

^{127}I and ^{129}I Species and Transformation in the Baltic Proper, Kattegat, and Skagerrak Basins

P. Yi,^{†,*} A. Aldahan,^{†,‡} G. Possnert,[§] X. L. Hou,^{⊥,||} V. Hansen,[⊥] and B. Wang[#]

[†]Department of Earth Sciences, Uppsala University, Uppsala, Sweden

[‡]Department of Geology, United Arab Emirates University, Al Ain, UAE

[§]Tandem Laboratory, Uppsala University, Uppsala, Sweden

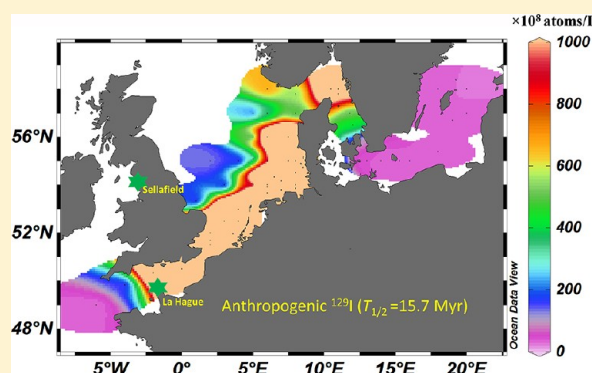
[⊥]Center for Nuclear Technologies, Technical University of Denmark, 4000 Risø Campus, Roskilde, Denmark

^{||}Xi'an AMS centre, SKLLQG, Institute of Earth Environment, CAS, Xi'an 710075, China

[#]Population Biology and Conservation Biology, Uppsala University, Uppsala, Sweden

Supporting Information

ABSTRACT: Occurrence of anthropogenic ^{129}I in seawater has provided invaluable information about water circulation and exchange rates, but results on ^{129}I species (iodide and iodate) are limited and only available for surface water. We here present the first extensive results on ^{129}I and ^{127}I species in samples of seawater depth profiles, which were collected in August 2006 and April 2007 in the Skagerrak, Kattegat, and Baltic Proper. The results expose $\leq 10\%$ annual reduction of iodate as ^{129}I is transported from the English Channel along the Dutch coast and German Bight into the Skagerrak and Kattegat. The results also suggest strong variability between surface and bottom seawater with respect to the predominant iodine species. Distribution of iodide and iodate of both ^{127}I and ^{129}I in the Kattegat mainly reflects water mixing process rather than speciation transformation. In water of the Baltic Proper, high $^{127}\text{I}^-/^{127}\text{IO}_3^-$ and $^{129}\text{I}^-/^{129}\text{IO}_3^-$ values suggest effective reduction of iodate with a maximum rate of 8×10^{-7} ($^{127}\text{IO}_3^-$) and 6×10^{-14} ($^{129}\text{IO}_3^-$) ($\text{g}/\text{m}^3\cdot\text{day}$). The reduction process of iodate seems to be related to decomposition of organic matter and photochemically induced reactions.



■ INTRODUCTION

^{127}I is a naturally occurring element and the only stable isotope of iodine, whereas ^{129}I is radioactive ($T_{1/2} = 15.7$ Ma) and is produced by both natural and anthropogenic pathways. Although iodine may exist in various oxidation states in natural environments, the predominant species in seawater are iodide, iodate, and a minor proportion of organic iodine.¹ The mechanism of conversion of iodate to iodide in highly oxygenated surface seawater or iodide to iodate in anoxic water is not yet fully understood, but organically mediated reactions have been suggested as dominant pathways.^{2–4} In tropical seas, transformation of iodine species was more effective^{5,6} than in polar and temperate seas.^{7–10} However, in view of iodate predominance in the marine systems, oxidation of iodide to iodate should be a common process.^{11–13} Even possible oxidation of iodide in the surface waters of the Black Sea (strongly anoxic conditions) was indicated by Truesdale et al.¹⁴ Some studies have suggested that the oxidation of iodide to iodate is an extremely slow chemical process, whereas modeling based estimates, using time series data, indicated relatively rapid rates.^{6,13}

All of the studies mentioned above have focused on ^{127}I , whereas the only results on ^{129}I speciation in seawater¹⁵ suggest significant differences in species distribution of iodine isotopes in surface water of the North Sea. Addition of anthropogenic ^{129}I to the Earth's surface environment through discharges from the nuclear fuel reprocessing facilities provided new avenue (since the late 1940s) for further understanding of iodine species transformation in seawater. Part of ^{129}I discharges from the Sellafield and La Hague nuclear reprocessing facilities has entered the Baltic Sea. Consequently, tracing the changes in the relative ratio of total $^{129}\text{I}/^{127}\text{I}$ along transects from the discharge points gave new information about iodine dispersion from the North Sea into the Baltic Sea.¹⁶

To our best knowledge, however, there are no published literatures about ^{129}I species in seawater depth profile. This means lack of vital information about the speciation transformation of the isotope below sea surface conditions. Results

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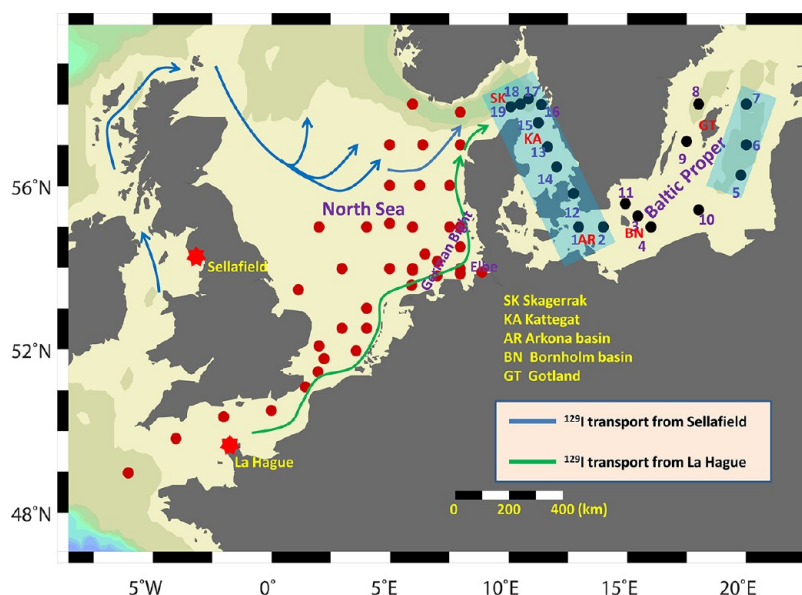


Figure 1. Map showing the sampling sites (black points) in the Skagerrak, Kattegat and Baltic Proper for August 2006 (1–15) and April 2007 (1–19) used in this study and those (red points) in the North Sea reported by Hou et al.¹⁵ Blue and green arrows show major surface ^{129}I pathways from the Sellafield and La Hague, respectively. Semitransparent blue rectangles delineate sites used in Figure 2 and in Figures S3, S4, and S5 of the Supporting Information.

from the data on ^{129}I species in the North Sea (Hou et al.)¹⁵ clearly show differences in the iodide and iodate behavior compared to total ^{129}I . It seems that some $^{129}\text{IO}_3^-$ is reduced to $^{129}\text{I}^-$, most commonly along the German Bight, thus providing specific signature for the surface water reaching the Skagerrak basin. Additionally, iodate and iodide of the two isotopes (^{129}I and ^{127}I) exhibit variable ratios that can be used to fingerprint water masses and consequently bioavailability of iodine species in the ecosystem.^{16,17} We present here extensive results of iodine species (^{127}I and ^{129}I) at different depths and even at two different sampling periods in seawater of the Skagerrak, Kattegat, and the Baltic Proper. These results are also compared with total iodine data of Yi et al.¹⁸ and influences of seawater oxygen concentration, salinity and temperature on the iodine species distribution. Furthermore, published data on iodine species in the surface water of the North Sea¹⁵ and the Baltic Sea¹⁹ are compared to the results of the depth profiles. The investigation exposes new information about ^{129}I and also ^{127}I species and effects of oxidation–reduction rates in the Baltic Sea and related basins (Skagerrak and Kattegat).

SAMPLING AND ANALYTICAL METHODS

Samples of seawater depth-profiles were collected from 15 sites in August 2006 and 19 sites in April 2007 (Figure 1). Sampling was carried out on board the research Vessel Argos, operated by the marine division of the Swedish Meteorological and Hydrological Institute. All seawater samples were collected in Nansen bottles (Hydro Bios) and the salinity was measured on board, using an AEG MINISAL 2100 salinometer. The seawater samples were filtered through a $0.45\ \mu\text{m}$ membrane (Sartorius AG, Gottingen, Germany) and then tightened and stored in clean polyethylene containers in cold dark conditions until analysis. All chemical reagents used were of analytical grade and all solutions were prepared using deionized water ($>18.2\ \Omega$). Measurements of ^{129}I and ^{127}I species were done using accelerator mass spectrometry and inductively coupled plasma mass spectrometry, respectively (Details of separation

and measurement techniques are provided in the Supporting Information).

RESULTS

Data on total iodine isotopes (^{127}I and ^{129}I) and their species ($^{127}\text{I}^-$, $^{129}\text{I}^-$, $^{127}\text{IO}_3^-$, and $^{129}\text{IO}_3^-$) in surface water (above 10 m depth) of the regions studied here were published by Yi et al.¹⁸ and Hansen et al.,¹⁹ respectively. Iodine analyses of depth profiles presented here (Table S1 of the Supporting Information) were done on samples collected simultaneously with those analyzed by Yi et al. and Hansen et al. and thus provide new information that can directly be compared with previous investigations. We also make use of iodine data analyzed in surface water of the North Sea (sampling locations are shown in Figure 1) for samples collected during August–September 2005¹⁵ to trace up sources and compare concentration levels and fluxes of iodine isotopes and species in the region studied here (Skagerrak, Kattegat, and Baltic Proper). Rather than repeat published knowledge, surface water data (above 10 m depth) of ^{127}I , ^{129}I , $^{127}\text{I}^-$, $^{129}\text{I}^-$, $^{127}\text{IO}_3^-$, $^{129}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{127}\text{I}^-/^{127}\text{IO}_3^-$, $^{129}\text{I}^-/^{129}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$, are used here just for comparison with the North Sea data (Figures S1 and S2 of the Supporting Information) thus covering a large domain of latitudes starting from 48°N (southern English Channel) and extending into 58°N (northern Baltic Proper).

Iodine Isotopes Variability with Depth. The concentrations of $^{127}\text{I}^-$ vary within 4–33 ppb in the Skagerrak and Kattegat (part a of Figure S3, part a of Figure S4, and Table S1 of the Supporting Information), whereas in the Baltic Proper, the range of $^{127}\text{I}^-$ is between 5 and 33 ppb (part a of Figure 2, and part a of Figure S5 of the Supporting Information). Variability in the $^{127}\text{IO}_3^-$ concentrations is 1–54 ppb in the Skagerrak-Kattegat and 0.3–10 ppb along the Baltic Proper depth profiles (part b of Figure 2, and parts b of Figures S3, S4, and S5 of the Supporting Information). The range of $^{129}\text{I}^-$ concentration is $11\text{--}215 \times 10^8$ atoms/L in the Baltic Proper,

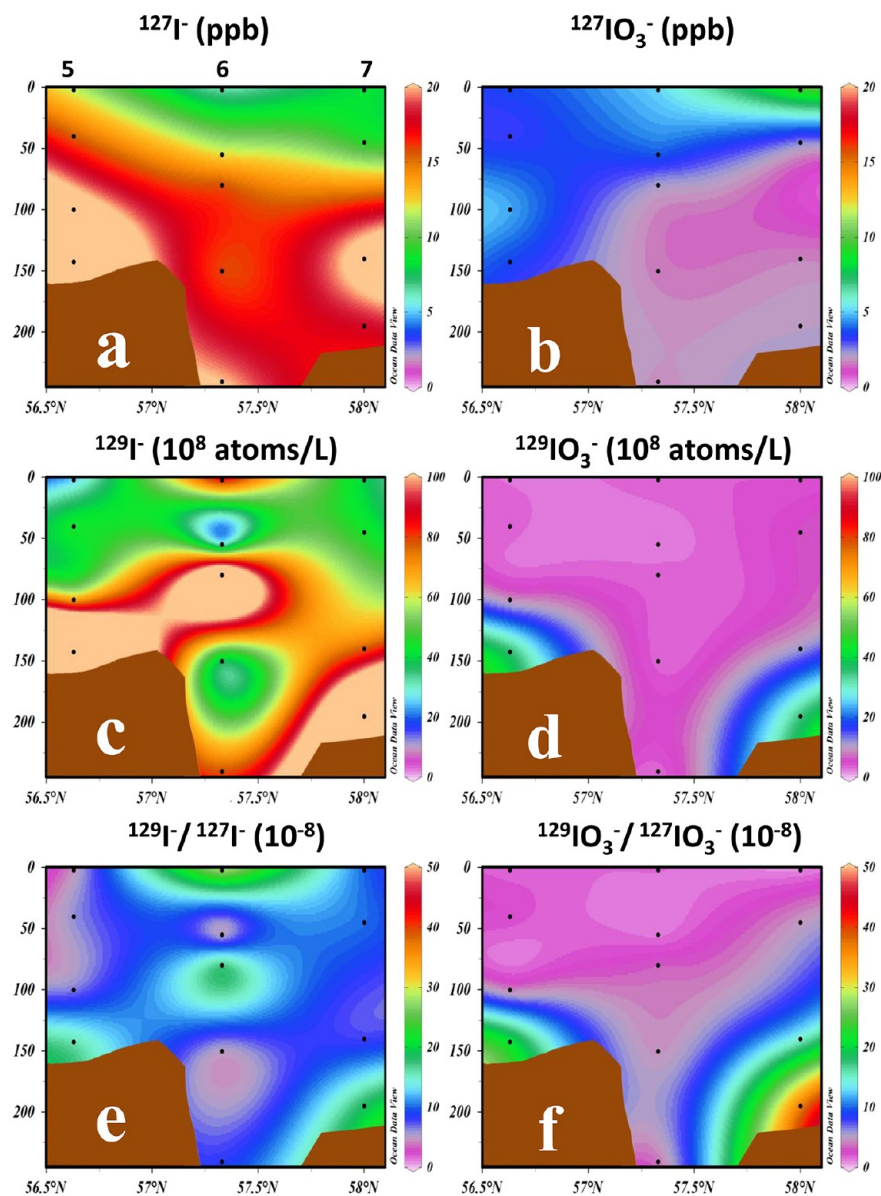


Figure 2. Depth Profiles of $^{127}\text{I}^-$, $^{127}\text{IO}_3^-$, $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ in the north part of the Baltic proper (eastern Gotland) for August 2006 (a–f) shown as an example of variability in iodine species and details of all depth profiles are given in the Supporting Information.

but a wider range ($31\text{--}1137 \times 10^8$ atoms/L) is found in the Skagerrak-Kattegat (part c of Figure 2 and parts c of Figures S3, S4, and S5 of the Supporting Information). The same behavior is also observed for the $^{129}\text{IO}_3^-$ concentration variability where a smaller range ($1\text{--}45 \times 10^8$ atoms/L) is exhibited in the Baltic Proper samples compared to the Skagerrak and Kattegat ($4\text{--}777 \times 10^8$ atoms/L). Changes in the $^{127}\text{I}^-/^{127}\text{IO}_3^-$ values along the different depth profiles vary between 0.4 and 10 in the Skagerrak-Kattegat and 1–43 in the Baltic Proper, and the ratios of $^{129}\text{I}^-/^{129}\text{IO}_3^-$ in these depth profiles are 0.4–16 and 2–96, respectively. In general, the $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ values ($0.4\text{--}235 \times 10^{-8}$) have wider range than the $^{129}\text{I}^-/^{127}\text{I}^-$ values ($2\text{--}150 \times 10^{-8}$).

The average concentration of iodide in bottom water of the Baltic Proper (Figure 3 and Figure S6 of the Supporting Information) is 21 ± 5 ppb for $^{127}\text{I}^-$ and $105 \pm 58 \times 10^8$ atoms/L for $^{129}\text{I}^-$ in August, whereas in April the average concentration is 14 ± 4 ppb for $^{127}\text{I}^-$ and $80 \pm 30 \times 10^8$ atoms/L for $^{129}\text{I}^-$. These concentrations are two times higher than

those in the surface water (depth above 10 m). Although iodate concentration is generally lower than iodide, some $^{129}\text{IO}_3^-$ and $^{127}\text{IO}_3^-$ values in the bottom water around Gotland reach up to 35×10^8 atoms/L in August (part d of Figure S6 of the Supporting Information) and 5 ppb in April (part b of Figure 3).

Regarding the ratio of $^{127}\text{I}^-/^{127}\text{IO}_3^-$, the results clearly indicate two separated zones in August; one is associated with low values (<5) characterizing the deep water in the Skagerrak-Kattegat and Arkona basins and the second is associated with relatively higher ratio (5–10) in the rest of the Baltic Proper (part e of Figure S6 of the Supporting Information). In April, the $^{127}\text{I}^-/^{127}\text{IO}_3^-$ values remained low in the Skagerrak-Kattegat basins, but values as high as 30 occur in the central parts of the Baltic Proper (part e of Figure 3). The distribution of $^{129}\text{I}^-/^{129}\text{IO}_3^-$ shows more variations than the $^{127}\text{I}^-/^{127}\text{IO}_3^-$ in deep water of the two sampling campaigns (part f of Figure 3 and part f of Figure S6 of the Supporting Information). The $^{129}\text{I}^-/^{129}\text{IO}_3^-$ values, however, remain below 30, and decreasing

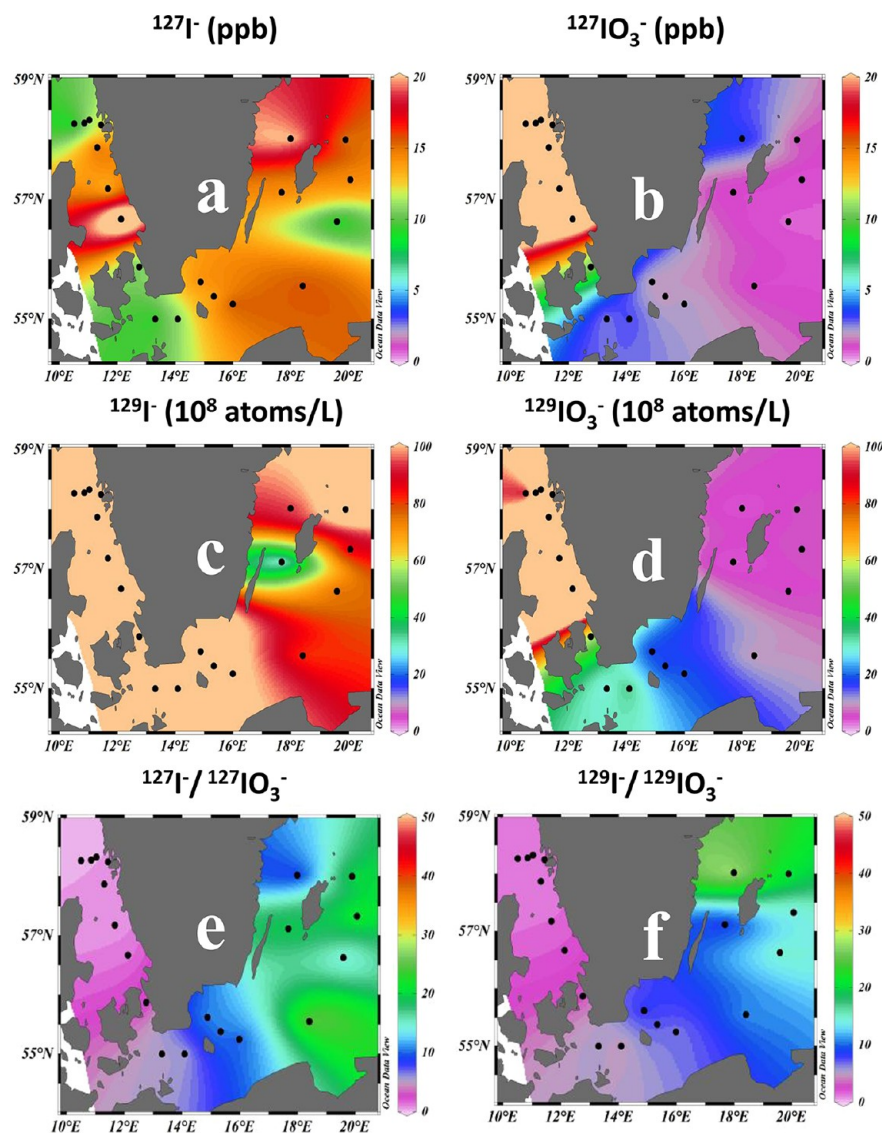


Figure 3. Distribution of $^{127}\text{I}^-$, $^{127}\text{IO}_3^-$, $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$, $^{127}\text{I}^-/^{127}\text{IO}_3^-$, $^{129}\text{I}^-/^{129}\text{IO}_3^-$ (a–f) in bottom water of the Skagerrak, Kattegat, and Baltic Proper for April 2007 shown as an example of variability in iodine species and details of distribution for August 2006 and other water depths are given in the Supporting Information.

as water masses move from higher ratio region (>20) in the whole Baltic Proper toward Kattegat. This trend is interrupted by low ratios (<10) in the Arkona basin.

Values of $^{129}\text{I}^-/^{127}\text{I}^-$ and $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ in the bottom waters generally decrease moving from the Kattegat ($>50 \times 10^{-8}$) into the Baltic Proper (Table S1 of the Supporting Information). The $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ are lower than $^{129}\text{I}^-/^{127}\text{I}^-$ values in the Skagerrak and Kattegat. Most $^{129}\text{I}^-/^{127}\text{I}^-$ and $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ values in the Baltic Proper are around 20×10^{-8} , except some that are $<10 \times 10^{-8}$ in west of Gotland.

Inventory of Iodine Species and Masses Exchanges from August 2006 to April 2007. Inventory of iodine species is estimated for the two sampling periods in the Kattegat and Baltic Proper. Lack of isotopes species data from depth profile in the Skagerrak during August 2006 sampling period forced us to avoid calculation of species inventory in the Skagerrak. The water column is divided as surface and deep water in the Kattegat and as surface, intermediate, and deep water in the Baltic Proper following theoretical wave base approximation.²⁰ The average depth of halocline (75 m) was

used to separate intermediate and deep water of the Baltic Proper. The two depth layers in the Kattegat are surface <40 m and deep >40 m, whereas the three ones for the Baltic Proper are surface <45 m, intermediate >45 m and <75 m, deep >75 m.

The inventory in each layer was calculated by multiplying average concentration by its corresponding water volume. The results (Table S2 of the Supporting Information) show that the inventory for each water layer in August is generally higher than that in April. This phenomena is well reflected by the iodide where differences of 5×10^7 kg and 5 kg is observed for $^{127}\text{I}^-$ and $^{129}\text{I}^-$ in the Baltic Proper, respectively. In terms of the two basins, the estimated inventory of $^{129}\text{I}^-$ in the Kattegat is about four times less than that in Baltic Proper, whereas $^{129}\text{IO}_3^-$ inventory is comparable between the two basins. The inventory of $^{127}\text{I}^-$ in the Kattegat basin is estimated to be $(7 \pm 1) \times 10^6$ kg which is slightly lower than $^{127}\text{IO}_3^-$ inventory $(10 \pm 2) \times 10^6$ kg. However, the situation is different in Baltic Proper where inventory of $^{127}\text{IO}_3^-$ $(30 \pm 10) \times 10^6$ kg is generally a factor of 4 less than that of $^{127}\text{I}^-$ $(160 \pm 22) \times 10^6$ kg.

Table 1. Comparison between the Estimated and Modeled Inventories of ¹²⁷I and ¹²⁹I Species in the Kattegat (KA) and Baltic Proper (BP) for the August 2006 to April 2007 Period

item	basin	estimated inventory (EIG)	KABP (inflow)	BPKA (outflow)	modeled inventory (MIA)	estimated inventory (EIA)	(EIA-MIA)	(EIA-MIA)/EIA (%)
¹²⁹ I ⁻	KA	3.6 ± 1.6		0.6 ± 0.4	2 ± 1.3	3 ± 1.4	1	30
	BP	18.7 ± 11.2	2.2 ± 0.7		20.3 ± 11.5	12.8 ± 4	-7.5	-60
¹²⁹ IO ₃ ⁻	KA	1.8 ± 1		<0.1	0.7 ± 0.6	1.9 ± 1	1.2	60
	BP	2.1 ± 1.9	1.1 ± 0.4		3.2 ± 2.3	1.2 ± 0.8	-2	-160
¹²⁷ I ⁻	KA	(7.8 ± 2.5) × 10 ⁶		(6.3 ± 1.9) × 10 ⁶	(8.2 ± 2.2) × 10 ⁶	(6.8 ± 2.9) × 10 ⁶	-1.4 × 10 ⁶	-20
	BP	(1.8 ± 0.5) × 10 ⁸	5.9 ± 2.2) × 10 ⁶		(1.8 ± 0.5) × 10 ⁸	(1.4 ± 0.4) × 10 ⁸	-0.4 × 10 ⁸	-30
¹²⁷ IO ₃ ⁻	KA	(1.1 ± 0.3) × 10 ⁷		(1.9 ± 1.3) × 10 ⁶	(5.9 ± 3.4) × 10 ⁶	(9.8 ± 4.2) × 10 ⁶	3 × 10 ⁶	40
	BP	(4.3 ± 2.4) × 10 ⁷	(7.4 ± 1.2) × 10 ⁶		(4.9 ± 2.4) × 10 ⁷	(1.9 ± 1.1) × 10 ⁷	-3 × 10 ⁷	-150
symbols	definition	descriptions						
estimated in-ventory (EIG and EIA)	obtained from inventory calculation	inventory of each of iodine species in August (EIG) and April (EIA) in kg, details in SI Table S2						
KABP (inflow)	$C_{ka_deep} \times Q_{ka_to_bp}$	iodine species inventory inflow from Kattegat (KA) to Baltic Proper (BP) from August 2006 to April 2007 in kg. C_{ka_deep} refers to average concentration of iodine species in deep water (Kattegat) from August 2006. $Q_{ka_to_bp}$ means water fluxes (km ³) transported from the KA to BP during the period from 15th August 2006 to 15th April 2007. Annual inflow ($Q_{ka_to_bp}$) 310 km ³ adjusted to a period of 8 months (15th August 2006 to 15th April 2007)						
BPKA (out-flow)	$C_{bp_surface} \times Q_{bp_to_ka}$	iodine species inventory outflow from Baltic Proper (BP) to Kattegat (KA) from August 2006 to April 2007 in kg. $C_{bp_surface}$ refers to average concentration of iodine species in surface water (Baltic Proper) from August 2006. $Q_{bp_to_ka}$ means water fluxes (km ³) transported from the BP to KA during the period from 15th August 2006 to 15th April 2007. Annual outflow ($Q_{bp_to_ka}$) 630 km ³ adjusted to a period of 8 months (15th August 2006 to 15th April 2007)						
modeled in-ventory (MIA)	For basin KA: EIG-KABP + BPKA For basin BP: EIG +KABP-BPKA	Modeled Inventory in April 2007 (MIA) in kg						
(EIA-MIA)	EIA-MIA	differences between Estimated Inventory and Modeled Inventory in April 2007 (kg)						
(EIA-MIA)/EIA (%)	$[(EIA-MIA)/EIA] \times 100$	percentage of inventory differences between Estimated Inventory and Modeled Inventory in April 2007 (%)						

DISCUSSION

Rate of Change in ^{129}I Species along Transport Pathways. $^{129}\text{IO}_3^-$ is a predominant species in the surface water of the English Channel, which apparently has overridden by relatively high concentrations of $^{129}\text{I}^-$ as the water mass moves across the Dutch coast and German Bight as well as in the central and northern parts of the North Sea (parts d and f of Figure S1 of the Supporting Information). This feature suggests that the reduction of iodate occurs during surface water transport from the English Channel to the Baltic Sea, especially in the Dutch coast area and German Bight.¹⁵ The transit time of ^{129}I transport from the La Hague to Kattegat is about 2 years,^{21,22} which implies that ^{129}I in the surface water near to La Hague (sampled in August–September 2005),¹⁵ would arrive at the Kattegat around late summer in 2007 and a few months ahead to the Skagerrak. Thus, ^{129}I in the Skagerrak water collected in April 2007 shares comparable discharge events with water around La Hague collected in August–September 2005.¹⁵ This analogous temporal discharge source will enable estimating rate of ^{129}I species transformation as water masses reach the Skagerrak-Kattegat basin. Two alternative estimation methods were carried out (for the details, see Supporting Information) and results of both methods reveal iodate annual reduction rate at $\leq 10\%$ as ^{129}I is transported from the English Channel along the middle of Dutch coast and German Bight into the Skagerrak and Kattegat.

Iodine Species in the Transitional Region. A particular attention has been given to the transitional region between the Skagerrak-Kattegat and Baltic Proper (Figure 1). In this region, the Arkona basin connects water masses exchange between the Skagerrak-Kattegat and the Baltic Proper. Cross sections of depth profiles show a plume of high iodide and iodate, of both isotopes, that occupies the central part, down to 150 m, between the Skagerrak and Kattegat during both sampling campaigns (parts a–d of Figure S3 and parts a–d of Figure S4 of the Supporting Information). ^{129}I concentration is reduced as the plume moves toward the Arkona basin. The origin of the plume is related to upwelling Jutland current that is rich in ^{129}I , which is gradually mixed with the North Atlantic deep water characterized with abundant $^{127}\text{IO}_3^-$ but poor in $^{129}\text{I}^-$ and $^{129}\text{IO}_3^-$. This feature is also reflected by higher $^{129}\text{I}^-/^{127}\text{I}^-$ compared to $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ values in deep water of the Skagerrak-Kattegat (parts e and f of Figure S4 of the Supporting Information).

A specific feature is observed upon transition of water masses from the Kattegat into the Arkona basin where the ratio of iodide to iodate of both isotopes, during both sampling campaigns, is generally increasing (parts h and i of Figure S1 and parts h and i of Figure S2 of the Supporting Information). This may result from either mixing with iodide dominated-Baltic water or a rapid iodate reduction process during transport. To explore the main reason for this iodide domination, we carried out the following calculation (Table 1). We considered mass transport of iodine species between the Kattegat and the Baltic Proper during the period August 2006 to April 2007 without diffusion and transformation or losses to the sediment pile. Accordingly, we used average concentration of iodine species in deep water of the Kattegat and surface water of the Baltic and fluxes of water inflow and outflow. Estimates of annual water inflow and outflow were at $470 \text{ km}^3/\text{y}$ and $950 \text{ km}^3/\text{y}$ ²³ respectively, which we have scaled to a period of eight months (15th August 2006 to 15th April 2007).

Furthermore, inflow and outflow inventories were related to total inventories in the Kattegat and the Baltic Proper (Details are provided in the Supporting Information).

The results show that estimated inventories (EIG and EIA, Table 1) during August 2006 and April 2007 are comparable for all iodine species ($^{127}\text{I}^-$, $^{129}\text{I}^-$, $^{127}\text{IO}_3^-$, and $^{129}\text{IO}_3^-$) in the Kattegat (basin KA). Water inflow inventories [KABP (inflow), Table 1], however, suggest transport of more $^{129}\text{I}^-$ than $^{129}\text{IO}_3^-$ compared to $^{127}\text{I}^-$, which was less than $^{127}\text{IO}_3^-$. This agrees with the fact that the $^{127}\text{IO}_3^-$ is expected to be the dominant species of iodine in the North Atlantic water,²⁴ whereas $^{129}\text{I}^-$ is the predominant species in the Jutland current water. Apparently, the $^{127}\text{IO}_3^-$ preserves the North Atlantic water signature in the inflow water from Kattegat into the Baltic Proper. Therefore, it seems that the consequence of different environmental conditions on ^{127}I and ^{129}I species in the Kattegat mainly reflects water mixing process rather than speciation transformation. The mixing process could be illustrated by the high salinity (>35) and ^{129}I concentration ($>1000 \times 10^8$ atoms/L) in surface eastern part of the North Sea water inflow into the Skagerrak which is mixed with the low salinity (<16) and ^{129}I concentration ($<300 \times 10^8$ atoms/L) outflow water from the Baltic Sea through the Kattegat (part b of Figure S1, and Figure S7 of the Supporting Information). Additionally, the negligible reduction of iodate in the Kattegat may have assisted in maintaining the high quantity of iodate in the inflow water [$(7.4 \pm 1.2) \times 10^6$ kg for $^{127}\text{IO}_3^-$ and 1.1 ± 0.4 kg for $^{129}\text{IO}_3^-$, Table 1]. When it comes to outflow water, then it is clear that iodide of both isotopes is the prevailing species [$(1.9 \pm 1.3) \times 10^6$ kg for $^{127}\text{IO}_3^-$ and <0.1 kg for $^{129}\text{IO}_3^-$, Table 1], which reflects the reduction conditions in the Baltic Proper. The calculation in Table 1 further indicates that there is a substantial difference between estimated inventory (EIA) and modeled inventory in April (MIA) of iodine species, particularly with respect to iodate in the Baltic Proper. This feature seems to be strongly related to the oxidation condition in the Baltic as it is further elaborated in the discussion below.

It is, however, important to mention that water masses in the Baltic Proper, having exchanged with the Kattegat, are also affected by several factors including local topography, seasonal variability and interaction with other three neighbor basins, Bothnian Sea, Gulf of Finland, and Gulf of Riga. Uncertainty in amounts of water exchange between Baltic Proper and Bothnian Sea is large and therefore average values (inflow $1900 \pm 1600 \text{ km}^3/\text{y}$ and outflow $2000 \pm 1600 \text{ km}^3/\text{y}$)²⁵ are adopted here to calculate masses of iodine species exchanged between the two basins from August 2006 to April 2007. To date, only one analysis was reported in the Bothnian Sea for ^{129}I species.²⁶ However, in view of the good correlation between salinity and ^{129}I ,^{15,18,27–29} the amount of ^{129}I in the surface water of the Bothnian Sea could be estimated by scaling typical salinity value (5.4 for Bothnian Sea and 7.0 for Baltic Proper) against ^{129}I in the Baltic Proper. Thereafter, a constant speciation ratio ($^{129}\text{I}^-/^{129}\text{IO}_3^- = 22$)²⁶ was adopted to estimate iodine species. The same estimation procedure was also performed for the water mass exchange from the Gulf of Finland and Gulf of Riga. Despite the rough estimate of iodine species concentration, the results (Table S3 of the Supporting Information) reveal about 0.2 kg inventory exchange between the Baltic Proper and the three basins, which is relatively small when compared to the 3 kg exchange between the Baltic Proper and Kattegat.

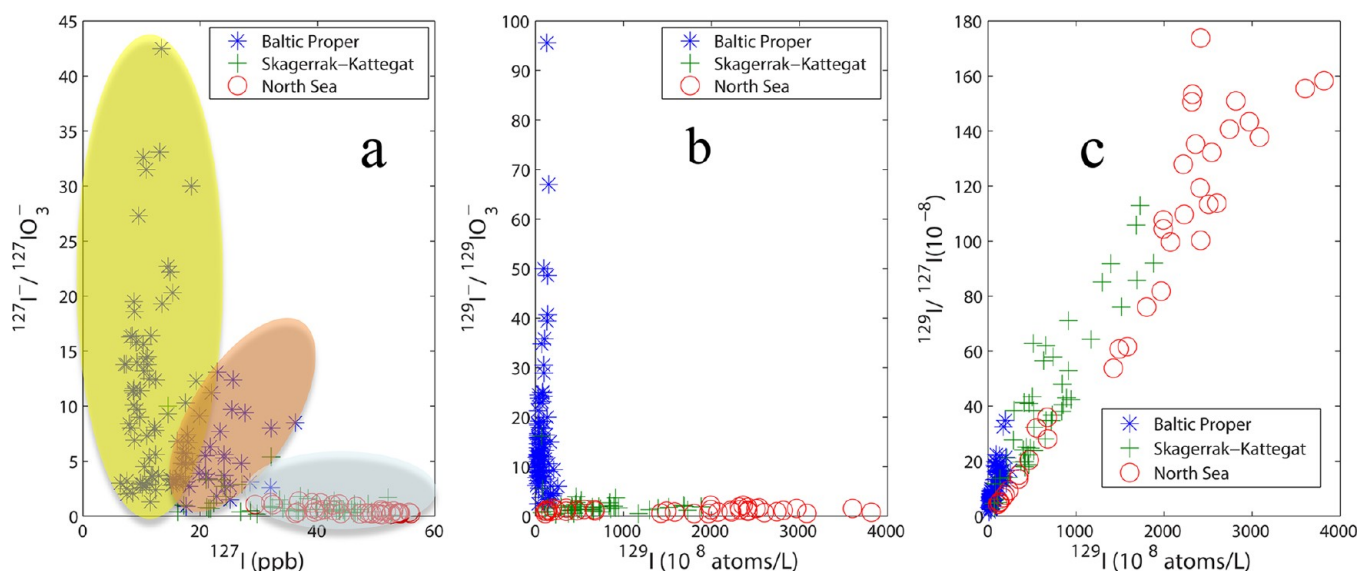


Figure 4. Plots of iodine species (a–c) for water samples analyzed here (Skagerrak, Kattegat, and Baltic Proper) and those of Hou et al.¹⁵ for the North Sea.

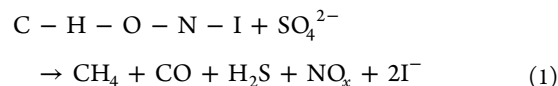
Figures 4 and Figure S8 of the Supporting Information indicate two end-member water masses (North Sea–North Atlantic and Baltic Sea) that occur in the mixing zone region of the Skagerrak–Kattegat. Fingerprint of the North Sea–North Atlantic water is shown by the high total ^{127}I (>30 ppb) and low (<1) $^{127}\text{I}^-/^{127}\text{IO}_3^-$ values, whereas the Baltic Sea water mass is characterized by relatively low ^{127}I (<20 ppb) and $^{127}\text{I}^-/^{127}\text{IO}_3^-$ values spreading between 1 and 40 (part a of Figure 4 and part a of Figure S8 of the Supporting Information). ^{129}I mixing diagram also shows strong imprint of North Sea water, which is separated from the other water masses (part b of Figure 4). The strong effect of ^{129}I on the relationship between $^{129}\text{I}^-/^{129}\text{IO}_3^-$ and ^{129}I (part c of Figure 4) suggests that the two isotopes are far from reaching equilibrium in seawater masses investigated here.

Dynamics of Iodine Species Transformation in the Baltic Proper. To estimate rate and possible processes of iodide formation in the Baltic Proper, we have used the inventory values in Table 1. The data show comparable relative losses in $^{127}\text{IO}_3^-$ and $^{129}\text{IO}_3^-$ between estimated (EIA) and modeled (MIA) inventories in April 2007 (–150% for $^{127}\text{IO}_3^-$ and –160% for $^{129}\text{IO}_3^-$ or in kg are 3×10^7 and 2, respectively). These losses point out reduction rates at 8×10^{-7} and 6×10^{-14} ($\text{g}/\text{m}^3 \cdot \text{day}$) for $^{127}\text{IO}_3^-$ and $^{129}\text{IO}_3^-$, respectively. Calculations based on percentage differences between EIA and MIA (Table 1) indicate, however, a remarkable discrepancy (30 to 60%) between iodide–EIA and iodide–MIA for both isotopes in the Baltic Proper. The source of this discrepancy may relate to effects of water masses mixing and stratification, oxidation–reduction process and residence time of each isotope. To illustrate the interplay of these factors, we selected the east of Gotland region as an example, where $^{127}\text{I}^-$ and $^{129}\text{I}^-$ concentrations in the water column tend to be separated by the halocline at a depth of about 75 m in April sampling period, resulting in stratification of water masses. The stratification boundary is, however, not clear in August sampling period (part c of Figure 2), but the process seems to enhance iodide concentration as observed by the relatively high $^{127}\text{I}^-/^{127}\text{IO}_3^-$ (part e of Figure 3) in deep water in April. This feature is, however, not well reflected in the $^{129}\text{I}^-/^{129}\text{IO}_3^-$,

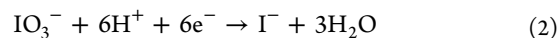
which may relate to continuous addition of new inflow water that is enriched with iodate. The new inflow may not have ample time to acquire ratio of $^{129}\text{I}^-/^{129}\text{IO}_3^-$ that is analogous to the pre-existing $^{129}\text{I}^-/^{129}\text{IO}_3^-$. The amount of new inflow water is expected to be too little to impose marked difference in the ratio of $^{127}\text{I}^-/^{127}\text{IO}_3^-$. This is due to the sensitivity of the two iodine isotopes where small amounts of water masses will have more profound effect on the concentration of ^{129}I with detection limit in atoms/L compared to the ^{127}I in ppb.

Iodate reduction is another process affecting the iodine isotopes in the Baltic Proper. The iodate to iodide reduction may be mediated by bacteria, photochemical or abiotic processes.⁹ Furthermore some studies have shown that iodide may be supplied to the water body through organic matter decay and diagenetic release from sediment by diffusion process.^{18,30,31} For abiotic reduction process, reducing agents such as iron and manganese can promote the removal of oxygen from iodate and the reduction into iodide in anoxic environment.³² The reduction may happen in deep or surface water depending on environmental conditions and several reactions have been proposed for the iodate reduction process including:

- (1) decomposition of organic matter³¹ with general expression as,

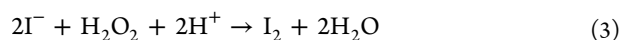


- (2) in presence of sun light, photochemical reduction of iodate is mediated by dissolved organic matter² as:

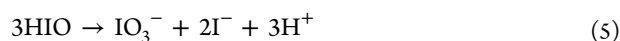
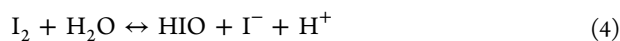


The photochemical process is expected to be extensive in the Baltic during summer when daylight is long and there is no ice cover, which seems consistent with high iodide in surface water collected during August 2006. Reduction of iodate could be also mediated by biological activity, but contradictory results on involvement of phytoplankton community in the process were reported.^{32–35}

Regardless of sampling period, some $^{127}\text{IO}_3^-$ and $^{129}\text{IO}_3^-$ concentrations were observed in surface and deep water of the Baltic Proper (parts b and d of Figure 2, part b of Figure 3; part e of Figure S1, part b of Figure S5, and part d of Figure S6 of the Supporting Information). A possible explanation for the occurrence of IO_3^- in oxygen depleted deep water of the Baltic Sea is inflow of iodate-rich Skagerrak-Kattegat water to the Baltic Sea and subsequent transport along the Bornholm and Gotland Basins. Additionally, decomposition of organic matter in bottom water of the Baltic Sea may enhance the level of iodine. However, presently we do not have information about iodine species in the Baltic Sea sediments, which makes estimate of iodine provided by the sediment difficult. Apparently, elevated iodate ($^{127}\text{IO}_3^-$, $^{129}\text{IO}_3^-$) concentrations occur only when marked iodide ($^{127}\text{I}^- > 20$ ppb or $^{129}\text{I}^- > 100 \times 10^8$ atoms/L) values exist (parts a–d of Figure 3 and parts a–d of Figure S6 of the Supporting Information). This feature suggests possibility of iodide oxidation in some deep waters in the Baltic Proper. Actually, the process of oxidizing iodide to iodate using oxygen requires at least 2 electron transfer steps,¹² which is also a thermodynamically difficult and sluggish process.^{36–39} Among the possible oxidation processes is involvement of strong oxidants such as hydrogen peroxide⁴ as shown in the equation below,



the molecular iodine may transform to iodate as follows,



H_2O_2 concentrations in the Baltic Sea reach up to 14.2 nmol/L⁴⁰ in the surface water, which can promote iodide oxidation and may explain part of the elevated $^{127}\text{IO}_3^-$ values in the surface water of northern Gotland (part b of Figures 2 and part e of Figure S1 of the Supporting Information). The sluggishness of the iodide oxidation process may explain effective oxidation of pre-existing ^{127}I compared to newly added ^{129}I .

Another less possible pathway for iodide oxidation is through biological mediation such as extracellular enzyme iodide oxidation in marine proteobacteria.⁴¹ Additionally, the process of CO_2 reduction to organic C aided by chemolithoautotrophic bacteria, particularly in the Gotland deep may extract needed electrons from oxidation of iodide.⁴²

To conclude, the ^{129}I and ^{127}I species data presented here indicate that: (1) Only less than 10% of iodate is annually reduced as ^{129}I is transported from the English Channel along the middle of Dutch coast and German Bight to the Skagerrak and Kattegat, (2) distribution of ^{127}I and ^{129}I species in the Kattegat is mainly reflecting water mixing process rather than speciation transformation, (3) a maximum reduction rate of 8×10^{-7} ($^{127}\text{IO}_3^-$) and 6×10^{-14} ($^{129}\text{IO}_3^-$) ($\text{g}/\text{m}^3 \cdot \text{day}$) is expected in the Baltic Proper, and (4) reduction process of iodate in the Baltic Proper seems to be related to decomposition of organic matter and photochemically induced reactions.

■ ASSOCIATED CONTENT

■ Supporting Information

Description of chemical separation and measurement of ^{127}I and ^{129}I species, iodine isotopes variability in surface water, estimating rate of change in ^{129}I species and inventory modeling and comparison, also including eight figures and three tables as

noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: peng.yi@geo.uu.se, peng2yi@gmail.com; tel.: +46(0)184712985; fax: +46(0)18555920.

Notes

Notes. The authors declare no competing financial interest. The authors declare no competing financial interest.

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■ REFERENCES

- Hou, X. L.; Hansen, V.; Aldahan, A.; Possnert, G.; Lind, O. C.; Lujanienė, G. A review on speciation of iodine-129 in the environmental and biological samples. *Anal. Chim. Acta* **2009**, *632* (2), 181–196.
- Spokes, L. J.; Liss, P. S. Photochemically induced redox reactions in seawater 0.2. Nitrogen and iodine. *Mar. Chem.* **1996**, *54* (1–2), 1–10.
- Wong, G. T. F.; Cheng, X. H. Dissolved organic iodine in marine waters: Determination, occurrence and analytical implications. *Mar. Chem.* **1998**, *59* (3–4), 271–281.
- Wong, G. T. F.; Zhang, L. S. The kinetics of the reactions between iodide and hydrogen peroxide in seawater. *Mar. Chem.* **2008**, *111* (1–2), 22–29.
- Jickells, T. D.; Boya, S. S.; Knap, A. H. Iodine cycling in the Sargasso Sea and the Bermuda inshore waters. *Mar. Chem.* **1988**, *24*, 61–82.
- Campos, M. L. A.; Farrenkopf, A. M.; Jickells, T. D.; Luther, G. W. A comparison of dissolved iodine cycling at the Bermuda Atlantic Time Series Station and the Hawaii Ocean Time-series. *Deep Sea Res., Part II* **1996**, *43*, 455–63.
- Truesdale, V. W. Iodine in inshore and offshore marine waters. *Mar. Chem.* **1978**, *6*, 1–13.
- Truesdale, V. W.; Jones, K. Steady-state mixing of iodine in shelf seas off the British Isles. *Cont. Shelf Res.* **2000**, *20*, 1889–1905.
- Truesdale, V. W.; Danielssen, D. S.; Waite, T. J. Summer and winter distributions of dissolved iodine in the Skagerrak. *Estuar. Coast. Shelf Sci.* **2003**, *57* (4), 701–713.
- Waite, T. J.; Truesdale, V. W.; Olafsson, J. The distribution of dissolved inorganic iodine in the seas around Iceland. *Mar. Chem.* **2006**, *101*, 54–67.
- Butler, E. C. V.; Smith, J. D.; Fisher, N. S. Influence of phytoplankton on iodine speciation in seawater. *Limnol. Oceanogr.* **1981**, *26*, 382–386.
- Allard, S.; von Gunten, U.; Sahli, E.; Nicolau, R.; Gallard, H. Oxidation of iodide and iodine on birnessite ($\delta\text{-MnO}_2$) in the pH range 4–8. *Water Res.* **2009**, *43* (14), 3417–3426.
- Edwards, A.; Truesdale, V. W. Regeneration of inorganic iodine species in Loch Etive, a natural leaky incubator. *Estuar. Coast. Shelf Sci.* **1997**, *45*, 357–366.
- Truesdale, V. W.; Watts, S. F.; Rendell, A. R. On the possibility of iodide oxidation in the near-surface of the Black Sea and its implications to iodine in the general ocean. *Deep Sea Res. Part I* **2001**, *48* (11), 2397–2412.

- (15) Hou, X. L.; Aldahan, A.; Nielsen, S. P.; Possnert, G.; Nies, H.; Hedfors, J. Speciation of 129I and 127I in seawater and implications for sources and transport pathways in the North Sea. *Environ. Sci. Technol.* **2007**, *41* (17), 5993–5999.
- (16) Moren, M.; Sloth, J. J.; Hamre, K. Uptake of iodide from water in Atlantic halibut larvae (*Hippoglossus hippoglossus* L.). *Aquaculture* **2008**, *285* (1–4), 174–178.
- (17) Moren, M.; Opstad, I.; Van Der Meeren, T.; Hamre, K. Iodine enrichment of *Artemia* and enhanced levels of iodine in Atlantic halibut larvae (*Hippoglossus hippoglossus* L.) fed the enriched *Artemia*. *Aquacult. Nutr.* **2006**, *12* (2), 97–102.
- (18) Yi, P.; Aldahan, A.; Hansen, V.; Possnert, G.; Hou, X. L. Iodine Isotopes (I-129 and I-127) in the Baltic Proper, Kattegat, and Skagerrak Basins. *Environ. Sci. Technol.* **2011**, *45* (3), 903–909.
- (19) Hansen, V.; Yi, P.; Hou, X. L.; Aldahan, A.; Roos, P.; Possnert, G. Iodide and iodate (129I and 127I) in surface water of the Baltic Sea, Kattegat and Skagerrak. *Sci. Total Environ.* **2011**, *412–413* (0), 296–303.
- (20) Hakanson, L.; Eckhell, J. Suspended particulate matter (SPM) in the Baltic Sea - New empirical data and models. *Ecol. Model.* **2005**, *189* (1–2), 130–150.
- (21) Hou, X. L.; Dahlgard, H.; Nielsen, S. P. Iodine-129 Time Series in Danish, Norwegian and Northwest Greenland Coast and the Baltic Sea by Seaweed. *Estuar. Coast. Shelf Sci.* **2000**, *51* (5), 571–584.
- (22) Alfimov, V.; Possnert, G.; Aldahan, A. Anthropogenic iodine-129 in the Arctic Ocean and Nordic Seas: Numerical modeling and prognoses. *Mar. Pollut. Bull.* **2006**, *52* (4), 380–385.
- (23) Witt, G. Occurrence and transport of polycyclic aromatic hydrocarbons in the water bodies of the Baltic Sea. *Mar. Chem.* **2002**, *79*, 49–66.
- (24) Bluhm, K.; Croot, P. L.; Huhn, O.; Rohardt, G.; Lochte, K. Distribution of iodide and iodate in the Atlantic sector of the southern ocean during austral summer. *Deep Sea Res.* **2011**, *58* (25–26), 2733–2748.
- (25) Leppäranta, M.; Myrberg, K. *Physical Oceanography of the Baltic Sea*; Springer: Berlin, 2009.
- (26) Lehto, J.; Rätty, T.; Hou, X. L.; Paatero, J.; Aldahan, A.; Possnert, G.; Flinkman, J.; Kankaanpää, H. Speciation of 129I in sea, lake and rain waters. *Sci. Total Environ.* **2012**, *419* (0), 60–67.
- (27) Alfimov, V.; Aldahan, A.; Possnert, G.; Kekli, A.; Meili, M. Concentrations of 129I along transect from the North Atlantic to the Baltic Sea. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2004**, *223–224*, 446–450, DOI: 10.1016/j.nimb.2004.04.084.
- (28) Aldahan, A.; Possnert, G.; Alfimov, V.; Cato, I.; Kekli, A. Anthropogenic 129I in the Baltic Sea. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *259* (1), 491–495, DOI: 10.1016/j.nimb.2007.01.242.
- (29) Aldahan, A.; Alfimov, V.; Possnert, G. 129I anthropogenic budget: Major sources and sinks. *Appl. Geochem.* **2007**, *22* (3), 606–618.
- (30) Hu, Q.; Zhao, P.; Moran, J. E.; Seaman, J. C. Sorption and transport of iodine species in sediments from the Savannah River and Hanford Sites. *J. Contam. Hydrol.* **2005**, *78* (3), 185–205.
- (31) Aldahan, A.; Englund, E.; Possnert, G.; Cato, I.; Hou, X. L. Iodine-129 enrichment in sediment of the Baltic Sea. *Appl. Geochem.* **2007**, *22* (3), 637–647.
- (32) Jia-Zhong, Z.; Whitfield, M. Kinetics of inorganic redox reactions in seawater: I. The reduction of iodate by bisulphide. *Mar. Chem.* **1986**, *192*, 121–137.
- (33) Wong, G. T. F.; Piumsomboon, A. U.; Dunstan, W. M. The transformation of iodate to iodide in marine phytoplankton cultures. *Mar. Ecol.: Prog. Ser.* **2002**, *237*, 27–39.
- (34) Waite, T. J.; Truesdale, V. W. Iodate reduction by *Isochrysis galbana* is relatively insensitive to de-activation of nitrate reductase activity—Are phytoplankton really responsible for iodate reduction in seawater? *Mar. Chem.* **2003**, *81* (3–4), 137–148.
- (35) Chance, R.; Malin, G.; Jickells, T.; Baker, A. R. Reduction of iodate to iodide by cold water diatom cultures. *Mar. Chem.* **2007**, *105* (1–2), 169–180.
- (36) Wong, G. T. F.; Zhang, L. S. Seasonal variations in the speciation of dissolved iodine in the Chesapeake Bay. *Estuar. Coast. Shelf Sci.* **2003**, *56* (5–6), 1093–1106.
- (37) Wong, G. T. F.; Cheng, X. H. The formation of iodide in inshore waters from the photochemical decomposition of dissolved organic iodine. *Mar. Chem.* **2001**, *74* (1), 53–64.
- (38) Truesdale, V. W.; Moore, R. M. Further-studies on the chemical-reduction of molecular-iodine added to seawater. *Mar. Chem.* **1992**, *40* (3–4), 199–213.
- (39) Truesdale, V. W.; Luther, G. W.; Canosamas, C. Molecular-iodine reduction in seawater - An improved rate-equation considering organic-compounds. *Mar. Chem.* **1995**, *48* (2), 143–150.
- (40) Breitbarth, E.; Gelting, J.; Walve, J.; Hoffmann, L. J.; Turner, D. R.; Hasseløw, M.; Ingri, J. Dissolved iron (II) in the Baltic Sea surface water and implications for cyanobacterial bloom development. *Biogeosciences* **2009**, *6* (11), 2397–2420.
- (41) Amachi, S.; Mishima, Y.; Shinoyama, H.; Muramatsu, Y.; Fujii, T. Active transport and accumulation of iodide by newly isolated marine bacteria. *Appl. Environ. Microbiol.* **2005**, *71*, 741–745.
- (42) Zic, V.; Truesdale, V. W.; Cukrov, N. The distribution of iodide and iodate in anchialine cave waters - Evidence for sustained localised oxidation of iodide to iodate in marine water. *Mar. Chem.* **2008**, *112* (3–4), 168–178.