Ballschmiter 1998) or the breakdown of higher molecular mass organohalogenes (Fenical 1982). Formation of monoiodinated organics has been observed via various pathways, including those involving alkylating enzymes or agents such as methylcobalamin (Manley 1994) and an abiotic reaction induced by the oxidation of organic matter by  $\text{Fe}^{3+}$  (Keppler et al. 2003). As in natural detrital particles (Simon et al. 2002), the aggregates incubated here are characterized by high rates of bacterial heterotrophic production (up to  $386 \mu\text{g C L}^{-1} \text{d}^{-1}$ ) compared with the surrounding seawater ( $\sim 13 \mu\text{g C L}^{-1} \text{d}^{-1}$ ). This enhanced microbial activity would be associated with increased rates of organic matter breakdown (Smith et al. 1992), which could supply the precursors required for  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  formation. In support of this, Amachi et al. (2001) demonstrate that bacterial activity in laboratory cultures increases the formation of monoiodinated iodocarbons.

The production of marine aggregates by concentrating plankton for experimental purposes is commonly used (e.g., Ploug and Grossart 2000) for understanding processes occurring on natural detrital particles. The level of concentration we use to produce aggregates ( $\sim 10^3$ ) is comparable to that seen in natural marine particles. For example, natural aggregates have been found to have between one and four orders of magnitude higher microbial densities than the surrounding seawater (Del Negro et al. 2005). Additionally, the rates of BHP observed in our study are within the range of those measured previously on natural detrital particles (Del Negro et al. 2005). However, marine aggregates are known to vary in organic matter content and microbial composition between different geographic locations and depths in the water column. Each of these characteristics could alter the iodocarbon production rate; hence, further study is required to assess this variability.

In support of our observation of iodocarbon production by the aggregates produced in this study, we carried out two studies examining  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  formation by natural aggregates. These included a diatom mucilage aggregation collected from the Celtic Sea and phytodetritus sampled from the top of a box core obtained in Kongsfjord on Svalbad, Norway. Diatom mucilage aggregations have been found in marine waters worldwide (e.g., Rinaldi et al. 1995). Phytodetritus is sedimentary material that collects on the seafloor after the termination of a phytoplankton bloom (Beaulieu 2002). Samples of each of these aggregates were incubated at a detritus-to-seawater volume ratio of 1:50 following the methods of Ploug and Grossart (2000), and iodocarbon concentrations were measured at various time intervals. As in the plankton concentrate, both the mucilage aggregation and phytodetritus were found to produce  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  but not the dihalogenated compounds. Observed iodocarbon production rates are reported in Table 1 and range from 0.03 to  $3.74 \text{ pmol L}^{-1} \text{h}^{-1}$ . These results provide additional evidence to

support the hypothesis that marine detrital particles are hotspots of iodocarbon production.

Marine aggregates are found in marine waters worldwide at a range of densities (Alldredge and Silver 1988). Hence, the degree by which the plankton concentrate, diatom mucilage aggregation, and phytodetritus were diluted in our incubations might be relevant to some ocean areas but not others. The high levels of biological material included in our experiments mean that the iodocarbon production rates we report are likely to apply to water masses containing dense aggregations of detrital particles. This could be in coastal regions after the termination of a phytoplankton bloom (Alldredge et al. 2002), during large aggregation events such as those observed in the Adriatic Sea (Rinaldi et al. 1995), or in density discontinuities in the water column (MacIntyre et al. 1995). Such marine areas or depths could be hotspots of iodocarbon production. For example, subsurface maxima in iodocarbon concentrations observed in previous studies (e.g., Moore and Groszko 1999) could be the result of an increased density of detrital particles at specific depths in the water column. Only the  $\text{CH}_3\text{I}$  production rate observed here in the phytodetritus ( $0.03 \text{ pmol L}^{-1} \text{h}^{-1}$ ) is comparable to those calculated for or observed in natural bulk water samples in previous studies. The  $\text{CH}_3\text{I}$  production rates observed in the plankton concentrate ( $0.27 \text{ pmol L}^{-1} \text{h}^{-1}$ ) and diatom mucilage aggregation ( $0.43 \text{ pmol L}^{-1} \text{h}^{-1}$ ) are approximately an order of magnitude greater than the maximum production rates reported for bulk water samples. For example, Moore and Groszko (1999) estimated  $\text{CH}_3\text{I}$  production rates in areas of the Atlantic and Pacific Oceans to be between  $1.3 \times 10^{-3}$  and  $2.9 \times 10^{-2} \text{ pmol L}^{-1} \text{h}^{-1}$ . Additionally, Moore (2006) observed  $\text{CH}_3\text{I}$  production rates of between  $4.0 \times 10^{-3}$  and  $4.0 \times 10^{-2} \text{ pmol L}^{-1} \text{h}^{-1}$  in incubations of natural water samples collected in the North Atlantic. Given that production rates are relatively low in the bulk water, the diffusion and dilution of iodocarbons produced by dense aggregate accumulations could make an important contribution to the  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CHICH}_3$ , and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  inventory of the surrounding seawater. In water samples that contain low densities of aggregates, the contribution of detrital particles to the iodocarbon production rate per volume of seawater could be relatively low. In such water samples, iodocarbon production might be dominated by other formation pathways, such as photochemistry (Richter and Wallace 2004).

In an ideal world, incubation experiments would not be done in enclosed containers because of the "bottle effects" that have been recognized for many years (Venrick et al. 1977). One particular issue in studies such as this that involve large amounts of biological material is oxygen consumption. Until the mechanisms for iodocarbon formation are better understood, we cannot eliminate the possibility that chemical changes, such as a switch to anoxic conditions, could alter  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  production rates. However, calculations that are based on the BHP measurements we made for the plankton concentrate experiment suggest that oxygen consumption resulting from bacterial activity would not have been sufficient to lead to anoxic conditions in the incubation syringes during the period of study. We estimate that only 5% of the total oxygen in the

syringes would have been consumed. Of course, respiration by other heterotrophic organisms such as protists and microalgae would further increase oxygen consumption, but this cannot be estimated with the information available. Although anoxia and other chemical changes could be induced during experimental incubations, we note that natural aggregates can become anoxic in the natural environment (Alldredge and Cohen 1987). Therefore, even if anoxia had occurred, this might not have produced results that are atypical of the natural situation. Ultimately, iodocarbon production should be studied under the range of environmental conditions that could occur in the aggregate microenvironment.

In this report of iodocarbon production by marine aggregates, we provide information on a possible source of  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and  $\text{CH}_3\text{CHICH}_3$  in seawater. Further study is required to understand the mechanisms and variability of iodocarbon formation in detrital particles, as well as the significance of this process in mediating sea-to-air iodine flux. Studying relationships between iodocarbon production and aggregate characteristics, such as particulate organic carbon, age, bacterial activity, or starting primary producer, will help to estimate the significance of the link between detrital particles and oceanic iodine emissions.

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