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# Spatial variation and species transformation of <sup>129</sup>I and <sup>127</sup>I in the Central Arctic Ocean



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# ABSTRACT

The spatial distributions of anthropogenic <sup>129</sup>I and natural <sup>127</sup>I in iodide (I<sup>-</sup>) and iodate (IO<sub>3</sub><sup>-</sup>) of anthropogenic <sup>129</sup>I and natural <sup>127</sup>I were investigated in the upper central Arctic Ocean. The results show that the molecular ratios of reductive iodide (I<sup>-</sup>) to oxidative iodate (IO<sub>3</sub><sup>-</sup>) ranged from 0.228 to 0.560 for <sup>127</sup>I and 0.383 to 0.827 for <sup>129</sup>I in the Polar Mixed Layer (PML). Greater <sup>127</sup>I<sup>-</sup> concentrations and markedly higher I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> ratios for both <sup>129</sup>I and <sup>127</sup>I were found in the PML over the Lomonosov and Alpha Ridges. This suggests that the in-situ formation of I<sup>-</sup> occurs as a result of enhanced reductive environments at these locations due to bacterial-mediated decomposition of dissolved organic matter (DOM) that likely originates from the inflow of river water into the central Arctic Ocean. Ratios of <sup>129</sup>I<sup>-</sup>/<sup>129</sup>IO<sub>3</sub><sup>-</sup> and <sup>127</sup>I<sup>-</sup>/<sup>127</sup>IO<sub>3</sub><sup>-</sup> decrease gradually along the main transport pathway of the Atlantic water, revealing that I<sup>-</sup> is gradually oxidized back to IO<sub>3</sub><sup>-</sup> at a slow net rate within the Atlantic Water Layer. Our study provides insights into the marine geochemical cycling of iodine and raises the potential for iodine species, notably of <sup>129</sup>I, to be used as indicators of changes in the redox condition of surface water in the Arctic Ocean, which may occur due to the predicted impacts of climate change.

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#### 1. Introduction

lodine is a biophilic and redox-sensitive element, with iodate  $(IO_3^-)$  as the dominant species under oxic conditions and iodide  $(I^-)$  under anoxic conditions in seawater, along with minor amounts of dissolved organic iodine existing in the marine environment (Wong, 1991). The conversion between  $IO_3^-$  and  $I^-$  in oxic seawater has been linked to biological processes including primary productivity, phytoplankton senescence during bloom collapse, and bacterial-mediated decomposition (Bluhm et al., 2010; Farrenkopf et al., 1997; Truesdale, 2008). In contrast to the total concentrations of iodine isotopes,  $I^-/IO_3^-$  ratios (species of iodine isotopes) have characteristic endmember values in various water bodies (e.g., low in open seawater, but high in coastal and river waters), which

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helps to identify the sources of water masses. The ratio of iodine species could also provide the information of redox changes of the water system. Numerous observations in seawater iodine species in the tropical and subtropical regions revealed that  $I^-/IO_3^-$  molecular ratios for stable <sup>127</sup>I in the surface layer of the open ocean decrease with increasing latitude (Chance et al., 2014, 2010; He et al., 2013; Hou et al., 2007; Luo, 2013; Truesdale et al., 2000; Tsunogai, 1971; Waite et al., 2006; Yi et al., 2012). The limited investigations into polar regions suggest that iodine species in surface layers were typically characterized by low  $I^-/IO_3^-$  ratios of less than 0.30 (Bluhm et al., 2011; Miwa et al., 2020).

Stable <sup>127</sup>I is typically homogeneous in seawater, limiting its use to understand different ocean processes across different water masses. Whereas the long-term authorized liquid discharges of <sup>129</sup>I (half-life of  $1.57 \times 10^7$  years) from European nuclear fuel reprocessing facilities at La Hague (France) and Sellafield (UK) have provided an ideal isotopic tracer for studying water mass transport, as well as the transformation of iodine species in the North

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Atlantic Ocean and the Arctic Ocean (Hou et al., 2007; Smith et al., 1999). Other sources of <sup>129</sup>I to the Arctic Ocean include releases from Russian nuclear facilities transported via the Ob and Yenisei rivers, global fallout of atmospheric nuclear weapons testing in 1945-1980, the Chernobyl and Fukushima accidents, and the dumping of radioactive waste (Beasley and Cooper, 1997; Buraglio et al., 1999; Cochran et al., 2000; Guilderson et al., 2014; Nielsen et al., 1997), but the contribution of these sources is dwarfed by the magnitude of <sup>129</sup>I that has been discharged from the two European nuclear reprocessing facilities. Up to 2018, the La Hague reprocessing plant has discharged around 6100 kg <sup>129</sup>I to the English Channel, with a further 1900 kg of <sup>129</sup>I discharged to the Irish Sea from Sellafield (Hou et al., 2007; OSPAR Data and Information Management System, 2022). The discharged <sup>129</sup>I from these reprocessing plants was transported first to the North Sea, then further northwards with the North Atlantic Current and Norwegian Coastal Current to the central Arctic Ocean via the Barents Sea and to a lesser degree via the West Spitsbergen Current (Smith et al., 1999). Additionally, <sup>129</sup>I has been released to the atmosphere in gaseous emissions from nuclear reprocessing facilities, but in an amount that is 2 to 3 orders of magnitude lower than by liquid discharges. In terms of sources of <sup>129</sup>I to the Arctic Ocean, analysis of sea ice has shown that atmospheric deposition is not a significant pathway, particularly when compared to the liquid discharges after long-range transport (Gómez-Guzmán et al., 2014).

Although inorganic iodine species of <sup>129</sup>I have been investigated along the transport pathways from the two European nuclear reprocessing facilities to the Arctic Ocean (He et al., 2013; Hou et al., 2007; Luo, 2013; Yi et al., 2012), there is only limited data available for the central Arctic Ocean. This work aims to investigate the spatial distribution of inorganic iodide and iodate species of <sup>129</sup>I and <sup>127</sup>I in the central Arctic Ocean and explores possible controls on their transformation.

# 2. Materials and methods

## 2.1. Research expeditions

The investigated region covers the southeastern Eurasian Basin including the Nansen Basin and the Amundsen Basin separated by the Gakkel Ridge, the Lomonosov Ridge, the Makarov Basin, the Alpha-Mendeleyev Ridge, and the northern Canada Basin in the central Arctic Ocean from 78°N to the North Pole (Fig. 1). Thirty-nine seawater samples from twelve stations were collected using a water sampling rosette from the central Arctic Ocean during the ARK-XXVI/3 cruise of the Polarstern expedition from 22 August to 22 September 2011. The detailed sampling procedure and methods have been reported elsewhere (Schauer, 2012). The sampling depths ranged from 10 m to 800 m, including the Polar Mixed Layer (PML) and the Atlantic Water Layer (AWL) of the central Arctic Ocean. Hydrographic data, including salinity and dissolved oxygen concentrations, were measured using the instrumentation installed on the water sampling rosette (Schauer et al., 2012). All seawater samples were transported to the Radioecological laboratory at Technical University of Denmark (Risø Campus), filtered through 0.45 µm filters without the addition of any chemical reagents, and stored in polyethylene bottles in the dark and below 10 °C until analysis.

# 2.2. Sample analysis

All seawater samples were analyzed within 8 months after the samples were collected. Multiple re-analyses of a seawater sample collected from an open sea area in the North Sea, have shown that inorganic species of iodine (iodide and iodate) for both <sup>127</sup>I and <sup>129</sup>I are guite stable (variation less than 5%) for at least 3 years



**Fig. 1.** Sampling stations (red dots) in the central Arctic Ocean during the ARK-XXVI/3 cruise of the R/V Polarstern in 2011 (red dot-dash line). (a) Circulation pathways of the surface Polar Mixed Layer (blue arrows) and the Atlantic Water Layer (light-blue dot arrows) in the Arctic (Karcher et al., 2012; Smith et al., 1999). For illustration in the context of the discussion, the locations of sampling stations from the NABOS-2005 cruise in September 2005 by the International Arctic Research Center (stations 7 and 8, dark blue open square) and the ARK XXII/2 cruise of the R/V Polarstern in August 2007 (station 25, violet open triangle) (Luo, 2013) are also shown. (b) Bathymetry of sampled sections, where AB, CB, MB, NB, AR, LR, and MR are Amundsen Basin, Canada Basin, Makarov Basin, Nansen Basin, Alpha Ridge, Lomonosov Ridge and Mendeleyev Ridge, respectively. ODV software was used for mapping (Schlitzer, 2021).

when stored in the dark even at room temperature (Hou, unpublished). The analytical methods for total iodine concentrations and inorganic species of iodine isotopes (<sup>129</sup>I and <sup>127</sup>I) were modified from the previous study (Hou et al., 2001, 2007), and the brief method is presented below.

# 2.2.1. Separation of inorganic iodine species

An anion exchange resin (AG  $1 \times 4$  resin, 50 mesh, Bio-Rad Laboratories Inc., USA) was converted from Cl<sup>-</sup> type to NO<sub>3</sub><sup>-</sup> type by rinsing with 2 M NaNO<sub>3</sub>. Due to the competitive binding of chloride with iodide in high salinity seawater, a column of 30 cm in length and 1 cm in internal diameter was used to avoid iodine breakthrough from the column. 200 Bq of  $^{125}$ I<sup>-</sup> as the chemical yield tracer was spiked to 600 mL seawater, and then the sample was loaded onto the anion exchange column with a flow rate of approximately 2 mL min<sup>-1</sup>. The column was rinsed with 30 mL of 0.2 mol L<sup>-1</sup> NaNO<sub>3</sub> and 20 mL of deionized water to remove iodate and any existing dissolved organic iodine that were weakly

adsorbed on the resin. lodide was eluted from the column with 100 mL of 5% NaClO and 30 mL of 3 mol  $L^{-1}$  HNO<sub>3</sub>.

# 2.2.2. Determination of <sup>127</sup>I

Prior to the ICP-MS measurement of stable <sup>127</sup>I, iodide fractions were neutralized with concentrated  $NH_3 \cdot H_2O$  to pH 7 due to the addition of HNO<sub>3</sub> for iodide elution. 1.0 mL of the original seawater samples and 1.0 mL of iodide fractions were diluted by 10-20 folds with 1%  $NH_3 \cdot H_2O$ . Cesium (2 ng g<sup>-1</sup>) was used as an internal standard to monitor the efficiency of sample introduction and iodine ionization during ICP-MS measurements. The diluted solutions were finally analyzed for <sup>127</sup>I by ICP-MS (Thermo Fisher, X Series II) using an Xt cone under normal mode (Hou et al., 2007).

# 2.2.3. Purification and determination of <sup>129</sup>I

For the measurement of <sup>129</sup>I, solvent extraction was used to extract iodine from the original seawater and iodide fractions. 400 mL of seawater sample was analyzed for the total <sup>129</sup>I concentration. The sample was first transferred to a separation funnel, and 2.0 mg of <sup>127</sup>I carrier prepared from iodine crystal (Woodward Company, Colorado, USA, with a <sup>129</sup>I/<sup>127</sup>I ratio of less than  $2 \times 10^{-14}$ ) was added. 1.0 mL of 1.0 mol L<sup>-1</sup> NaHSO<sub>3</sub> solution was added and then 6.0 mol  $L^{-1}$  HNO<sub>3</sub> was added to acidify the sample solution to pH 1-2 to convert all inorganic iodine species to iodide. 1.0 mol  $L^{-1}$  NaNO<sub>2</sub> solution was added to the sample to oxidize iodide to I<sub>2</sub> which was then extracted from the water phase to the CHCl<sub>3</sub> phase. This extraction step was repeated twice, and all the CHCl<sub>3</sub> phases were combined and transferred to a clean separation funnel. 10 mL H<sub>2</sub>O and 0.5 mL of 0.1 mol L<sup>-1</sup> NaHSO<sub>3</sub> were added to reduce I<sub>2</sub> to iodide, and iodide was back extracted to the water phase. The extraction and back-extraction steps were repeated. The separated iodine in the aqueous phase as iodide was transferred to a centrifuge tube, and 1.0 mL of 0.5 mol  $L^{-1}$  AgNO<sub>3</sub> solution was added to precipitate iodide as AgI, which was separated by centrifugation.

Agl precipitates were then dried at 70 °C in an oven and mixed with niobium powder (325 mesh, Alfa Aesar, Karlsruhe, Germany). The mixture of Agl and niobium was pressed into a copper holder. The prepared Agl targets were measured for <sup>129</sup>I by accelerator mass spectrometry (AMS, 3 MV, High Voltage Engineering Europa B.V., the Netherlands) at Xi'an AMS Center, China. Iodine in a charge state of 5<sup>+</sup> (I<sup>5+</sup>) was selected for the measurement of <sup>127</sup>I by a Faraday cup and <sup>129</sup>I by a gas ionization detector. Procedural blanks were prepared in parallel with the samples. <sup>129</sup>I/<sup>127</sup>I ratios of the procedural blanks were below  $5 \times 10^{-13}$  (for iodide and total inorganic iodine), which is two orders of magnitude lower than all sample targets. Measurements of the total <sup>129</sup>I in three samples in this study show good agreement with reported values in the samples that were taken from the same stations during the same cruise by an independent study (Casacuberta et al., 2016), confirming the reliability of our data.

Since dissolved organic iodine presents at extremely low concentrations in open ocean waters (Wong and Cheng, 1998), iodate concentrations for <sup>127</sup>I and <sup>129</sup>I were simply calculated as the difference between total inorganic iodine and iodide.

# 3. Results

# 3.1. Spatial distributions of total <sup>127</sup>I and <sup>129</sup>I

The depth profiles of total <sup>127</sup>I showed a rapid increase from  $380 \pm 35$  nmol L<sup>-1</sup> at 10 to 50 m to  $448 \pm 22.9$  nmol L<sup>-1</sup> at 200 m, with values thereafter remaining relatively constant to the maximum sampling depth of 800 m at all stations (Fig. 2a, Fig. S1a and Table S1). This trend is similar to those observed in the Pacific Ocean, Atlantic Ocean, and Black Sea (Nakayama et al., 1989;

Tsunogai and Sase, 1969; Wong, 1977). The <sup>127</sup>I concentrations in the PML (0 to 50 m) over the Lomonosov and Alpha ridges (station 230; 310 nmol  $L^{-1}$  and station 249; 350 nmol  $L^{-1}$ ) were lower than those at other stations (350 to 420 nmol  $L^{-1}$ ) in this study. A significantly positive correlation between <sup>127</sup>I concentrations and salinity in the PML was observed (R = 0.712, p = 0.031, Fig. S2a), while such a correlation was not found in the AWL (200 to 800 m).

Unlike <sup>127</sup>I, the concentrations of <sup>129</sup>I in the PML were typically higher, albeit over a wide range from 1.36  $\times$  10<sup>8</sup> to 72.6  $\times$  10<sup>8</sup> atoms  $L^{-1}$ , than those in the AWL which were within a range of  $2.89 \times 10^8$  to  $32.8 \times 10^8$  atoms L<sup>-1</sup> (Fig. 2b and Fig. S1b). No significant correlation was observed between <sup>129</sup>I concentrations and salinity in the PML (Fig. S2b). The vertical distribution of <sup>129</sup>I typically showed two distinct patterns. In the Eurasian and Makarov Basins, <sup>129</sup>I concentrations decreased from the PML to 200 to 300 m in the AWL by a factor of 2 to 4, before slowly decreasing further with depth. In the Canada Basin, a sub-surface <sup>129</sup>I maximum was observed at 244 m, one order of magnitude higher than that observed at 25 m (station 234, Fig. 2b).  $^{129}I/^{127}I$  ratios fell within the range of 6.03  $\times$  10<sup>-10</sup> to 311  $\times$  10<sup>-10</sup> in the PML and 10.6  $\times 10^{-10}$  to 118  $\times 10^{-10}$  in the AWL, with vertical distribution patterns similar to total <sup>129</sup>I concentrations (Fig. 2c and Fig. S1c).  $^{129}I/^{127}I$  ratios in the studied sites were 1 to 2 orders of magnitude higher than the background environmental level in global surface seawater (ca.  $1 \times 10^{-10}$ ) for the post-nuclear bomb era (Snyder et al., 2010), and can be attributed mainly to the authorized liquid discharges of <sup>129</sup>I from the European nuclear fuel reprocessing facilities.

Horizontally, <sup>129</sup>I concentrations in the PML decreased from the Eurasian Basin to the Makarov Basin, with the lowest values observed in the Canada Basin, reflecting the transport and gradual mixing of <sup>129</sup>I-rich Atlantic Water and <sup>129</sup>I-poor Pacific Water (Karcher et al., 2012; Smith et al., 2011, 1999). The dramatic decrease in <sup>129</sup>I concentrations and <sup>129</sup>I/<sup>127</sup>I ratios from station 227 to the adjacent station 230 by a factor of 5 clearly demarcates the interface between the Atlantic and Pacific Waters in the PML over the Makarov Basin flank of the Alpha Ridge. This is consistent with other <sup>129</sup>I observations and the front position between Atlantic and Pacific Waters during the GEOTRACES oceanographic expeditions in 2015 (Smith et al., 2021). The slight decrease in <sup>129</sup>I concentrations in the surface water from the Eurasian Basin margin (station 285) to the interior (stations 271 and 276) could provide evidence of a weak surface current flowing from the margin to the interior along the Gakkel Ridge, as has been suggested by a previous observation and modeling study (Smith et al., 2021).

Compared to the PML, significantly lower <sup>129</sup>I concentrations were observed in the AWL (17 × 10<sup>8</sup> to 25 × 10<sup>8</sup> atoms L<sup>-1</sup>) with smaller gradients across the Eurasian Basin, Lomonosov Ridge, and Makarov Basin (Fig. 2b and Fig. S1b). The results indicate a well-mixed <sup>129</sup>I signal in this layer and limited water exchange between the AWL and the PML. The highest <sup>129</sup>I concentration in the Canada Basin (station 234) was observed at 244 m, which is similar to the values observed along the Lomonosov Ridge, indicating the intrusion of the AWL into the Canada Basin, as proposed by Karcher et al. (2012).

In the eastern Eurasian Basin, it has been reported that <sup>129</sup>I concentrations in the PML have increased six-fold from approximately  $12 \times 10^8$  atoms L<sup>-1</sup> in the mid-1990s to around  $65 \times 10^8$  atoms L<sup>-1</sup> in late 2000s (Buraglio et al., 1999; Cooper et al., 2001; Smith et al., 2011). In this study, we report a further increase in the PML to  $72.6 \times 10^8$  atoms L<sup>-1</sup> by 2011. Furthermore, <sup>129</sup>I concentrations in the AWL had increased around four-fold from  $5 \times 10^8$  atoms L<sup>-1</sup> in 1995 (Smith et al., 2011) to  $22 \times 10^8$  atoms L<sup>-1</sup> in 2011. The overall increase in <sup>129</sup>I concentrations in both PML and AWL since the 1990s is attributed to the increased marine



Fig. 2. Depth profiles of total <sup>127</sup>I, <sup>129</sup>I, and <sup>129</sup>I/<sup>127</sup>I ratios (a, b, and c), inorganic iodine species (d, e, g, and h), and molecular ratios of I<sup>-</sup> to IO<sub>3</sub><sup>-</sup> (f and i) for <sup>127</sup>I and <sup>129</sup>I in the central Arctic Ocean. The legends in subplots a to i for the corresponding locations are indicated in the map on the top right.

discharges of <sup>129</sup>I from European nuclear fuel reprocessing plants since 1990 and consistently higher discharges since 2000 (OSPAR Data and Information Management System, 2022). <sup>129</sup>I concentrations in the North Pacific, Bering Sea, and Chukchi Sea have been reported to be less than  $1.4 \times 10^8$  atoms L<sup>-1</sup> during 1993-1994 and 2012-2013 (Cooper et al., 2001; Nagai et al., 2015). The <sup>129</sup>I concentration in the PML of the northern Canada Basin (station 234) in 2011 observed in this study is comparable with these values, indicating that the surface water in the Canada Basin is dominated by Pacific Water characterized with a signature of global fallout <sup>129</sup>I (Cooper et al., 2001; Nagai et al., 2015). However, <sup>129</sup>I concentrations in the PML of the northern Canada Basin have increased from 0.5  $\times$   $10^8$  atoms  $L^{-1}$  in 1995 (Smith et al., 1999) to  $1.36 \times 10^8$  atoms L<sup>-1</sup> in 2011, indicating a slow rate of lateral mixing or diffusion between Atlantic and Pacific Water over the Mendeleyev and Alpha Ridges.

# 3.2. Variation in chemical species of iodine isotopes

Depth profiles of I<sup>-</sup> and IO<sub>3</sub><sup>-</sup> for both <sup>129</sup>I and <sup>127</sup>I in the central Arctic Ocean (Fig. 2d-i and Fig. S1d-i) show that iodate was the dominant species of both <sup>127</sup>I and <sup>129</sup>I in all analyzed samples. Depth profiles of <sup>127</sup>IO<sub>3</sub><sup>-</sup> concentration displayed increasing trends from the PML to the AWL, similar to that seen for the to-

tal <sup>127</sup>I. In contrast, <sup>127</sup>I<sup>-</sup> concentrations decreased by a factor of about seven from the PML to the AWL (Table 1). In the PML, the minimum <sup>127</sup>I<sup>-</sup> concentration (75.9 nmol L<sup>-1</sup>) occurred at station 285 close to the eastern shelf edge of the Eurasian Basin, with the maximum (113 nmol  $L^{-1}$ ) at station 249 over the Lomonosov Ridge. In the AWL, the highest <sup>127</sup>l<sup>-</sup> concentration was observed at 800 m at station 285. The depth profiles of the two inorganic species of <sup>129</sup>I showed clear decreasing trends from the PML to the AWL at all sampling stations except station 234, where a maximum was observed at 244 m. The mean <sup>129</sup>I<sup>-</sup> concentration in the AWL was about 9-fold lower than that of the PML, while the mean  $^{129}IO_3^-$  concentration was only about two-fold lower. A negative correlation between  ${}^{127}I^-$  and salinity (p = 0.024), and a positive correlation between  ${}^{127}IO_2^-$  and salinity (p = 0.011) was observed, while there was no significant correlation between either <sup>129</sup>I inorganic species (<sup>129</sup>I<sup>-</sup> and <sup>129</sup>IO<sub>3</sub><sup>-</sup>) and salinity (Fig. S2).

The measured  $I^-/IO_3^-$  ratios for both <sup>127</sup>I and <sup>129</sup>I in all analyzed seawater samples were less than 1 (Fig. 2 and Table S1), indicating that  $IO_3^-$  was the major iodine species as predicted under oxic conditions. <sup>129</sup>I<sup>-</sup>/<sup>129</sup>IO\_3^- ratios were about 1 to 12 times greater than <sup>127</sup>I<sup>-</sup>/<sup>127</sup>IO\_3^- due to the different sources of the two iodine isotopes (Hou et al., 2007). The highest ratios (0.560 and 0.476 for <sup>127</sup>I, 0.728 and 0.827 for <sup>129</sup>I) in the PML were found

Table 1
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Summary of inorganic iodine species of <sup>127</sup>I and <sup>129</sup>I in the central upper Arctic Ocean<sup>a</sup>.

Isotope	Layer	I-	$IO_3^-$	$I^-/IO_3^-$ molecular ratio
<sup>127</sup> I,	PML	75.8 - 113	199 - 334	0.228 - 0.560
nmol L <sup>-1</sup>		(92.8 ± 14.9)	$(287 \pm 45)$	$(0.338 \pm 0.113)$
	AWL	5.63 - 32.6	348 - 496	0.013 - 0.078
		$(13.3 \pm 6.0)$	$(434 \pm 24)$	$(0.031 \pm 0.015)$
<sup>129</sup> I,	PML	0.385 - 29.5	0.978 - 43.6	0.383 - 0.827
$10^8$ atoms $L^{-1}$		(19.7 ± 10.9)	(31.5 ± 16.0)	$(0.608 \pm 0.144)$
	AWL	0.147 - 6.54	2.75 - 29.5	0.054 - 0.392
		$(2.25 \pm 1.49)$	$(17.1 \pm 6.21)$	$(0.126 \pm 0.076)$

<sup>a</sup> The values are expressed as "minimum - maximum (mean  $\pm$  1 standard deviation)".

over the Lomonosov and Alpha ridges (stations 230 and 249), which were higher by 81% for <sup>127</sup>I, and 39% for <sup>129</sup>I, than the mean values for all other stations (0.287 for <sup>127</sup>I and 0.560 for <sup>129</sup>I) (Fig. 3a). Far lower I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> ratios were found in the AWL compared to the PML, with ratios lower than 0.08 for <sup>127</sup>I and lower than 0.40 for <sup>129</sup>I. Ratios of I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> for both <sup>129</sup>I and <sup>127</sup>I in the AWL typically decreased in the order of the Lomonosov Ridge, Eurasian Basin, Makarov, and Canada Basins, and the Alpha Ridge (Fig. 4), but with different trends due to the different sources of the two isotopes.

Exceptions were observed in the eastern part of the Eurasian Basin, with  $^{129}I^-/^{129}IO_3^-$  ratios of 0.146 at 700 m at station 271, 0.392 at 800 m at station 276, and 0.294 to 0.322 at 400 to 800 m at station 285. Such elevated I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> ratios for  $^{129}I$  and  $^{127}I$  have been previously reported in the AWL of the southern Eurasian Basin between Franz Josef Land and Severnaya Zemlya (station 7 and station 25 in Fig. 1) (Luo, 2013) and could be attributed to the off-shelf transport of sediment derived I<sup>-</sup> (Miwa et al., 2020), and/or vertical mixing of iodide-containing surface waters.

# 4. Discussion

# 4.1. Source and formation of iodide in the PML

Previous studies have reported a wide range of <sup>127</sup>I<sup>-</sup> concentrations of 0 to 300 nmol  $L^{-1}$  in the near-surface layer of the open ocean, with an overall decreasing trend with increasing latitude (Chance et al., 2014; He et al., 2013; and references therein). In the northern North Atlantic Ocean (>60°N), almost all reported <sup>127</sup>I<sup>-</sup> concentrations were below 60 nmol  $L^{-1}$  (Chance et al., 2014; He et al., 2013; Hou et al., 2007; Truesdale et al., 2000; Tsunogai and Henmi, 1971; Waite et al., 2006). In this study, relatively higher  $^{127}I^-$  concentrations of 75.8-113 nmol  $L^{-1}$  and  $I^-/IO_3^-$  ratios of 0.22-0.56 for <sup>127</sup>I and 0.38-0.83 for <sup>129</sup>I were found in the central Arctic Ocean from 78°N to the North Pole. Similarly, elevated  $I^-/IO_3^-$  ratios for <sup>127</sup>I (0.21) and <sup>129</sup>I (0.40) in the PML have been previously reported over the Lomonosov Ridge (Station 8 in Fig. 1) and over the Gakkel Ridge of the eastern Eurasian Basin (0.45 and 0.42, respectively at Station 25 in Fig. 1) (Luo, 2013). These results indicate that concentrations of  $^{127}I^-$  in surface water in the Arctic Ocean have reached levels that are far higher than previously expected. It has recently been predicted by a modeling study that <sup>127</sup>I<sup>-</sup> concentrations exceeding 100 nmol L<sup>-1</sup> could occur in the surface water in the Arctic Ocean (Wadley et al., 2020). This was attributed to the retention of I<sup>-</sup> that is transported into the Arctic Ocean in the PML due to a shallow mixed layer depth and little seasonal variation (Wadley et al., 2020), which would be enhanced by the relatively slow oxidation rate of  $I^-$  to  $IO_3^-$  in the open seas (Hou et al., 2007). However, there remains a question as to whether these observed elevated levels of I<sup>-</sup> in the PML are solely the result of I<sup>-</sup> transported into the Arctic Ocean or in situ converted.

**Influence of the Atlantic waters.** Concentrations of <sup>127</sup>I<sup>-</sup> in surface water of the northern Atlantic Ocean (inflowing water to the central Arctic) were reported to be 21 to 82 nmol  $L^{-1}$  (He et al., 2013), which is lower than those observed in the central Arctic Ocean in this study (Table S2). Elevated levels of <sup>127</sup>I<sup>-</sup> observed in the marginal seas of the northeast Atlantic Ocean (39 to 177 nmol  $L^{-1}$  in the North Sea and 93.8 to 183.8 nmol  $L^{-1}$  in the Baltic Sea) were attributed to the rather fast reduction of  $IO_2^-$  to I<sup>-</sup> in coastal areas of the North Sea and anoxic condition in the Baltic Sea (Hou et al., 2007; Yi et al., 2012). Further north in the Norwegian Sea (62 to 71°N),  $^{127}I^-$  concentrations were reported to be 35.1 to 161 nmol L<sup>-1</sup>, but with  $^{127}I^-$  concentrations lower than 75 nmol  $L^{-1}$  at locations further than 150 km from the coast (Luo, 2013). The  ${}^{127}I^{-}/{}^{127}IO_{3}^{-}$  ratios of the surface water in the central Arctic Ocean were within the range of those in the aforementioned marginal seas, but higher than those in the open seas of the northeast Atlantic Ocean. On the contrary,  ${}^{129}I^{-}/{}^{129}I^{-}_{-3}$  ratios in the Arctic were comparable to the northeast Atlantic Ocean, but far lower than those in marginal seas, which is attributed to the fact that I<sup>-</sup> is the dominant species of <sup>129</sup>I in liquid discharges to the English Channel and the Irish Sea from the European nuclear fuel reprocessing plants at La Hague and Sellafield (Hou et al., 2007) (Table S2). The observations in this study and the previously reported results support the slow oxidation of  $^{129}I^-$  to  $^{129}IO_3^-$  during the transport from the northeast Atlantic Ocean to the Arctic Ocean.

**Influence of the Pacific waters.** Although concentrations of <sup>127</sup>I<sup>–</sup> of 211-255 nmol L<sup>-1</sup> have been reported at depths of 0 to 150 m at 52°N in the northeast Pacific Ocean (Barkley and Thompson, 1960), lower <sup>127</sup>I<sup>–</sup> concentrations (ca. 50 nmol L<sup>-1</sup>) were reported in the upper layer (0 to 100 m) further north in the North Pacific Ocean (Chance et al., 2014; Miwa et al., 2020; Nakayama et al., 1989). In Bering and Chukchi Seas shelf waters, a range of 10-157 nmol L<sup>-1</sup> for <sup>127</sup>I<sup>–</sup> has been reported, with the higher values in bottom waters linked to the release of <sup>127</sup>I<sup>–</sup> from sediments in the southern Chukchi Sea (Miwa et al., 2020). In this study, we observed a <sup>127</sup>I<sup>–</sup> concentration of 97.9 nmol L<sup>-1</sup> in the Canada Basin (station 234), which was higher than the reported values for Pacific surface waters entering the Arctic Ocean (Miwa et al., 2020).

Based on available evidence and the potential retention of  $I^-$  in the Arctic Ocean, it is clear that inflowing Atlantic and Pacific waters and shelf sediments contribute to the observed levels of  $I^{27}I^-$  in the central Arctic Ocean. However, the observation of enhanced levels of  $I^-/IO_3^-$  ratios in the PML suggests that additional in-situ production of  $I^-$  is also occurring in surface waters.

**Influence by biological and atmospheric processes.** The highest <sup>127</sup>I<sup>-</sup> concentrations and I<sup>-</sup>/IO<sub>3</sub><sup>-</sup> ratios for <sup>127</sup>I and <sup>129</sup>I in the PML were observed over the Alpha Ridge and Lomonosov Ridge (stations 230 and 249) (Fig. 3a). In terms of known biological processes that mediate the conversion from IO<sub>3</sub><sup>-</sup> to I<sup>-</sup> in surface waters, there was no evidence of greater primary production at the two stations with sea-ice cover at 100% for most of the sampling



**Fig. 3.** Comparison of iodine species ratios to biological, physical, and nutrient parameters in the Polar Mixed Layer. (a)  $I^{-}/IO_{3}^{-}$  ratios for <sup>127</sup>I and <sup>129</sup>I. (b) Net community production (NCP) and sea ice cover (Ulfsbo et al., 2014). (c) Nitrate and (d) molecular ratios of nitrogen species including nitrite to nitrate, and ammonium to nitrate (Kattner and Ludwichowski, 2014).

section (Fig. 3b). The concentrations of chlorophyll a were as low as 0.106-0.194 µg L<sup>-1</sup>, and there was no difference in net primary production with the exception of station 271 located at the seaice edge (Fig. 3b) (Kattner and Ludwichowski, 2014; Miwa et al., 2020; Nöthig et al., 2015; Ulfsbo et al., 2014). Besides, the deposition of atmospheric iodine isotopes on the seawater iodine species in the central Arctic Ocean can be ignored due to the negligible contribution of <sup>127</sup>I and <sup>129</sup>I deposited onto the surface seawater comparing to their inventory in the upper Arctic Ocean (Gómez-Guzmán et al., 2014; Saiz-Lopez et al., 2012).

Influence of freshwater. Salinities of 28.3 to 32.9‰ were observed in the PML at our sampling stations, which are far lower than the values typical for Atlantic water  $(34.87 \pm 0.03\%)$  and Pacific Water  $(32.5 \pm 0.2\%)$  (Yamamoto-Kawai et al., 2008). The negative correlation between  ${}^{127}I^-$  and salinity (as well as a positive correlation between total <sup>127</sup>I and salinity) observed in this work might suggest that freshwater input (river water, sea ice meltwater, and precipitation) may have contributed to the elevated <sup>127</sup>I<sup>-</sup> concentrations in the PML (Fig. S1a and d). Of all the sources of freshwater to the Arctic Ocean, river runoff accounts for around 55%, with a total amount of 4800 km<sup>3</sup> yr<sup>-1</sup> (Arnell, 2005). Total <sup>127</sup>I concentrations are typically below 100 nmol  $L^{-1}$  in river water and rain, and lower than 400 nmol  $L^{-1}$  in sea ice (Atkinson et al., 2012; Hou et al., 2009). Although  $I^-$  is the dominant species of iodine isotopes in river water (Abdel-Moati, 1999; Hou et al., 2007; Smith and Butler, 1979), it only accounts for less than 30% of the total <sup>127</sup>I in precipitation and sea ice (Atkinson et al., 2012; Hou et al., 2009). When compared to the far greater overall background level of  $127 I^-$  in seawater, it is unlikely then that freshwater-derived <sup>127</sup>I<sup>-</sup> could contribute to the elevated levels of <sup>127</sup>I<sup>-</sup> observed in this study, and certainly would not explain the similar observations for <sup>129</sup>I<sup>-</sup>.

However,  $\delta^{18}$ O data revealed that riverine water accounts for about 14-22% of the surface waters near the two stations over the Alpha Ridge and Lomonosov Ridge where the highest levels of Iwere observed, but less than 10% at all other stations (Casacuberta et al., 2016). This might suggest another link between elevated levels of I<sup>-</sup> and the presence of river water in the PML. Available information on nutrient levels at the two stations revealed that the observed lower  $NO_3^-$  concentrations (Fig. 3c) were consistent with lower total <sup>127</sup>I concentrations, and that  $NO_2^-/NO_3^-$  ratios varied synchronously with  ${}^{127}I^{-}/{}^{127}IO_{3}^{-}$  ratios (R = 0.898, p = 0.002) and  $^{129}I^{-}/^{129}IO_{3}^{-}$  ratios (R = 0.631, p = 0.093) (Fig. S3). In addition,  $NH_{4}^{+}/NO_{3}^{-}$  ratios showed similar increases as  ${}^{127}I^{-}/{}^{127}IO_{3}^{-}$  ratios over station 249, but not at station 230 (Fig. 3d). The changes in inorganic nitrogen species ratios suggest that bacteria mediated decomposition of dissolved organic material (DOM) was occurring at these locations, which is known to drive the reduction of  $IO_2^$ to I<sup>-</sup> (Holmes et al., 2012; Rich et al., 1998). The lack of evidence of primary production along the sampling section would suggest that the source of DOM is not autochthonous. It is known that river water is a major source of DOM to the central Arctic Ocean (Holmes et al., 2012; Rich et al., 1998), and this may provide the link between elevated levels of I<sup>-</sup> we have observed in the PML at stations 230 and 249 and the reported increased fractions of river water at these locations.

Interestingly, freshwater, particularly river water, typically exhibits low redox potentials, with values below 300 mV in the Ob River system for example that drains into the Kara Sea (Frank et al., 2021). Since the stability of iodine species are affected by the redox condition of seawater, the presence of riverine water in the Arctic Ocean can have further implications for  $I^-/IO_3^-$  ratios. As freshwater storage in the upper layer over the Arctic basins has increased over the period from 1992 to 2012 by  $600 \pm 300 \text{ km}^3$  $yr^{-1}$ , partially due to an average increase in the rate of riverine discharge of 2.0  $\pm$  0.7 km<sup>3</sup> yr<sup>-1</sup> from the six largest Eurasian rivers to the Arctic Ocean over the period from 1936 to 1999 (Peterson et al., 2002; Rabe et al., 2014), it might be expected that the conditions favorable for the production and stability of I<sup>-</sup> in the upper layers of the Arctic Ocean have increased in recent times. Indeed, redox potentials down to 107 mV have been observed in the eastern Eurasian Basin (Rachor and Nalbandov, 2003), which would favor the stabilization of iodide, leading to longer residence times for any imported and in-situ produced I<sup>-</sup>. Under the prognoses for further increases in the input of riverine water to the Arctic Ocean under the impact of climate change (Pörtner et al., 2019), it might be anticipated that the redox condition of surface water in the Arctic Ocean will be more reductive in the future, leading to even higher levels of I<sup>-</sup>.

# 4.2. Iodide oxidation in the AWL

Distinct from high  $I^-/IO_3^-$  ratios in the PML, the  ${}^{129}I^-/{}^{129}IO_3^$ and  ${}^{127}I^-/{}^{127}IO_3^-$  ratios in the AWL in most of the investigated regions were lower than 0.15 and 0.05, respectively. However, high  ${}^{129}I^-/{}^{129}IO_3^-$  ratios up to 0.39 were found in the AWL of the eastern Eurasian Basin, particularly at stations 271 (700 m), 276 (800 m), and 285 (400 m and 800 m) (Fig. 2i, Fig. S1i, and Fig. 4). Such elevated  $I^-/IO_3^-$  ratios for  ${}^{129}I$  and  ${}^{127}I$  have been previously reported in the AWL of the southern Eurasian Basin between Franz Josef Land and Severnaya Zemlya (station 7 and station 25 in Fig. 1) (Luo, 2013). This suggests that higher  $I^-$  levels are occurring in the upper AWL at the margins of the eastern Eurasian Basin, which could be linked to the further transport of shelf sediment derived  $I^-$  such as that observed in the Chukchi Sea (Miwa et al., 2020), and/or the subduction of  $I^-$  in surface waters when dense



**Fig. 4.** Plot of  ${}^{129}I^{-}/{}^{129}IO_3^{-}$  ratios against  ${}^{127}I^{-}/{}^{127}IO_3^{-}$  ratios in the AWL of the central Arctic Ocean. The results show decreasing trends following the order of the Lomonosov Ridge (LR), the Eurasian Basin (EB), the Makarov and Canada Basins (MB&CB), and the Alpha Ridge (AR). Three outliers of the  ${}^{129}I^{-}/{}^{129}IO_3^{-}$  ratios were observed in the eastern Eurasian Basin (stations 276 and 285). For comparison with the other investigated areas, more data can be found in Table S2.

shelf waters cascade downslope and feed into the AWL (Koenig et al., 2018; Schauer et al., 1997).

Except for the high  $I^-/IO_3^-$  values of the eastern Eurasian Basin, the  $I^-/IO_3^-$  ratios for both <sup>129</sup>I and <sup>127</sup>I in the AWL show a clear decreasing trend from the Lomonosov Ridge, the Eurasian Basin, the Makarov, and Canada Basins to the Alpha Ridge (Fig. 4), that follows the transport pathway of the Atlantic Water. Any differences observed in the rate of changes for species ratios of <sup>127</sup>I and <sup>129</sup>I are probably simply a reflection of the point source nature of <sup>129</sup>I versus the ubiquitous abundance of <sup>127</sup>I in seawater and the mixing of different water masses.

The overall decreasing trends for both <sup>127</sup>I and <sup>129</sup>I provide direct observational evidence for the gradual net oxidation of I<sup>-</sup> to  $IO_3^-$  in the AWL along the transport pathway of the Atlantic Water in the Arctic. Even though observations on iodine species have been widely reported in the deep ocean (Bluhm et al., 2011; Tsunogai, 1971; Waite et al., 2006), the mechanism regulating I<sup>-</sup> oxidation in sub-surface layers is not clear. Given that <sup>127</sup>I<sup>-</sup> concentrations decreased by about 15 nmol L<sup>-1</sup> from the Eurasian Basin to the Canada Basin in this study, and that the transit time of Atlantic Water from the Eurasian Basin to the Canada Basin has been estimated to be over one decade by <sup>129</sup>I/<sup>137</sup>Cs tracers (Smith et al., 2011), a net oxidation rate of I<sup>-</sup> to IO<sub>3</sub><sup>-</sup> of 2.7 nmol L<sup>-1</sup> year<sup>-1</sup> at maximum can be roughly estimated when simply assuming a transit time of 10 years. This is far lower than values reported for surface and shelf waters elsewhere (up to 270 nmol L<sup>-1</sup> year<sup>-1</sup>) (Campos et al., 1996; Hardisty et al., 2020), indicating a rather slow oxidation of iodide to iodate in the AWL of the central Arctic Ocean.

# 5. Conclusions

The spatial distribution of <sup>129</sup>I in the Arctic Ocean in this study compares favorably with previous observational and modeling studies, with a clear front between Atlantic and Pacific Waters over the Makarov Basin flank of the Alpha Ridge in the PML, and an intrusion of the AWL into the Canada Basin. Based on our observation and the above discussion of the distribution of  $IO_3^-$  and  $I^$ for <sup>127</sup>I and <sup>129</sup>I, we propose a simple mechanism to schematically illustrate the interconversion of the two inorganic jodine species in the upper central Arctic Ocean (Fig. 5). Elevated I<sup>-</sup> concentrations, above the background of the inflowing Atlantic and Pacific Waters, are produced in situ in the PML and driven by bacterially mediated decomposition of river-input DOM. Shelf sediment and surface water derived I<sup>-</sup> are transported downwards along the shelf slopes into the AWL, where  $I^-$  is slowly oxidized back to  $IO_3^$ as the Atlantic water transports through the Arctic Ocean. Under the influence of climate change, the predicted increase in fluxes of riverine water and any subsequent increase in fluxes of DOM to the Arctic Ocean might be expected to further promote the reduction of  $IO_2^-$  to  $I^-$  as well as the stabilization of  $I^-$  in the upper layers of the Arctic Ocean. The liquid discharges of <sup>129</sup>I from the two European reprocessing plants provide a unique opportunity to investigate the marine geochemical cycling of iodine and provide insights into any changes to the redox condition of surface water in the Arctic Ocean.



**Fig. 5.** Schematic diagram showing the conversion of inorganic iodine species in the upper central Arctic Ocean. Yellow and pink balls denote  $I^-$  and  $IO_3^-$ , respectively. The Atlantic and Pacific water inflows into the PML are represented with yellow and white solid arrowed lines, respectively, and currents within the AWL are represented with yellow dotted lines. The downwelling of surface water masses is represented by a green dashed line. The thick blue arrow represents the input of riverine dissolved organic matter (DOM).  $I^-$  in the PML is partly derived from  $I^-$  signatures in inflowing Atlantic and Pacific Water, and partly by in-situ transformation from  $IO_3^-$  to  $I^-$  that may be driven by bacterially mediated decomposition of riverine DOM. In the AWL,  $I^-$  is slowly oxidized to  $IO_3^-$  as Atlantic Water is transported through the Arctic Ocean.

# **CRediT** authorship contribution statement

L.Y. Zhang carried out the experiments, interpreted the data, drew figures and drafted the manuscript. X.L. Hou supervised, conceptualized, designed the project, interpreted the data, and revised the manuscript. J.P. Gwynn and M. Karcher provided the samples, discussed the analytical results, and revised the manuscript. Y.K. Fan, N. Chen and Q. Liu conducted target preparation, AMS measurement, and data reduction. All authors contributed to the paper writing.

# **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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# Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2023.118165.

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