Isoprene production in the water column and sediment in Funka Bay, Hokkaido, Japan

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Abstract

We conducted shipboard observations in Funka Bay, Hokkaido, Japan, in 2015, 2016 and 2019 to observe temporal variations of isoprene (C$_5$H$_8$) concentration in water and sediment. We found increases in C$_5$H$_8$ concentrations below and within the euphotic zone, which were associated with chl-a peaks and changes in nutrient and dissolved oxygen (DO). We found a C$_5$H$_8$ peak in the subsurface layer within the euphotic zone at 20–30 m depth in May–June 2019 that coincided with a decrease in DO, suggesting that there was net oxygen consumption. We hypothesize that the rapid cycle of regenerated production in the subsurface layer in early summer resulted in C$_5$H$_8$ production (1.00–1.75 pmol (μg chl-a) d$^{-1}$ at 30 m), decreased DO, relatively high chl-a levels, and nutrient depletion. We propose that C$_5$H$_8$ can be used as a new chemical parameter reflecting primary production, in addition to the common parameters of chlorophyll-a, nutrients, and oxygen. We attributed a C$_5$H$_8$ peak at the surface in May–June 2019 to photosynthetic production of C$_5$H$_8$ associated with new production, likely stimulated by the sporadic input of nutrients to the sea surface. In addition, this is the first study to report the presence of C$_5$H$_8$ in seafloor sediments. We found very high C$_5$H$_8$ concentrations in the sediment from the surface to 5 cm depth. We propose that C$_5$H$_8$ production and degradation by the bacterial community in coastal marine sediments are approximately in balance.

Keywords

phytoplankton, volatile organic compound (VOC), nutrient, coastal ocean, primary production

Dates

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Introduction

Isoprene (C$_5$H$_8$) is the most abundant biogenic volatile organic compound (BVOC) emitted to the atmosphere, mainly from terrestrial vegetation (Guenther et al., 2012). C$_5$H$_8$ affects the oxidation capacity of the atmosphere by reacting with other reactive gases (Lelieveld et al., 2008) and contributes to the formation of secondary organic aerosols (Carlton et al., 2009). Although terrestrial plants account for much of the global C$_5$H$_8$ emissions to the atmosphere, marine-derived C$_5$H$_8$ can also influence atmospheric chemistry over remote parts of the
Methods

the basis of these previous studies, we expect that oligotrophic subtropical oceans with low chl-\(\text{a}\) changes in C\(_{5}\) (~17 pmol L\(^{-1}\)). In contrast, the lowest levels (~17 pmol L\(^{-1}\)) have been found in the surface waters of oligotrophic subtropical oceans with low chl-\(\text{a}\) (~0.05 \(\mu g\) L\(^{-1}\); Ooki et al., 2015). As for C\(_{5}\) production rates, Booge et al. (2018) estimated a significantly higher rate for the tropical Atlantic Ocean, where it seems that there had been relatively high primary production, with average NO\(_{3}^-\) concentrations <3 pmol L\(^{-1}\) (read from their Fig. 6 and Fig. 7), than for the coastal Indian Ocean. On the basis of these previous studies, we expect that changes in C\(_{5}\) in seawater are synchronized with changes in other biochemical parameters related to primary production such as concentrations of chlorophyll-\(\text{a}\), nutrients, and dissolved oxygen. The first purpose of this study, then, is to propose the use of C\(_{5}\) as a parameter reflecting marine primary production.

The second purpose of this study is to investigate the possibility of marine C\(_{5}\) emissions in the water column and sediment that are not directly related to photosynthesis by marine plants. Non-photosynthetic C\(_{5}\) production in terrestrial and marine environments has been suggested by some studies. C\(_{5}\) is formed by terrestrial plants via the breakdown of stored carbohydrates when photosynthesis is blocked (Lerdau et al., 1997), and C\(_{5}\) is emitted by cells of all living organisms (Sanadze, 2004). Terrestrial soils can act as strong sinks and sources of C\(_{5}\) through bacterial activity (Fall and Copley, 2000). However, Wang et al. (2018) found no significant C\(_{5}\) flux between forest soil and air, whereas there were significant emissions of the other, heavier non-methane hydrocarbons from the soil. This suggests that C\(_{5}\) production and degradation in soil may be approximately in balance. Recently, Ooki et al. (2019) reported the oceanic production of C\(_{5}\) by diatoms under dark conditions from repetitive observations in Funka Bay, Hokkaido, Japan in 2014. They concluded that diatom aggregates on the seafloor released C\(_{5}\) in darkness, resulting in increased concentrations in bottom water. Then, we hypothesized that marine sediment is a source of C\(_{5}\) and aimed to firstly measure the C\(_{5}\) concentration in pore water of marine sediment.

Methods

Shipboard observations and sample collection

Shipboard observations were conducted in Funka Bay, Hokkaido, Japan, in 2015, 2016, and 2019 using the training ship (T/S) Ushio-maru. Water samples were collected at station 30 located near the center of the bay with a bottom depth of 96 m (Fig. 1). Seawater samples were collected along with conductivity-temperature-depth (CTD) observations at depths of 0, 5, 10, 20, 30, 40, 50, 60, 65, 70, 75, 80, 85, 95 (1 m above the seafloor), and 96 m (just above the seafloor). The seawater samples at 96 m depth just above the seafloor were collected from sediment core samples, and the samples at 95 m (approximately 1 m above the seafloor) were collected with a Van-Dorn sampling bottle (Rigo Co. Ltd., Saitama, Japan). The sediment core samples were collected by gravity-type core sampler (Rigo Co. Ltd., Saitama, Japan) in 2019. Sediment cores were cut into 1 cm sections from the surface (seafloor, 0 cm) to a depth of 5 cm. The pore water was collected from each section by using a syringe and pulling the water through a porous ceramic filter cup using a soil water sampler (DIK-8393, Daiki Rica Kogyo Co. Ltd., Saitama, Japan). To stop microbial activity, 100 \(\mu L\) and 50 \(\mu L\) of saturated mercuric chloride (HgCl\(_{2}\)) solutions were added to the seawater bottle (120 mL) and pore water bottle (32 mL), respectively.

Analytical procedures

Chl-\(\text{a}\) concentrations in the discrete seawater samples were measured by the fluorometric method using a fluorometer (model 10-AU, Turner Designs, Inc.). Concentrations of nutrients (NO\(_{3}^-\), NO\(_{2}^-\), NH\(_{4}^+\), Si(OH)\(_{4}\), and PO\(_{4}^{3-}\)) were measured by colorimetric methods using a QuAAtro system (BL-Tec, Osaka, Japan). Dissolved oxygen (DO) was determined by Winkler titration and the apparent oxygen utilization (AOU) was calculated by subtracting the measured oxygen concentration from the dissolved oxygen concentration at saturation under in situ temperature and salinity. Dissolved organic gases in seawater and pore water sample were collected by the purge-and-trap method. The total volume of seawater (125 or 32 mL) in the sample bottle was introduced into a purge vessel by a high-purity nitrogen carrier, and the dissolved...
gases were consecutively purged by bubbling with nitrogen at 65 mL min\(^{-1}\) for 35 min. The purged gas sample was collected in a cold-trap containing adsorption resin (Tenax TA, 10 mg) cooled to \(-90^\circ\)C. The cold-trap samples were stored in a freezer (\(-30^\circ\)C) until analysis by gas chromatography–mass spectrometry (GC–MS). Concentrated C\(_5\)H\(_8\) in the cold-trap were thermally desorbed and transferred to an automated pre-concentration GC–MS analytical system (capillary column: Porabond Q, 0.32 mm, 50 m; GC–MS: Agilent 5973, 6890). The analytical procedure for C\(_5\)H\(_8\) is described elsewhere (Ooki and Yokouchi, 2011; Ooki et al., 2019).

**Results and Discussion**

We focus on the temporal variation of biogeochemical parameters in 2019. Time sections of all years and vertical profiles in 2019 are shown in supplementary figures (Fig. s3–s5) and observation data in 2019 are provided in supplementary data (FB-2019-data-bottle, FB-2019-data-CTD).

### Hydrographic features

In Funka Bay, there are two source water-masses, Oyashio (O) water and Tsugaru (T) water, and two modified water masses, winter (W) water and summer (S) waters. The transitional waters are defined as W-O, O-S, S-T, and WOT. The mixed-layer depth and euphotic-zone depth (1% of surface photosynthetically active radiation [PAR]) are also shown. The numbered rectangles outlined with red and white dotted lines indicate the time–depth ranges where we analysed temporal changes in biogeochemical parameters; the numbers 1, 2, and 3 correspond to the time–depth ranges described in the main text.

![Fig. 2. Temporal change of water-mass structure in 2019 at station 30 in Funka Bay, Japan. The two main source water masses are Tsugaru (T) and Oyashio (O) waters and the two modified waters are winter (W) and summer (S) waters. The transitional waters are defined as W-O, O-S, S-T, and WOT. The mixed-layer depth and euphotic-zone depth (1% of surface PAR) are also shown. The numbered rectangles outlined with red and white dotted lines indicate the time–depth ranges where we analysed temporal changes in biogeochemical parameters; the numbers 1, 2, and 3 correspond to the time–depth ranges described in the main text.](image-url)
dates. The time periods and depth ranges over which the temporal changes in biogeochemical parameters were examined were (1) 30–50 m between 4 and 15 March 2019, (2) 0–5 m between April and August 2019, and (3) 20–30 m between April and June 2019 (Fig. 2).

**Changes in biogeochemical parameters in the water column**

We prepared time sections of the biogeochemical parameters chl-a, AOU, DO, NO$_3^-$, and C$_8$H$_{16}$ in 2019 (Fig. 3a-h). Time sections for all years (Fig. s3) and vertical profiles for 2019 (Fig. s4, s5) are also provided in supplementary figures. Overall, we found very high chl-a concentrations (>15 μmol L$^{-1}$) in March (Fig. 3a, s4b), suggesting the occurrence of a spring diatom bloom. NO$_3^-$ concentrations decreased in the surface mixed layer after the peak of the bloom on 4 March 2019 (Fig. 3c, s4a). After the bloom, small chl-a peaks were found below the surface mixed layer within the euphotic zone on 12 May and 12 June 2019 (Fig. 3b, s5b). We found large negative values of AOU (<−40 μmol L$^{-1}$) in March–May 2019 (Fig. 3c, s4c, s5c), suggesting net O$_2$ production by photosynthesis, in the surface mixed layer during the bloom and post-bloom (March–April), and below the surface mixed layer within the euphotic zone on 14 April. Details of changes in biogeochemical parameters within depth–time ranges (1)–(3), which are indicated by rectangles outlined by red and white dotted lines with numbers (1–3) in Fig. 3, are described below.

**Range (1): 30–50 m between 4 and 15 March 2019**

The depth range of 30–50 m was below the surface mixed-layer (i.e. a subsurface layer) and euphotic-zone depths. The euphotic-zone depths (1% PAR depth) were 11 m and 18 m on 4 March and 15 March, respectively. And, the depths at which PAR was 0.1% of the surface PAR were 18 m and 30 m on 4 March and 15 March respectively. We considered that the depth range (30–50 m) was substantially dark. NO$_3^-$ concentrations at 30–50 m decreased substantially at these dates (Fig. 3c, s4a). The reason for the NO$_3^-$ decrease is discussed in another paper. The lack of any substantial change in DO between these dates (Fig. 3d, s4d) indicates that there was no net O$_2$ production by photosynthesis. Although we did not detect photosynthetic activity in the dark subsurface layer (30–50 m), we found an increase in C$_8$H$_{16}$ concentrations at that layer from 22.3–30.2 pmol L$^{-1}$ to 31.1–52.6 pmol L$^{-1}$ between these two dates (Fig. 3g, s4e). We attribute the peaks in C$_8$H$_{16}$ concentration at the surface (0 m) to photosynthetic production by phytoplankton associated with the primary production stimulated by sporadic NO$_3^-$ input. On 29 August 2019, although a substantial peak of C$_8$H$_{16}$ was found at the surface (147 pmol L$^{-1}$ at 0 m; 54 pmol L$^{-1}$ at 5 m) and 12 June (43 pmol L$^{-1}$ at 0 m; 37 pmol L$^{-1}$ at 5 m (Fig. 3g, s5e). We attribute the peaks in C$_8$H$_{16}$ concentration at the surface (0 m) to photosynthetic production by phytoplankton which had fully consumed sporadically supplied NO$_3^-$ to the surface before the observation date. Enhanced regenerated production at the surface would have caused the C$_8$H$_{16}$ production in August. In contrast, there were not any peaks of C$_8$H$_{16}$ and NO$_3^-$ at the surface in 2015 and 2016 (Fig. s3b, s3d). We conclude that sporadic input of NO$_3^-$ to the surface water in May–June stimulated photosynthetic production of C$_8$H$_{16}$ forming the obvious peak at the surface in August.

**Range (2): 0–5 m between April and August 2019**

We examine the range (2) in 2019. The chl-a concentration at 0 m gradually increased from 14 April 2019 (below the detection limit [DL, 0.05 μg L$^{-1}$]) to 12 May (0.40 μg L$^{-1}$) and 12 June (1.1 μg L$^{-1}$). On 14 April, sufficient amount of PO$_4^{3-}$ (0.31–0.40 μmol L$^{-1}$) remained in the euphotic zone (within 18 m), although, NO$_3^-$ (<0.05 μmol L$^{-1}$) and Si(OH)$_4$ (<0.1 μmol L$^{-1}$) were not detected. On 12 May and 12 June, we found relatively high concentrations of NO$_3^-$ at 0 m (0.29 μmol L$^{-1}$ on 12 May; 0.24 μmol L$^{-1}$ on 12 June) compared with the lowest levels (<0.05 μmol L$^{-1}$) at 5–20 m on both dates. In contrast to the NO$_3^-$ depletion at 5–20 m in May–June, Si(OH)$_4$ was detected at low levels (0.32–0.58 μmol L$^{-1}$). We assumed that there was sporadic input of nutrients to the surface layer in May–June (e.g. riverine input, rainfall input) and that this nutrient input had stimulated the surface primary production.

Corresponding to the NO$_3^-$ enhancement at the surface, there were obvious peaks of C$_8$H$_{16}$ at the surface (0 m) compared with the concentrations at 5 m: 12 May (54 pmol L$^{-1}$ at 0 m; 22 pmol L$^{-1}$ at 5 m) and 12 June (43 pmol L$^{-1}$ at 0 m; 37 pmol L$^{-1}$ at 5 m (Fig. 3g, s5e). We attribute the peaks in C$_8$H$_{16}$ concentration at the surface (0 m) to photosynthetic production by phytoplankton which had fully consumed sporadically supplied NO$_3^-$ to the surface before the observation date. Enhanced regenerated production at the surface would have caused the C$_8$H$_{16}$ production in August. In contrast, there were not any peaks of C$_8$H$_{16}$ and NO$_3^-$ at the surface in 2015 and 2016 (Fig. s3b, s3d). We conclude that sporadic input of NO$_3^-$ to the surface water in May–June stimulated photosynthetic production of C$_8$H$_{16}$ forming the obvious peak at the surface in August.

**Range (3): 20–30 m between April and June 2019**

We examine the range (3) in 2019. Chl-a showed an obvious peak at 20–30 m (below the surface mixed layer but within the euphotic zone) on 12 May and 12 June 2019 (Fig. 3b, s5b), where NO$_3^-$ levels were below the detection limit (<0.05 μmol L$^{-1}$). DO concentration slightly decreased from 14 April (379–383 μmol L$^{-1}$) to 30–50 m were close to this estimated range. We therefore conclude that the emission of C$_8$H$_{16}$ from suspended diatoms in the dark subsurface layer resulted in the observed concentration increase when a massive diatom bloom occurred in the upper surface layer.
12 May (366–378 μmol L\(^{-1}\)), suggesting that production and consumption of O\(_2\) were approximately balanced between the two dates. By 12 June, DO concentration at 30 m was decreased from 378 μmol L\(^{-1}\) (12 May) to 364 μmol L\(^{-1}\) (12 June), suggesting net O\(_2\) consumption after 12 May. C\(_5\)H\(_8\) increased from 14 April (48.5–48.6 pmol
chl-a to 12 May (52.1–54.5 pmol L\(^{-1}\)) and 12 June (52.4–86.3 pmol L\(^{-1}\)) at 20–30 m (Fig. 3g, s5e), forming peaks at that depth range on 12 May and 12 June. We attribute the increased C\(_{3}\)H\(_{8}\) to photosynthetic production by phytoplankton, which would have experienced limited growth due to a lack of NO\(_{3}^{-}\) because PO\(_{4}^{3-}\) and Si(OH)\(_{4}\) were not depleted.

The community production in summer in Funka Bay is reportedly dominated by regenerated primary production, which is fueled by recycling ammonium in the euphotic zone (Kudo and Matsunaga, 1999). Thus, we consider the increased chl-a (Δchl-a = +0.44 μg L\(^{-1}\)) at 30 m from 12 May to 12 June to have been partially sustained by regenerated production. Another reason for the chl-a increase at 30 m is new production supported by diffusive transport of nutrients from the deeper layer. Here, we estimate the diffusive transport of NO\(_{3}^{-}\) between 30 m and 40 m from 12 May to 12 June. There is not any previous study to have measured diffusive coefficients (K\(_{p}\)) in Funka Bay. We referred a range of K\(_{p}\) (10\(^{-6}–10^{-3}\) m\(^{2}\) s\(^{-1}\)) measured just below the mixed layer (30 m) at the western subarctic Pacific in summer (Dobashi et al., 2021). The range of diffusive transport of NO\(_{3}^{-}\) was calculated to be 0.00014–0.0014 μmol m\(^{-1}\) s\(^{-1}\) between 30 m and 40 m, which could result in concentration increase of 0.036–0.36 μmol L\(^{-1}\) at 30 m for 31 days. Using Redfield ratio (C/N = 106/16) and carbon content (μg-C) per unit chlorophyll-a (μg chl-a) of 11.6 μg-C (μg Chl-a\(^{-1}\)) (Ban et al., 2000), the diffusive transport of NO\(_{3}^{-}\) could result in chl-a increase of 0.25–2.5 μg L\(^{-1}\). The observed increase of chl-a (+0.44 μg L\(^{-1}\)) at 30 m was within this calculated range.

We conclude that in the stratified, oligotrophic subsurface water within the euphotic zone in early summer, the rapid cycle of regenerated production and new production supported by diffusive transport of nutrients resulted in C\(_{3}\)H\(_{8}\) production and occurrence of obvious C\(_{3}\)H\(_{8}\) peak, following a decrease in DO, relatively high chl-a concentrations, and low nutrient levels. Similarly, the subsurface maximums of C\(_{3}\)H\(_{8}\) just above the euphotic-zone depth were found in summer (May–August) of all years (Fig. s3d).

We estimated the C\(_{3}\)H\(_{8}\) production rate per unit chl-a to be 1.00–1.75 pmol (μg chl-a\(^{-1}\)) d\(^{-1}\) at 30 m between these dates using chl-a concentration range of 0.59–1.02 μg L\(^{-1}\) at 30 m of both dates, which were similar to the rate (0.82 pmol [μg chl-a\(^{-1}\)]d\(^{-1}\)) at the surface during the 2014 bloom in the bay (Ooki et al., 2019). This rate is much lower than the rate of 7.4 pmol (μg chl-a\(^{-1}\)) d\(^{-1}\) at 20–40 m between July and August 2014 in the bay, when the chl-a level was considerably lower (0.16 μg L\(^{-1}\)) (Ooki et al., 2019). From these findings, we suggest that the rapid cycle of regenerated production with lower chl-a levels leads to a higher C\(_{3}\)H\(_{8}\) production rate per unit chl-a.

### Production and loss of C\(_{3}\)H\(_{8}\) in the euphotic zone

We calculate the sea-to-air flux (loss to the air) and net production of C\(_{3}\)H\(_{8}\) in the euphotic zone between 12 May and 12 June 2019. The sea-to-air flux calculation was according to Johnson (2010) using transfer velocity (K\(_{soa}\) = 0.222 u\(^{2}\) + 0.333u) by Nightingale et al. (2000). We used hourly wind speed (u) collected at the Muroran meteorological weather station located at the coastal site of the Funka bay. Daily sea surface temperature of Funka Bay was obtained from Sapporo regional headquarters of Japan meteorological agency. We used Henry’s law constant of C\(_{3}\)H\(_{8}\) in seawater by Ooki and Yokouchi (2011). Atmospheric C\(_{3}\)H\(_{8}\) concentration was assumed to be 80 ppt according to Ooki et al. (2019). The hourly sea surface C\(_{3}\)H\(_{8}\) concentration was linearly interpolated from the observation data on 12 May and 12 June. The average sea-to-air flux of C\(_{3}\)H\(_{8}\) was calculated to be 30.5 nmol m\(^{-2}\) d\(^{-1}\), where the average wind speed was 3.4 m s\(^{-1}\). The calculated sea-to-air flux leads to concentration loss of 94.4 pmol L\(^{-1}\) in the surface mixed layer (0–10 m) between 12 May and 12 June, which is much higher than the surface concentrations (42.9–53.7 pmol L\(^{-1}\)). Even though the considerable amount of C\(_{3}\)H\(_{8}\) were emitted to the air, concentration maximum was maintained at the surface (Fig. 3g, s5e). It suggests that phytoplankton production of C\(_{3}\)H\(_{8}\) at the surface water overwhelmed the loss to the air.

We have obtained net production rate per unit chl-a to be 1.00–1.75 pmol (μg chl-a\(^{-1}\)) d\(^{-1}\) at 30 m. Considering this rate and the surface chl-a concentrations (0.40–1.04 μg L\(^{-1}\)), net C\(_{3}\)H\(_{8}\) production of 12.4–56.1 pmol L\(^{-1}\) could occur at the surface between 12 May and 12 June. The calculated net production at the surface could explain only 13–59% of the sea-to-air flux loss (94.4 pmol L\(^{-1}\)). We considered that actual C\(_{3}\)H\(_{8}\) production rate at the surface was higher than the 30-m depth because of higher biological productivity stimulated by stronger light intensity at the surface (27 times of PAR at 30-m depth) and higher concentrations of NO\(_{3}^{-}\) (0.24–0.29 μmol L\(^{-1}\)) at the surface (approximately 6 times of NO\(_{3}^{-}\) at 30-m depth). Although many uncertainties remain, we propose that C\(_{3}\)H\(_{8}\) can be used as a new chemical parameter reflecting new and regenerated production, in addition to the common parameters of chlorophyll-a, nutrients, and oxygen.

### Sediment source of C\(_{3}\)H\(_{8}\)

We determined C\(_{3}\)H\(_{8}\) concentrations in sediment pore water on the seafloor of Funka Bay (Fig. 3h). The overall average C\(_{3}\)H\(_{8}\) concentration in pore water (260 pmol L\(^{-1}\)) was 5 times the water-column average (44 pmol L\(^{-1}\)). We found quite high C\(_{3}\)H\(_{8}\) concentrations in pore water on 15 February, 14 April, and 29 August at the sediment surface and in deeper sediment layers. High concentrations were also found in the bottom water just above the sea-
floor at depths of 95 and 96 m, where the overall averages of $C_{2}H_{8}$ were 93 pmol L$^{-1}$ (SD = 98, n = 18) at 95–96 m and 31 pmol L$^{-1}$ (SD = 16, n = 9) at 85 m. These results convinced us that the sediment is a source of bottom-water $C_{2}H_{8}$. Because living diatoms produce $C_{2}H_{8}$ in darkness (Ooki et al., 2019), we hypothesize that fresh diatom aggregates that settle on the seafloor can produce $C_{2}H_{8}$. In addition, $C_{2}H_{8}$ can be produced from organic matter that had been buried in the deeper sediment. From the same sediment core samples collected at the Funka Bay, high concentrations of iodoethane, which is a volatile organic iodine gas derived from sedimented diatom aggregate, have been also found in pore water of the sediment surface after the spring bloom 2019 (Ooki et al., accepted).

The influence of $C_{2}H_{8}$ from source sediment seems to be limited to within the bottom water just above the seafloor. In contrast, the influence of nutrients regenerated from organic matter on the seafloor, for example NO$_3^{-}$ in Fig. 3c, extended to the upper bottom layer (75 m) in summer. Kudo et al. (2007) reported that the decomposition of organic matter produced during the spring bloom in Funka Bay, which then settled to the seafloor, was mostly complete by August and resulted in a supply of regenerated nutrients throughout the bottom layer. It is possible that a specific type of $C_{2}H_{8}$ decomposer in the sediment created a patchy pattern of high and low $C_{2}H_{8}$ concentrations in the sediment over time (Fig. 3h) and prohibited the expansion of sediment-derived $C_{2}H_{8}$ to the upper bottom layer. Alvarez et al. (2009) reported the rapid degradation of $C_{2}H_{8}$ from estuarine sediment by $C_{2}H_{8}$-degrading bacteria that can use n-alkanes as a carbon source or energy. They also found that the most rapid $C_{2}H_{8}$ degradation coincides with the highest rate of $C_{2}H_{8}$ production in the sediment. As we summarized in the introduction to this article, $C_{2}H_{8}$ production and degradation in terrestrial soil is approximately balanced. Similarly, we propose that $C_{2}H_{8}$ production and degradation in marine sediment are also approximately in balance. Since all archaea have membrane lipids composed of isoprenoids (Koga and Morii, 2007), $C_{2}H_{8}$ could be emitted from archaea through their biosynthesis of isoprenoid or break down of their membrane lipids. Crenarchaeota accounted for approximately 11% of bacterial amplicons collected from marine sediment surface (Zhang et al., 2017), and marine sediment is abundant in methane-consuming archaeabacteria that was detected by lipid biomarker having specific isoprenoid chain (Hinrichs et al., 1999). We deduced that $C_{2}H_{8}$ production could occur in marine sediment from the surface to deeper sediment associated with bacterial activity including archaea.

### Influence of bacterial degradation of $C_{2}H_{8}$ in water column

Since the ubiquitous marine hydrocarbon-degrader, Alcanivorax borkumensis, can degrade isoprene (Alvarez et al., 2009), bacterial degradation of $C_{2}H_{8}$ could occur in water column of Funka Bay. Average concentrations of $C_{2}H_{8}$ in water column (0–85 m) decreased from 39.1 pmol L$^{-1}$ on 28 October to 26.3 pmol L$^{-1}$ on 14 December when the Tsugaru (T) water remained in the bay. The decreased amount of $C_{2}H_{8}$ in the water column (1088 nmol m$^{-2}$) was much less than the sea-to-air loss of 4060 nmol m$^{-2}$ between the two observation dates. It implies that phytoplankton production of $C_{2}H_{8}$ compensated the sea-to-air loss and was much greater than bacterial degradation of $C_{2}H_{8}$ in water column.

### Conclusion

We conducted repetitive observations in Funka Bay in 2015, 2016, and 2019. We found increases in $C_{2}H_{8}$ concentrations (1) in the dark subsurface layer after the peak of the phytoplankton bloom in March 2019, (2) at the surface (0 m) from April to June 2019 when there was sporadic nutrient input, and (3) below the surface mixed layer within the euphotic zone in summer of all years. We also found very high concentrations in the sediment from the surface to deeper layers (5 cm) and in the bottom water just above the seafloor (4). From these findings, we reached the following conclusions.

1. Because photosynthetic O$_2$ production was not detected below the euphotic zone between 4 and 15 March 2019, we attribute the $C_{2}H_{8}$ increase to dark production by diatoms that had grown in the surface waters and sank to the subsurface layer at 30–50 m. This is the first study to present observational evidence of dark production of $C_{2}H_{8}$ in the subsurface layer.

2. We detected an obvious peak of $C_{2}H_{8}$ at the surface (0 m), compared with 5 m depth, from April to June 2019. An increase in the NO$_3^{-}$ supply was also detected at the surface in May and June. We conclude that the peaks in $C_{2}H_{8}$ at the surface were due to photosynthetic production of $C_{2}H_{8}$ by phytoplankton associated with new production stimulated by sporadic nutrient input.

3. We found a peak of $C_{2}H_{8}$ at 20–30 m on 12 May, which is consistent with our detections of a chl-a peak. We conclude that the increased $C_{2}H_{8}$ was due to photosynthetic production by phytoplankton. We also found an obvious peak of $C_{2}H_{8}$ at 30 m on 12 June, where we detected net O$_2$ consumption between 12 May and 12 June. We conclude that the increased $C_{2}H_{8}$ was produced by photosynthesis associated with regenerated production. We propose that $C_{2}H_{8}$ can be used as a new chemical parameter reflecting features of new and regenerated productions.

4. We found very high concentrations of $C_{2}H_{8}$ in the...
sediment from the surface (0 cm) to deeper layers (5 cm) and in bottom water just above the seafloor. We are certain that the sediment is a source of C\textsubscript{6}H\textsubscript{10} to bottom water, however, its influence was limited to within the bottom water just above the seafloor. In addition, the high C\textsubscript{6}H\textsubscript{10} concentrations occurred only occasionally and were patchy in the sediment. We conclude that C\textsubscript{6}H\textsubscript{10} is produced by fresh diatom aggregates on the surface of the marine sediment as well as by heterotrophic bacteria and/or archaea decomposing organic matter buried in the sediment. We propose that C\textsubscript{6}H\textsubscript{10} production and degradation by the bacterial community in coastal marine sediments are approximately in balance.

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\textbf{References}


**Supplementary Materials**

https://www.jstage.jst.go.jp/article/geochemj/56/5/56_GJ22013/_article

• Figures S1–S5