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Concentration maxima of volatile organic iodine compounds in the bottom layer water and the cold, dense water over the Chukchi Sea in the western Arctic Ocean: a possibility of production related to degradation of organic matter

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Abstract

We conducted a shipboard observation over the Chukchi Sea and the Canada Basin in the western Arctic Ocean in September and October 2012 to obtain vertical distributions of four volatile organic iodine compounds (VOIs) in seawater. VOIs are believed to play a role in ozone destruction in the troposphere and lower stratosphere. The VOIs observed in this study were iodomethane (CH_3I), iodoethane (C_2H_5I), diiodomethane (CH_2I_2) and chloroiodomethane (CH_2ClI). Maximum concentrations of the four VOIs were found in the bottom layer water over the Chukchi Sea shelf, in which layer the maximum concentration of ammonium (NH_4^+) also occurred. A significant correlation was observed between C_2H_5I and NH_4^+ (correlate coefficient $R = 0.93$) and between CH_3I and NH_4^+ ($R = 0.77$), suggesting production of these VOIs increased with degradation of organic matter. Over the northern Chukchi Sea shelf–slope area, concentration maxima of CH_2I_2, CH_2ClI, and CH_3I were found in the subsurface cold, dense water (CDW). A large nitrogen deficit (N-deficit = $NH_4^+ + NO_3^- + NO_2^- - 16PO_4^{3-}$) simultaneously occurred in this water, suggesting production of the three VOIs in the sediment or the bottom layer water over the shelf, probably in association with degradation of organic matter. We conclude that VOI production over the Chukchi Sea shelf can be largely attributed to the degradation of organic matter that is produced in the highly productive shelf water. High concentrations of CH_2ClI were also found in the Alaskan Coastal Water (ACW) from the Bering Strait to the surface of the northern Chukchi slope. The VOIs that originated at the Chukchi Sea shelf are expected to be laterally transported to the Arctic Ocean Basin though the subsurface CDW and the surface ACW.

1 Introduction

Volatile organic iodine compounds (VOIs) such as iodomethane (CH_3I), iodoethane (C_2H_5I), diiodomethane (CH_2I_2) and chloroiodomethane (CH_2ClI) are known to pro-

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vide iodine atoms to the atmosphere, resulting in catalytic ozone destruction in the troposphere and lower stratosphere (World Meteorological Organization (WMO), 2010). These VOIs have the potential to deplete ozone in boundary layer air on a wide scale (e.g., Carpenter et al., 1999). Arctic ozone depletion during polar sunrise has been indicated, by both observational and theoretical studies (e.g., Spicer et al., 2002), to result from the release of gaseous Br_2 and BrCl from the surface of sea ice and/or snow. More recent theoretical studies have indicated that reactive VOIs such as CH_2I_2 would be extremely effective agents for tropospheric Arctic ozone depletion in polar sunrise, and that iodine compounds added to a Br_2/BrCl mixture have a significantly greater ozone depletion effect than additional Br_2 and BrCl molecules only (Carpenter et al., 2005). To understand the flux patterns of VOIs emitted from the ocean to the Arctic air, it is necessary to investigate VOI distribution in seawater and VOI production and loss processes.

The concentrations of VOIs in seawater of the Arctic Ocean have been measured in the following studies. CH_3I, CH_2I_2, CH_2ClI, and C_3H_7I were measured around Ny Ålesund (80° N) in Spitzbergen, Norway in September (Schall and Heumann, 1993). CH_3I was measured in the Greenland and Norwegian Seas (63–75° N) in November (Happell and Wallace, 1996). CH_2ClI was measured in the Arctic Ocean Basin from Barrow, Alaska to Svalbard (71–90° N) (Karlsson et al., 2013). CH_3I, C_2H_5I, CH_2ClI, and C_3H_7I were measured in the Greenland and Norwegian Seas (78–82° N) in June and July (Atkinson et al., 2014). As can be seen, each of these studies considered VOIs in the Atlantic sector of the Arctic Ocean. In contrast, there have been very few measurements of VOIs in the western (Pacific sector) Arctic Ocean, which has vast continental shelves.

In recent global mapping of VOIs in the surface mixed layer (Ooki et al., 2015), the Chukchi Sea shelf in the western Arctic Ocean was found to have the second-highest concentration of CH_2ClI (ave. 5.7 pmol L^{-1}) among all water types (tropical, subtropical, transitional, subpolar and polar) and ocean areas (shelf, slope, and basin). In the shelf–slope areas, CH_2ClI had the largest flux to the atmosphere among three VOIs

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(CH_3I, C_2H_5I, and CH_2ClI). The vast Chukchi Sea shelf and the adjacent sea areas might have an impact on organic iodine flux to the Arctic atmosphere. Although these various studies have measured distribution of VOIs, there is no established approach that will enable us to determine how VOI distributions and processes that produce them are impacted by the environmental conditions – including water mass structure and biochemical parameters, such as nutrients and chlorophyll *a*.

The vast Chukchi Sea shelf and the adjacent Canada Basin characterize the geography of the western Arctic Ocean. The Bering and Chukchi Sea shelves in the western Arctic Ocean, which are among the largest continental shelves in the world, are known to have high biological productivity (e.g., Cota et al., 1996). Three Pacific-origin water masses – the Anadyr Water (AnW), Bering Shelf Water (BSW) and Alaskan Coastal Water (ACW) – flow through the Bering Strait into the Chukchi Sea (Grebmeier et al., 1988, 1989). The AnW and BSW form a modified Bering Shelf–Anadyr Water (BSAW). BSAW flowing over the Chukchi shelf is characterized by low temperature (−1 to +2.0 °C) and relatively high salinity (> 31.8). It is originally enriched in nutrients, and occupies the bulk of the central Chukchi Sea. ACW flowing over the eastern Chukchi shelf along the coastline of the Alaskan Peninsula is characterized by higher temperatures (> +2 °C) and lower salinity (< 31.8). The nutrient level of ACW is originally low compared with that of BSAW. ACW and BSAW are described as the Pacific-origin Summer Water (PSW) in the western Arctic Ocean. The surface mixed layer in the Arctic Ocean has a seasonally low salinity signature in the summer as a result of sea ice melt and river runoff. In the Canada basin, the surface mixed layer has a seasonally low salinity signature (< 30) with relatively low temperature (< +2 °C) in the summer as a result of sea ice melting and river runoff, is called Polar Mixed Layer Water (PMLW) (Codispoti et al., 2005). The PMLW covering the surface layer contributes to sea ice formation in the fall and winter. Cold, dense water (CDW), which is characterized by its low temperature (−1.7 to −1.0 °C) and relatively high salinity (> 31.8), is created as a result of sea ice formation and brine production, forming upper and lower halocline layers (Anderson et al., 2013). The CDW that is transported

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northward on the bottom of the Chukchi Sea shelf is described as the Pacific-origin Winter Water (PWW). This CDW (or PWW) flows in the subsurface layer of the Canada Basin. Atlantic Water (AW) with high salinity (> 34.2) extends from below the halocline layer to the bottom of the Canada Basin.

In the present study, we conducted shipboard observation on the R/V *Mirai* (MR12-E03) over the Chukchi Sea and the Canada Basin in the western Arctic Ocean in September and October 2012. We identified the vertical distributions of four VOIs (CH_3I, C_2H_5I, CH_2ClI, and CH_2I_2) in relation to the water mass structure. We also attempted to find a clue that will help explain the production processes of VOIs in seawater in association with biochemical parameters, such as nutrients and Chl *a*.

2 Method

2.1 Shipboard observation and seawater sampling

Shipboard observation was conducted on the R/V *Mirai* (MR12-E03), which is owned and operated by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), between 15 September and 04 October 2012 in the western Arctic Ocean as a part of GRENE Arctic Climate Change Research Project initiated by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan. A general description of the R/V *Mirai* is provided in the cruise report, which is available to the public on the JAMSTEC data website (http://www.godac.jamstec.go.jp/darwin/e). The locations of the 19 sampling stations for the present study are shown in Fig. 1.

Seawater samples for VOI measurement were collected in Teflon-coated, 10-L Niskin-X sampling bottles attached to CTD-RMSs (conductivity-temperature-depth probe-rosette multi-samplers). The sampling depths were 0 (bucket sampling), 5, 10, 20, 30, 40, 50, 100, 200, 500, 1000, 2000, and 3000 m (or bottom depth −5 m).

Seawater aliquots (125 mL) were collected in dark glass bottles, overflowing approximately 250 mL of seawater. To arrest microbial activity, 50 µL of saturated mercuric

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chloride ($HgCl_2$) solution, which had been previously bubbled with high-purity nitrogen for 30 min at 90–100 °C to remove any contaminating gases, was added to each bottle. The bottles were crimp-sealed with 0.5 mL headspace using a butyl rubber-lined septum and an aluminum cap. The sample bottles were kept in the dark at 0–4 °C until pre-treatment, typically within one month.

Dissolved halocarbons were collected from the seawater samples by the purge-and-trap method. The total volume of seawater (125 mL) in the sample bottle was introduced to a purge vessel by a high-purity nitrogen carrier at 65 mL L^{-1}, and the dissolved gases were consecutively purged by bubbling with nitrogen for 35 min. The purged gas sample was collected in a cold-trap containing Tenax TA (10 mg) cooled to −90 °C. This cold-trap sample was sealed with 1/16 in. screw nuts (Swagelok©) and stored in a freezer (−30 °C) until gas chromatography–mass spectrometry (GC–MS) analysis, typically within 7 days. The purge efficiencies for CH_3I, C_2H_5I, CH_2ClI and CH_2I_2 were 94, 95, 83, and 66 %, respectively.

Concentrated VOIs in the cold-trap were thermally (200 °C) desorbed and transferred to an automated pre-concentration GC–MS analytical system. Details of the GC-MS analysis are described elsewhere (Ooki and Yokouchi, 2011a, b). Briefly, the thermally desorbed sample was collected in a trap containing Carboxene 1000 and Carbopak B cooled to −50 °C in a small freezer. Concentrated VOIs in this first trap were thermally (200 °C) desorbed and transferred to a second trap, which contained Tenax TA and Carboxene 1000 cooled to −50 °C. Then, the second trap was heated to 200 °C, and the desorbed components were transferred to a capillary column (Porabond Q, 0.32 mm, 50 m) in preparation for GC–MS analysis (Agilent 5973, 6890).

To check the possibility of losses and contaminations of VOIs in the cold-trap during storage in the freezer (−30 °C), two types of standard gases were separately concentrated in each cold-trap. The first type is a purge-and-trap standard containing three VOIs in a water bottle (125 mL). The VOIs standard in a standard bottle (125 mL) was collected in a cold-trap using the purge-and-trap method mentioned above. The second type is mixed standard gases containing 13 halocarbons in a high-pressure cylin-

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der. The mixed standard diluted with high-purity nitrogen was introduced to a cold-trap. Blank cold-traps (no VOI standard) and the two types of standard cold-traps were stored in a freezer (−30 °C) for 7 to 30 days. The results of the GC–MS analysis of the standard and blank traps showed that no significant losses or contaminations occurred during storage.

2.2 Chlorophyll *a* and nutrients

Chl *a* concentrations were measured with a fluorescence sensor attached to the CTD observation system. The fluorescence data were calibrated with Chl *a* concentrations in discrete seawater samples measured using the fluorometric Welshmeyer method (Welshmeyer, 1994). Nutrient (NO_3, NO_2, NH_4, SiO_2, and PO_4) concentrations were measured by the colorimetric method using a QuAAtro system and in accordance with "The GO-SHIP Repeat Hydrography Manual" (Hydes et al., 2010). Analytical precision was 0.12 % for NO_3^-, 0.21 % for NO_2^-, 0.19 % for PO_4^{3-}, 0.11 % for SiO_2, and 0.34 % for NH_4^+.

We calculated the value of nitrogen deficit relative to phosphate, N-deficit ($= [NH_4^+] + [NO_3^-] + [NO_2^-] - r \times [PO_4^{3-}]$), where r is a Redfield ratio of 16. We regard the large N-deficit as an indicator of the influence of organic matter decomposition in the sediment over the shelf.

3 Results

3.1 Overview of hydrographic condition

The spatial distribution of surface seawater temperature (SST) is shown in Fig. 1. The water masses were classified according to Grebmeier et al. (1989). The warm ACW with temperature > +2 °C, as shown in light blue–red color in the figure, and salinity < 31.8, was found extensively in the east Chukchi Sea shelf–slope area. The main flow

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of ACW (temp. > 4 °C), shown in both orange and red color in the figure, was along the coastline of the Alaskan Peninsula. This flow covered the sampling locations of St1, St14, St76, and St74. The ACW seemed to distribute westward around 70° N, covering the sampling locations of St78–80. Its eastward flow reached the Barrow Canyon (St53–60) and branched to the northwest along the Chukchi Sea slope from St48–45 (light blue in the figure). The PMLW (−1 < temp. < 2 °C, sal. < 30) occupied the surface over the northern Chukchi Sea and the Canada Basin, covering the sampling locations of St72, St24, St64, St39, St29, St33, and St32.

Geographical information is summarized in Table 1. This information includes sampling position (Lat., Long.), bottom depth, area type (shelf with bottom depth < 200 m, slope with bottom depth 200–2000 m or basin with bottom depth > 2000 m). The table also includes hydrographic conditions, which include SST, sea surface salinity (SSS), surface mixed layer depth (MLD), and water mass types (ACW, BSAW, PMLW, CDW, or AW). The sampling stations are listed in order of latitude from the southernmost St1 to the northernmost St45 under the influence of ACW and in order of bottom depth from the shallowest St72 to the deepest St64 under the influence of PMLW. The MLD was defined as the depth where the potential density increases by 0.125 kg m^{-3} compared with the reference depth of 5 m. The subsurface layer was defined as the layer between the surface mixed layer and the CDW or ocean floor.

In the present study, the southern Chukchi Sea area (St1–74) was defined as the area between the Bering Strait and 71° N, where there is a shallow continental shelf. The central Chukchi Sea area (St53–24) was defined as the area between 71° N and 74° N, and the northern slope–basin area (St29–64) was defined as the northern area (74° N).

In the water structure analysis, the ACW occupied the water column under the main flow of ACW (St1, St14, St76, St74), and the BSAW was found in the subsurface layer at the other stations. The CDW (or PWW) was found below the subsurface layer at the central Chukchi Sea and the northern areas. The AW underlaid the CDW at the deeper stations (bottom depth > 124 m) of the central and northern areas.

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3.2 Distributions of Chlorophyll *a* (Chl *a*), Ammonium (NH_4^+), N-deficit, and VOIs

The average concentrations of Chl *a*, NH_4^+, N-deficit, and the four studied VOIs (CH_3I, C_2H_5I, CH_2I_2 and CH_2ClI) in the surface mixed layer, subsurface layer, CDW and AW at each station are listed in Tables 2–7. The vertical distributions of potential density, NH_4^+, N-deficit and the four VOIs in the southern Chukchi Sea shelf (St10, St80, St80 and St76), and the central Chukchi Sea and northern areas (St24, St29, St64, St32, and St68) are shown in Fig. 2a–g and Fig. 3a–g, respectively.

3.2.1 Chlorophyll *a* (Chl *a*)

The total average concentration of Chl *a* in all Pacific-origin Water (ACW + BSAW + PMLW + CDW) was 0.42 $\mu g\,L^{-1}$. We regard any Chl *a* concentration above 0.42 $\mu g\,L^{-1}$ as "high" in the western Arctic Ocean. The ACW had high Chl *a* concentrations, with averages of 0.75 ($\pm 0.33\sigma$) $\mu g\,L^{-1}$ in the surface mixed layer and 0.67 ($\pm 0.26\sigma$) $\mu g\,L^{-1}$ in the subsurface layer. The PMLW and BSAW had lower Chl *a* concentrations, with averages of 0.19 ($\pm 0.17\sigma$) $\mu g\,L^{-1}$ in the surface mixed layer and 0.31 ($\pm 0.16\sigma$) $\mu g\,L^{-1}$ in the subsurface layer. In the northern slope–basin stations (St64, St39, St29, St33, St32), where the PMLW occupied the surface layer, the Chl *a* concentrations were very low (0.08–0.16 $\mu g\,L^{-1}$) in the surface layer. But, concentration maxima were found in the subsurface layer at station St29 (0.53 $\mu g\,L^{-1}$) and the CDW at St33 (0.48 $\mu g\,L^{-1}$) (Table 2).

3.2.2 Ammonium (NH_4^+) and N-deficit

The total average concentration of NH_4^+ in all Pacific-origin Water (ACW + BSAW + PMLW + CDW) was 1.0 $\mu mol\,L^{-1}$. We regard any NH_4^+ concentration above 1.0 $\mu mol\,L^{-1}$ as "high" in the western Arctic Ocean. Over the southern Chukchi Sea shelf (St1–74), the concentration maxima (1.0–5.8 $\mu mol\,L^{-1}$) were found

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in the bottom layer water as shown in Fig. 2b for St10, St80 and St76. The highest concentration (5.8 $\mu mol\,L^{-1}$) was found near the bottom of the BSAW around the Hope Valley over the Chukchi Sea shelf (St10), where the "Hope Valley biological hotspot" is known to exist (Grebmeier et al., 2015). The dissolved oxygen minimum (243 $\mu mol\,Kg^{-1}$) and large N-deficit (−12.3 $\mu mol\,L^{-1}$) occurred simultaneously near the bottom in this area.

Over the central Chukchi Sea shelf–slope area, concentration maxima (1.3–3.8 $\mu mol\,L^{-1}$) were found in the subsurface BSAW and CDW above AW at St53, St60, St68, St72 and St24 (Table 3). The vertical distributions at St68 and St24 are shown in Fig. 3b.

In the northern slope–basin areas (St29–64), NH_4^+ concentrations were very low, with an average of 0.05 ($\pm 0.07\sigma$) $\mu mol\,L^{-1}$. Note that small concentration peaks were found in the CDW at St29 (027 $\mu mol\,L^{-1}$) at 60 m depth, as shown in Fig. 3b. The same were found in the CDW at St33 (0.56 $\mu mol\,L^{-1}$) at 51 m depth over the Chukchi Sea slope. The latter is the location where Chl *a* peaks (0.48–0.53 $\mu g\,L^{-1}$) also occurred.

The high NH_4^+ concentration in the Chukchi Sea shelf–slope areas can be explained as follows. Ammonium regenerated from the organic matter in sediment is added to the bottom layer water over the Chukchi Sea shelf in summer. The CDW, which has an added high amount of NH_4^+ from the sediment of the northernmost end of the Chukchi Sea shelf, has been moved to the slope area (Nishino et al., 2005). The supply of NH_4^+ regenerated from organic matter in the ocean sediment contributes to keeping the NH_4^+ concentration at several $\mu mol\,L^{-1}$ in the water column. In contrast, the low concentrations of NH_4^+ in the northern slope–basin area can be explained by the biological consumption of NH_4^+ (NH_4^+ oxidation as a first step of nitrification) in the water column.

Large N-deficits (−11.1 ~ −20.4 $\mu mol\,L^{-1}$) were found in the bottom layer water of the BSAW and CDW from the southern Chukchi Sea shelf to the northern slope–basin area. The largest N-deficit (−20.4 $\mu mol\,L^{-1}$) occurred in the CDW at the northern tip of the Chukchi Sea shelf (St24), as shown in Fig. 3c. These N-deficits largely resulted

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from denitrification in the ocean sediment over the shelf. Within a narrow depth range in the subsurface waters of the BSAW and CDW over the northern Chukchi Sea shelf–slope area and the Canada Basin, the N** minima (or N-deficit minima) were coincident with the remarkably high maxima of nutrients, humic-like F-DOM, and dissolved Fe – which are all attributed to emissions from the bottom sediment, which in turn are linked to organic matter decomposition (Hioki et al., 2014).

3.2.3 Iodomethane (CH_3I)

The total average concentration of CH_3I in all Pacific-origin water (ACW + BSAW + PMLW + CDW) was 2.2 pmol L^{-1}, which corresponds to the global ocean surface average values in the range of 2.3–2.6 pmol L^{-1} in shelf-slope areas (Ooki et al., 2015). Globally, the polar surface waters had the lowest concentrations of CH_3I (1.0–1.5 pmol L^{-1}) among all water types from tropical to polar (total average 2.3–3.7 pmol L^{-1}). We regard any CH_3I concentration above 2.2 pmol L^{-1} as "high" in the Arctic Ocean.

High concentration peaks of CH_3I were occasionally found in the bottom layer water over the southern Chukchi Sea shelf (Fig. 2d), with average values in the range of 2.1–5.2 pmol L^{-1}, and in the subsurface ACW/BSAW and CDW over the central Chukchi Sea, with average values in the range of 1.5–8.1 pmol L^{-1} (Table 4). These concentrations are consistent with the surface mixed layer averages of 2.5 (1.2–4.3) pmol L^{-1} in the Amundsen Sea and 3.0 (2.1–4.7) pmol L^{-1} in the Ross Sea in Antarctica. In summer, considerable algal bloom occurs, and maximum Chl *a* concentrations are 8.4–10 µg L^{-1} (Mattson et al., 2012).

The highest concentration of CH_3I (8.1 pmol L^{-1}) occurred in the CDW, near the bottom over the northern tip of the Chukchi Sea shelf (St24), where the largest N-deficit (−20.4 µmol L^{-1}) also occurred. A significant peak (4.0 pmol L^{-1}) occurred in the CDW above the AW over the northern Chukchi Sea slope (St68 in Table 4), coincident with the concentration peak of NH_4^+ (3.2 µmol L^{-1}), as shown in Fig. 2b and d. In the north-

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ern slope–basin area (St29–64), the CH_3I concentrations were low with average values in the range of 0.37–1.9 pmol L^{-1}.

3.2.4 Iodoethane (C_2H_5I)

The total average concentration of C_2H_5I in all Pacific-origin water (ACW + BSAW + PMLW + CDW) was 0.84 pmol L^{-1}. We regard any C_2H_5I concentration above 0.84 pmol L^{-1} as "high" in the western Arctic Ocean. This threshold is 1.5–3 times the global ocean surface average values in the range of 0.23–0.59 pmol L^{-1} in shelf–slope areas (Ooki et al., 2015).

High concentration peaks of C_2H_5I were occasionally found in the bottom layer water over the southern Chukchi Sea shelf (average values in the range of 0.9–3.9 pmol L^{-1} in Table 5), as shown in Fig. 2e, and in subsurface BSAW and CDW over the central shelf–slope areas (average values in the range of 1.2–4.4 pmol L^{-1}), as shown in Fig. 3e.

The highest concentration of C_2H_5I (4.4 pmol L^{-1}) occurred in the CDW over the central Chukchi Sea slope (St68), at which depth a large N-deficit (−13.2 µmol L^{-1}) and high concentration of NH_4^+ (3.2 µmol L^{-1}) simultaneously occurred. In the northern slope–basin area, the C_2H_5I concentrations were low (DL–0.70 pmol L^{-1}). A small peak of C_2H_5I (1.5 pmol L^{-1}) was found in the CDW over the northern tip of the Chukchi Sea shelf (St24), where the CH_3I maximum and a large N-deficit simultaneously occurred.

3.2.5 Diiodomethane (CH_2I_2)

Very high levels of CH_2I_2 (30–47 pmol L^{-1}) were found in the ACW at the Bering Strait (St1). Similar high levels of CH_2I_2 (ave. 23 pmol L^{-1}, min–max: DL (< 0.9)–48 pmol L^{-1}) were reported in the macro-algal field seawater in the fjord of the NyÅlesund (80° N, 12° E) on Spitzbergen, Norway (Schall and Heumann, 1993). The total average concentration of CH_2I_2 in all Pacific-origin water (ACW + BSAW + PMLW + CDW) except for the Bering Strait water (St1) was 4.4 pmol L^{-1}. We regard any CH_2I_2 concentration

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above 4.4 pmol L^{-1} as "high" in the western Arctic Ocean. This threshold is within the range of surface averages from 2.5 pmol L^{-1} in the coastal area (10 km offshore) of the English Channel (50° N, 4° W) (Archer et al., 2007) to 6.2 pmol L^{-1} in the fjord of the Ny Ålesund (Schall and Heumann, 1993). High concentrations were found in the bottom layer water of the southern Chukchi Sea shelf and the subsurface layer of the ACW, BSAW, and CDW over the central to northern Chukchi shelf–slope areas, as shown in Figs. 2f and 3f. The low concentrations (0.80–1.50 pmol L^{-1}) occasionally found in the surface mixed layer water over the shelf (St76 and St45 in Table 6) are probably due to the photolysis of CH_2I_2 in seawater (Jones and Carpenter, 2005).

A significant peak of CH_2I_2 (20.9 pmol L^{-1}), which is the highest concentration other than the Bering Strait samples, was found in the CDW, near the bottom over the northern tip of the Chukchi Sea shelf (St24 in Fig. 3f). The largest N-deficit and the CH_3I maximum also occurred in this water. In the northern slope–basin area, the lowest levels of CH_2I_2 (DL–0.05 pmol L^{-1}) were found in the surface mixed layer and the underlying deeper AW. In contrast, significant peaks of CH_2I_2 (0.47–14 pmol L^{-1}) were found in the subsurface BSAW and CDW over the slope–basin area. The peak concentrations decreased with increasing bottom depth from the shelf (St24) to the far basin (St64).

3.2.6 Chloroiodomethane (CH_2ClI)

The total average concentration of CH_2ClI in all Pacific-origin water (ACW + BSAW + PMLW + CDW) was 5.0 pmol L^{-1}. We regard any CH_2ClI concentration above 5.0 pmol L^{-1} as "high" in the western Arctic Ocean. This threshold is within the global ocean surface average values in the range of 3.7–6.6 pmol L^{-1} in shelf–slope areas (Ooki et al., 2015). High concentrations of CH_2ClI were found in all the ACW samples except for St76, with an average of $8.7 \pm 3.6 (1\sigma)$ pmol L^{-1} from the Bering Strait to the central Chukchi Sea slope area (Table 7). Low concentrations of CH_2I_2 in the surface ACW were occasionally found over the shelf (St76) and slope

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(St45). The occasional low concentrations of CH_2I_2 in the surface layer are attributed to photochemical degradation. Since the photolysis rate of CH_2ClI is much slower than that of CH_2I_2 in seawater (Jones and Carpenter, 2005), CH_2ClI in the surface layer would exist for a longer time than CH_2I_2. The lateral transport of CH_2ClI and CH_2I_2 will be discussed in Sect. 4.4.

A high concentration peak of CH_2ClI (11.0 pmol L^{-1}) was found in the CDW, near the bottom over the northern tip of the Chukchi Sea shelf (St24 in Fig. 3g). Significant peaks of CH_2I_2 and CH_3I, and the largest N-deficit also occurred in this water.

4 Discussion

4.1 Correlation analysis and VOI production

Correlation analysis was performed to identify potential correlation between VOIs, Chl *a*, NH_4^+, and N-deficit for all the samples and ACW and BSAW/PMLW/CDW samples. The correlate coefficients are summarized in Table 8. Scattering diagrams of VOIs as compared to NH_4^+ are shown in Fig. 4.

High correlations were found in the BSAW/PMLW/CDW between NH_4^+ and three VOIs: CH_3I (R = 0.77), C_2H_5I (R = 0.93) and CH_2ClI (R = 0.66). High correlations were also found between N-deficit and CH_2I_2 (R = 0.67). Other nutrient components (NO_3^-, NO_2^-, PO_4^{3-}, SiO_2) showed lower correlations with VOIs than NH_4^+ and N-deficit.

We could not find any correlation between VOIs and Chl *a*, even though former incubation experiments have indicated that many marine phytoplankton species produce VOIs as they grow (Tokarczyk and Moore, 1994; Moore et al., 1996; Manley and de la Cuesta, 1997). However, high and low concentrations of VOIs in surface seawater have also been attributed to varying high and low biological productivity in different types of water (e.g., from tropical to polar) and different sea areas (shelf, slope, basin) (Ooki et al., 2015). It seems that Chl *a* is not a main factor in the vertical–horizontal

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distributions of VOIs on a regional scale, such as the Chukchi Sea and adjacent sea area.

4.1.1 Production of Iodomethane (CH_3I) and Iodoethane (C_2H_5I)

The significant correlation between C_2H_5I and NH_4^+ implies that C_2H_5I production in seawater is occurring at the same time as regeneration of NH_4^+ from organic matter. The C_2H_5I consumption, which is probably bacterial consumption, might occur at a rate similar to the biological NH_4^+ consumption. The consumption rates for NH_4^+ in seawater over the Chukchi Sea shelf are reported to vary widely from 0.15–3.6 nmol L^{-1} d^{-1} (Christman et al., 2011) to 0.24–7.2 µmol L^{-1} d^{-1} (Souza et al., 2014), with a variable turnover from within a day to over ten days. The high correlation between CH_3I and NH_4^+ (R = 0.77) would also be attributable to the CH_3I production linked to the degradation of organic matter.

Note that two plots below the linear regression line in Fig. 4 are the data collected from the bottom layer water at the Hope Valley biological hotspot (St10) with high nutrients and low dissolved oxygen. We do not currently propose a reason for this exceptional plot.

The production of C_2H_5I and CH_3I associated with the bacterial degradation of organic matter was first demonstrated by an incubation experiment for marine biogenic aggregates, which mainly consisted of diatom collected from the Arctic seawater. The concentrations of C_2H_5I and CH_3I in the incubation vessel increased sharply, simultaneously with the enhancement of bacterial heterotrophic production rate (Hughes et al., 2008).

Previously, NH_4^+ concentrations in coastal subarctic seawater have been observed to increase in the bottom layer water (~ 90 m depth) after the spring bloom of diatoms (Kudo et al., 2007). Therefore, we suggest that the production of C_2H_5I and CH_3I associated with the degradation of organic matter occurs in the bottom layer water, probably after the diatom bloom, over the Chukchi Sea shelf.

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4.1.2 Production of Diiodomethane (CH_2I_2) and Chloroiodomethane (CH_2ClI)

The notable feature of CH_2I_2 and CH_2ClI distributions was that high concentration peaks were found (1) in the CDW and subsurface BSAW over the Chukchi Sea shelf (St24, St53, St60, St72) and slope (St68), where large N-deficit and high NH_4^+ concentration occurred simultaneously, and (2) at the northern Chukchi Sea slope (St29), where large N-deficit and low NH_4^+ concentration occurred simultaneously. Concentration peaks of C_2H_5I and CH_3I were not found over the northern slope area (St29) where NH_4^+ concentration was low.

From the marine biogenic aggregates incubation (Hughes et al., 2008) mentioned in the last section, the concentrations of CH_2I_2 and CH_2ClI did not increase in the incubation vessel during the incubation period of 70 h, whereas C_2H_5I showed significant increases in concentration with the enhancement of bacterial production rate after 30 h of incubation. It is possible that the production processes of CH_2I_2 in bottom layer water are quite different from those of C_2H_5I, even if the production of both VOIs is associated with the degradation of organic matter in the sediment or the bottom layer water.

Recent studies have suggested that the production of CH_2I_2 in seawater occurs after the reaction of organic matter with I_2, which is known as the "iodoform (CHI_3) reaction." The production of CHI_3 and CH_2I_2 has been clarified to occur after the reaction of dissolved organic matter with I_2, which is produced by I^- oxidizing bacteria in a culture vessel (Fuse et al., 2003; Amachi et al., 2005). It is noted that small amounts of CH_2ClI and CH_3I have been detected in the culture vessel with drastic increases of CH_2I_2, whereas C_2H_5I production has not yet clarified from the iodoform reaction.

The production of I_2 in seawater is believed to be initiated with I^- oxidations. However, it remains unclear where the I^- oxidations occur in the ocean environment. Recently, iodide-oxidizing bacteria, which oxidize iodide (I^-) to molecular iodine (I_2), have been detected in natural seawater samples after incubation under the iodide-rich condition ($\sim 1\,mmol\,L^{-1}$) (Amachi et al., 2005). The iodide-rich condition has been found in pore water of ocean sediment, with I^- concentration of $\sim 7\,\mu mol\,L^{-1}$, which is 70 to 700 times

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the seawater concentration (10–100 nmol L^{-1}) (Anschutz et al., 2000). Iodide-oxidizing bacteria might actively produce I_2 in pore water of the ocean sediment. Therefore, it is supposed that I_2 production by I^--oxidizing bacteria in the sediment over the Chukchi Sea shelf has resulted in the production of CH_2I_2, CH_2ClI, and CH_3I in the sediment or the bottom layer water.

Moreover, iodide can be oxidized by nitrate in a reaction that yields N_2 and I_2 in marine sediments (Anschutz et al., 2000).

$$I^- + 1/5NO_3^- + 6/5H^+ = 1/10N_2 + 1/2I_2 + 3/5H_2O$$

This reaction, which is thermodynamically favorable at all pH encountered in marine sediments (pH < 8), would promote denitrification. Therefore, we suppose that the high concentrations of CH_2I_2 and CH_2ClI in the bottom layer water and CDW over the Chukchi Sea shelf–slope area, with the large N-deficit, were linked to denitrification in the sediment.

4.2 Lateral transport of VOIs

The significant concentration peaks of the four VOIs in the CDW over the northern shelf–slope area suggest the lateral transport of VOIs through the CDW layer from the shelf to the basin area, as well as the transport of humic-like DOM, nutrients, and dissolved Fe (Hioki et al., 2014) – which are all believed to be derived from organic matter decomposition in the sediment over the shelf.

High concentrations of CH_2ClI in the surface mixed layer over the central Chukchi Sea slope would be due to the lateral transport of ACW from the Bering Strait and the southern Chukchi Sea. Lateral transport of CH_3I, C_2H_5I, and CH_2I_2 in ACW through the surface mixed layer to the central slope area was not observed.

The lateral transport of CH_2ClI from the Chukchi Sea to the northern Canada Basin in ACW through the mixed layer, and to the Alpha Rigde (85° N) in the Pacific-origin CDW through the subsurface upper halocline layer, has recently been reported by Karlsson

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et al. (2013). The VOIs produced over the Chukchi Sea shelf might have the potential to supply iodine to Arctic air far from the shelf.

5 Summary

Shipboard observation was conducted over the Chukchi Sea shelf-slope and the Canada Basin in the western Arctic Ocean in September and October 2012 by the R/V *Mirai* (MR12-E03) as part of GRENE Arctic Climate Change Research Project. The purpose of the study was to obtain vertical distributions of iodomethane (CH_3I), iodoethane (C_2H_5I), diiodomethane (CH_2I_2) and chloroiodomethane (CH_2ClI) in seawater. The following is a summary of the characteristics of the vertical distributions of these VOIs, and hypotheses concerning lateral transport of VOIs in the area and mechanisms responsible for their production in relation to the degradation of organic matter.

High concentrations of four VOIs were found in the bottom layer water over the Chukchi Sea shelf, in which layer the concentration maximum of ammonium (NH_4^+) simultaneously occurred. High correlations were found between NH_4^+ and C_2H_5I with correlate coefficient $R = 0.93$, and between NH_4^+ and CH_3I with $R = 0.77$. These results suggest that production of these VOIs is related to degradation of organic matter. The significant correlation between C_2H_5I and NH_4^+ implies similar consumption rates for both compounds in seawater, probably owing to bacterial consumption. Over the northern Chukchi Sea shelf–slope, concentration maxima of CH_2I_2, CH_2ClI, and CH_3I were found in the subsurface BSAW and CDW alongside large N-deficits and low concentrations of NH_4^+. These results suggest that the production of the three VOIs are quite different from the production process of C_2H_5I, while the productions of the four VOIs are all suspected to be relevant to the decompositions of organic matter in the sediment or the bottom layer water over the shelf.

Concentration peaks of four VOIs in the subsurface BSAW and CDW over the northern Chukchi Sea slope, and the peaks of CH_2ClI in the surface ACW over the central

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Chukchi Sea slope, suggest lateral transport from the Chukchi Sea shelf to slope–basin areas. The production of VOIs over the Chukchi Sea, in relation to decomposition of organic matter created in the high productive Chukchi Sea shelf, would have the potential to supply iodine to Arctic air far from the shelf.

Author contributions. A. Ooki and S. Kawasaki measured VOIs in seawater, and analyzed the data. K. Kuma, S. Nishino, and T. Kikuchi designed the ship observation. A. Ooki, S. Kawasaki, S. Nishino, and T. Kikuchi carried out the observation. A. Ooki prepared the manuscript with contributions from all co-authors.

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Table 1. Hydrographic conditions in the Chukchi Sea and the Arctic Ocean Basin.

St.	Location	Lat.	Long.	Bottom depth (m)	Area type	SST (°C)	SSS	MLD (m)	Surface mixed layer (m)	Subsurface layer (m)	CDW (m)	AW (m)
1	Southern	*65.7*	*191.8*	*43*	*Shelf*	*8.1*	*24.1*	*5*	*0–5 (ACW)*	*6–36 (ACW)*	–	–
10	Chukchi	*68.0*	*192.0*	*55*	*Shelf*	*3.9*	*28.9*	*6*	*0–6 (ACW)*	*7–22 (ACW), 23–48 (BSAW)*	–	–
14	shelf	*68.3*	*193.0*	*38*	*Shelf*	*7.1*	*28.0*	*7*	*0–6 (ACW)*	*7–32 (ACW)*		
80		*70.8*	*192.0*	*48*	*Shelf*	*2.7*	*31.9*	*20*	*0–20 (ACW)*	*21–22 (ACW), 23–39 (BSAW)*	–	–
78		*70.7*	*194.0*	*40*	*Shelf*	*3.1*	*31.2*	*11*	*0–11 (ACW)*	*12–28 (ACW), 29–33 (BSAW)*	–	–
76		*70.8*	*196.0*	*47*	*Shelf*	*4.5*	*29.6*	*15*	*0–15 (ACW)*	*16–39 (ACW)*	–	–
74		*70.8*	*198.0*	*43*	*Shelf*	*4.5*	*31.1*	*33*	*0–33 (ACW)*	*34–35 (ACW)*	–	–
53	Central	*71.4*	*202.5*	*124*	*Shelf*	*3.6*	*29.7*	*9*	*0–9 (ACW)*	*10–24 (ACW), 25–36 (BSAW)*	*37–99*	*> 100*
60	Chukchi	71.7	204.9	257	Slope	3.2	30.3	6	0–6 (ACW)	7–25 (ACW), 26–54 (BSAW)	55–111	> 112
48	shelf –	72.5	204.0	1896	Slope	4.0	26.7	9	0–9 (ACW)	10–40 (ACW), 41–70 (BSAW)	71–207	> 208
68	slope	72.9	202.0	1573	Slope	2.6	28.4	14	0–14 (ACW)	15–20 (ACW), 21–55 (BSAW)	56–151	> 152
45		73.3	200.0	1390	Slope	2.7	26.9	10	0–10 (ACW)	11–13 (ACW), 14–81 (BSAW)	82–203	204
72		*72.0*	*200.0*	*30*	*Shelf*	*0.2*	*28.2*	*8*	*0–8 (PMLW)*	*9–15 (BSAW)*	*16–20*	–
24		*73.5*	*191.3*	*118*	*Shelf*	*−0.2*	*26.9*	*9*	*0–8 (PMLW)*	*9–32 (BSAW)*	*32–105*	
29	Northern	75.2	187.4	453	Slope	−0.3	26.6	13	0–13 (PMLW)	14–51 (BSAW)	52–192	> 193
33	slope –	75.2	182.5	721	Slope	0.0	26.7	18	0–18 (PMLW)	19–45 (BSAW)	46–162	> 163
39	basin	75.0	198.1	1987	Slope	0.8	25.7	20	0–20 (PMLW)	21–91 (BSAW)	92–240	> 240
32		76.0	186.0	2137	Basin	−0.4	25.8	23	0–20 (PMLW)	21–83 (BSAW)	84–225	> 226
64		74.5	206.0	3851	Basin	0.1	25.1	17	0–18 (PMLW)	19–105 (BSAW)	106–263	> 264

Shelf area with bottom depth < 200 m, slope area with bottom depth between 200 and 2000 m, basin area with bottom depth > 2000 m.
Sampling stations in the shelf area are displayed in italics.
ACW: Alaskan Coastal Water (SST > +2 °C; S < 31.8).
BSAW: Bering Shelf–Anadyr Water (T = −1 ~ 2.0 °C).
PMLW: Polar Mixed Layer Water (T < +2 °C, S < 30).
Subsurface layer: between ML and CDW.
CDW: Cold, Dense Water (Halocline Layer) (T = −1 ~ −1.7 °C; S = 32 ~ 34).
AW: Atlantic Water (S > 34.2).

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Table 2. Concentrations of Chl *a*.

St.	ML ACW	ML PMLW	bML ACW	bML BSAW	CDW	AW
	Southern Chukchi shelf					
1	**1.28**		**1.24**			
10	**1.14**		**0.66**	0.23		
14	**0.98**		**0.46**			
80	**0.71**			0.21		
78	**0.64**		**0.85**	0.22		
76	0.24		0.29			
74	**0.73**		**0.69**			
	Central Chukchi shelf – slope					
53	**0.93**		**0.59**	0.18	0.20	0.21
60	**0.97**		**0.58**	0.14	0.12	0.12
48	**0.47**		**0.51**		0.08	0.06
68	**0.63**		**0.81**	0.20	0.10	0.06
45	0.22			0.28	0.03	0.02
72		**0.56**		**0.69**	0.27	
24		0.14		**0.46**	0.13	
	Northern slope – basin					
29		0.14		**0.53**	0.11	0.07
33		0.13		0.31	**0.48**	0.03
39		0.16		0.38	0.10	0.06
32		0.08		0.29	0.04	0.01
64		0.12		0.16		0.05

High Chl *a* ($> 0.42\,\mathrm{ug\,L^{-1}}$) concentrations are denoted in bold.

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Table 3. Concentrations of NH_4^+ and N-deficit, (NH_4^+/N-deficit).

St.	ML ACW	ML PMLW	bML ACW	bML BSAW	CDW	AW
	Southern Chukchi shelf					
1	0.91/−10.0		**1.03/**−10.8			
10	**1.38/**−9.8		**2.73/**−10.9	**5.77/−15.2**		
14	0.31/−9.1		**2.08/**−9.9			
80	**1.01/**−7.9			**4.58/−16.8**		
78	0.47/−7.6		0.52/−8.0	**3.35/−14.3**		
76	**1.01/**−8.1		**2.28/−11.4**			
74	**1.40/**−11.5		**1.61/−11.6**			
	Central Chukchi shelf-slope					
53	0.74/−10.7		**1.49/−12.1**	**3.39/−15.5**	**3.83/−15.0**	0.67/−7.7
60	0.17/−9.3		**1.36/−11.6**	**1.67/−13.7**	**2.15/−11.9**	0.03/−2.9
48	0.04/−8.5		0.56/−10.2		0.11/**−11.1**	DL/−2.3
68	0.11/−8.0		0.50/−9.2	**1.44/−13.6**	**3.22/−16.1**	0.07/−2.1
45	DL/−8.8			DL/**−13.2**	DL/−10.9	DL/−2.1
72		DL/−7.5		DL/−8.0	**1.34/−15.6**	
24		0.05/−9.3		0.13/**−11.1**	**1.81/−20.4**	
	Northern slope-basin					
29		0.02/−10.0		**0.12/−12.5**	DL/**−15.5**	DL/−4.7
33		0.05/−9.6		0.02/−10.2	**0.29/−15.5**	DL/−2.3
39		0.03/−9.2		0.05/**−13.2**	0.02/**−13.6**	0.01/−2.0
32		0.05/−9.1		0.02/**−12.4**	0.02/**−13.6**	DL/−2.1
64		0.05/−8.5		0.02/**−12.4**		DL/−2.2

High NH_4^+ (> 1.0 µmol L^{-1}) concentrations and large N-deficits (< −11 µmol L^{-1}) are denoted in bold.

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Table 4. Concentrations of CH_3I in each water type.

St.	ML ACW	ML PMLW	bML ACW	bML BSAW	CDW	AW
	Southern Chukchi shelf					
1	**3.4**		**5.20**			
10	1.7		**3.35**	**4.70**		
14	**2.5**		**4.05**			
80	1.7			**4.05**		
78	1.2		1.45	**2.75**		
76	0.9		2.13			
74	**2.2**		**2.40**			
	Central Chukchi shelf-slope					
53	1.5		**2.30**	**4.30**	**4.45**	1.10
60	2.0		**2.35**	**2.65**	2.10	0.30
48	1.4		**3.13**		0.65	0.50
68	1.7		**2.60**	**2.65**	**4.00**	0.58
45	1.1			1.50	0.60	0.27
72		1.30		1.50	**3.70**	
24		1.10		**2.57**	**8.10**	
	Northern slope-basin					
29		1.00		1.80	1.20	0.75
33		1.15		1.40	1.60	0.63
39		0.93		1.20	0.70	0.50
32		0.80		1.90	0.60	0.37
64		0.87		1.03		0.48

High CH_3I ($> 2.2\,pmol\,L^{-1}$) concentrations are denoted in bold.

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Table 5. Concentrations of C_2H_5I in each water type.

St.	ML ACW	ML PMLW	bML ACW	bML BSAW	CDW	AW
	Southern Chukchi shelf					
1	0.50		**1.58**			
10	0.45		**1.45**	**2.70**		
14	0.30		0.70			
80	0.53			**3.90**		
78	0.30		0.35	**2.55**		
76	0.17		**1.40**			
74	0.83		**0.90**			
	Central Chukchi shelf-slope					
53	0.40		**0.85**	**2.70**	**2.95**	0.70
60	0.30		**0.85**	**1.30**	**1.90**	0.10
48	0.15		0.43		0.30	0.07
68	0.20		0.50	**1.15**	**4.40**	0.10
45	0.13			0.17	0.25	0.07
72		0.23		0.30	**2.10**	
24		0.10		0.17	**1.50**	
	Northern slope-basin					
29		0.10		0.25	0.70	0.20
33		0.05		0.10	0.55	0.00
39		0.13		0.20	0.25	0.10
32		0.10		0.15	0.45	0.07
64		0.10		0.17		0.08

High C_2H_5I ($> 0.84\,pmol\,L^{-1}$) concentrations are denoted in bold.

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Table 6. Concentrations of CH_2I_2 in each water type.

St.	ML ACW	ML PMLW	bML ACW	bML BSAW	CDW	AW
	Southern Chukchi shelf					
1	**47.40**		**30.00**			
10	0.65		2.45	4.00		
14	**7.20**		**9.95**			
80	2.63			**9.10**		
78	3.80		**6.10**	**6.30**		
76	0.80		**6.20**			
74	**9.38**		**13.90**			
	Central Chukchi shelf-slope					
53	2.77		**5.40**	**10.10**	**9.80**	1.70
60	4.20		**5.55**	4.20	**7.60**	0.20
48	4.10		**11.30**		0.60	0.27
68	3.60		**6.90**	**5.15**	**13.40**	0.20
45	1.50			1.60	0.85	0.10
72		0.27		1.00	**5.90**	
24		0.10		2.37	**20.90**	
	Northern slope-basin					
29		0.00		**7.40**	1.30	0.45
33		0.00		0.60	2.30	0.03
39		0.05		1.45	0.15	0.00
32		0.03		1.55	0.35	0.03
64		0.00		0.47		0.04

High CH_2I_2 ($> 4.4\,pmol\,L^{-1}$) concentrations are denoted in bold.

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Table 7. Concentrations of CH_2ClI in each water type.

St.	ML ACW	ML PMLW	bML ACW	bML BSAW	CDW	AW
	Southern Chukchi shelf					
1	**10.95**		**7.70**			
10	**5.90**		**7.10**	3.95		
14	**17.80**		**13.35**			
80	**5.97**			4.80		
78	**8.37**		**9.40**	**5.65**		
76	3.50		4.83			
74	**12.68**		**14.60**			
	Central Chukchi shelf-slope					
53	**6.93**		**6.05**	**5.10**	4.30	0.70
60	**9.60**		**6.55**	3.10	2.90	0.20
48	**10.60**		**7.50**		0.50	0.13
68	**10.45**		**8.00**	3.10	4.60	0.08
45	4.23			1.37	0.60	0.00
72		2.00		3.50	**5.30**	
24		0.50		3.70	**11.00**	
	Northern slope-basin					
29		0.20		2.10	1.90	0.25
33		0.25		1.30	2.15	0.13
39		0.58		1.10	0.55	0.00
32		0.17		1.35	0.70	0.03
64		0.23		1.00		0.02

High CH_2ClI ($> 5.0\,pmol\,L^{-1}$) concentrations are denoted in bold.

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Table 8. Correlate coefficients R (all water types (n = 147)/warm ACW (n = 54)/cold BSAW-PMLW-CDW (n = 64)).

	CH_3I	C_2H_5I	CH_2I_2	CH_2ClI	NH_4^+	Chl *a*	N-deficit
CH_3I		**0.73/0.71/0.76**	0.55/0.47/**0.84**	0.55/0.21*/**0.91**	**0.70**/0.43/ **0.77**	0.41/0.28*/0.09*	**0.61**/0.49/**0.63**
C_2H_5I	**0.73/0.71/0.76**		0.27/0.08*/**0.73**	0.24/0.10*/**0.70**	**0.90/0.79/0.93**	0.05*/0.07*/0.11*	0.59/**0.76/0.61**
CH_2I_2	0.55/0.47/**0.84**	0.27/0.08*/**0.73**		0.50/0.27*/**0.85**	0.23/0.05*/**0.64**	**0.62/0.64**/0.13*	0.22/0.01*/**0.67**
CH_2ClI	0.55/0.21*/**0.91**	0.24/0.10*/**0.70**	0.50/0.27*/**0.85**		0.31/0.10*/**0.66**	**0.69**/0.30*/0.18*	0.29/0.03*/**0.63**
NH_4^+	**0.70**/0.43/**0.77**	**0.90/0.79/0.93**	0.23/0.05*/0.64	0.31/0.10*/0.66		0.06/0.32*/0.08*	0.52/**0.68**/0.55
Chl *a*	0.41/0.28*/0.09*	0.05*/0.07*/0.11*	0.62/0.64/0.13*	0.69/0.30*/0.18*	0.06/0.32*/0.08*		0.20*/0.18*/0.04*
N-deficit	0.61/0.49/0.63	0.59/**0.76**/0.61	0.22/0.01*/0.67	0.29/0.03*/0.63	0.52/0.68/0.55	0.20*/0.18*/0.04*	

All water types: ACW + BSAW + PMLW + CDW + AW.
p value < 0.01, * p value > 0.01.

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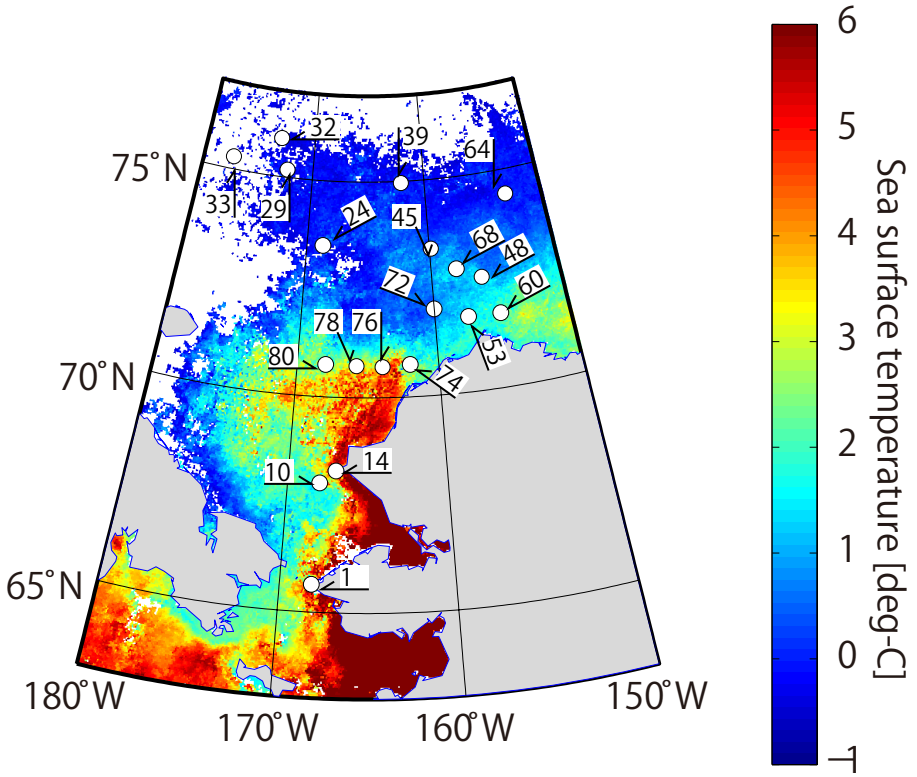

Figure 1. Sampling stations in the present study and sea surface temperature (color) by satellite images on October 2012 (NASA Goddard Space Flight Center Ocean Color; http://oceancolor.gsfc.nasa.gov/cms/).

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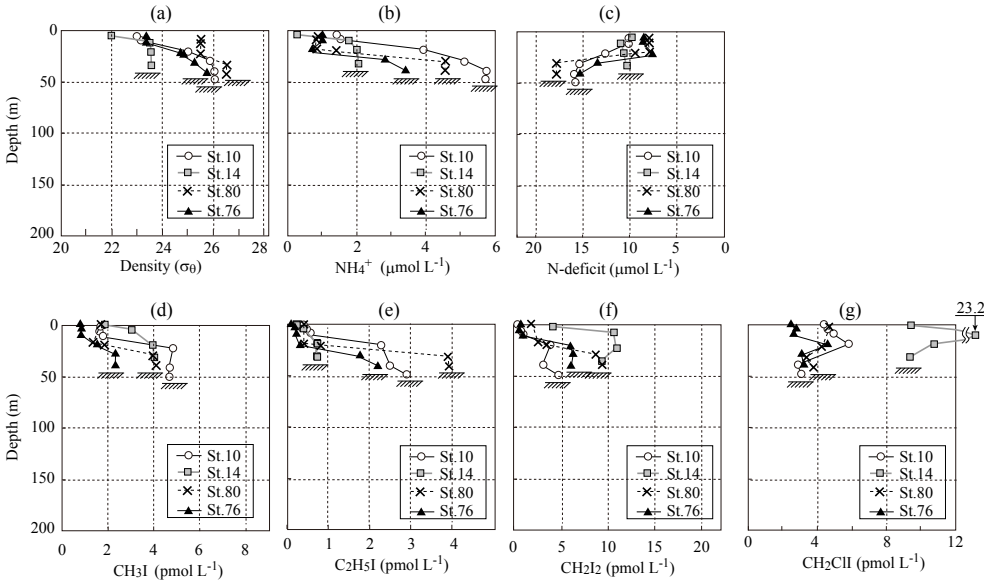

Figure 2. Vertical distributions of potential density **(a)**, NH_4^+ **(b)**, N-deficit **(c)**, CH_3I **(d)**, C_2H_5I **(e)**, CH_2I_2 **(f)**, CH_2ClI **(g)** at St10, St14, St80, and St76 over the southern Chukchi Sea shelf.

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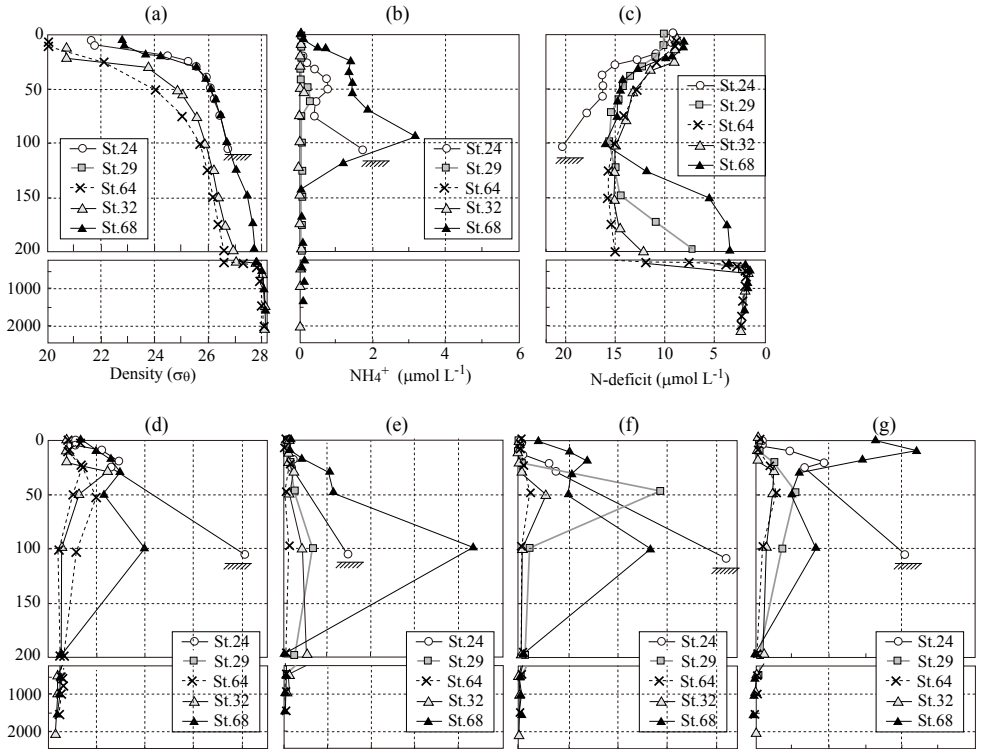

Figure 3. Vertical distributions of potential density **(a)**, NH_4^+ **(b)**, N-deficit **(c)**, CH_3I **(d)**, C_2H_5I **(e)**, CH_2I_2 **(f)**, CH_2ClI **(g)** at St24, St29, St64, St32, and St68 over the central Chukchi Sea shelf – slope area and the northern slope – basin area.

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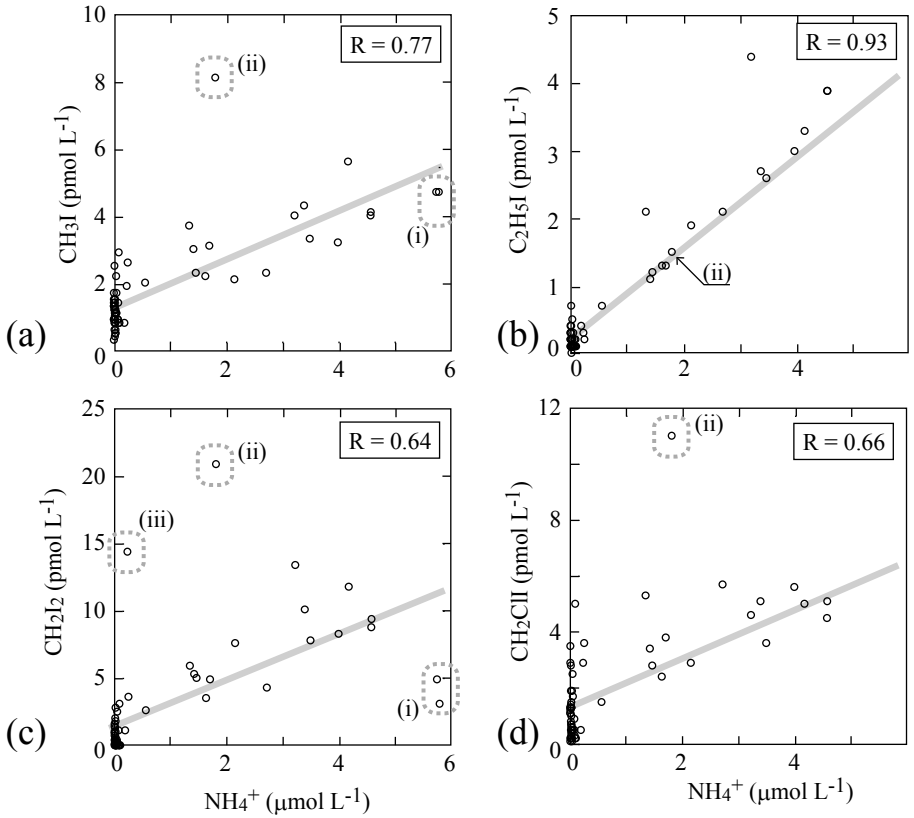

Figure 4. Scatter plots of CH_3I and NH_4^+ **(a)**, C_2H_5I and NH_4^+ **(b)**, CH_2I_2 and NH_4^+ **(c)**, and CH_2ClI and NH_4^+ **(d)**. The data for St10 in the subsurface bottom layer water of the Hope Valley biological hotspot are enclosed with a dashed line (i); data for St24 in the bottom layer water over the northern tip of the Chukchi Sea shelf is enclosed with a dashed line (ii); and data for St29 in the subsurface BSAW (48 m) over the northern slope area is enclosed with a dashed line (iii).

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