

# 1 Speciation of $^{127}\text{I}$ and $^{129}\text{I}$ in atmospheric aerosols at Risø, 2 Denmark: Insight into sources of iodine isotopes and their 3 species transformations

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## 14 Abstract

15 Speciation analysis of iodine in aerosols is a very useful approach for understanding  
16 geochemical cycling of iodine in the atmosphere. In this study, overall iodine species,  
17 including water-soluble iodine species (iodide, iodate and water-soluble organic iodine),  
18 NaOH-soluble iodine and insoluble iodine have been determined for  $^{129}\text{I}$  and  $^{127}\text{I}$  in the  
19 aerosols collected at Risø, Denmark, between March and May, 2011 (shortly after the  
20 Fukushima nuclear accident) and in December, 2014. The measured concentrations of total  
21 iodine are in the range of 1.04-2.48 ng m<sup>-3</sup> for  $^{127}\text{I}$  and (11.3-97.0)×10<sup>5</sup> atoms m<sup>-3</sup> for  $^{129}\text{I}$ ,  
22 corresponding to  $^{129}\text{I}/^{127}\text{I}$  atomic ratios of (17.8-86.8)×10<sup>-8</sup>. The contribution of  
23 Fukushima-derived  $^{129}\text{I}$  (peak value of 6.3×10<sup>4</sup> atoms m<sup>-3</sup>) is estimated to be negligible (less  
24 than 6%) compared to the total  $^{129}\text{I}$  concentration in northern Europe. The concentrations and  
25 species of  $^{129}\text{I}$  and  $^{127}\text{I}$  in the aerosols are found to be strongly related to their sources and  
26 atmospheric pathways. Aerosols that were transported over the contaminated seas  
27 containing higher amounts of  $^{129}\text{I}$  than aerosols transported over the European continent. The  
28 high  $^{129}\text{I}$  concentrations of the marine aerosols are attributed to secondary emission

1 from  $^{129}\text{I}$ -contaminated seawater besides the primary gaseous release from the two European  
2 nuclear reprocessing plants. Water-soluble iodine was found to be a minor fraction to the total  
3 iodine for both  $^{127}\text{I}$  (7.8-13.7%) and  $^{129}\text{I}$  (6.5-14.1%) in ocean-derived aerosols, but accounted  
4 for 20.2-30.3% for  $^{127}\text{I}$  and 25.6-29.5% for  $^{129}\text{I}$  in land-derived aerosols. Iodide was the  
5 predominant form of water-soluble iodine, accounting for more than 97% of the water-soluble  
6 iodine. NaOH-soluble iodine seems to be independent of the sources of aerosols. The  
7 significant proportion of  $^{129}\text{I}$  and  $^{127}\text{I}$  found in NaOH-soluble fractions is likely bound with  
8 organic substances. In contrast to water-soluble iodine however, the sources of air masses  
9 exerted distinct influences on insoluble iodine for both  $^{129}\text{I}$  and  $^{127}\text{I}$ , with higher values for  
10 marine air masses and lower values for terrestrial air masses.

## 11 **1 Introduction**

12 The atmospheric chemistry of iodine has attracted increasing attention in recent years, in part  
13 because of its central role in governing the geochemical cycling of iodine, and also for its  
14 influences on ozone depletion, primary particle formation, and global climate (Carpenter 2003;  
15 O'Dowd et al., 2002; Saiz-Lopez et al., 2012). Most atmospheric iodine studies to date have  
16 concentrated on laboratory smog chamber experiments and modeling studies, with a paucity  
17 of field measurements of atmospheric samples. Apart from gaseous iodine (e.g. molecular  
18 iodine, iodocarbons) in the atmosphere, aerosols, which are colloids of fine solid particles or  
19 liquid droplets in air and include dust, fume, mist, smoke and fog, contain a significant  
20 fraction of iodine, and play an important role for iodine transportation from ocean to land. In  
21 particular, speciation analysis of iodine in aerosols is one of critical issue to understand the  
22 reactions and atmospheric processes of iodine, and develop a comprehensive understanding of  
23 biogeochemical cycles of iodine in nature.

24 Most of the work on aerosol iodine speciation has focused on water-soluble iodine (WSI)  
25 (Baker 2004; Baker 2005; Gilfedder et al., 2008). Early modeling studies suggested that  
26 aerosol iodate should be the only stable iodine specie as a by-product of iodine oxides  
27 production, with negligible iodide due to transformation into gaseous iodine (McFiggans et al.,

1 2000; Vogt et al., 1999). However, this prediction went against several previous observations  
2 that showed significant iodide and soluble organic iodine, accounting for 10%-100% of WSI  
3 in aerosols (Baker 2004; Baker 2005; Gabler and Heumann 1993). An improved model was  
4 then developed, primarily by increasing the proportion of iodide in the aerosols (Pechtl et al.,  
5 2007). Few studies have addressed water-insoluble iodine in aerosols (Gilfedder et al., 2010;  
6 Tsukada et al., 1987), which might be not easily converted to gaseous iodine before being  
7 deposited on the Earth's surface. Previous observational data suggest that water-insoluble  
8 iodine is abundant in aerosol particles, representing 17-53% of the total iodine (Gilfedder et  
9 al., 2010). However, there is no comprehensive investigation of aerosol iodine species that  
10 encompasses aqueous-soluble and insoluble iodine species. This constitutes a significant gap  
11 in our understanding of the interaction among atmospheric iodine species.

12 Due to the difficulty of source identification of natural  $^{127}\text{I}$ ,  $^{129}\text{I}$  ( $T_{1/2}=15.7$  Ma) has proven  
13 being an especially useful geochemical tracer both in the marine environment and in the  
14 atmosphere (He et al., 2013b; Hou et al., 2007; Jabbar et al., 2012; Michel et al., 2012). A  
15 large amount of  $^{129}\text{I}$  has been released to the environment by nuclear reprocessing plants  
16 (NRPs). These dominate all other anthropogenic sources, with 6000 kg released as of 2009,  
17 from Sellafield (United Kingdom) and La Hague (France) (Hou et al., 2007; Raisbeck et al.,  
18 1995). Anthropogenic  $^{129}\text{I}$  is currently distributed unevenly around the world in water,  
19 atmosphere and terrestrial systems (Hou et al., 2009b). Above-ground nuclear explosions also  
20 produced  $^{129}\text{I}$ , injecting it into the troposphere and stratosphere. The proportion that entered to  
21 the stratosphere became mixed globally before re-entering the troposphere. From the  
22 troposphere, about one half of the radioactive particles is deposited onto the earth's surface  
23 within 20 days (Tölgyessy 1993). Gaseous releases from reprocessing plants and accidents are  
24 primary sources of  $^{129}\text{I}$  to the local environment (Hou et al., 2009a; Xu et al., 2013).  
25 Re-emission of iodine as the forms of inorganic and organic iodine (e.g.  $\text{I}_2$ ,  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ )  
26 from sea surface plays a significant role in the atmospheric budget of  $^{129}\text{I}$  (Englund et al.,  
27 2010b). Gaseous iodine compounds photodissociate rapidly in the atmosphere to generate  
28 iodine atoms. Iodine atoms are oxidized by atmospheric oxidants (e.g.  $\text{O}_3$ ,  $\text{NO}_x$ ) to iodine  
29 oxides, which then incorporate with particles either by nucleation or by reaction/trap

1 mechanisms (Saiz-Lopez et al., 2012). As with stable iodine ( $^{127}\text{I}$ ),  $^{129}\text{I}$  also disperses in the  
2 atmosphere in both gaseous and particulate forms. Particulate  $^{129}\text{I}$  has been used successfully  
3 in monitoring studies, and as an atmospheric tracer (Englund et al., 2010b; Jabbar et al., 2012;  
4 Santos et al., 2005; Tsukada et al., 1987). While, speciation analysis of  $^{129}\text{I}$  in aerosols is  
5 extremely scarce with the only one being our previous study (Xu et al., 2015).

6 Here, we present the results of speciation analysis of stable  $^{127}\text{I}$  and radioactive  $^{129}\text{I}$  in aerosols  
7 collected in Denmark, in order to understand how the iodine is carried in the atmosphere and  
8 to investigate transformation mechanisms between iodine species in aerosols, as well as  
9 gas-aerosol exchange processes involving iodine. To our knowledge, this is the first paper to  
10 address the conversion among overall iodine species in aerosols.

## 11 **2 Materials and methods**

### 12 **2.1 Aerosol sampling**

13 Aerosol samples were collected on 0.45  $\mu\text{m}$  polypropylene filters (Type G-3, PTI, Germany),  
14 attached to an in-house aerosol collector at Risø campus, Technical University of Denmark,  
15 Denmark (55°41.77'N, 12°05.39'E) (Fig. 1). The sampling filters are normally replaced every  
16 week, but during the Fukushima nuclear accident, the changing frequency was increased to  
17 every 3-4 days. Seven aerosol samples were collected from 31 March - 2 May 2011 (local  
18 time, the same below), shortly after the Fukushima accident on 11 March 2011. One sample  
19 was collected from 8 December - 15 December 2014. The samples were put into plastic bags  
20 and stored in the dark before analysis. The sample information is listed in Table 1.

### 21 **2.2 Speciation analysis of $^{127}\text{I}$ and $^{129}\text{I}$ in aerosols**

22 **Separation of iodine species from aerosol.** The aerosol samples were analyzed for species  
23 of  $^{127}\text{I}$  and  $^{129}\text{I}$  using a newly developed method (Zhang et al., 2015). In brief, iodine was  
24 extracted sequentially using deionized water and sodium hydroxide solutions for  
25 water-soluble and NaOH-soluble iodine (WSI and NSI). Total iodine (TI) and residual  
26 insoluble iodine (RII) were separated by alkaline ashing from the original air filters and the

1 residual filters after NaOH solution leaching, respectively. Iodide and iodate in the water  
2 leachate were separated using anion exchange chromatography. Fig. 2 shows a diagram of the  
3 separation procedure for speciation analysis of iodine isotopes.

4 **Determination of  $^{127}\text{I}$  by ICP-MS and  $^{129}\text{I}$  by AMS.**  $^{127}\text{I}$  in all fractions were diluted by  
5 factors from 1 to 20 using ammonium depending on the iodine concentration in each fraction  
6 and the matrix of the leachates. Cesium was added as internal standard to a final concentration  
7 of  $2 \text{ ng g}^{-1}$  to normalize measurement efficiency of iodine in the ICP-MS measurement.  
8 Standard addition method was employed for the measurement of  $^{127}\text{I}$  in ash leachates of total  
9 iodine and the insoluble fraction. An iodine standard solution (NaI, CPI International,  
10 California, USA) was spiked into the reserved aliquots and diluted with 1%  $\text{NH}_3\cdot\text{H}_2\text{O}$  to a  
11 final concentration of  $2 \text{ ng g}^{-1}$ .  $^{127}\text{I}$  in the diluted solution was measured by ICP-MS (Thermo  
12 Fisher, X Series II) using an Xt cone under normal mode, as described elsewhere (Hou et al.,  
13 2007).

14  $^{129}\text{I}$  was measured using a 5 MV accelerator mass spectrometry (NEC, Wisconsin, USA) at  
15 Scottish University Environmental Research Center, UK (Xu et al., 2013). The prepared AgI  
16 precipitates were mixed with silver powder (Sigma-Aldrich Co., USA) with an AgI:Ag mass  
17 ratio of 1:2 and pressed into copper holders. A terminal voltage of 3.5 MV and  $\text{I}^{5+}$  ions were  
18 chosen for  $^{129}\text{I}$  detection. The measured  $^{129}\text{I}/^{127}\text{I}$  ratios were corrected against a standard with  
19 a  $^{129}\text{I}/^{127}\text{I}$  ratio of  $1.138\times 10^{-10}$ , prepared from a  $^{129}\text{I}$  standard solution (NIST 4949C) and  
20 an  $^{127}\text{I}$  carrier. The analytical precision of standards and samples are within 5%.  $^{129}\text{I}/^{127}\text{I}$  ratios  
21 in the procedural blanks were measured to be about  $5\times 10^{-13}$ , 1-3 orders of magnitude lower  
22 than those measured for the samples. All results were corrected for procedural blanks.

### 23 **3 Results**

24 The concentrations of total iodine in aerosols from Risø, Denmark ranged at  $1.04\text{-}2.48 \text{ ng m}^{-3}$   
25 (average of  $1.8\pm 0.5 \text{ ng m}^{-3}$ ) for  $^{127}\text{I}$  and  $11.3\text{-}72.9\times 10^5 \text{ atoms m}^{-3}$  (average of  $(44\pm 19)\times 10^5$   
26  $\text{atoms m}^{-3}$ ) for  $^{129}\text{I}$ , during March-May 2011 (Table 2). Total  $^{127}\text{I}$  concentration of  $2.36 \text{ ng m}^{-3}$   
27 during 8-15 December 2014 fell within the range in 2011, while  $^{129}\text{I}$  concentration of

1  $97.0 \times 10^5$  atoms  $m^{-3}$  was about two times higher than the average value in 2011. Much lower  
2 values of  $^{129}I$  and  $^{127}I$  concentrations were observed during 18 April- 2 May 2011 compared to  
3 those before 18 April (Fig. 3), but  $^{129}I$  levels didn't show a synchronous variation with  $^{127}I$   
4 concentrations. The results of  $^{127}I$  concentrations in the studied aerosols are compatible with  
5 those from an inland city, Regensburg, Germany and from some Pacific islands ((Gabler and  
6 Heumann 1993) and references therein).  $^{129}I/^{127}I$  atomic ratios in the investigated aerosols  
7 were  $(17.8-86.8) \times 10^{-8}$ , which are consistent with those found at Foehr island, north of  
8 Germany in April 2002 (Michel et al., 2012) and in southern Sweden during 1983-2008  
9 (Englund et al., 2010b; Michel et al., 2012). However, the measured  $^{129}I$  concentrations  
10 and  $^{129}I/^{127}I$  ratios are 1-2 orders of magnitude higher than those observed in Vienna, Austria  
11 during 2001-2002, and in the high altitude eastern Alps (2700 m) during 2001 (Jabbar et al.,  
12 2011; Jabbar et al., 2012).

13 For  $^{127}I$ , the WSI fraction of aerosols collected in 2011 occurred predominantly as iodide,  
14 ranging from 0.12-0.33  $ng\ m^{-3}$ . Minor iodate of 0.02-0.03  $ng\ m^{-3}$  was detected only in two  
15 samples (AE11-12 during 4-7 April and AE11-17 during 26 April-2 May) (Table 1 and Fig. 4).  
16 The highest measured  $^{127}I$  concentration (0.74  $ng\ m^{-3}$ ) was observed in aerosol collected in  
17 2014, and there was no measurable water-soluble organic iodine. Water-soluble  $^{129}I$  shows a  
18 similar species pattern as water-soluble  $^{127}I$  except that iodate-129 was below the detection  
19 limit in all the analyzed samples. The concentrations of  $^{129}I$  varied in  $(3.26-5.91) \times 10^5$  atoms  
20  $m^{-3}$  with an average value of  $4.41 \times 10^5$  atoms  $m^{-3}$  in the aerosols from 2011. This value is  
21 about 8 times lower than that in the sample collected in 2014 ( $30.1 \times 10^5$  atoms  $m^{-3}$ ). High NSI  
22 concentrations were observed in all of the aerosol samples, with an average of  $0.64 \pm 0.21$   $ng$   
23  $m^{-3}$  for  $^{127}I$  and  $(13.64 \pm 10.1) \times 10^5$  atoms  $m^{-3}$  for  $^{129}I$ . RII is the dominant species in aerosol  
24 samples for both iodine isotopes, with concentration range of 0.34-1.66  $ng\ m^{-3}$  for  $^{127}I$  and  
25  $(4.27-39.9) \times 10^5$  atoms  $m^{-3}$  for  $^{129}I$ .

26 There is no available standard reference material for iodine isotopes in aerosols which can be  
27 used for validation of the analytical method. While, the sums of all of iodine species in the  
28 analyzed samples are comparable with the measured total iodine in the corresponding samples

1 for both  $^{127}\text{I}$  and  $^{129}\text{I}$  in a range of 85-110%, indicating the reliability of our analytical results  
2 (Fig. 5).

3 For the samples collected before 18 April 2011, the proportion of  $^{129}\text{I}$  and  $^{127}\text{I}$  species follows  
4 an order of  $\text{RII} > \text{NSI} > \text{iodide}$ . For the samples collected later in April 2011 and in the winter  
5 2014, the three iodine fractions for both  $^{129}\text{I}$  and  $^{127}\text{I}$  account for almost equivalent proportion  
6 of total iodine (Fig. 5). Compared to the former sampling period (31 March-18 April 2011),  
7 the most apparent feature of the latter sampling period is a dramatic diminution of iodine in  
8 the RII fraction, by 38.7% for  $^{127}\text{I}$  and 26.8% for  $^{129}\text{I}$ . This was compensated by a  
9 corresponding increase in the iodide fraction of the aerosol particles. Iodate, as the least  
10 abundant iodine specie ( $< 3\%$ ), was only observed in two aerosol samples for  $^{127}\text{I}$ , and  
11 no  $^{129}\text{IO}_3^-$  was detectable in all aerosol samples investigated in this work.

12  $^{129}\text{I}/^{127}\text{I}$  atomic ratios of  $(15.6-102.0)\times 10^{-8}$  were determined for the different iodine species in  
13 the aerosols. The variations of  $^{129}\text{I}/^{127}\text{I}$  ratio in iodide, NSI and RII are similar to those in  
14 total  $^{129}\text{I}/^{127}\text{I}$ , with high values observed prior to 18 April 2011 and December 2014 (Table 2  
15 and Fig. 3).

## 16 **4 Discussion**

### 17 **4.1 Sources of $^{127}\text{I}$ and $^{129}\text{I}$ in aerosols**

18 Variation of  $^{127}\text{I}$  and  $^{129}\text{I}$  concentration in aerosols against meteorological parameters (i.e.  
19 wind direction, wind speed and temperature) during the sampling period shows that wind  
20 direction has a dominant influence (Fig. 3). Back trajectory model analysis shows that  $^{127}\text{I}$   
21 and  $^{129}\text{I}$  in the aerosols was directly controlled by the sources and pathways of air masses (Fig.  
22 6, Figs. S-1 and S-2 in supplementary material). The relatively high  $^{127}\text{I}$  and  $^{129}\text{I}$   
23 concentrations was observed in the aerosols collected early April 2011 and December 2014,  
24 when the air mass was mainly transported from the Atlantic Ocean cross the North Sea by  
25 prevailing westerly winds. Relatively low concentrations of iodine isotopes were observed in  
26 the aerosols collected later in April, when the air masses were dominated by prevailing

1 easterly winds and passed over the European continent and the Baltic Sea.

2 Marine emission of volatile iodine species is a major source of iodine in the atmosphere. It  
3 results in relatively elevated  $^{127}\text{I}$  concentrations in the marine atmosphere, as compared to the  
4 terrestrial atmosphere (Saiz-Lopez et al., 2012). During the sampling period of 11-14 April,  
5 the sampled air mass was transported by westerly winds from a vast area over the northern  
6 Atlantic Ocean. This caused an elevated  $^{127}\text{I}$  concentration. Except for the Norwegian Sea and  
7 the North Sea, most areas of the northern Atlantic have low seawater  $^{129}\text{I}$  concentrations (He  
8 et al., 2013a), which is what we observed for the 11-14 April aerosol sample.

9 The highest measured  $^{129}\text{I}$  concentrations in spring 2011,  $72.98 \times 10^5 \text{ atoms m}^{-3}$ , was observed  
10 in the aerosol sample collected in 4 -7 April 2011. These samples reflect that air masses were  
11 transported from two directions, west/northwest and south/southwest (Fig. 6). The dominant  
12 south/southwesterly wind passed over regions of elevated  $^{129}\text{I}$ , including the North Sea and  
13 reprocessing sites at Sellafield and La Hague. In contrast to ocean source for  $^{127}\text{I}$ , more than  
14 95% of environmental  $^{129}\text{I}$  originates from releases of Sellafield and La Hague reprocessing  
15 plants, located at west and southwest of Denmark, respectively (Fig. 1). A large fraction  
16 of  $^{129}\text{I}$  (200 -300 kg year $^{-1}$  since 1995) has been discharged to the sea as liquid form from  
17 these two reprocessing plants. After being introduced into the English Channel and Irish  
18 Sea,  $^{129}\text{I}$  follows surface ocean currents to the North Sea, Kattegat, and Baltic Sea, and  
19 continues to the Arctic along the Norwegian coast (Alfimov et al., 2004a; Buraglio et al.,  
20 1999; Hou et al., 2007; Raisbeck et al., 1995; Yi et al., 2012). Remarkably, elevated  $^{129}\text{I}$   
21 concentrations of up to  $10^{10}$  - $10^{11}$  atoms L $^{-1}$  have been found in the North Sea,  $10^9$  - $10^{10}$   
22 atoms L $^{-1}$  in Norwegian coastal waters and the Kattegat, and  $10^8$  - $10^9$  atoms L $^{-1}$  in the Baltic  
23 Sea (Aldahan et al., 2007; Alfimov et al., 2004b; He et al., 2014; Hou et al., 2007; Michel et  
24 al., 2012; Yi et al., 2011). Only a small fraction of  $^{129}\text{I}$  (about 0.5 -5 kg year $^{-1}$  in the past 20  
25 years) has been released as gaseous form to the atmosphere from Sellafield and La Hague  
26 reprocessing plants, and it has dispersed over a large area, in particular in Europe (Ernst et al.,  
27 2003; Hou et al., 2007; Persson et al., 2007; Jabbar et al., 2012). Direct gaseous release of  $^{129}\text{I}$   
28 is suggested as a major source of  $^{129}\text{I}$  in aerosols and precipitation in Zurich and Seville, Spain



1 (Schnabel et al. 2001, Lopez-Gutierrez et al., 2004). In this work, the results present a direct  
2 observation of  $^{129}\text{I}$  source in the Danish aerosol. The aerosol samples collected in 41 March-4  
3 April and 4-7<sup>th</sup> April, which as air mass passed over Sellafield and La Hague, as well as the  
4 North Sea, but the air mass in the aerosol collected in 4-7<sup>th</sup> April were also passed through the  
5 English Channel where was highly contaminated by marine discharged  $^{129}\text{I}$  from La Hague  
6 reprocessing plant. A  $^{129}\text{I}$  concentration of  $25.9 \times 10^5 \text{ atoms m}^{-3}$  was observed in the aerosol  
7 sample in 31 March-4 April, 2.6 times lower than that in 4-7 April ( $72.98 \times 10^5 \text{ atoms m}^{-3}$ ).  
8 The aerosol in 7-11 April, when air mass didn't passed above Sellafield and La Hague, but  
9 over a narrow sea surface of the North Sea contained similar high level  $^{129}\text{I}$  concentration as  
10 that in 31 March - 4 April. In contrast, the two aerosols collected in 11-18 April, which the air  
11 mass did not pass over Sellafield and La Hague, had relatively high  $^{129}\text{I}$  concentrations  
12 ( $(43.81-47.21) \times 10^5 \text{ atoms m}^{-3}$ ) (Figs. 6 and S1). These results indicates that secondary  
13 emission from  $^{129}\text{I}$ -contaminated seawater, in particular in the North Sea, Kattegat and the  
14 Norwegian Sea, is a dominant source of  $^{129}\text{I}$  in the aerosols from Denmark, as well as part of  
15 north Europe. Emission process of volatile iodine from seawater can be facilitated by  
16 sea-spray and biological activity of macroalgae and microalgae (McFiggans, 2005; O'Dowd et  
17 al., 2002). This conclusion is also supported by  $^{129}\text{I}$  measurements in aerosols from high  
18 altitude European sites (Jabbar et al., 2012), as well as in precipitation from Denmark,  
19 Sweden and Germany (Buraglio et al., 2001; Hou et al., 2009a; Krupp and Aumann, 1999;  
20 Michel et al. 2012), as well as in two Irish lake waters influenced by precipitation  
21 (Atarashi-Andoh et al., 2007; Keogh et al., 2010).

22 The lowest  $^{129}\text{I}$  concentrations,  $(11-13) \times 10^5 \text{ atoms m}^{-3}$ , were observed in the aerosol samples  
23 collected in 18 -26 April and 26 April -2 May 2011. Back trajectory analysis (Fig. S1) shows  
24 that in this period the air masses at the sampling site were mainly transported by easterly or  
25 northwesterly winds, i.e. from the European continent. Terrestrial emissions of iodine occur  
26 through vegetation and terrestrial microorganisms (Bewers and Haysom, 1974). Low  $^{129}\text{I}/^{127}\text{I}$   
27 ratio of terrestrial system can be observed in those areas distant from nuclear reprocessing  
28 plant and highly  $^{129}\text{I}$ -contaminated marine source (Jabbar, 2011 and 2012). This is reflected in  
29 these two aerosol samples by their relatively low  $^{129}\text{I}$  concentrations. An elevated  $^{210}\text{Pb}$  level

1 (249 -253  $\mu\text{Bq m}^{-3}$ ) (Table 1) for this period is also consistent with a continental origin  
2 ( $^{210}\text{Pb}$  in the air is a decay product of  $^{222}\text{Rn}$  which is mainly released from the soil in the  
3 continental area). The highest value of  $^{129}\text{I}$ ,  $97.00\times 10^5$  atoms  $\text{m}^{-3}$ , in 8-15 December 2014 is  
4 also related with  $^{129}\text{I}$  re-emission mainly from the North Sea, where the air masses passed  
5 over (Fig. S2). Because of the possibilities, including probably increased releases from  
6 Sellafield and La Hague and seasonal difference of iodine re-emission from seawater, the  $^{129}\text{I}$   
7 concentration in winter 2014 is higher than that in spring 2011.

#### 8 **4.2 Species of $^{129}\text{I}$ and $^{127}\text{I}$ in aerosols**

9 WSI is virtually pure iodide in the aerosols investigated, with iodate and water-soluble  
10 organic iodine accounting for less than 3% of total iodine, and these are only measureable in  
11 two samples. Iodate was once considered to be the only WSI species in aerosol (Vogt et al.,  
12 1999). This was supported by earlier field observations demonstrating that iodate was  
13 dominant in size-segregated aerosols from the tropical Atlantic (Wimschneider and Heumann  
14 1995). However, this iodate-dominant feature was not found in other aerosol samples, e.g. in  
15 the northwest Atlantic Ocean and in tropical atmospheric aerosols (Baker 2004; Baker 2005).  
16 In these cases, iodide was the dominant water soluble iodine species in the aerosols, as  
17 observed in this study. Significant amounts of soluble organic iodine, accounting for 83-97%  
18 of WSI, has been reported in aerosols collected at the Mace Head atmospheric research station  
19 on the west coast of Ireland (Gilfedder et al., 2008). Water-soluble organic iodine accounting  
20 for 4%-75% of WSI were also measured in aerosols collected from a cruise from the UK to  
21 the Falkland Islands in 2003 (Baker 2005). This suggests that the proportion of soluble  
22 organic iodine in aerosols varies regionally and depends on particular aerosol sources and  
23 formation processes. Some of this variability might also be related to the analytical methods  
24 employed for speciation analysis (Zhang et al., 2015).

25 It is not clear how iodide is formed in the atmosphere, in an oxidizing environment containing  
26 oxygen and ozone. Early models predicted a negligible iodide concentration in particle phases  
27 based on the assumption that the iodide in aerosols only originates from the low levels of  
28 gaseous HI (McFiggans et al., 2000; Vogt et al., 1999). This work in combination with the

1 previous reports (Baker 2004; Xu et al., 2015) suggests that there must be other primary  
2 pathways that contribute to iodide formation at the observed levels. It's generally accepted  
3 that iodine atoms are photochemically produced by photolysis of gaseous iodinated  
4 compounds, and oxidized by ozone to form reactive iodine oxides (Carpenter 2003;  
5 Saiz-Lopez et al., 2012; Vogt et al., 1999). The formation of iodide from iodine atoms and  
6 other reactive iodine compounds must rely on electron-donors that are capable of reducing  
7 high valence iodine species to iodide. One possibility is the involvement of sulfur compounds  
8 (Chatfield and Crutzen 1990). Possible reaction pathways are given in Table 3. Gaseous  $\text{SO}_2$   
9 can be formed in nature by reactions of dimethyl sulfate (DMS) with hydroxide and nitrate.  
10 Human activity is a major source of atmospheric  $\text{SO}_2$ , globally about three times as much  
11  $\text{SO}_2$  as natural processes (Galloway, 1995). By associating with  $\text{H}_2\text{O}$ , these reactions produce  
12  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  (Eqs.s 1 and 2). Native iodine and other reactive species (not shown) can be  
13 reduced to  $\text{I}^-$  on gas-aerosol interfaces (Eq. 3). Other iodine species in aerosols can also  
14 reduced by reductive sulfur compounds to form iodide (Eq. 4). The electron-donors are not  
15 limited to sulfur compounds either, for example, nitrogen in the form of gaseous ammonia  
16 ( $\text{NH}_3 \rightarrow \text{NO}_2/\text{NO}_3$ ) (McFiggans et al., 2000; Saiz-Lopez and Plane 2004) and elemental  
17 mercury ( $\text{Hg}^0 \rightarrow \text{HgO}/\text{HgX}$ , where X is a halogen,  $\text{I}^-$ ,  $\text{Br}^-$  or  $\text{Cl}^-$ ) (Lindberg et al., 2002;  
18 Simpson et al., 2007) are also candidates responsible for iodide formation.

19 We note that the percentage of WSI  $^{129}\text{I}$  and  $^{127}\text{I}$  in marine-sourced aerosol from the North Sea  
20 is relative lower than that in the continental aerosol, as compared to the European  
21 continent-sourced aerosols (Figs. 4 and 5). This is consistent with the findings drawn from an  
22 iodine speciation study of coastal aerosol samples from England (Baker et al., 2001), where  
23 the concentrations of total water-soluble iodine from continental aerosols were significantly  
24 higher than those from marine aerosols.

25 A large proportion of  $^{129}\text{I}$  and  $^{127}\text{I}$  in our aerosol samples were NaOH-soluble, which is  
26 consistent with the results of aerosol from Tsukuba, Japan, collected shortly after the  
27 Fukushima nuclear accident in March 2011 (Xu et al., 2015). Abundant NaOH-soluble  $^{129}\text{I}$   
28 (32%-44% of total  $^{129}\text{I}$ ) in Fukushima-derived aerosols was attributed to coarse  
29 vegetation-related organic particles concentrated during spring. The measured NaOH-soluble

1 iodine (NSI) fractions of  $^{129}\text{I}$  and  $^{127}\text{I}$  during the entire sampling period in the spring of 2011  
2 and winter of 2014 are similar. This indicates that NSI is relatively stable and less affected by  
3 the source and pathways of air masses than WSI. NaOH leaching is often used to extract  
4 organic substance in fractionation analysis of soil and sediment (Englund et al., 2010a; Hou et  
5 al., 2003) based on the high solubility of organic matter, such as humic substances, as well as  
6 on nucleophilic substitution and decomposition of organic matter. Organic compounds are  
7 important contributors to aerosols, such as lipidic, saccharides and proteinaceous materials  
8 (O'Dowd et al., 2004; Quinn et al., 2014). A significant portion of atmospheric aerosols was  
9 found to be humic-like substances (HULIS), named for their strong structural similarity to  
10 humic and fulvic acids (Havers et al., 1998). Most of these organic compounds are  
11 water-soluble, but a significant water-insoluble fraction of the HULIS material is hydrophobic  
12 and acidic in character, and can be dissolved in an alkaline solvent, like NaOH (Feczko et al.,  
13 2007; Havers et al., 1998). On the other hand, the hydroxide anion can also initiate a  
14 nucleophilic substitution or elimination of iodine-containing organic compounds, which  
15 releases iodine from the organic substances. Therefore, NaOH-soluble iodine is suggested to  
16 be likely associated with organic substances in aerosols.

17 RII in aerosols has received less attention than WSI (Gilfedder et al., 2010; Tsukada et al.,  
18 1987). The early report on water-insoluble iodine fraction in aerosol particles showed that  
19 water-insoluble iodine accounted for 27-58% of total iodine bound in aerosols from Tokyo,  
20 Japan, collected in 1983-84 (Tsukada et al., 1987). Another similar result of 17-53% of total  
21 iodine as insoluble species was reported for aerosols from the west coast of Ireland in 2007,  
22 and from a ship transect from China to Antarctica in 2005-2006 (Gilfedder et al., 2010).  
23 Taking the alkaline-leachable iodine in aerosols into account, these results are very consistent  
24 with our observations from Risø (Fig. 5). The residual insoluble  $^{129}\text{I}$  fractions were reported to  
25 be 4-23% of total  $^{129}\text{I}$  in Fukushima-derived aerosol particles (Xu et al., 2015), less than the  
26 proportion in the aerosols collected in Denmark. This discrepancy might reveal the different  
27 formation processes of RII species for the NRPs-derived  $^{129}\text{I}$  in this study as compared to  
28 those from Fukushima. A significant difference is the timing of the  $^{129}\text{I}$  releases. NRPs have  
29 releasing  $^{129}\text{I}$  into the European environment for about 50 years, allowing  $^{129}\text{I}$  to follow

1 geochemical pathways on timescales ranging from days to decades. In contrast, RII in  
2 Fukushima-derived aerosols had only days to react with their environment prior to sampling,  
3 15-22 March, 2011.

4 The origin of the RII fraction is not well understood at present. It's possible that part of the  
5 RII fraction is derived from suspended soil particles (Xu et al., 2013). It has been  
6 demonstrated that iodine can be associated with metal oxide (notably iron and manganese). A  
7 relatively large fraction of iodine (about 38%) in soil and sediment has been observed in  
8 Fe/Mn oxides associated form (Hou et al., 2003). Our data show that RII fraction is as high as  
9 67% of total aerosol iodine. In addition to metal oxides associated iodine, speciation analysis  
10 of  $^{129}\text{I}$  in soil shows that residual iodine after leaching with NaOH and weak acid accounts for  
11 less than 10% of the total, and this component is assumed to be associated with minerals (Hou  
12 et al., 2003; Qiao et al., 2012). As stated above, the aerosols collected in early April 2011 and  
13 winter of 2014 were mainly marine-derived aerosols with relatively higher RII percentage  
14 than those continental-derived aerosols (Fig. 5). This might be attributed that some marine  
15 components facilitate the association of gaseous iodine with oxides and minerals.

### 16 **4.3 Fukushima-derived $^{129}\text{I}$ signal in the European atmosphere**

17 The Fukushima Dai-ichi nuclear power plant accident on March 11, 2011 released radioiodine  
18 to the atmosphere, primarily as  $^{131}\text{I}$  and  $^{129}\text{I}$ , which was mainly transported eastwards by  
19 prevailing westerly winds. Based on  $^{129}\text{I}$  levels in the Fukushima offshore seawater, the  
20 released  $^{129}\text{I}$  from this accident was estimated to be 1.2 kg (Hou et al., 2013). Radioactive  
21 iodine in the air dispersed across the Pacific Ocean, American continent and Atlantic Ocean,  
22 and some fraction arrived in the European continent after 1-2 weeks (Clemenza et al., 2012;  
23 Leon et al., 2011; Manolopoulou et al., 2011; Pittauerová et al., 2011). Anthropogenic  $^{129}\text{I}$  has  
24 been reported from a variety of environmental samples in Japan, including soil, seawater,  
25 precipitation and aerosols (Buessler et al., 2012; Hou et al., 2013; Muramatsu et al., 2015;  
26 Xu et al., 2013; Xu et al., 2015). The level of  $^{129}\text{I}$  in aerosols collected in Tsukuba, about 170  
27 km from the Fukushima Dai-ichi NPP, reached  $5 \times 10^8$  atoms  $\text{m}^{-3}$  (Xu, et al. 2015). While the

1 Fukushima-derived  $^{129}\text{I}$  in environmental samples outside of Japan was less  
2 well-characterized.  $^{131}\text{I}$  in the aerosol samples collected at Risø, Denmark, 10 days after the  
3 Fukushima accident have been observed (Fig. 7) (Nielsen et al., 2011). The radioactivity  
4 of  $^{131}\text{I}$  reached the peak on 24-30 March 2011 ( $763 \mu\text{Bq m}^{-3}$  in aerosol), then fell to below  
5 detection limits for  $^{131}\text{I}$  in the middle of May. Based on the measured  $^{131}\text{I}$  radioactivity in the  
6 aerosol samples and an  $^{129}\text{I}/^{131}\text{I}$  atomic ratio of  $16.0 \pm 2.2$  deduced from the aerosol samples  
7 collected at Tsukuba, Japan shortly after the Fukushima accident (Xu et al., 2015), the  
8 Fukushima-derived  $^{129}\text{I}$  signal in Denmark can be reconstructed (Fig. 7). The highest  $^{129}\text{I}$   
9 concentration in the aerosols in Denmark from the Fukushima accident is estimated to be  
10  $6.3 \times 10^4 \text{ atoms m}^{-3}$  on 30-31 March 2011, which accounts for less than  $\sim 6\%$  of total  $^{129}\text{I}$   
11 ( $1.1\text{-}9.7 \times 10^6 \text{ atoms m}^{-3}$ ) in Denmark when the Fukushima  $^{131}\text{I}$  peak was measured.  
12 Considering the rapid decline of  $^{129}\text{I}$  levels in aerosols and precipitation in Japan to nearly  
13 pre-accident levels within two years (Xu et al., 2013), the contribution of  
14 Fukushima-derived  $^{129}\text{I}$  to the  $^{129}\text{I}$  level and inventory in the Europe is now negligible in  
15 comparison to NRPs-derived  $^{129}\text{I}$  in the European atmosphere.

## 16 **5 Conclusions**

17 Based on the analytical results on speciation analysis of  $^{129}\text{I}$  and  $^{127}\text{I}$  in aerosols collected in  
18 Denmark immediately after the Fukushima accident and the discussion above, the following  
19 conclusions can be drawn:

- 20 1) Iodide is the dominant species ( $>97\%$ ) of the water-soluble iodine in the aerosols of this  
21 study, its formation might be related to atmospheric reductants, such as reductive  $\text{SO}_2$  and  
22 disulfites. The most dominant species of iodine in aerosols are NSI and RII, accounting  
23 for up to 80% of total iodine, NSI is predominantly bound to organic matter, such as  
24 HULIS, while RII might be associated with inorganic components, such as metal oxides.
- 25 2) Westerly-dominated air masses from the Atlantic Ocean contribute to high  $^{129}\text{I}$   
26 concentrations compared to easterly air masses from the northeastern European  
27 continent.  $^{129}\text{I}$  in aerosols in Denmark is primarily derived from European nuclear

1 reprocessing plants. This includes secondary emission of  $^{129}\text{I}$  from seawater in the North  
2 Sea, Norwegian coastal water and Kattegat, which has been contaminated by marine  
3 discharges of  $^{129}\text{I}$  from NRPs.

4 3) Fukushima-derived  $^{129}\text{I}$  contributed less than ~6 % to the total  $^{129}\text{I}$  in the European  
5 atmosphere immediately after the Fukushima accident, a negligible quantity when  
6 compared to  $^{129}\text{I}$  levels released from Sellafield and La Hague nuclear reprocessing plants.

7 4) Water-insoluble iodine (NSI and RII) in aerosols that is primarily associated with organic  
8 compounds is crucial for investigation of geochemical cycling of iodine in the atmosphere  
9 due to its large fraction. This requires more intensive studies to extend our observations on  
10 both temporal and spatial scales.

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1 Table 1. Sampling information of aerosols collected at Risø, Denmark in 2011 and 2014. Data  
 2 of  $^{131}\text{I}$  and  $^{210}\text{Pb}$  in the aerosol samples are adopted from the DTU Nutech report (Nielsen et al.,  
 3 2011). The reference time was the mid-point of the sampling period, and analytical  
 4 uncertainties were 5% for  $^{131}\text{I}$ , and within 1% for  $^{210}\text{Pb}$ ).

Sample No	Sampling date	Air flux, $\text{m}^3$	Air flux, $\text{m}^3 \text{h}^{-1}$	Weigh t, g	$^{131}\text{I}$ , $\mu\text{Bq m}^{-3}$	$^{210}\text{Pb}$ , $\mu\text{Bq m}^{-3}$
AE11-1	31 <sup>st</sup> Mar-4 <sup>th</sup> Apr, 2011	88833	2757	72.5	205	66
AE11-2	4-7 <sup>th</sup> Apr, 2011	64339	2751	79.2	218	47
AE11-3	7-11 <sup>th</sup> Apr, 2011	55911	1744	79.5	147	47
AE11-4	11-14 <sup>th</sup> Apr, 2011	27083	1096	70.9	110	172
AE11-5	14-18 <sup>th</sup> Apr, 2011	48317	1505	77.9	58.3	172
AE11-6	18-26 <sup>th</sup> Apr, 2011	101400	1593	80.8	20.9	249
AE11-7	26 <sup>th</sup> Apr-2 <sup>nd</sup> May, 201	54600	1117	77.7	14.8	253
AE14-1	8-15 <sup>th</sup> Dec, 2014	37917	2727	21.7	< D.L.	54.9

5

1 Table 2. Analytical results of chemical species of  $^{127}\text{I}$  and  $^{129}\text{I}$  in aerosols collected from Risø,  
 2 Denmark during spring 2011 and winter 2014 <sup>a</sup>.

Sample	TI	WSI	Iodate	Iodide	NSI	RII
$^{127}\text{I}$ concentration, $\text{ng m}^{-3}$						
AE11-1	$1.187 \pm 0.062$	$0.152 \pm 0.002$	ND	$0.158 \pm 0.008$	$0.340 \pm 0.019$	$0.606 \pm 0.042$
AE11-2	$1.797 \pm 0.116$	$0.141 \pm 0.01$	$0.022 \pm 0.012$ <sup>b</sup>	$0.119 \pm 0.006$	$0.556 \pm 0.037$	$0.977 \pm 0.049$
AE11-3	$1.927 \pm 0.115$	$0.264 \pm 0.004$	ND	$0.259 \pm 0.013$	$0.813 \pm 0.027$	$0.983 \pm 0.05$
AE11-4	$2.480 \pm 0.129$	$0.258 \pm 0.013$	ND	$0.276 \pm 0.014$	$0.825 \pm 0.049$	$1.664 \pm 0.085$
AE11-5 <sup>c</sup>	$2.027 \pm 0.104$	$0.221 \pm 0.011$	ND	$0.237 \pm 0.012$	$0.638 \pm 0.036$	$1.308 \pm 0.087$
AE11-6	$1.506 \pm 0.112$	$0.305 \pm 0.007$	ND	$0.327 \pm 0.017$	$0.624 \pm 0.033$	$0.585 \pm 0.03$
AE11-7 <sup>c</sup>	$1.041 \pm 0.055$	$0.316 \pm 0.019$	$0.033 \pm 0.024$ <sup>b</sup>	$0.283 \pm 0.014$	$0.377 \pm 0.027$	$0.343 \pm 0.018$
AE14-1	$2.356 \pm 0.127$	$0.618 \pm 0.019$	ND	$0.739 \pm 0.039$	$0.929 \pm 0.057$	$0.802 \pm 0.041$
$^{129}\text{I}$ concentration, $\times 10^5$ atoms $\text{m}^{-3}$						
AE11-1	$28.57 \pm 1.11$	$3.07 \pm 0.08$	ND	$3.60 \pm 0.43$	$8.33 \pm 0.84$	$14.14 \pm 0.64$
AE11-2	$72.98 \pm 5.64$	$4.72 \pm 0.41$	ND	$4.63 \pm 0.27$	$20.55 \pm 1.43$	$39.94 \pm 1.64$
AE11-3	$25.60 \pm 0.98$	$3.60 \pm 0.15$	ND	$4.11 \pm 0.72$	$10.80 \pm 0.40$	$13.49 \pm 2.83$
AE11-4	$47.27 \pm 1.55$	$4.78 \pm 0.23$	ND	$5.27 \pm 0.57$	$13.43 \pm 1.24$	$30.26 \pm 4.24$
AE11-5 <sup>c</sup>	$43.81 \pm 1.28$	$5.55 \pm 0.27$	ND	$5.91 \pm 0.74$	$12.58 \pm 0.46$	$27.51 \pm 1.28$
AE11-6	$12.73 \pm 0.42$	$3.26 \pm 0.10$	ND	$3.26 \pm 0.30$	$4.60 \pm 0.49$	$5.91 \pm 0.36$
AE11-7 <sup>c</sup>	$11.31 \pm 0.43$	$3.34 \pm 0.11$	ND	$4.08 \pm 0.24$	$3.36 \pm 0.25$	$4.27 \pm 0.74$
AE14-1	$97.00 \pm 3.01$	$26.85 \pm 0.65$	ND	$30.12 \pm 1.68$	$34.74 \pm 0.80$	$39.01 \pm 1.49$
$^{129}\text{I}/^{127}\text{I}$ atomic ratio, $\times 10^{-8}$						
AE11-1	$50.78 \pm 3.31$	$42.73 \pm 1.28$	ND	$48.04 \pm 6.23$	$51.70 \pm 5.98$	$49.19 \pm 4.07$
AE11-2	$85.70 \pm 8.63$	$70.73 \pm 8.06$	ND	$81.93 \pm 6.36$	$78.03 \pm 7.50$	$86.21 \pm 5.62$
AE11-3	$28.03 \pm 1.99$	$28.82 \pm 1.26$	ND	$33.49 \pm 6.13$	$28.04 \pm 1.40$	$28.94 \pm 6.25$
AE11-4	$40.21 \pm 2.48$	$39.11 \pm 2.72$	ND	$40.29 \pm 4.84$	$34.34 \pm 3.78$	$38.37 \pm 5.72$
AE11-5 <sup>c</sup>	$45.60 \pm 2.70$	$52.85 \pm 3.66$	ND	$52.50 \pm 7.16$	$41.58 \pm 2.79$	$44.36 \pm 3.61$
AE11-6	$17.84 \pm 1.46$	$22.59 \pm 0.89$	ND	$21.08 \pm 2.24$	$15.56 \pm 1.85$	$21.32 \pm 1.69$
AE11-7 <sup>c</sup>	$22.92 \pm 1.48$	$22.30 \pm 1.55$	ND	$30.43 \pm 2.38$	$18.81 \pm 1.93$	$26.28 \pm 4.73$
AE14-1	$86.84 \pm 5.40$	$91.70 \pm 3.55$	ND	$86.03 \pm 6.63$	$78.84 \pm 5.20$	$102.63 \pm 6.51$

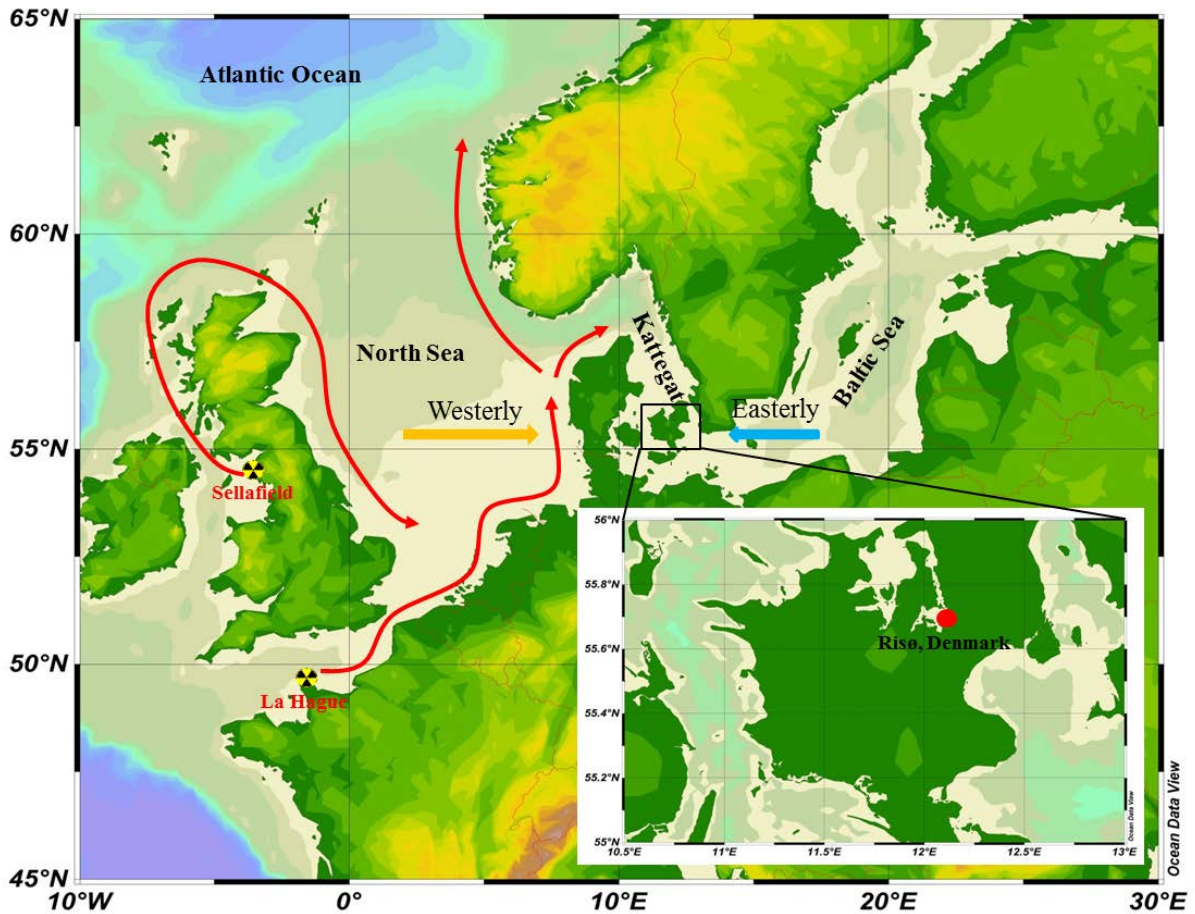
3 a. Analytical uncertainties ( $1\sigma$ ). b. The values are for reference. c. Data from Zhang et al., 2015.

1 Table 3. Possible pathways of formation of iodide by reduction of sulfur compounds

Phase	Reactions	Equations	References
Gas	DMS + OH $\rightarrow$ SO <sub>2</sub>	(1)	(Chatfield and Crutzen 1990)
	DMS + NO <sub>3</sub> $\rightarrow$ SO <sub>2</sub>		
Gas/Aerosol	SO <sub>2</sub> + H <sub>2</sub> O $\rightarrow$ HSO <sub>3</sub> <sup>-</sup>	(2)	
	SO <sub>2</sub> + H <sub>2</sub> O $\rightarrow$ SO <sub>3</sub> <sup>2-</sup>		
Gas-Aerosol interface	I + HSO <sub>3</sub> <sup>-</sup> $\rightarrow$ I <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>	(3)	
	I + SO <sub>3</sub> <sup>2-</sup> $\rightarrow$ I <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>		
Aerosol	HOI + HSO <sub>3</sub> <sup>-</sup> / SO <sub>3</sub> <sup>2-</sup> $\rightarrow$ I <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>	(4)	(Saiz-Lopez et al., 2012)
	HOI + SO <sub>3</sub> <sup>2-</sup> $\rightarrow$ I <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>		
	HOI <sub>2</sub> + HSO <sub>3</sub> <sup>-</sup> / SO <sub>3</sub> <sup>2-</sup> $\rightarrow$ I <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>		
	HOI <sub>2</sub> + SO <sub>3</sub> <sup>2-</sup> $\rightarrow$ I <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup>		

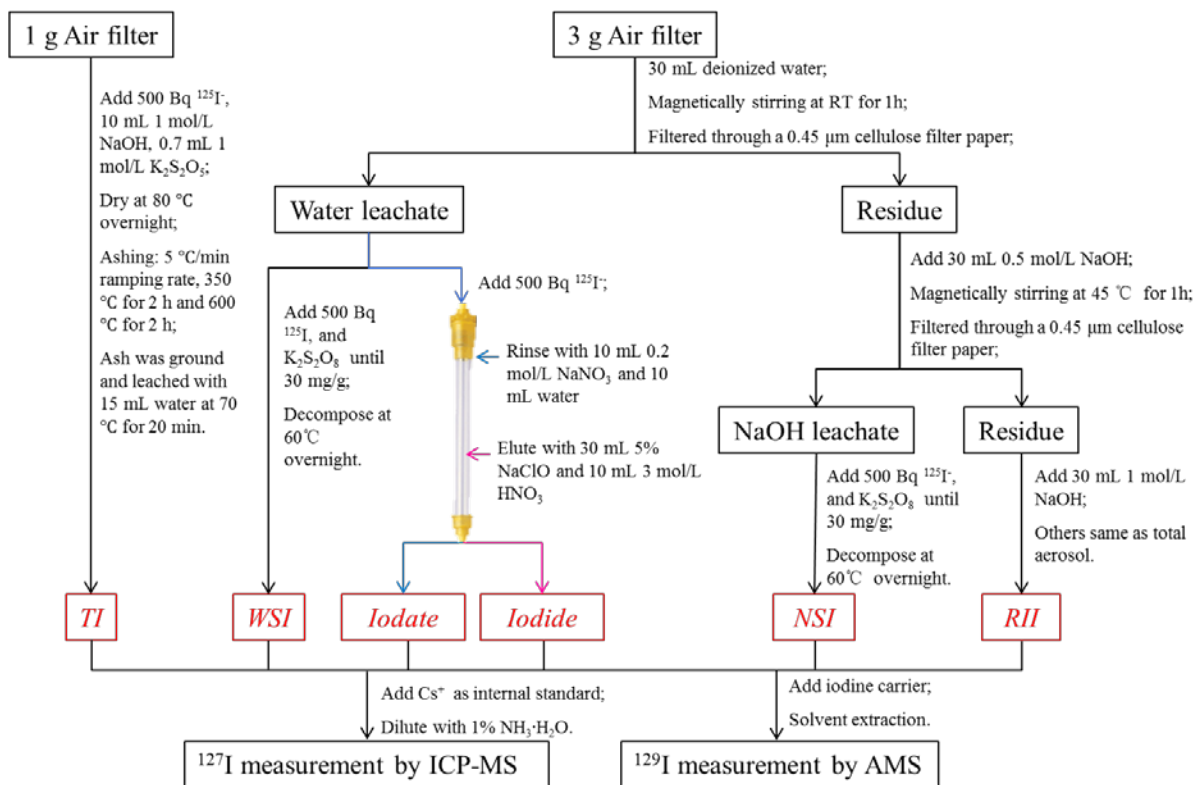
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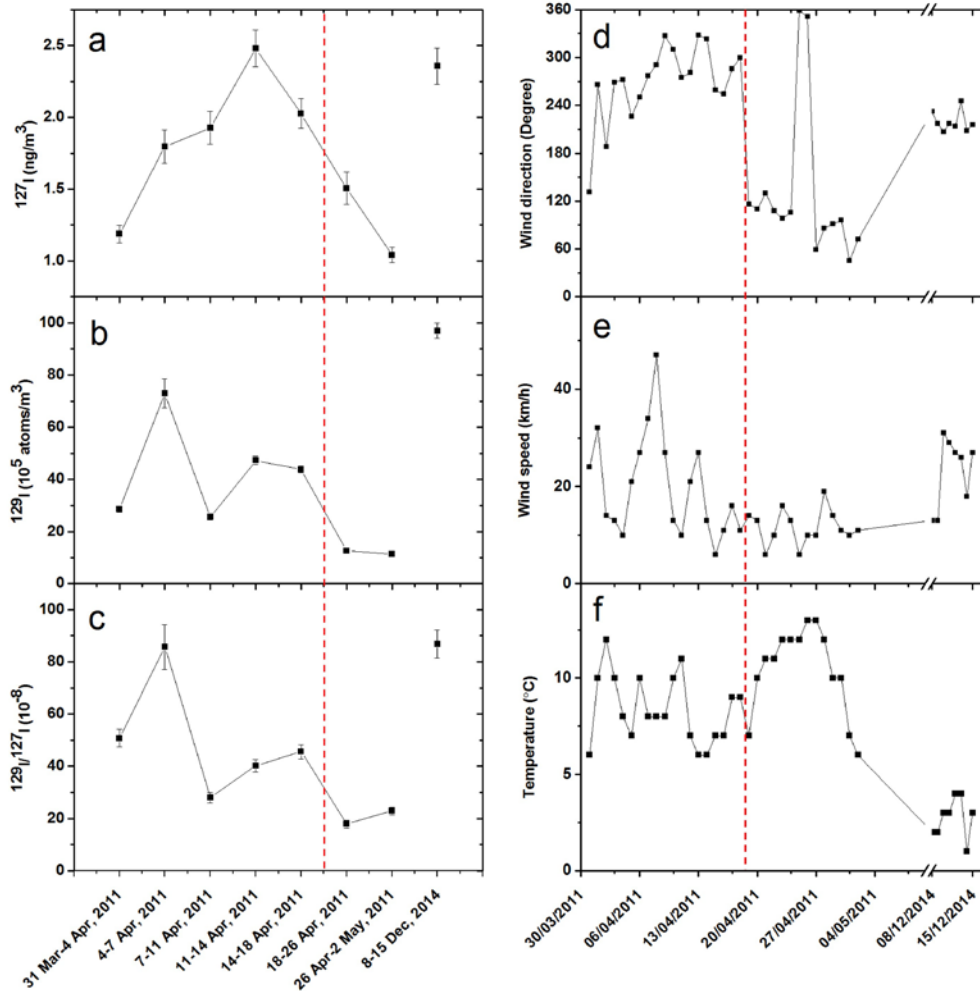
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3 Figure 1. Map showing the sampling site (red dot in the inset) at Risø, Denmark for aerosol  
 4 collection. The two nuclear reprocessing plants (radioactivity labels), Sellafield (United  
 5 Kingdom) and La Hague (France) have released a large quantity of  $^{129}\text{I}$  to the marine and  
 6 atmospheric environment. This anthropogenic  $^{129}\text{I}$  discharged to marine systems has been  
 7 transported to the North Sea, Baltic Sea, Norwegian Sea, and beyond, by ocean currents (red  
 8 lines). Yellow and blue arrows show the westerly wind and easterly wind, respectively.



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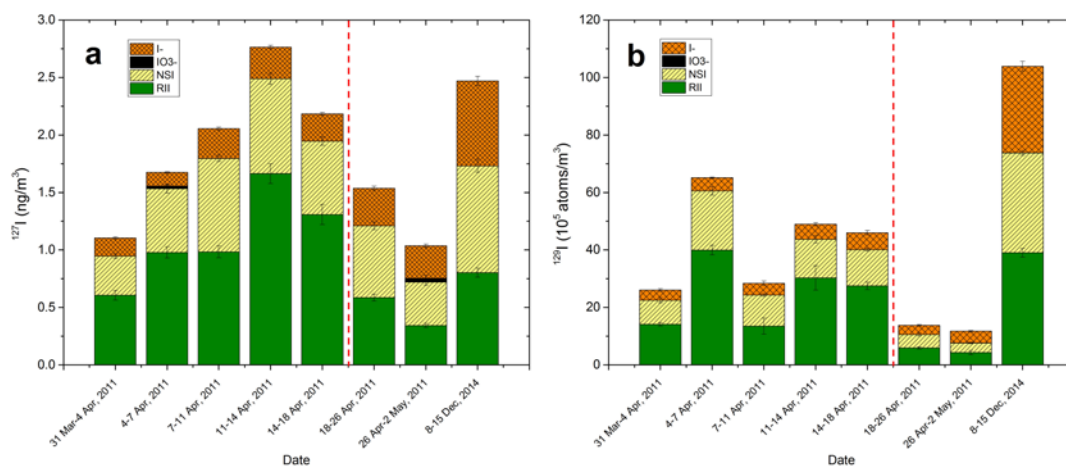
4 Figure 2. Schematic diagram of the analytical procedure for the determination of  $^{127}\text{I}$  and  $^{129}\text{I}$   
5 species in aerosols (adapted from Zhang et al., 2015). TI for total iodine, WSI for  
6 water-soluble iodine, NSI for NaOH-soluble iodine and RII for residual-insoluble iodine.



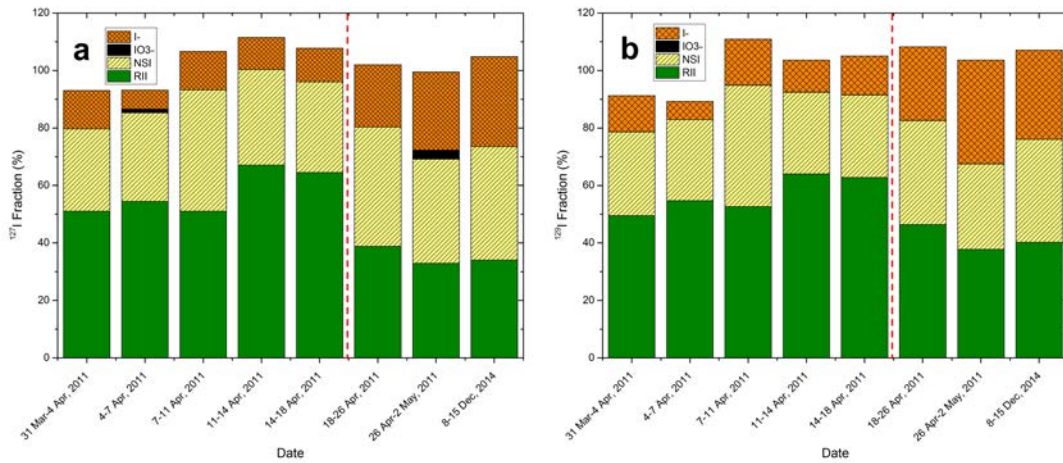
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3 Figure 3. Variation of  $^{127}\text{I}$  concentrations (a),  $^{129}\text{I}$  concentrations (b),  $^{129}\text{I}/^{127}\text{I}$  ratios in aerosols  
 4 (c), wind direction (d), wind speed (e) and temperature (f) during the sampling period. The  
 5 historical meteorological data, including temperature, wind direction and wind speed were  
 6 obtained from the observation station of Hangarvej in Roskilde, Denmark ( $55.594^{\circ}\text{N}$   
 7  $12.128^{\circ}\text{E}$ ) based on 41 m ASL (Above sea level) (Weather Wunderground webpage, 2015).  
 8 Dot red lines are used to separate the episode of westerly wind and easterly wind in spring  
 9 2011.

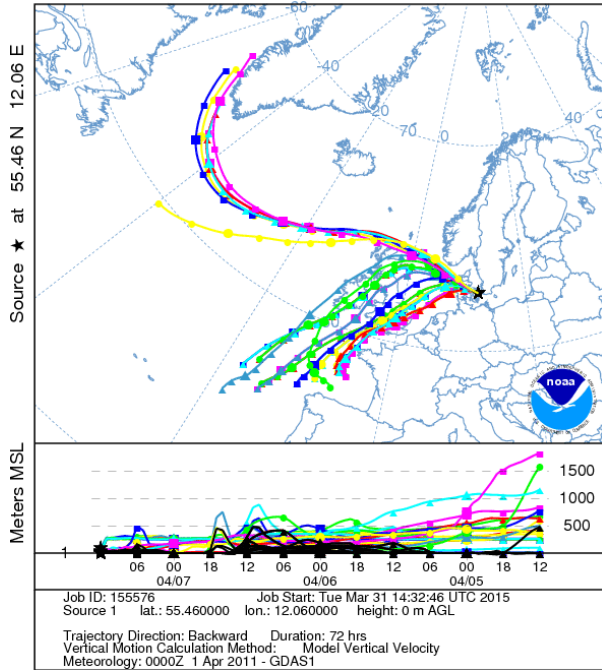


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 2 Figure 4. Concentrations of iodine species in the aerosol samples for <sup>127</sup>I (a) and <sup>129</sup>I (b),  
 3 indicating that NSI and RII are major iodine species and that iodide is the dominant fraction  
 4 of water-soluble iodine. Dot lines are same as those in Figure 3.

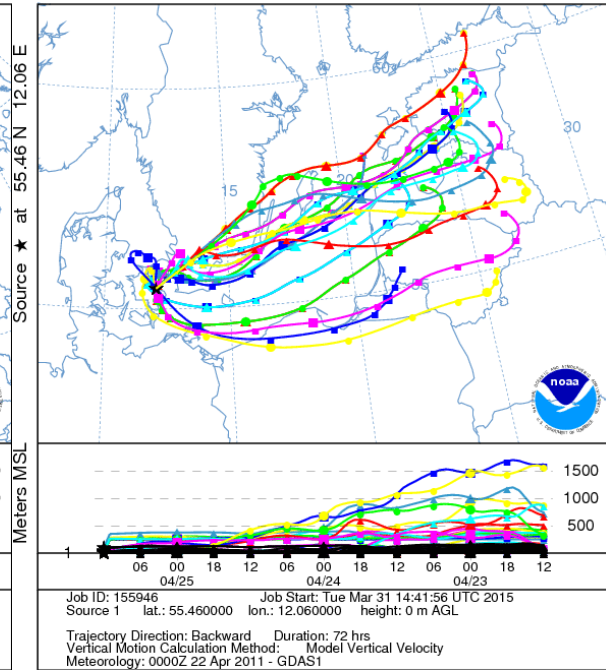


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 2 Figure 5. Distribution of iodine species in the aerosol samples for <sup>127</sup>I (a) and <sup>129</sup>I (b),  
 3 compared with the measured concentrations of total <sup>127</sup>I and <sup>129</sup>I in bulk aerosols. Dot lines are  
 4 same as those in Figure 3.

NOAA HYSPLIT MODEL  
Backward trajectories ending at 1200 UTC 07 Apr 11  
GDAS Meteorological Data

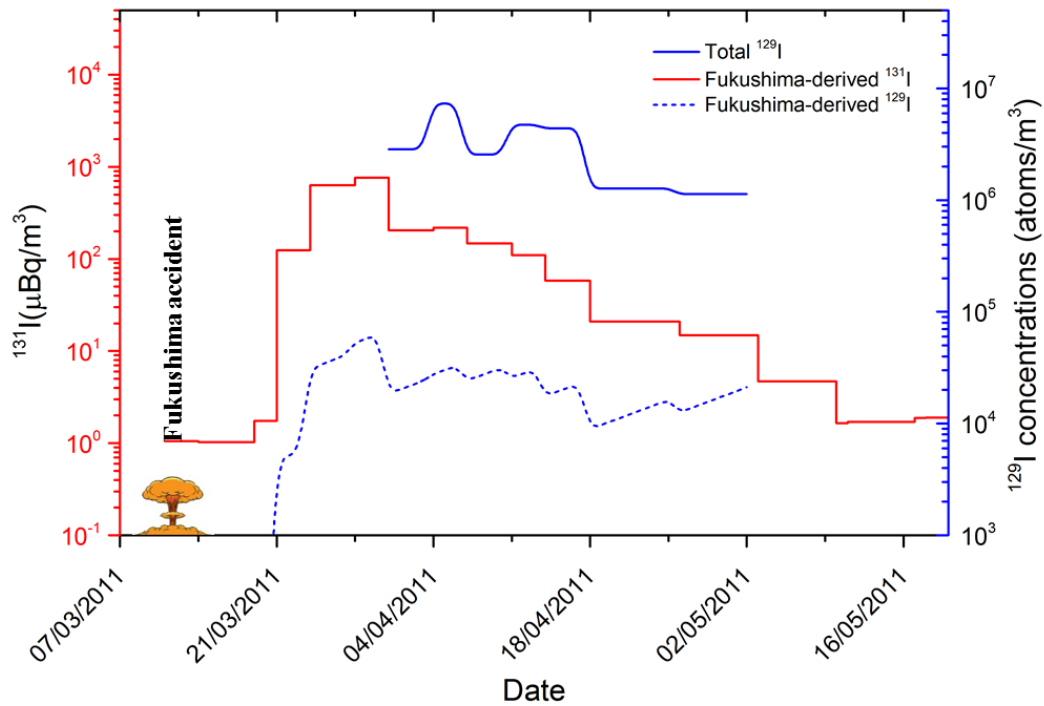


NOAA HYSPLIT MODEL  
Backward trajectories ending at 1200 UTC 25 Apr 11  
GDAS Meteorological Data



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Figure 6. The 72 h (3 days) air mass back trajectories for starting altitudes of 0 m above ground level (AGL) calculated from the FNL database of the National Ocean and Atmospheric Administration (NOAA) and simulated by using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HY-SPLIT) model. 4-7 April 2011 (left) and 21-25 April 2011 (right).



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3 Figure 7.  $^{131}\text{I}$  radioactivity (red),  $^{129}\text{I}$  concentrations (blue) in aerosols from Risø, Denmark  
 4 after the Fukushima accident (Nielsen et al., 2011). The Fukushima-derived  $^{129}\text{I}$   
 5 concentrations are calculated based on  $^{129}\text{I}/^{131}\text{I}$  atomic ratio of  $16.0 \pm 2.2$  deduced from  
 6 Fukushima-affected aerosol samples (Xu et al., 2015).