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Iodine isotopes species fingerprinting environmental conditions in surface water along the northeastern Atlantic Ocean

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Concentrations and species of iodine isotopes (^{127}I and ^{129}I) provide vital information about iodine geochemistry, environmental conditions and water masses exchange in oceans. Despite extensive investigations of anthropogenic ^{129}I in the Arctic Ocean and the Nordic Seas, concentrations of the isotope in the Atlantic Ocean are, however, still unknown. We here present first data on ^{129}I and ^{127}I, and their species (iodide and iodate) in surface water transect along the northeastern Atlantic between 30° and 50°N. The results show iodate as the predominant species in the analyzed marine waters for both ^{127}I and ^{129}I. Despite the rather constant ratios of ^{127}I$^-$/^{127}IO$_3^-$, the ^{129}I$^-$/^{129}IO$_3^-$ values reveal variations that apparently response to sources, environmental conditions and residence time. These findings provide a new tracer approach that will strongly enhance the application of anthropogenic ^{129}I in ocean environments and impact on climate at the ocean boundary layer.

Atmospheric chemistry shows that iodine plays a significant role in the depletion of ozone and aerosol particles for cloud nucleation[1,2]. Thus, considerable attention has been paid to understanding sources of inventory and distribution of iodine in natural environments. Oceans represent the main source of iodine to the Earth's surface environments and it is apparent that tracing the chemical species of iodine in ocean water provides further clue for incorporation in the atmosphere. As most of iodine atmospheric interaction is strongly linked to releases from ocean surface water, identifying iodine species in this compartment of the ocean is becoming important. Iodate is the predominant species in oxic ocean water with a comparable iodide concentration especially in the tropical surface waters. Data from the Atlantic and Pacific Oceans reveal occurrence of minimum iodate concentrations along the equatorial regions that increase polar wards[3,4].

The addition of anthropogenic long-lived radioactive isotope of iodine, ^{129}I ($T_{1/2} = 15.7$ Myr), to the marine environment provided another interesting tracer that can be used to shed further light on the ^{127}I distribution and its geochemical behavior in ocean surface water. Huge amount of ^{129}I has been released to the environment as a result of human nuclear activities since the 1940s. The nuclear fuel reprocessing facilities (NRFs) at Sellafield (UK) and La Hague (France), have together released >6000 kg of ^{129}I both to the atmosphere and marine environment until 2010. The discharge rate of ^{129}I from these two facilities increased and remained high after 1990 and peaked in 1997, but declined slightly during the past 10 years. Although concerns about ^{129}I hazardous environmental impacts are there, the releases from Sellafield and La Hague also provided an ideal source point oceanographic tracer to investigate transport and circulation of water masses in specific areas.

Several studies show that the discharges of ^{129}I from the English Channel and the Irish Sea are transported into the North Atlantic via the Norwegian Coastal Current (NCC) and the Arctic Ocean[5–7]. A twofold increase of ^{129}I concentration was observed in the central Arctic since 1996[7] and has been used to trace Polar Water transport into the Atlantic Ocean[8]. However, most of these studies have focused on the Nordic Seas and the Arctic region, and there is little information about concentration and/or inventory of ^{129}I in other parts of the North Atlantic Ocean. He et al.[9] summarized all available ^{129}I data in the ocean's surface water and pointed out that there are many shortcomings in the data sets which need to be completed in future work.

Speciation analyses of [129]I represent a new powerful tool for gaining detailed information on identifying redox rate of I^-/IO_3^- pair in environmental conditions as well as sources and exchanges of seawater masses. This potential has been successfully applied in the North Sea and the Baltic Sea[10–12]. However, at present we have no idea on distribution and conversion patterns of [129]I species in the open sea environment. In addition, to our best knowledge, there is no clear conclusions on whether [129]I that originated from Sellafield and La Hague has influenced the middle latitudes of the North Atlantic Ocean or even more remote regions (i.e. South Atlantic Ocean and Southern Ocean), though evidence revealed elevated [129]I/[127]I ratio in the Deep Western Boundary Current[13,14]. Orre et al.[15] simulated the spread of [129]I contamination from the west of the North Atlantic Ocean to the east over a 10 years period using Ocean General Circulation Model (OGCM). They concluded a possible transport of high [129]I-labelled surface water from the Labrador Sea that can influence the eastern part of the Atlantic Ocean. This hypothesis has, however, not yet been supported and confirmed by experimental observations. In the study presented here, we provide first data on iodine isotopes ([129]I and [127]I) and their species (iodate and iodide) in the northeastern Atlantic Ocean (Fig. 1), aiming at identifying effects of environmental conditions, sources and pathways on [129]I distribution in this region.

Results

Distribution of total iodine and its species ([127]I⁻ and [127]IO₃⁻). The concentrations of total iodine ([127]I) and its species ([127]I⁻ and [127]IO₃⁻) in the sampled surface water of the North Atlantic Ocean are shown in Fig. 2a and listed in Supplementary Table S1. In general, surface concentrations of total iodine and its species (iodate and iodide),

show a fairly small variation in the samples from the break of Celtic Slope to the east of Madeira Archipelago. It seems that [127]I and its species, iodate and iodide, show rather constant values in the surface water of the open sea, with mean concentrations of 0.39, 0.35 and 0.05 μM, respectively. The range of iodide is 0.02 to 0.08 μM and the lowest concentration of iodide occurred along the shelf break of the Celtic Sea (sample 1) while the two pronounced peaks (sample 6 and 14) appear in the north and middle parts of the Portugal coastal region. Unlike the iodide, the concentrations of total iodine is positively correlated with iodate ($r^2 = 0.5$), which suggests rather similar distribution trend for both [127]I and [127]IO₃⁻. The highest concentrations are in the area off the Cape St Vicente, whereas the minimum values occurred in the northeast of Madeira. More than 75% of [127]I-iodate is observed in these surface waters, which is comparable to seawaters collected in any other ocean regions (Supplementary Table S2).

Distribution of [129]I and its species ([129]I⁻ and [129]IO₃⁻). Data on [129]I and its species ([129]I⁻ and [129]IO₃⁻) in the surface water samples are listed in Supplementary Table S1. It is apparent that, as a sensitive radioactive tracer, the concentration of [129]I (including [129]I⁻ and [129]IO₃⁻) shows a larger variation in the seawater compared with that of [127]I (Fig. 2c). More than one order of magnitude difference in [129]I concentration is shown in the studied region, with an average of 1.53×10^8 atoms/L. The highest concentration occurred in the middle of the Biscay Bay (12.67×10^8 atoms/L) and all the [129]I data here are higher than 4.0×10^7 atoms/L. Five pronounced peaks of [129]I ($>2 \times 10^8$ atoms/L) are observed along the surface water transect. However, if these distinct peaks are not taken into consideration, concentration of [129]I in the sampled transect is less than 1×10^8 atoms/L (mean 6.9×10^7 atoms/L) and also does not
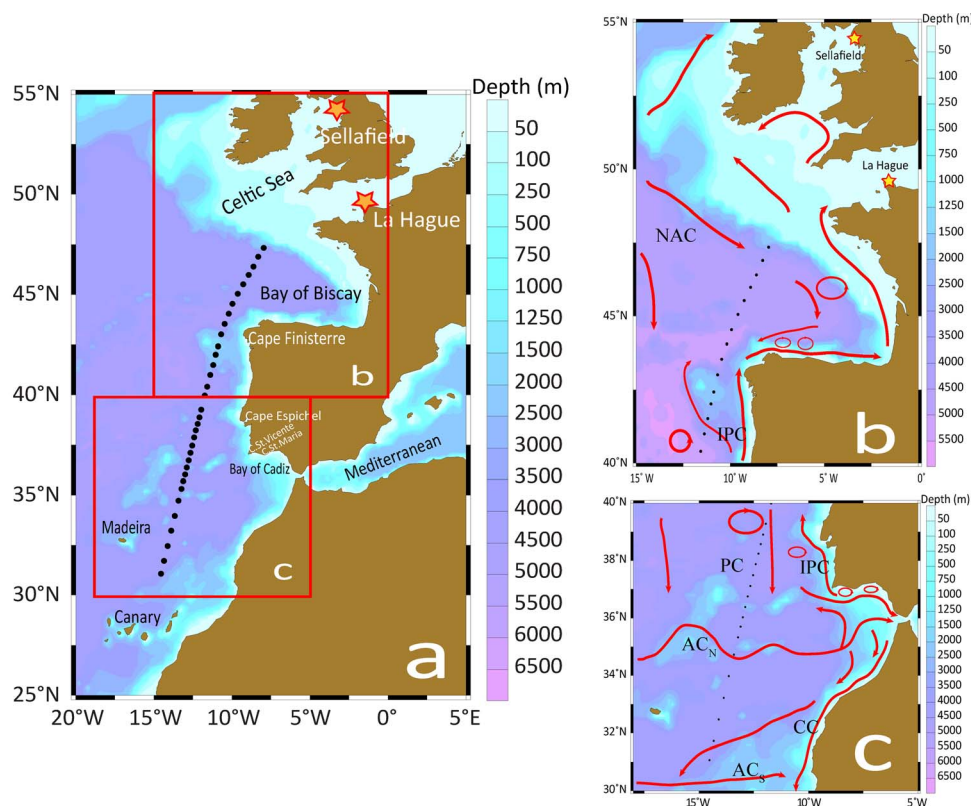

Figure 1 | General bathymetric chart of the investigated area in the North Atlantic Ocean. (a) Sampling transect of [129]I along the northeastern Atlantic Ocean. Sampling locations are expressed as blank dots. Two European nuclear reprocessing facilities (NRFs) Sellafield and La Hague, are highlighted with stars. (b) General scheme of surface water circulation in the region of Bay of Biscay and (c) the Gulf of Cadiz. NAC = North Atlantic Current, IPC = Iberian Poleward Current, PC = Portuguese Current, AC_N = Azores Current, northern branch, AC_S = Azores Current, southern branch and CC = Canary Current. The bathymetry and coastal lines were created using Ocean Data View (ODV 4.5.3).
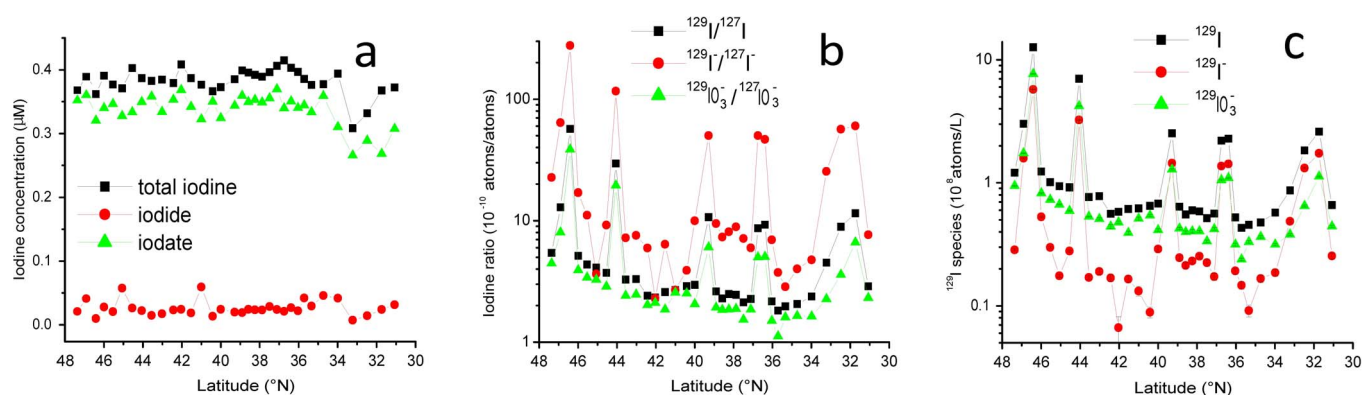
Figure 2 | Iodine isotopes (^{127}I and ^{129}I) and their species in the Atlantic seawaters. (a) Concentration of total iodine (^{127}I) and its species (^{127}I$^-$ and ^{127}IO$_3^-$) along the sampled transect in the northeastern Atlantic Ocean. (b) Variations of isotopic ratio of ^{129}I/^{127}I, ^{127}I$^-$/^{129}I$^-$ and ^{127}IO$_3^-$/^{129}IO$_3^-$ in the sampled transect along the northeastern Atlantic Ocean. (c) Concentration of ^{129}I and its species (^{129}I$^-$ and ^{129}IO$_3^-$) along the sampled transect in the northeastern Atlantic Ocean.

vary a lot in the open sea surface water. Despite nearly similar behavior for ^{129}I$^-$ and ^{129}IO$_3^-$ in the sampled surface water, the concentrations of ^{129}I$^-$ show a relatively wider range (0.07–5.73 × 10^8 atoms/L). Additionally, ^{129}IO$_3^-$ concentrations are normally higher than that of ^{129}I$^-$ in the sampled region with a few exceptions. The isotopic ratio of ^{129}I/^{127}I has the same trend as with that of ^{129}I and varies between 1.82 × 10^{-10} and 5.69 × 10^{-9} with an average value of 6.63 × 10^{-10} (Fig. 2b). Both ^{129}I and ^{129}I/^{127}I values are 2–4 orders of magnitude higher than the natural levels in the ocean (estimated as ~10^5 atoms/L for ^{129}I and ~10^{-12} for ^{129}I/^{127}I). Similarly, there are five peaks found at sampling locations 3, 8, 17, 24 and 33. The same pattern also appears for the ratios of ^{129}I$^-$/^{127}I$^-$ and ^{129}IO$_3^-$/^{127}IO$_3^-$ and that the atomic ratio of ^{129}I/^{127}I for iodide is significantly higher than that for iodate in the investigated region.

Distribution of ^{129}I$^-$/^{129}IO$_3^-$ and ^{127}I$^-$/^{127}IO$_3^-$. The ratios of ^{129}I$^-$/^{129}IO$_3^-$ are generally higher than ^{127}I$^-$/^{127}IO$_3^-$ (Fig. 3c). This discrepancy between abundance of iodine species for ^{127}I and ^{129}I likely reflects different sources of the isotopes. Some ^{129}I$^-$/^{129}IO$_3^-$ values, however, are close to the corresponding ^{127}I$^-$/^{127}IO$_3^-$ levels which are expected to reflect a local effect. This may either be related to older water ventilated to the surface during winter, or the small-scale accelerated redox cycle induced by local chemical or biological characters in these waters. The ^{129}I$^-$/^{129}IO$_3^-$ value varies from 0.14 to 2.02 in the samples where the highest level occurs in the region

between Madeira and Africa coast (sample 32). Most of the ratios for ^{129}I$^-$/^{129}IO$_3^-$ lie at 0.3–0.7 while the ^{127}I$^-$/^{127}IO$_3^-$ values are normally below 0.2. High values of ^{129}I$^-$/^{129}IO$_3^-$ (above 0.7) are thought to be directly linked to the large-scale circulation pattern as described in the next section. Similar to ^{129}I and ^{129}I/^{127}I, there are five peaks observed for ^{129}I$^-$/^{129}IO$_3^-$ and the intensity of the peaks generally decreases towards the north. Unlike the ^{129}I$^-$/^{129}IO$_3^-$, the ratios of iodide to iodate for ^{127}I remain nearly constant in the sampled surface water transect. On average the value for ^{127}I$^-$/^{127}IO$_3^-$ is 0.14, which is a factor of five lower than that of ^{129}I$^-$/^{129}IO$_3^-$ (0.65).

Discussion

It is well established that marine discharges from Sellafield and La Hague (NRFs) are the main source of ^{129}I in the North Sea, Baltic Sea, Nordic Seas and the Arctic Ocean[8,16,17]. Whether the discharges have influenced the northeastern Atlantic Ocean and, if so, on what magnitude was not fully investigated. The natural ^{129}I/^{127}I of the pre-nuclear era is estimated at 1.5 × 10^{-12} based on analysis of marine sediment cores[18] and consequently the inventory of natural ^{129}I in the world ocean is calculated to be 100 kg using average iodine concentration of 0.4 μM from our Atlantic data presented here. About 90 kg of ^{129}I were released to the environment by atmospheric nuclear weapons tests in the 1950s and 1960s which raised the ^{129}I concentration to ~10^7 (atoms/L) and ^{129}I/^{127}I to ~10^{-10} (atoms/atoms)[19]

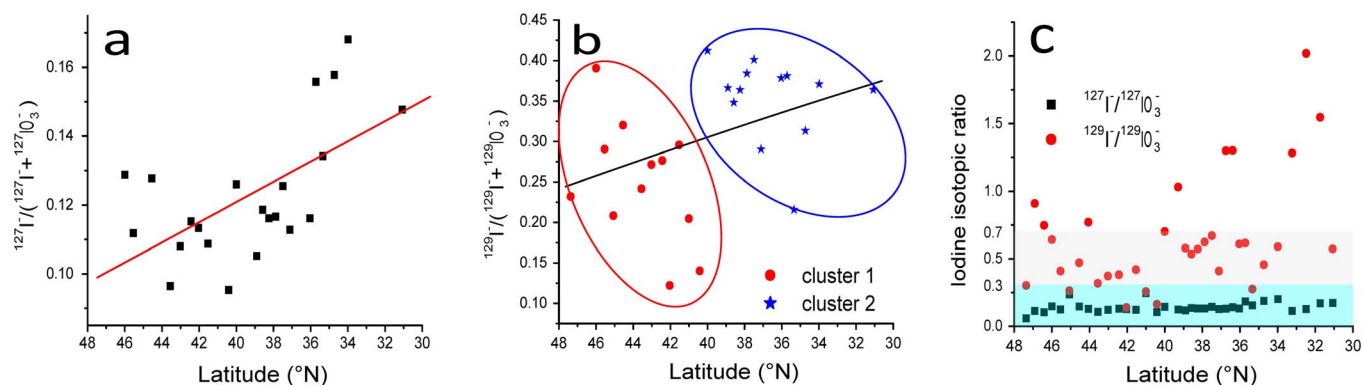**Figure 3 | Ratios of Iodine species in the Atlantic seawaters.** (a) Variations of ^{127}I$^-$/(^{127}IO$_3^-$ + ^{127}I$^-$) as a function of latitude along the sampled transect in the northeastern Atlantic Ocean. Linear fit shows a significant increase of ^{127}I$^-$ proportion southwards ($r = -0.61$; $P < 0.005$). (b) Negative correlation between ^{129}I$^-$/(^{129}IO$_3^-$ + ^{129}I$^-$) ratio and latitude towards south along the sampled transect of the northeastern Atlantic Ocean ($r = -0.39$; $P < 0.05$). Clusters in blue and red that separated by 40°N may attribute to different sources of ^{129}I (Mediterranean source and English Channel source, respectively). (c) Variations of ^{129}I$^-$/^{129}IO$_3^-$ and ^{127}I$^-$/^{127}IO$_3^-$ along the sampled transect of the northeastern Atlantic Ocean. Colored zones represent ^{129}I species in samples that is close to (<0.3, cyan), approaching (0.3–0.7, gray) and far from reaching (>0.7, white) the iodine redox equilibrium in seawaters.

and account for about 10% of the concentration found in our samples. This finding indicates that the [129]I in surface water of the northeastern Atlantic Ocean had been labeled by mainly marine and/or atmospheric discharges from the nuclear fuel reprocessing.

Atmospheric [129]I emission from many NRFs is a possible source to the North Atlantic Ocean. Hanford nuclear fuel reprocessing plant located in the west coast of USA has released about 260 kg [129]I into the atmosphere during its operation[20]. Meanwhile, the major European NRFs (i.e Marcoule (France), Sellafield (UK) and La Hague (France)), have combined release of 400 kg [129]I into the atmosphere until 2007[20] and estimation of total atmospheric discharges from major Russian facilities (Mayak, Seversk and Zheleznogorsk) are about 210 kg[21]. A large portion of atmospheric [129]I may attach to aerosols and be washed out and deposited in the vicinity of the point sources while long-distance transport of [129]I atoms will be continuously removed by precipitation along their journey. Concentration [129]I in precipitation and surface soil in Europe together with the fallout pattern of ^{137}Cs after Chernobyl accident suggest that more than 90% of the radionuclides are deposited within 1500 km of the nuclear power plant[22–24]. Thus the contribution from Hanford reprocessing plant (~4000 km away from east coast of America) to the Atlantic Ocean must be negligible and the same applies for the atmospheric releases from the Russian facilities. Furthermore, precipitation collected in Europe suggests that only tiny portion (<1%) of [129]I atmospheric releases occurs in the atmosphere which again supports insignificant effect of gaseous emission from the European NRFs[25]. Thus for the [129]I inventory, the influence of direct marine discharges and later transport by ocean currents system play a major role for the concentration in the surface water of the investigated area. The [129]I concentration and [129]I/[127]I value in samples north of Cape Finisterre (Spain) analyzed here also confirm the influence from north, where a gradually decreasing pattern is documented southward. Therefore, the [129]I level in the north part of the investigated region exhibited a combined contribution from both Sellafield and La Hague, and may likely be advection effect further south.

Except the two high [129]I concentrations in the north part of our transect, three peaks are also found in water samples south of 40°N (Fig. 2). These waters exhibit relatively high [129]I concentration (1.8–2.6 × 10^8 atoms/L) and high [129]I/[127]I values (8.7–11.5 × 10^{−10} atoms/atoms), which are about one order of magnitude higher than the level of atmospheric nuclear weapons test (~10^{−10}) and 4–6 times higher than surrounding waters. These three isolated peaks do not seem linked to waters from the north due to the general pattern of meridional water movement with respect to the Portugal Current system in this region[26]. This is also confirmed by speciation analysis of [129]I that shows, iodide as the main species, in the southern three peaks, whereas in samples 3 and 8 the iodate species dominates. Accordingly, waters with high [129]I concentration south of 40°N clearly imply a source other than the influence of Sellafield and La Hague from the north. In addition to the two NRFs mentioned above, the Marcoule facility (France), which is located on the banks of Rhone river, directly released 45 kg of liquid [129]I to the river and 145 kg of [129]I to the atmosphere during its operation until 1997[20]. Considering 50% of atmospheric [129]I deposited in the vicinity of the plant and assume all [129]I has eventually injected into the Mediterranean Sea through continental runoff, about 120 kg of [129]I would be in the Mediterranean Sea. As a result, the average concentration of [129]I is estimated at 1.46 × 10^8 atoms/L on the assumption that the [129]I is homogeneously mixed in the Mediterranean water. The large amount of [129]I released by Marcoule and the relatively long residence time of iodine (~1800 y) compared with the water turnover time (~1000 y) in the Mediterranean Sea, point out the Mediterranean water as a source of [129]I to the North Atlantic Ocean. Seawater and algae samples taken from the Mediterranean Sea show a comparable [129]I level with our samples that show high [129]I level in the south part of the transect. This similarity suggests a Mediterranean source in these waters[27,28]. To our

best knowledge, there is no [129]I speciation data in the Mediterranean Sea, but data from the English Channel (close to the La Hague facility) indicate high [129]I^−/[129]IO_3^− values[10] and it is reasonable to conclude high [129]I^−/[129]IO_3^− values for Mediterranean seawater. Moreover, high iodide concentration is normally found in the coasts, bays, estuaries and semi-enclosed basin[10,29,30]. Therefore, our transect seawater samples south of 40°N that are characterized by high [129]I and [129]I^−/[129]IO_3^− may represent direct influence from Mediterranean water plume.

Saline and dense Mediterranean Outflow Water (MOW) that passes through the Strait of Gibraltar descends as Mediterranean Undercurrent in the Gulf of Cadiz along the continental slope and interacts with local bottom topography, and spreads towards the Azores, the Canary Islands and the coast of Portugal[31]. Two major Mediterranean cores with maxima in the temperature and salinity can be well detected in the depth of 800 and 1200 m[32]. This feature is also shown by two peaks of [129]I/[127]I ratio in a water profile taken from the northeastern Atlantic Ocean[33]. The dense Mediterranean Water typically settles at depth of 800–1200 m in the North Atlantic Ocean, which is physically separated by a salinity-minimum layer of Subpolar Mode Water (S < 36) above[34]. The isolated Mediterranean layer should not have direct influence on the surface and the North Atlantic Central Water (NACW) that control the surface circulation. Thus, those high [129]I samples (>2 × 10^8 atoms/L) in the south of our transect seem to originate from the Gulf of Cadiz and Portugal coast rather than local upwelling effect in the open sea. Intensive in situ hydrographic data and sea surface temperature (SST) satellite observations, as well as numerical models reveal that the eastward Azores Current, combined with equatorial Portuguese Current that flows parallel to the west Iberia coast, enters the Gulf of Cadiz along the continental slope towards the Strait of Gibraltar. The easternmost part of this anticyclonic circulation eventually feeds the Canary Current (Fig. 1c). This general feature of circulation pattern was thought to be weakened in winter and enhanced in summer[35–37]. Mediterranean Outflow Water (MOW) overflows the sills of Gibraltar in a shallow depth (~200 m) and intense local vertical mixing and entrainment processes taken place at the mouth of the strait are even capable to induce and maintain the eastward surface Azores Current[38,39]. Mauritzen et al.[40] hypothesized a cross-isopycnal MOW towards the surface in the vicinity of the Strait of Gibraltar, which they referred to 'detrainment' process and later confirmed by a rotating tank experiment. Thus the high [129]I concentration may occur in the surface water as a result of Mediterranean water upwelled in this turbulent and instable fluid condition within the eastern Gulf of Cadiz. In addition to the double-core structure of the MOW, a shallow layer is identified through salinity and temperature field at depths between 400 m and 700 m[36,41], or depicted in the geostrophic velocity field[42,43] along the upper continental slope of the Gulf of Cadiz and off the southern half of the Iberian western coast[41,44]. Therefore, upwarping of this Mediterranean shallow core, in association of coastal upwelling that is especially occurring off the Capes St. Vicente and St. Maria, by favored westerlies during summer[45], probably bring the Mediterranean-labeled [129]I from mid-depth to the surface. Accordingly, we suggest the surface water in location 24 and 25 may reflect the propagation of a branch of this onshore water westwards towards the open ocean after leaving Cape St. Vicente when easterlies dominated (Fig. 4). Seasonal and regional variations of wind system in the transition zone between westerlies and trade wind highly influences the surface circulation pattern in most parts of our sampling transect. Based on buoy and hydrographic data, large-scale movement of upper water between subpolar and subtropical gyres is week, flowing slowly towards east and south[46]. However, a poleward surface current has been reported off the west coast of Portugal during winter when the wind blowing northward[47]. Although the origin and variability of this slope-flow current is still unclear, it may be connected with the coastal counter flow in the western of Cadiz,
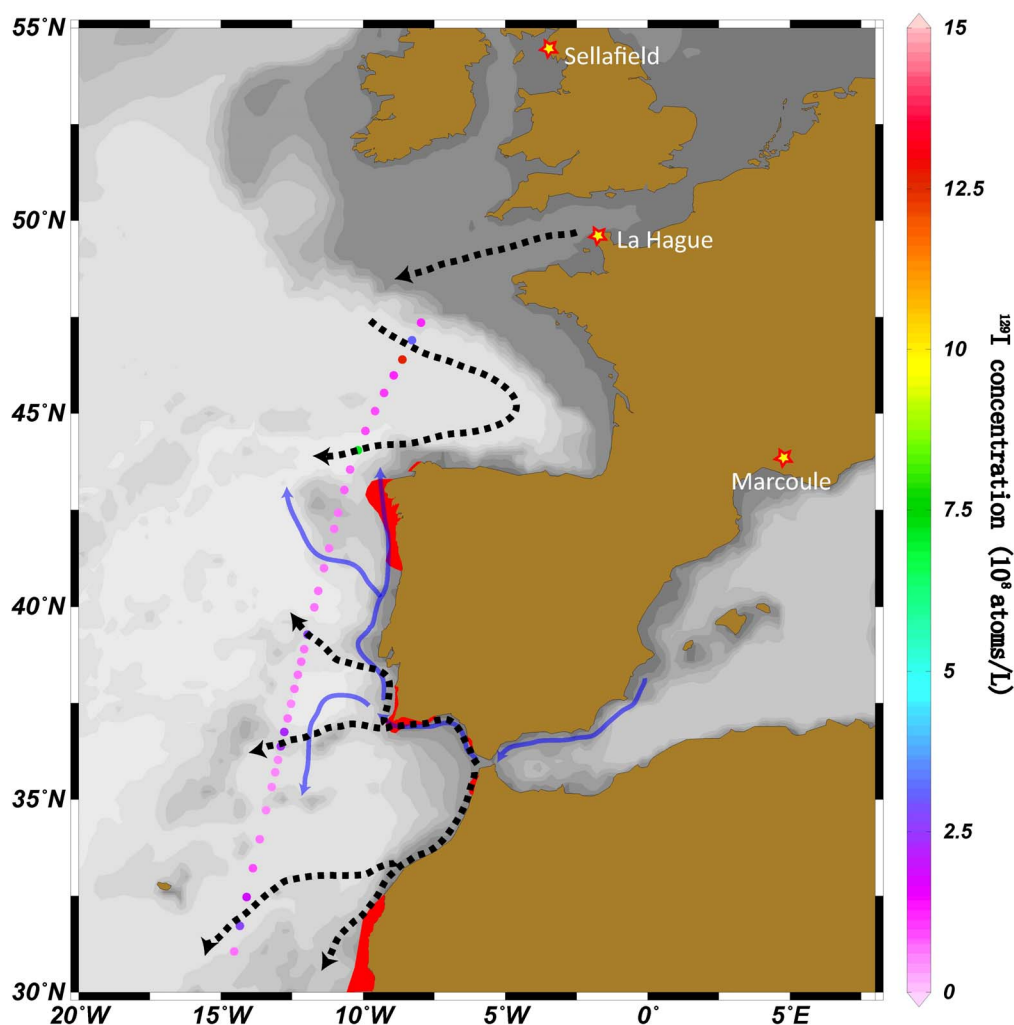
Figure 4 | Concentrations of ^{129}I (10^8 atoms/L) along the transect and suggested surface ^{129}I pathways from the English Channel and the Strait of Gibraltar (dashed arrows). Red regions represent major coastal upwelling and solid blue lines show the spread pathways of deep Mediterranean water. Major nuclear reprocessing facilities (NRFs) are marked as stars. The original map was constructed by a free software Ocean Data View (ODV 4.5.3).

which flow anticyclonically around Cape St. Vicente and thus bearing high ^{129}I signal from MOW[48]. When this water reaches the Cape Espichel, local coastal morphology, shelf/slope bathymetry as well as propagation of eddies make the ^{129}I plume extends seaward, which is reflected in our sample 17. The other two high-^{129}I samples, which occur in the middle of Madeira and African coast (location 32 and 33), however, are likely related to the onshore flow of Canary Current, which with one branch separated from the northern Morocco coast[37], transports ^{129}I from the Strait of Gibraltar to further west around 14°W (Fig. 4).

Iodate is found to be predominated species in ocean waters, however, since some biological-mediated processes may be active on iodate reduction, significant amounts of iodide have also been observed in the surface water of the open sea. By combining available inorganic iodine species data in the different ocean regions, total iodine concentration is fairly constant in the world ocean ($\sim$0.45 μM) whereas ^{127}I$^-$/^{127}IO$_3^-$ ratio shows a meridional variation (Supplementary Fig. S1). This feature implies reduction of iodate in the tropical areas, though how fast this conversion is in the open sea is still unclear. Our results (iodide/total iodine) also show a 50% increase of iodide from 50 to 30°N for both ^{127}I and ^{129}I (Fig. 3a, b). It seems that the water samples show a different behavior in terms of ^{129}I$^-$ proportion at the two sides of latitude 40°N (Fig. 3b). This could be explained either by different sources of ^{129}I (English Channel and Mediterranean Sea) or different degrees of biological activity in

each cluster. Marked discrepancies of iodide/iodate ratio for ^{127}I and ^{129}I (Fig. 3c) suggest that the ^{129}I speciation system is not kinetically and thermally at equilibrium in the investigated area. Thus, given the transit time between source and sampled region, speciation of ^{129}I can be used as an ideal temporal and spatial tracer to distinguish ^{129}I sources as well as to evaluate iodine redox processes in the ocean.

Compared to iodate, iodide is a thermodynamically unfavorable species under oxic conditions. Thus theoretically the spontaneous oxidation of iodide should occur in the ocean surface until dynamic equilibrium has been achieved for the iodide-iodate couple. However, kinetic barrier prevents this mechanism and natural oxidation process in ocean waters is thought to be rather sluggish once newly iodide is formed[10,49]. Regarding available ratio of ^{129}I$^-$/(^{129}I$^-$ + ^{129}IO$_3^-$), the decreasing trend from the source of ^{129}I indeed suggests iodide oxidation occurred in ocean surface water as the water is transported (Fig. 5 and Supplementary Table S3). Considering a constant level of ^{129}I speciation in the source water and 6.5-years transport of ^{129}I plume from the northern North Sea (Location B, Fig. 5) to the Nansen Basin in the Arctic Ocean (Location C, Fig. 5)[50], 7.3–10.3% (mean 8.9%) of iodide is annually oxidized as the ^{129}I-contaminant water masses move. Seawater transit times from the northern North Sea to the Denmark Strait and the interior of Labrador Sea are estimated at 3.5–6.5 and 5.5–8.5 years, respectively[51–53]. The ^{129}I$^-$/(^{129}I$^-$ + ^{129}IO$_3^-$) values in the surface water of the Denmark Strait and the Labrador Sea are 0.19–0.42 (mean 0.32)
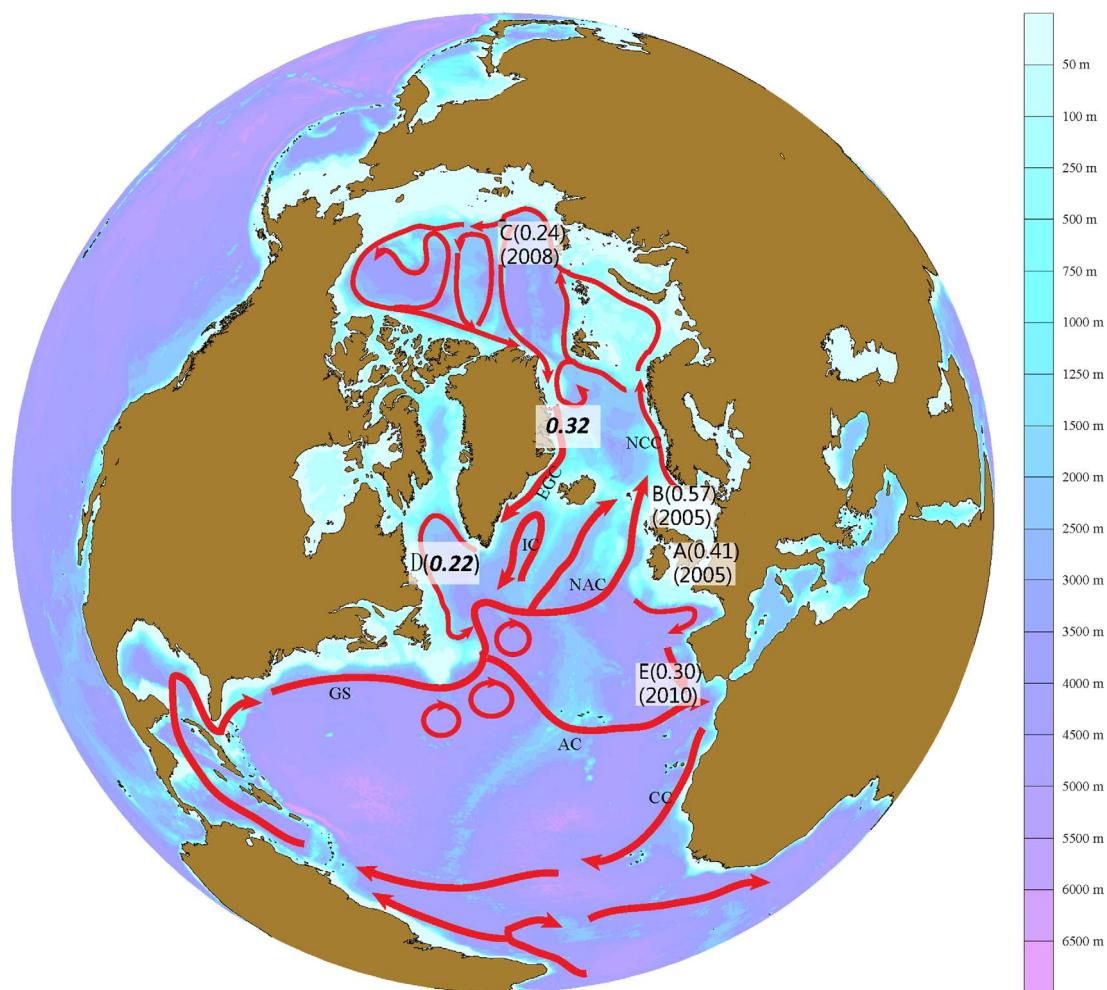
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Figure 5 | Scheme of surface water circulation in the North Atlantic Ocean and the variation of $^{129}I^-/(^{129}IO_3^- + ^{129}I^-)$ (upper parenthesis) in the (A) English Channel, (B) the North Sea, (C) the Arctic Ocean, (D) the Labrador Sea and (E) the eastern North Atlantic Ocean. NCC = Norwegian Coastal Current, NAC = North Atlantic Current, AC = Azores Current, CC = Canary Current, GS = Gulf Stream, EGC = East Greenland Current and IC = Irminger Current. Background map was created using Ocean Data View (ODV 4.5.3). Numbers in lower parenthesis refer to the sampling year and the bold italic number represent estimated $^{129}I^-/(^{129}IO_3^- + ^{129}I^-)$ value.

and 0.07–0.34 (mean 0.22) when analogous annual oxidation rate is applied. Regarding species for ^{127}I, concentration of iodide seems rather homogenous and remains at low value in the seawaters (<0.01 μM) at high and middle latitude. Similarly, the average ratio of $^{127}I^-/(^{127}I^- + ^{127}IO_3^-)$ remains fairly constant (0.13) both in the Arctic Ocean and the North Atlantic Ocean (Supplementary Table S3), which suggests an equilibration for iodine species in these waters. Thus, if we simply assume there is no upwelling or vertical mixing, as well as no additional redox processes occurring during the transport of ^{129}I plume in the open ocean, it takes 7.5–10.6y (mean 8.7 y) for $^{129}I^-/(^{129}I^- + ^{129}IO_3^-)$ to reach the about 0.13 seawater equilibrium ratio as they transport from the northern North Sea (Location B, Fig. 5). Given 2 years transport from the Labrador Sea to the northeastern Atlantic region, via the Azores Current[54,55], it will take about 7.5–10.5 y for ^{129}I to be transported from the northern North Sea, via the Greenland Sea and the Labrador Sea, to the northeastern Atlantic Ocean. In addition, even much longer time is estimated (>10 y) for ^{129}I in the upper 200 m from the Labrador Sea to reach our sampling transect using Ocean General Circulation Model[15]. This indicates that the ratio of $^{129}I^-/(^{129}I^- + ^{129}IO_3^-)$ in our sampled transect should be in a state of geochemically balanced value (~0.13). However, this feature is not the fact in collected water samples as the observed $^{129}I^-/(^{129}I^- + ^{129}IO_3^-)$ ratio varies at 0.12–0.41 (mean 0.30), which is far from reaching their thermodynamic

equilibrium. This suggests that a dominated source of ^{129}I in the northeastern Atlantic Ocean (sampled transect) from the Nordic Seas and the Labrador Sea seems doubtful. We suggest that ^{129}I is mainly originated from outflow in the English Channel and possibly the Irish Sea rather than transport from the northwestern Atlantic. Transit time of 2.6–3.7 y (mean 3.0 y) was calculated for water transport from the English Channel to the northeastern Atlantic Ocean, via the Bay of Biscay, based on the same iodine oxidation rate used in the open ocean. This hypothesis is quite possible because of the relatively stagnant circulation in this region[56].

At present concentration levels in the northeastern Atlantic, ^{129}I does not pose a risk to human health. However, because of its high mobility and long half life, as well as continuous release from NRFs, anthropogenic ^{129}I can easily dispersed and redistributed in the Atlantic Ocean, thus affects marine ecosystem. Accumulation of ^{129}I has been reported in the marine organisms such as algae, mussel and fish[57,58]. This seafood with elevated ^{129}I can therefore find its way into food chain and eventually into the human, which makes ^{129}I monitoring important. In addition, as algae blooming in coastal areas is linked to nutrient concentration associated with stratification and upwelling effects, it is possible to couple ^{129}I distribution with respect to biotic processes and subsequent anoxic environment. Rather similar nutrient (e.g. phosphorus) geochemical behavior as that of iodine is suggested in seawater[59].

Fish otolith has been used as environmental marker for fish life-time and migration pathway[60]. Majority of elements deposited in otolith originate from water, with a minor fraction comes from food sources. [127]I was already found in otolith[61] and [129]I has been detected in fish flesh reference IAEA[58], then [129]I may also be incorporated into the otolith. Thus, variations of iodine isotopes ([129]I and [129]I) and their species in seawater are expected to be reflected in growth of otolith (e.g. Atlantic cod and Atlantic herring). This possibility can open a new interesting approach where growth and migration pathways of fish can be traced using the ratio of [129]I/[127]I. For example, fishes that inhabit the English Channel, the Nordic Seas and the Arctic Ocean are expected to build up higher [129]I/[129]I levels than those inhabit other parts of the Atlantic Ocean or even at different depths in the ocean or originate in a fresh water environment like salmon. Therefore, levels of [127]I/[129]I and speciation analysis in seawater can add new dimensions in otolith chemistry to investigate fish migration pathways, [129]I contamination history and marine environmental change. The same ideas could also be implied to other calcified structures, such as coral reef growth rings.

The data presented here are the first study on iodine isotopes ([129]I and [127]I) and their species (iodate and iodide) in the water of the northeastern Atlantic Ocean. Generally, iodate is the dominant species of dissolved iodine for both [127]I and [129]I in the surface waters of the sampled northeastern Atlantic. Although relatively low level of [129]I appears in the studied area at present, continuous [129]I releases from La Hague and Sellafield make monitoring of this radionuclide valuable in the Atlantic Ocean since the concentration of [129]I in the subpolar gyre tends to be increased by ocean circulation. This study also indicates that [129]I and species could be used as an ideal oceanographic tracer not only in the Arctic and Nordic regions, but also in the North Atlantic Ocean.

Multiple sources of [129]I are suggested to be received in the northeastern Atlantic Ocean as revealed by the [129]I speciation data. Among these sources, occurrence of Mediterranean seawater contribution is exposed as three narrow jets south of 40°N. Mediterranean water is commonly difficult to detect in the Atlantic surface water using salinity and temperature distribution. Here we show the potential implication of [129]I and its species to label MOW in the Atlantic surface and even deeper water. As most of MOW descends within the Gulf of Cadiz, depth profiles are needed in the vicinity of the Strait of Gibraltar for further research.

Methods

Samples collection. Surface seawater samples (47.4–31.1°N, 7.6–14.5°W) were collected in the North Atlantic Ocean from October to November, 2010 (Fig. 1a). The sampling transect was done onboard the Ice Breaker *Oden* during the passage from Sweden to Ponta Arenas (Chile) as part of the 2010/2011 Antarctica expedition jointly funded by the Swedish Polar Research Secretariat and the US National Science Foundation. Sampling was performed using a Teflon intake direct surface water sampling system that has been tested for possible memory effect and contamination[62]. At the same time an automatic continuous measurements of parameters such as salinity, temperature, and wind speed were conducted. Each 2-L sample was instantly filtered onboard through a 0.45 μm membrane (Sartorius AG, Gottingen, Germany) and filled in a clean polyethylene container under cold and dark conditions. All chemical reagents used were of analytical grade and all solutions were prepared using deionized water (18.2 MΩ·cm).

Iodine speciation analysis. A method for separation of iodine species (iodate and iodide) developed by Hou et al.[63] was used for both [127]I and [129]I (Supplementary Fig. S2). The filtered seawater mixed with 250 Bq of [125]I⁻ (Amersham Pharmacia Biotech, Little Chalfout, Buckinghamshire, UK) was loaded to a column (Ø 1.0 × 20 cm) filled with prepared NO_3^- form of AG1- × 4 anion exchange resin (50–100 mesh, Bio-Rad laboratories, Richmond, CA). 30 ml deionized water and a 50 ml of 2 M NaNO₃ were used to wash the column and the effluent and two washes were collected for solvent extraction of iodate. Iodide absorbed on the resin was eluted using 60 ml of 10% NaClO solution. One milliliter of each fraction (original seawater, iodate effluent and iodide eluate) was diluted with Cs internal standard (~200 ppb) and 1% NH₃·H₂O solution.

About 250 Bq of [125]I⁻ tracer and 0.1 ml 2 mg/ml of Woodward iodine (MICAL Specialty Chemicals, New Jersey, USA) were added to iodate effluent for chemical separation of [129]I species. To convert all the iodine to iodide form, 5 ml of 3 mol/L HNO₃ and 1.0 ml of 1 mol/L Na₂S₂O₅ were added, to ensure a fast reduction. CHCl₃

was used for solvent extraction of iodine. Iodine was first extracted to CHCl₃ phase (as I₂) by adding 2–5 ml of 1 mol/L NaNO₂ solution and then back-extracted to water with Na₂S₂O₅. This procedures was repeated several times until no I₂ in CHCl₃ phase was observed. The extraction of iodide from the eluate is much the same, the differences are that we use 1.0 mol/L NH₂OHHCl solution to reduce iodate to molecular iodine and no [125]I⁻ was added during the first extraction. The analytical uncertainty is 5%–10%.

Iodine determination. The concentration of total iodine, iodate and iodide were determined using X-Series[II] ICP-MS (Thermal Electron Corporation) under hot plasma conditions with Xt interface. The detection limit calculated as 3SD of blanks was 0.02 ppb. [125]I activity was measured using a NaI gamma detector (well type, Bicron) at channels 25–115 in 26–36 keV.

The dried iodine precipitation (AgI) was mixed with Nb powder in a mass ratio of 1 : 2 and the mixture was transferred into a copper holder and pressed for the AMS measurement using a 5 MV Pelletron machine at the Tandem Laboratory, Uppsala University. The [129]I/[127]I isotopic ratio in the [129]I standard (diluted NIST SRM 4949C) is $(1.1 \pm 0.1) \times 10^{-11}$ and the background of the AMS system is 4×10^{-14}. The statistical error of the measurements was <7% (one standard deviation).

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Author contributions

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Additional information

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