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

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## Abstract

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

discharged $^{129}$I in the contaminated seawater in the North Sea, North Atlantic Ocean, English Channel, Kattegat, etc, rather than direct gaseous release from the European nuclear reprocessing plants (NRPs). Water-soluble iodine was found to be a minor fraction to the total iodine for both $^{127}$I (7.8-13.7%) and $^{129}$I (6.5-14.1%) in ocean-derived aerosols, but accounted for 20.2-30.3% for $^{127}$I and 25.6-29.5% for $^{129}$I in land-derived aerosols. Iodide was the predominant form of water-soluble iodine, accounting for more than 97% of the water-soluble iodine. NaOH-soluble iodine seems to be independent of the sources of aerosols. The significant proportion of $^{129}$I and $^{127}$I found in NaOH-soluble fractions is likely bound with organic substances. In contrast to water-soluble iodine however, the sources of air masses exerted distinct influences on insoluble iodine for both $^{129}$I and $^{127}$I, with higher values for marine air masses and lower values for terrestrial air masses.

## 1 Introduction

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

Most of the work on aerosol iodine speciation has focused on water-soluble iodine (WSI) (Baker 2004; Baker 2005; Gilfedder et al., 2008). Early modeling studies suggested that aerosol iodate should be the only stable iodine specie as a by-product of iodine oxides production, with negligible iodide due to transformation into gaseous iodine (McFiggans et al., 2000; Vogt et al., 1999). However, this prediction went against several previous observations that showed significant iodide and soluble organic iodine, accounting for 10%-100% of WSI in aerosols (Baker 2004; Baker 2005; Gabler and Heumann 1993). An improved model was then developed, primarily by increasing the proportion of iodide in the aerosols (Pechtl et al., 2007). Few studies have addressed water-insoluble iodine in aerosols (Gilfedder et al., 2010; Tsukada et al., 1987), which might be not easily converted to gaseous iodine before being deposited on the Earth's surface. Previous observational data suggest that water-insoluble iodine is abundant in aerosol particles, representing 17-53% of the total iodine (Gilfedder et al., 2010). However, there is no comprehensive investigation of aerosol iodine species that encompasses aqueous-soluble and insoluble iodine species. This constitutes a significant gap in our understanding of the interaction among atmospheric iodine species.

Due to the difficulty of source identification of natural $^{127}$I, $^{129}$I ($T_{1/2}$=15.7 Ma) has proven being an especially useful geochemical tracer both in the marine environment and in the atmosphere (He et al., 2013; Hou et al., 2007; Jabbar et al., 2012; Michel et al., 2012). A large amount of $^{129}$I has been released to the environment by nuclear reprocessing plants (NRPs). These dominate all other anthropogenic sources, with 6000 kg released as of 2009, from Sellafield (United Kingdom) and La Hague (France) (Hou et al., 2007; Raisbeck et al., 1995). Anthropogenic $^{129}$I is currently distributed unevenly around the world in water, atmosphere and terrestrial systems (Hou et al., 2009b). Above-ground nuclear explosions also produced $^{129}$I, injecting it into the troposphere and stratosphere. The proportion that entered to the stratosphere became mixed globally before re-entering the troposphere. From the troposphere, about one half of the radioactive particles is deposited onto the earth's surface within 20 days (Tölgyessy 1993). Gaseous releases from reprocessing plants and accidents are primary sources of $^{129}$I to the local environment (Hou et al., 2009a; Xu et al., 2013). Re-emission of iodine as the forms of inorganic and organic iodine (e.g. $I_2$, $CH_3I$, $C_2H_5I$) from sea surface plays a significant role in the atmospheric budget of $^{129}$I (Englund et al., 2010b). Gaseous iodine compounds photodissociate rapidly in the atmosphere to generate iodine atoms. Iodine atoms are oxidized by atmospheric oxidants (e.g. $O_3$, $NO_x$) to iodine oxides, which then incorporate with particles either by nucleation or by reaction/trap mechanisms (Saiz-Lopez et al., 2012). As with stable iodine ($^{127}$I), $^{129}$I also disperses in the atmosphere in both gaseous and particulate forms. Particulate $^{129}$I has been used successfully in monitoring studies, and as an atmospheric tracer (Englund et al., 2010b; Jabbar et al., 2012; Santos et al., 2005; Tsukada et al., 1987). While, speciation analysis of $^{129}$I in aerosols is extremely scarce with the only one being our previous study (Xu et al., 2015).

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

## 2 Materials and methods

### 2.1 Aerosol sampling

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

### 2.2 Speciation analysis of $^{127}$I and $^{129}$I in aerosols

**Separation of iodine species from aerosol.** The aerosol samples were analyzed for species of $^{127}$I and $^{129}$I using a newly developed method (Zhang et al., 2015). In brief, iodine was extracted sequentially using deionized water and sodium hydroxide solutions for water-soluble and NaOH-soluble iodine (WSI and NSI). Total iodine (TI) and residual insoluble iodine (RII) were separated by alkaline ashing from the original air filters and the residual filters after NaOH solution leaching, respectively. Iodide and iodate in the water leachate were separated using anion exchange chromatography. Fig. 2 shows a diagram of the separation procedure for speciation analysis of iodine isotopes.

**Determination of $^{127}$I by ICP-MS and $^{129}$I by AMS.** $^{127}$I in all fractions were diluted by factors from 1 to 20 using ammonium depending on the iodine concentration in each fraction and the matrix of the leachates. Cesium was added as internal standard to a final concentration of 2 ng g$^{-1}$ to normalize measurement efficiency of iodine in the ICP-MS measurement. Standard addition method was employed for the measurement of $^{127}$I in ash leachates of total iodine and the insoluble fraction. An iodine standard solution (NaI, CPI International, California, USA) was spiked into the reserved aliquots and diluted with 1% $NH_3 \cdot H_2O$ to a final concentration of 2 ng g$^{-1}$. $^{127}$I in the diluted solution was measured by ICP-MS (Thermo Fisher, X Series II) using an Xt cone under normal mode, as described elsewhere (Hou et al., 2007).

$^{129}$I was measured using a 5 MV accelerator mass spectrometry (NEC, Wisconsin, USA) at Scottish University Environmental Research Center, UK (Xu et al., 2013). The prepared AgI precipitates were mixed with silver powder (Sigma-Aldrich Co., USA) with an AgI:Ag mass ratio of 1:2 and pressed into copper holders. A terminal voltage of 3.5 MV and $I^{5+}$ ions were chosen for $^{129}$I detection. The measured $^{129}I/^{127}I$ ratios were corrected against a standard with a $^{129}I/^{127}I$ ratio of $1.138\times10^{-10}$, prepared from a $^{129}$I standard solution (NIST 4949C) and an $^{127}$I carrier. The analytical precision of standards and samples are within 5%. $^{129}I/^{127}I$ ratios in the procedural blanks were measured to be about $5\times10^{-13}$, 1-3 orders of magnitude lower than those measured for the samples. All results were corrected for procedural blanks.

## 3 Results

The concentrations of total iodine in aerosols from Risø, Denmark ranged at 1.04-2.48 ng m$^{-3}$ (average of 1.8±0.5 ng m$^{-3}$) for $^{127}$I and $11.3\text{-}72.9\times10^5$ atoms m$^{-3}$ (average of $(44\pm19)\times10^5$ atoms m$^{-3}$) for $^{129}$I, during March-May 2011 (Table 2). Total $^{127}$I concentration of 2.36 ng m$^{-3}$

during 8-15 December 2014 fell within the range in 2011, while $^{129}$I concentration of 97.0×10$^{5}$ atoms m$^{-3}$ was about two times higher than the average value in 2011. Much lower values of $^{129}$I and $^{127}$I concentrations were observed during 18 April- 2 May 2011 compared to those before 18 April (Fig. 3), but $^{129}$I levels didn't show a synchronous variation with $^{127}$I concentrations. The results of $^{127}$I concentrations in the studied aerosols are compatible with those from an inland city, Regensburg, Germany and from some Pacific islands (Gabler and Heumann, 1993 and references therein). $^{129}$I/$^{127}$I atomic ratios in the investigated aerosols were (17.8-86.8)×10$^{-8}$, which are consistent with those found at Foehr island, north of Germany in April 2002 (Michel et al., 2012) and in southern Sweden during 1983-2008 (Englund et al., 2010b; Michel et al., 2012). However, the measured $^{129}$I concentrations and $^{129}$I/$^{127}$I ratios are 1-2 orders of magnitude higher than those observed in Vienna, Austria during 2001-2002, and in the high altitude eastern Alps (2700 m) during 2001 (Jabbar et al., 2011; Jabbar et al., 2012).

For $^{127}$I, the WSI fraction of aerosols collected in 2011 occurred predominantly as iodide, ranging from 0.12-0.33 ng m$^{-3}$. Minor iodate of 0.02-0.03 ng m$^{-3}$ was detected only in two samples (AE11-12 during 4-7 April and AE11-17 during 26 April-2 May) (Table 1 and Fig. 4). The highest measured $^{127}$I$^{-}$ concentration (0.74 ng m$^{-3}$) was observed in aerosol collected in 2014, and there was no measurable water-soluble organic iodine. Water-soluble $^{129}$I shows a similar species pattern as water-soluble $^{127}$I except that iodate-129 was below the detection limit in all the analyzed samples. The concentrations of $^{129}$I$^{-}$ varied in (3.3-5.9)×10$^{5}$ atoms m$^{-3}$ with an average value of 4.41×10$^{5}$ atoms m$^{-3}$ in the aerosols from 2011. This value is about 8 times lower than that in the sample collected in 2014(30.1×10$^{5}$ atoms m$^{-3}$). High NSI concentrations were observed in all of the aerosol samples, with an average of 0.64±0.21 ng m$^{-3}$ for $^{127}$I and (13.6±10.1)×10$^{5}$ atoms m$^{-3}$ for $^{129}$I. RII is the dominant species in aerosol samples for both iodine isotopes, with concentration range of 0.34-1.66 ng m$^{-3}$ for $^{127}$I and (4.3-39.9)×10$^{5}$ atoms m$^{-3}$ for $^{129}$I.

There is no available standard reference material for iodine isotopes in aerosols which can be used for validation of the analytical method. While, the sums of all of iodine species in the analyzed samples are comparable with the measured total iodine in the corresponding samples for both $^{127}$I and $^{129}$I in a range of 85-110%, indicating the reliability of our analytical results (Fig. 5).

For the samples collected before 18 April 2011, the proportion of $^{129}$I and $^{127}$I species follows an order of RII > NSI > iodide. For the samples collected later in April 2011 and in the winter 2014, the three iodine fractions for both $^{129}$I and $^{127}$I account for almost equivalent proportion of total iodine (Fig. 5). Compared to the former sampling period (31 March-18 April 2011), the most apparent feature of the latter sampling period is a dramatic diminution of iodine in the RII fraction, by 38.7% for $^{127}$I and 26.8% for $^{129}$I. This was compensated by a corresponding increase in the iodide fraction of the aerosol particles. Iodate, as the least abundant iodine specie (< 3%), was only observed in two aerosol samples for $^{127}$I, and no $^{129}IO_3^-$ was detectable in all aerosol samples investigated in this work.

$^{129}$I/$^{127}$I atomic ratios of $(15.6\text{-}102.0)\times10^{-8}$ were determined for the different iodine species in the aerosols. The variations of $^{129}$I/$^{127}$I ratio in iodide, NSI and RII are similar to those in total $^{129}$I/$^{127}$I, with high values observed prior to 18 April 2011 and December 2014 (Table 2 and Fig. 3).

# 4 Discussion

## 4.1 Sources of $^{127}$I and $^{129}$I in aerosols

Variation of $^{127}$I and $^{129}$I concentrations in aerosols against meteorological parameters (i.e. wind direction, wind speed and temperature) during the sampling period shows that wind direction has a principle influence (Fig. 3). Back trajectory model analysis shows that $^{127}$I and $^{129}$I concentrations in the aerosols were directly controlled by the sources and pathways of air masses (Fig. 6, Figs. S-1 and S-2 in supplementary material). The relatively high $^{127}$I and $^{129}$I concentrations were observed in the aerosols collected in early April 2011, when air masses were mainly transported from the Atlantic Ocean across the North Sea by prevailing westerly winds. While, relatively low concentrations of iodine isotopes were observed in the aerosols collected in later April, when air masses were dominated by prevailing easterly winds and passed over the European continent and the Baltic Sea (Fig. 6 and Figs S-1). Marine emission of volatile iodine species (e.g. inorganic $I_2$ and HOI, organic $CH_3I$, $CH_2I_2$) is a major source of iodine in the atmosphere (Prados-Román et al., 2015). It results in relatively elevated $^{127}I$ concentrations in the marine atmosphere, as compared to the terrestrial atmosphere (Saiz-Lopez et al., 2012). During the sampling period of 11-14 April, air masses were transported by westerly winds from a vast area over the northern Atlantic Ocean. This caused the highest $^{127}I$ concentration in the sampling period.

Distinct from source of $^{127}I$, $^{129}I$ concentrations in the aerosols were significantly influenced by aqueous and gaseous discharge of the two European NRPs at Sellafield (UK) and La Hague (France) that contribute more than 95% of $^{129}I$ inventory in the environment. The two European NRPs locate at west and southwest direction of Denmark, respectively (Fig. 1). Of the total release of $^{129}I$ from the two European NRPs, about 99% of $^{129}I$ (200-300 kg year$^{-1}$ since 1995) has been discharged as aqueous form to the English Channel and Irish Sea, respectively (Hou et al., 2007; Raisbeck et al., 1995). Only a small fraction of $^{129}I$ (about 0.5-2 kg year$^{-1}$after 2004 and 3-10 kg/y in 1981-2004) has been released as gaseous form to the atmosphere and dispersed over a large area, in particular in Europe (Schnabel et al. 2001; Ernst et al., 2003; Persson et al., 2007; Jabbar et al., 2012). Aqueous $^{129}I$ was carried by ocean currents and transported to the North Sea, Kattegat, and Baltic Sea, and continues to the Arctic along the Norwegian coast (Alfimov et al., 2004a; Buraglio et al., 1999; Hou et al., 2007; Raisbeck et al., 1995; Yi et al., 2012). Remarkably elevated $^{129}I$ concentrations of up to $10^{10}$ -$10^{11}$ atoms L$^{-1}$ have been found in the North Sea (with $^{129}I/^{127}I$ atomic ratios of $10^{-7}$-$10^{-6}$), $10^{9}$ -$10^{10}$ atoms L$^{-1}$ in Norwegian coastal waters and the Kattegat (with $^{129}I/^{127}I$ atomic ratios of $10^{-8}$-$10^{-7}$), and $10^{8}$ -$10^{9}$ atoms L$^{-1}$ in the Baltic Sea (Aldahan et al., 2007; Alfimov et al., 2004b; He et al., 2014; Hou et al., 2007; Michel et al., 2012; Yi et al., 2011). Besides the directly atmospheric releases of $^{129}I$ from European NRPs at La Hague and Sellafield, the relatively high $^{129}I$ concentrations in the aerosols influenced by westerly wind might also attributed to the secondary emission of marine discharged $^{129}I$ in the European seas (the North Sea, Irish Sea, Norwegian coastal water). The back trajectories analysis (Fig. 6 and Fig. S-1) shows that the aerosol samples collected in 31 March-4 April, 4-7 April and 11-14 April were directly influenced by westerly and southwesterly air masses that passed over not only the high $^{129}$I contaminated North Sea, Irish Sea and English Channel, but also above Sellafield and La Hague NRPs. However, $^{129}$I concentration and $^{129}$I/$^{127}$I ratio in aerosol collected in 4-7 April were 2.6-fold and 1.7-fold higher than that aerosols collected in 31 March-4 April and 1.6-fold and 2.1 fold that in 7-11 April, respectively. This might be attributed to that most of air masses during 4-7 April mainly passed over both Sellafield and La Hague as well as the high $^{129}$I contaminated North Sea, Irish sea and English Channel, while air masses during 31 March-4 April passed over only Sellafield, south part of the highly $^{129}$I contaminated of the North Sea and low $^{129}$I level northern Atlantic Ocean, and air masses during 7-11 April passed over Sellafield, north part of the highly contaminated North Sea and low $^{129}$I level Atlantic Ocean. However, the $^{129}$I directly atmospheric released and secondary emitted from the $^{129}$I contaminated sea cannot be isolated and identified based on the trajectories analysis of these 3 samples, because the air masses of these 3 aerosols passed over both reprocessing plant(s) and high contaminated seas. For the aerosol collected in 14-18 April, the air masses passed over only the north part of the highly contaminated North Sea and low $^{129}$I level North Atlantic Ocean (Fig. 6c), the $^{129}$I/$^{127}$I ratio in this aerosol is comparable with the samples collected in 11-14 April and 31 March-4 April ($(4\text{-}5)\times10^{-7}$), and the $^{129}$I concentration is higher than that in 31 March-4 April sample by a factor of 1.5. This result suggests that secondary emission of marine discharged $^{129}$I in the contaminated seawater (the English Channel, North Sea, Kattegat and the Norwegian costal water) is the major source of $^{129}$I in the westerly wind-influenced aerosols in Denmark in 2011 rather than the directly gaseous release of the two European NRPs. A relative lower $^{129}$I concentration ($2.6\times10^{6}$ atoms m$^{-3}$) and $^{129}$I/$^{127}$I ratio ($2.8\times10^{-7}$) were observed in the aerosol collected in 7-11 April compared to other 4 aerosol samples influenced by westerly wind. This might be attributed that the air masses during this period is mainly from northwest and mainly passed over to the lower $^{129}$I North Atlantic Ocean and small area of the northern North Sea (Alfimov et al. 2004a).

The $^{129}$I/$^{127}$I atomic ratios in the studied aerosols ($(1.8\text{-}8.6)\times10^{-7}$) fell well in the range of $^{129}$I/$^{127}$I ratios in the North Sea surface water in 2005 and 2009 ((1-10) )×$10^{-7}$) (Hou et al. 2007; Christl et al. 2015). This also supports the above conclusion that the main source of $^{129}$I in the aerosols in Denmark in 2011 is re-emission of marine discharged $^{129}$I in the surface water of the North Sea, Irish Sea and Kattegat.

There was a debate for a long time on either atmospheric releases or re-emission of marine discharged $^{129}$I from the two European NRPs as the dominant source of $^{129}$I in the European atmosphere (Schnabel et al. 2001, Jabbar et al., 2011, 2012; Lopez-Gutierrez et al. 2004; Ernst et al., 2003; Persson et al., 2007; Hou et al. 2009; Reithmeier et al. 2010; Michel et al. 2012). High $^{129}$I concentrations of (3-445)×$10^{8}$ at/L in rain water collected at Zürich, Switzerland in 1994-1997, corresponding to estimated average $^{129}$I/$^{127}$I ratios of (3.2-4.0)×$10^{-7}$, have been reported. Based on the estimated annual re-emission of $^{129}$I from the contaminated European water (1.37 kg) in the 1990's and combined atmospheric releases of $^{129}$I of about 6.5 kg in 1991-1996 from the two European NRPs (Schnabel et al. 2001), as well as the relative positive correlation of $^{129}$I concentration in the aerosols from Vienna, Austria with the integrated monthly atmospheric releases of $^{129}$I from Sellafield NRP (Jabbar et al. 2011), the direct atmospheric release of $^{129}$I was proposed as the dominant source of $^{129}$I in the atmosphere in the central Europe (Schnabel 2011; Jabbar et al. 2011).

An investigation on $^{129}$I in rain water (1994-2005) over Germany has shown a high but slightly decreasing gradient of $^{129}$I concentrations and $^{129}$I/$^{127}$I ratios from coastal to inland areas (Krupp and Aumann, 1999, Szidat et al., 2000; Michel et al. 2012). A high $^{129}$I level ($^{129}$I/$^{127}$I ratio of (2-8)×$10^{-7}$) was also measured in air samples (gas and particle associated iodine) collected at an island in the North Sea (Foehr) in April 2002, which is similar to the $^{129}$I/$^{127}$I ratio measured in the seawater surrounding the Island (Ernst, 2003; Michel et al. 2012). This $^{129}$I level in the aerosol is also comparable with those in precipitation in the inland Germany. A significant correlations of $^{129}$I with marine-derived chlorine ($R^2$=0.62) and bromine ($R^2$=0.62) were measured in precipitation in Denmark in 2001-2006 (Hou et al. 2009). All these investigations suggested that $^{129}$I in the European atmosphere, at least in the central and north Europe, mainly originates from the re-emission of marine discharged $^{129}$I in the European seawater (Krupp and Aumann, 1999, Szidat et al., 2000; Michel et al. 2012, Ernst, 2003; Hou et al. 2009; Persson et al., 2007).

The reported $^{129}I/^{127}I$ ratios in the atmosphere (aerosol and precipitation) in the central and north Europe keeps constant high from about (3-4)×$10^{-7}$ at Zurich in 1994-1997 (Schnabel et al. 2001), (3-14) ×$10^{-7}$ in 1988-1995 (Krupp & Aumann 1999; Bachhuber et al. 1992) and (2-11)×$10^{-7}$ in 1997-2005 (Michel et al. 2012; Szidat et al. 2000) in Germany, (0.8-5.2)×$10^{-7}$ in 2001-2002 in south Sweden, to (0.5-8 )×$10^{-7}$ in 2001-2006 in Denmark. The $^{129}I/^{127}I$ ratios measured in the investigated aerosol samples in 2001 ((1.8-8.7) ×$10^{-7}$) are also comparable to the value in the precipitation in 2001-2006 in Denmark and other locations in central and north Europe in 1988-2005. However, the atmospheric releases of $^{129}I$ from the two NRPs at La Hague and Sellafield have significantly reduced since 2002, from peak value of 5-10 kg/y in 1981-2000 to less than 2 kg after 2004 (Michel et al. 2012), if the contribution from another European NRP at Marcoule (France), which was operated in 1960-1997, is included, the atmospheric releases of $^{129}I$ were 9-17 kg/y in 1980-1997 (Reithmeier et al. 2006). The insignificant influence of the remarkably reduced atmospheric releases of $^{129}I$ from the European NRPs since 2002 on the $^{129}I/^{127}I$ ratios in the atmosphere in central and north Europe confirms that the atmospheric releases $^{129}I$ from the two European NRPs at La Hague and Sellafield is not the dominant source of $^{129}I$ in the European atmosphere, at least after 2002. However, this does not conflict with the suggestion that $^{129}I$ in the atmosphere in Zürich in 1994-1997 and Vienna in 2001 mainly originated from the atmospheric releases of the European NRPs due to the relative high atmospheric releases of $^{129}I$ from the European NRPs in 1980-2002, and relative lower marine discharges of $^{129}I$ from the two European NRPs before 1990. The marine discharges of $^{129}I$ from the two European NRPs has significantly increased from less than 60 kg/y before 1990 to more than 100 kg/y in 1995 and keeping relative constant at about 250 kg/y from 1998 until now (Reithmeier et al. 2006). The $^{129}I$ discharged to the English Channel from the La Hague NRP and to the Irish Sea from the Sellafield NRP has dispersed to a large area in the North Sea, Kattegat, Norwegian Sea and further to the Arctic by sea currents, and mainly remains in the surface water (less than 100 m) in this area. It is not like the atmospheric released $^{129}I$ which is quickly dispersed in the atmosphere and deposited on the land in a short time (a few weeks/months), the marine discharged $^{129}$I is integrated in the marine system with much less and slow removal from the water body to the sediment as particle associated form and to the atmosphere in gaseous forms. Therefore, the huge amount and constantly increased inventory of $^{129}$I in the marine system has made the marine discharged $^{129}$I the major source of $^{129}$I in the present environment, the continuous re-emission of $^{129}$I from the contaminated seawater to the atmosphere makes the marine discharged $^{129}$I the dominated source in the atmosphere in the Europe, and probably all over the world after 2002. The very well matched trend of $^{129}$I/$^{127}$I ratio in the atmosphere in central and north Europe with the marine discharges of $^{129}$I from the two European NRPs (Michel et al. 2012) and constantly high $^{129}$I level in the precipitation in the north hemisphere outside Europe (e.g. in Japan before 2011, China) also confirmed this assumption (Toyama et al. 2013, Zhang et al. 2011). In addition, the measurement of $^{129}$I in the aerosol collected in the high altitude Alps sites in 2001 and back trajectories analysis of air masses reached to these locations have also confirmed that re-emission of marine discharged $^{129}$I from the contaminated European seawater was the major source of $^{129}$I in these aerosols (Jabbar et al. 2012).

The low $^{129}$I concentrations, $(11 - 13)\times10^5$ atoms m$^{-3}$, were observed in the aerosol samples collected in 18 -26 April and 26 April -2 May 2011. Back trajectory analysis shows that in this period the air masses at the sampling site were mainly transported by easterly or northwesterly winds, i.e. from the European continent (Fig. S-1). Terrestrial emissions of iodine occur through vegetation and terrestrial microorganisms (Bewers and Haysom, 1974). The related lower $^{129}$I/$^{127}$I ratios in the terrestrial samples in the Europe ($10^{-8}$-$10^{-7}$) (Osterc et al. 2013; Ezerinsk et al. 2016) compared to that in the contaminated European seawater ($10^{-7}$-$10^{-6}$) have been reported. This is reflected in these two aerosol samples by their relatively low $^{129}$I concentrations. An elevated $^{210}$Pb level (249 -253 μBq m$^{-3}$) (Table 1) for this period is also consistent with a continental origin ($^{210}$Pb in the air is a decay product of $^{222}$Rn which is mainly released from the soil in the continental area). However, it should be mentioned that the $^{129}$I level in the European soil is still much higher than that in the uncontaminated area such as in the China and Chile ($^{129}$I/$^{127}$I ratio of $10^{-10}$-$10^{-9}$) (Zhang et al.

2011; Daraoui et al. 2012), this is attributed to the high $^{129}$I level in the atmosphere in the Europe. Consequently, the $^{129}$I level in the aerosols with air masses from terrestrial area is lower than that from the contaminated European seas, but it is still much higher than that in other places with less contamination. It should be mentioned that the conclusion of re-emission of the NRPs marine discharged $^{129}$I in the contaminated seas as the dominant $^{129}$I source in the atmosphere in the Europe and other locations in the north hemisphere suggested in this work does not exclude the contribution of the directly atmospheric releases of $^{129}$I from the NRPs. In the local area surround the NRPs, the atmospheric releases might become the dominant source.

The highest $^{129}$I concentration ($97.0\times10^{5}$ atoms m$^{-3}$) found in 8-15 December 2014 might be related to the increased $^{129}$I re-emission from the North Sea since 2011, where the air masses passed over (Fig. S-2), as well as probably increased liquid releases of NRPS which needs further investigation.

## 4.2 Species of $^{129}$I and $^{127}$I in aerosols

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

It is not clear how iodide is formed in the atmosphere, in an oxidizing environment containing oxygen and ozone. Early models predicted a negligible iodide concentration in particle phases based on the assumption that the iodide in aerosols only originates from the low levels of gaseous HI (McFiggans et al., 2000; Vogt et al., 1999). This work in combination with the previous reports (Baker 2004; Xu et al., 2015) suggests that there must be other primary pathways that contribute to iodide formation at the observed levels. It's generally accepted that iodine atoms are photochemically produced by photolysis of gaseous iodinated compounds, and oxidized by ozone to form reactive iodine oxides (Carpenter, 2003; Saiz-Lopez et al., 2012; Vogt et al., 1999). The formation of iodide from iodine atoms and other reactive iodine compounds must rely on electron-donors that are capable of reducing high valence iodine species to iodide. One possibility is the involvement of sulfur compounds (Chatfield and Crutzen, 1990). Possible reaction pathways are given in Table 3. Gaseous $SO_2$ can be formed in nature by reactions of dimethyl sulfate (DMS) with hydroxide and nitrate. Human activity is a major source of atmospheric $SO_2$, globally about three times as much $SO_2$ as natural processes (Galloway, 1995). By associating with $H_2O$, these reactions produce $HSO_3^-$ and $SO_3^{2-}$ (Eqs. 1 and 2 in Table 3). Native iodine and other reactive species (not shown) can be reduced to $I^-$ on gas-aerosol interfaces (Eq. 3 in Table 3). Other iodine species in aerosols can be also reduced by reductive sulfur compounds to form iodide (Eq. 4 in Table 3). The electron-donors are not limited to sulfur compounds either, for example, nitrogen in the form of gaseous ammonia ($NH_3 \rightarrow NO_2/NO_3$) (McFiggans et al., 2000; Saiz-Lopez and Plane 2004) and elemental mercury ($Hg^0 \rightarrow HgO/HgX$, where X is a halogen, $I^-$, $Br^-$ or $Cl^-$) (Lindberg et al., 2002; Simpson et al., 2007) are also candidates responsible for iodide formation.

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

A large proportion of $^{129}$I and $^{127}$I in our aerosol samples were NaOH-soluble, which is consistent with the results of aerosol from Tsukuba, Japan, collected shortly after the Fukushima nuclear accident in March 2011 (Xu et al., 2015). Abundant NaOH-soluble $^{129}$I (32%-44% of total $^{129}$I) in Fukushima-derived aerosols was attributed to coarse vegetation-related organic particles concentrated during spring. The measured NaOH-soluble iodine (NSI) fractions of $^{129}$I and $^{127}$I during the entire sampling period in the spring of 2011 are similar. This indicates that NSI is relatively stable and less affected by the source and pathways of air masses than WSI. NaOH leaching is often used to extract organic substance in fractionation analysis of soil and sediment (Englund et al., 2010a; Hou et al., 2003) based on the high solubility of organic matter, such as humic substances, as well as on nucleophilic substitution and decomposition of organic matter. Organic compounds are important contributors to aerosols, such as lipidic, saccharides and proteinaceous materials (O'Dowd et al., 2004; Quinn et al., 2014). A significant portion of atmospheric aerosols was found to be humic-like substances (HULIS), named for their strong structural similarity to humic and fulvic acids (Havers et al., 1998). Most of these organic compounds are water-soluble, but a significant water-insoluble fraction of the HULIS material is hydrophobic and acidic in character, and can be dissolved in an alkaline solvent, like NaOH (Feczko et al., 2007; Havers et al., 1998). On the other hand, the hydroxide anion can also initiate a nuclephilic substitution or elimination of iodine-containing organic compounds, which releases iodine from the organic substances. NaOH-soluble iodine is therefore suggested to be likely associated with organic substances in aerosols.

RII in aerosols has received less attention than WSI (Gilfedder et al., 2010; Tsukada et al., 1987). The early report on water-insoluble iodine fraction in aerosol particles showed that water-insoluble iodine accounted for 27-58% of total iodine bound in aerosols from Tokyo, Japan, collected in 1983-84 (Tsukada et al., 1987). Another similar result of 17-53% of total iodine as insoluble species was reported for aerosols from the west coast of Ireland in 2007, and from a ship transect from China to Antarctica in 2005-2006 (Gilfedder et al., 2010).

Taking the alkaline-leachable iodine in aerosols into account, these results are very consistent with our observations from Risø (Fig. 5). The residual insoluble $^{129}$I fractions were reported to be 4-23% of total $^{129}$I in Fukushima-derived aerosol particles (Xu et al., 2015), less than the proportion in the aerosols collected in Denmark. This discrepancy might reveal the different formation processes of RII species for the NRPs-derived $^{129}$I in this study as compared to those from Fukushima. A significant difference is the timing of the $^{129}$I releases. NRPs have releasing $^{129}$I into the European environment for about 50 years, allowing $^{129}$I to follow geochemical pathways on timescales ranging from days to decades. In contrast, RII in Fukushima-derived aerosols had only days to react with their environment prior to sampling, 15-22 March, 2011.

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

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

The Fukushima Dai-ichi nuclear power plant accident on March 11, 2011 released radioiodine to the atmosphere, primarily as $^{131}$I and $^{129}$I, which was mainly transported eastwards by prevailing westerly winds. Based on $^{129}$I levels in the Fukushima offshore seawater, the released $^{129}$I from this accident was estimated to be 1.2 kg (Hou et al., 2013). Radioactive iodine in the air dispersed across the Pacific Ocean, American continent and Atlantic Ocean, and some fraction arrived in the European continent after 1-2 weeks (Clemenza et al., 2012; Leon et al., 2011; Manolopoulou et al., 2011; Pittauerová et al., 2011). Anthropogenic $^{129}$I has been reported from a variety of environmental samples in Japan, including soil, seawater, precipitation and aerosols (Buesseler et al., 2012; Hou et al., 2013; Muramatsu et al., 2015; Xu et al., 2013; Xu et al., 2015). The level of $^{129}$I in aerosols collected in Tsukuba, about 170 km from the Fukushima Dai-ichi NPP, reached $5\times10^8$ atoms m$^{-3}$ (Xu, et al. 2015). While the Fukushima-derived $^{129}$I in environmental samples was less presented outside of Japan. $^{131}$I in the aerosol samples collected at Risø, Denmark, 10 days after the Fukushima accident have been observed (Fig. 7) (Nielsen et al., 2011). The radioactivity of $^{131}$I reached the peak on 24-30 March 2011 (763 μBq m$^{-3}$ in aerosol), then fell to below detection limits for $^{131}$I in the middle of May. Based on the measured $^{131}$I radioactivity in the aerosol samples and an $^{129}$I/$^{131}$I atomic ratio of $16.0\pm2.2$ deduced from the aerosol samples collected at Tsukuba, Japan shortly after the Fukushima accident (Xu et al., 2015), the Fukushima-derived $^{129}$I signal in Denmark can be reconstructed (Fig. 7). The highest $^{129}$I concentration in the aerosols in Denmark from the Fukushima accident is estimated to be $6.3\times10^4$ atoms m$^{-3}$ on 30-31 March 2011, which accounts for less than ~6% of total $^{129}$I ($1.1\text{-}9.7\times10^6$ atoms m$^{-3}$) in Denmark when the Fukushima $^{131}$I peak was measured. Considering the rapid decline of $^{129}$I levels in aerosols and precipitation in Japan to nearly pre-accident levels within two years (Xu et al., 2013), the contribution of Fukushima-derived $^{129}$I to the $^{129}$I level and inventory in the Europe is now negligible in comparison to NRPs-derived $^{129}$I in the European atmosphere.

## 5 Conclusions

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

1) Iodide is the dominant species (>97%) of the water-soluble iodine in the aerosols of this study, its formation might be related to atmospheric reductants, such as reductive $SO_2$ and

disulfites. The most dominant species of iodine in aerosols are NSI and RII, accounting for up to 80% of total iodine, NSI is predominantly bound to organic matter, such as HULIS, while RII might be associated with inorganic components, such as metal oxides.

2) Westerly-dominated air masses from the North Sea contribute to high $^{129}$I concentrations compared to easterly air masses from the northeastern European continent. $^{129}$I in aerosols in Denmark is strongly influenced by the European nuclear reprocessing plants, in which secondary emission of $^{129}$I from surface seawater in the North Sea, Norwegian coastal water and Kattegat is a main contributor.
3) Fukushima-derived $^{129}$I contributed less than ~6 % to the total $^{129}$I in the European atmosphere immediately after the Fukushima accident, a negligible quantity when compared to $^{129}$I levels released from Sellafield and La Hague nuclear reprocessing plants.
4) Water-insoluble iodine (NSI and RII) in aerosols that is primarily associated with organic compounds is crucial for investigation of geochemical cycling of iodine in the atmosphere due to its large fraction. This requires more intensive studies to extend our observations on both temporal and spatial scales.

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## References

Aldahan, A., Possnert, G., Alfimov, V. and Cato, K.: Anthropogenic $^{129}$I in the Baltic Sea, Nucl. Instrum. Meth. B, 259, 491-495, 2007.

Alfimov, V., Aldahan, A., Possnert, G., Kekli, A. and Meili, M.: Concentrations of $^{129}$I along a transect from the North Atlantic to the Baltic Sea, Nucl. Instrum. Meth. B, 223-224, 446-450, 2004a.

Alfimov, V., Aldahan, A., Possnert, G. and Winsor, P.: Anthropogenic iodine-129 in seawater along a transect from the Norwegian coastal current to the North Pole, Mar. Pollut. Bull., 49, 1097-1104, 2004b.

Bachhuber, H., Bunzl, K.: Background levels of atmospheric deposition to ground and temporal variations of $^{129}$I, $^{127}$I, $^{137}$Cs and $^{7}$Be in a rural area of Germany. J. Environ. Radioact. **16**, 77-89, 1992

Baker, A. R., Tunnicliffe, C. and Jickells, T. D.: Iodine speciation and deposition fluxes from the marine atmosphere, J. Geophys. Res., 106, 28743-28749, 2001.

Baker, A. R.: Marine Aerosol Iodine Chemistry: The Importance of Soluble Organic Iodine, Environ. Chem., 2, 295-298, 2005.

Baker, A. R.: Inorganic iodine speciation in tropical Atlantic aerosol, Geophys. Res. Lett., 31, L23S02, 2004.

Bewers, J. M. and Haysom, H. H.: The terrigenous dust contribution to fluoride and iodide in atmospheric precipitation, J Rech Atmos, 8, 689-697, 1974.

Buesseler, K. O., Jayne, S. R., Fisher, N. S., Rypina, I. I., Baumann, H., Baumann, Z., Breier, C. F., Douglass, E. M., George, J., Macdonald, A. M., Miyamoto, H., Nishikawa, J., Pike, S. M. and Yoshida, S.: Fukushima-derived radionuclides in the ocean and biota off Japan, Proc. Natl. Acad. Sci. U. S. A., 109, 5984-5988, 2012.

Buraglio, N., Aldahan, A. and Possnert, G.: Distribution and inventory of $^{129}$I in the central Arctic Ocean, Geophys. Res. Lett., 26, 1011-1014, 1999.

Carpenter, L. J.: Iodine in the Marine Boundary Layer, Chem. Rev., 103, 4953-4962, 2003.

Chatfield, R. B. and Crutzen, P. J.: Are there interactions of iodine and sulfur species in marine air photochemistry?, J. Geophys. Res. - Atmos., 95, 22319-22341, 1990.

Christl, M., Casacuberta, N., Lachner, J., Maxeiner, S., Vockenhuber, C., Synal, H.-A., Gorncy, I., Herrmann, J., Daraoui, A., Walther, C., Michel, R.: Status of $^{236}$U analyses at ETH Zurich and the distribution of $^{236}$U and $^{129}$I in the North Sea in 2009. Nucl. Instr. Method Phys. Res., B 36, 510-516, 2015

Clemenza, M., Fiorini, E., Previtali, E. and Sala, E.: Measurement of airborne $^{131}$I, $^{134}$Cs and $^{137}$Cs due to the Fukushima reactor incident in Milan (Italy), J. Environ. Radioact., 114, 113-118, 2012.

Daraoui, A., Michel, R., Gorny, M., Jakob, D., Sachse, R., Synal, H. –A., Alfimov, V. : Iodine-129, iodine-127 and caesium-137 in the environment: soil from Germany and Chile. J. Environ. Radioact., 112, 8-22, 2012.

Englund, E., Aldahan, A., Hou, X., Petersen, R. and Possnert, G.: Speciation of iodine (I-127 and I-129) in lake sediments, Nucl. Instrum. Meth. B, 268, 1102-1105, 2010a.

Englund, E., Aldahan, A., Hou, X., Possnert, G. and Soderstrom, C.: Iodine (I-129 and I-127) in aerosols from northern Europe, Nucl. Instrum. Meth. B, 268, 1139-1141, 2010b.

Ernst, T.; Szidat,S.; Handl,J.; Jakob,D.; Michel,R.; Schnabel,C.; Synal,H. A.; Arevalo, F.J.; Benne, I.; Boess, J.; Gehrt, E.; Capelle, A.; Schneider,J.; Schafer, W.; Bottcher, J.: Migration of iodine-129 and iodine-127 in soils, Kerntechnik (Germany), 68, 155-167, 2003.

Ezerinskis, Z., Hou, X.L., Druteikiene, R., Puzas, A., Sapolaite, J., Gvozdaite, R., Gudelis, A., Buivydas, S., Remeikis, V.: Distribution and source of $^{129}$I, $^{239,240}$Pu, $^{137}$Cs in the environment of Lithuania, J. Environ. Radioact., 151, 166-173, 2016.

Feczko, T., Puxbaum, H., Kasper-Giebl, A., Handler, M., Limbeck, A., Gelencsér, A., Pio, C., Preunkert, S. and Legrand, M.: Determination of water and alkaline extractable atmospheric humic-like substances with the TU Vienna HULIS analyzer in samples from six background sites in Europe, J. Geophys. Res. - Atmos., 112, 1-9, 2007.

Gabler, H. E. and Heumann, K. G.: Determination of particulate iodine in aerosols from different regions by size fractionating impactor sampling and IDMS, Intern. J. Anal. Chem., 50(2), 129-146, 1993.

Galloway, J. N.: Acid deposition：perspectives in time and space, Water, Air and Soil Pollut., 85, 15-24, 1995.

Gilfedder, B. S., Chance, R., Dettmann, U., Lai, S. C. and Baker, A. R.: Determination of total and non-water soluble iodine in atmospheric aerosols by thermal extraction and spectrometric detection (TESI), Anal. Bioanal. Chem., 398, 519-526, 2010.

Gilfedder, B. S., Lai, S. C., Petri, M., Biester, H. and Hoffmann, T.: Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases, Atmos. Chem. Phys., 8, 6069-6084, 2008.

Havers, N., Burba, P., Lambert, J. and Klockow, D.: Spectroscopic Characterization of Humic-Like Substances in Airborne Particulate Matter, J. Atmos. Chem., 29, 45-54, 1998.

He, P., Hou, X., Aldahan, A., Possnert, G. and Yi, P.: Iodine isotopes species fingerprinting environmental conditions in surface water along the northeastern Atlantic Ocean, Scientific Reports, 3: 2685, 1-8, 2013.

He, P., Aldahan, A., Possnert, G. and Hou, X.: Temporal Variation of Iodine Isotopes in the North Sea, Environ. Sci. Technol., 48, 1419-1425, 2014.

Hou, X., Aldahan, A., Nielsen, S. P. and Possnert, G.: Time Series of I-129 and I-127 Speciation in Precipitation from Denmark, Environ. Sci. Technol., 43, 6522-6528, 2009a.

Hou, X., Aldahan, A., Nielsen, S. P., Possnert, G., Nies, H. and Hedfors, J.: Speciation of I-129 and I-127 in seawater and implications for sources and transport pathways in the North Sea, Environ. Sci. Technol., 41, 5993-5999, 2007.

Hou, X., Fogh, C. L., Kucera, J., Andersson, K. G., Dahlgaard, H. and Nielsen, S. P.: Iodine-129 and Caesium-137 in Chernobyl contaminated soil and their chemical fractionation, Sci. Total Environ., 308, 97-109, 2003.

Hou, X., Hansen, V., Aldahan, A., Possnert, G., Lind, O. C. and Lujanienė, G.: A review on speciation of iodine-129 in the environmental and biological samples, Anal. Chim. Acta, 632, 181-196, 2009b.

Hou, X., Povinec, P. P., Zhang, L., Shi, K., Biddulph, D., Chang, C., Fan, Y., Ješkovský, M., Liu, Q., Luo, M., Steier, P., Zhou, W. J., Hou, Y. and Golser, R.: Iodine-129 in Seawater Offshore Fukushima: Distribution, Inorganic Speciation, Sources, and Budget, Environ. Sci. Technol., 47, 3091-3098, 2013.

Jabbar, T., Steier, P., Wallner, G., Kandler, N. and Katzlberger, C.: AMS analysis of iodine-129 in aerosols from Austria, Nucl. Instrum. Meth. B, 269, 3183-3187, 2011.

Jabbar, T., Steier, P., Wallner, G., Priller, A., Kandler, N. and Kaiser, A.: Iodine Isotopes ($^{127}$I and $^{129}$I) in Aerosols at High Altitude Alp Stations, Environ. Sci. Technol., 46, 8637-8644, 2012.

Krupp G., Aumann D. C.: Iodine-129 in rainfall over Germany, J. Environ. Radiat. 46, 287 -299, 1999.

Leon, J. D., Jaffe, D. A., Kaspar, J., Knecht, A., Miller, M. L., Robertson, R. G. H. and Schubert, A. G.: Arrival time and magnitude of airborne fission products from the Fukushima, Japan, reactor incident as measured in Seattle, WA, USA, J. Environ. Radioact., 102, 1032-1038, 2011.

Lindberg, S. E., Brooks, S., Lin, C., Scott, K. J., Landis, M. S., Stevens, R. K., Goodsite, M. and Richter, A.: Dynamic Oxidation of Gaseous Mercury in the Arctic Troposphere at Polar Sunrise, Environ. Sci. Technol., 36, 1245-1256, 2002.

Lopez-Gutierrez J.M., Santos F.J., Garcia-Leon M., Schnabel Ch., Synal H.-A., Ernst Th., Szidat S.: Levels and temporal variability of $^{129}$I concentrations and $^{129}$I/$^{127}$I isotopic ratios in atmospheric samples from southern Spain, Nucl. Instrum. Meth. B, 223 -224, 495 -500, 2004.

Manolopoulou, M., Vagena, E., Stoulos, S., Ioannidou, A. and Papastefanou, C.: Radioiodine and radiocesium in Thessaloniki, Northern Greece due to the Fukushima nuclear accident, J. Environ. Radioact., 102, 796-797, 2011.

McFiggans, G., Plane, J. M. C., Allan, B. J., Carpenter, L. J., Coe, H. and O'Dowd, C.: A modeling study of iodine chemistry in the marine boundary layer, Journal of Geophysical Research: Atmospheres, 105, 14371-14385, 2000.

Michel, R., Daraoui, A., Gorny, M., Jakob, D., Sachse, R., Tosch, L., Nies, H., Goroncy, I., Herrmann, J., Synal, H. A., Stocker, M. and Alfimov, V.: Iodine-129 and iodine-127 in European seawaters and in precipitation from Northern Germany, Sci. Total Environ., 419, 151-169, 2012.

Muramatsu, Y., Matsuzaki, H., Toyama, C. and Ohno, T.: Analysis of $^{129}$I in the soils of Fukushima Prefecture: preliminary reconstruction of $^{131}$I deposition related to the accident at Fukushima Daiichi Nuclear Power Plant (FDNPP), J. Environ. Radioact., 139, 344-350, 2015.

Nielsen, S. P., Anderson, K. P. and Miller, A.: December 2011Radioactivity in the Risø District January-June 2011, Risø Report, Risø-R-1800(EN), 2011.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J. and Putaud, J.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676-680, 2004.

O'Dowd, C.,D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hämeri, K., Pirjola, L., Kulmala, M., Jennings, S. G. and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, Nature, 417, 632-636, 2002.

Osterc, A., Stibilj V.: 129I level in soil from Ukraine and Slovenia in the last decade, Intern. J. Environ. Anal. Chem., 93, 553-564, 2013.

Pechtl, S., Schmitz, G. and von Glasow, R.: Modelling iodide–iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry, Atmos. Chem. Phys., 7, 1381-1393, 2007.

Persson S., Aldahan A., Possnert G., Alfimov V., Hou X.: $^{129}$I Variability in precipitation over Europe, Nucl. Instrum. Meth. B 259, 508 -512, 2007.

Pittauerová, D., Hettwig, B. and Fischer, H. W.: Fukushima fallout in Northwest German environmental media, J. Environ. Radioact., 102, 877-880, 2011.

Prados-Román, C., Cuevas, C. A., Hay, T., Fernandez, R. P., Mahajan, A. S., Royer, S.-J., Galí, M., Simó, R., Dachs, J., Großmann, K., Kinnison, D., Lamarque, J.-F. and Saiz-Lopez, A.: Iodine oxide in the global marine boundary layer, Atmos. Chem. Phys., 15, 583–593, 2015.

Qiao, J., Hansen, V., Hou, X., Aldahan, A. and Possnert, G.: Speciation analysis of $^{129}$I, $^{137}$Cs, $^{232}$Th, $^{238}$U, $^{239}$Pu and $^{240}$Pu in environmental soil and sediment, Appl.Radial.Isot., 70, 1698-1708, 2012.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W. C. and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol, Nature Geosci, 7, 228-232, 2014.

Raisbeck, G. M., Yiou, F., Zhou, Z. Q. and Kilius, L. R.: $^{129}$I from nuclear fuel reprocessing facilities at Sellafield (U.K.) and La Hague (France); potential as an oceanographic tracer, J. Mar. Syst., 6, 561-570, 1995.

Saiz-Lopez, A., Gómez Martín, J. C., Plane, J. M. C., Saunders, R. W., Baker, A. R., Von Glasow, R., Carpenter, L. J. and McFiggans, G.: Atmospheric chemistry of iodine, Chem. Rev., 112, 1773-1804, 2012.

Saiz-Lopez, A. and Plane, J. M. C.: Novel iodine chemistry in the marine boundary layer, Geophys. Res. Lett., 31, L04112, 2004.

Santos, F. J., López-Gutiérrez, J. M., García-León, M., Suter, M. and Synal, H. A.: Determination of $^{129}$I/$^{127}$I in aerosol samples in Seville (Spain), J. Environ. Radioact., 84, 103-109, 2005.

Schnabel,C., Lopez-Gutierrez,J.M., Szidat,S., Sprenger,M., Wernli,H., Beer,J., Synal H. -A.: On the origin of $^{129}$I in rain water near Zürich, Radiochim. Acta 89, 815-822, 2001.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., FrieÃŸ, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H. -., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T. and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, Atmos. Chem. Phys., 7, 4375-4418, 2007.

Szidat, S., Schmidt, A., Handl, J., Jakob, D., Botsch, W., Michel, R., Synal, H. A., Schnabel, C., Suter, M., López-Gutiérrez, J. M. and Stade, W.: Iodine-129: Sample preparation, quality control and analyses of pre-nuclear materials and of natural waters from Lower Saxony, Germany, Nucl.Instrum.Meth.B, 172, 699–710, 2000.

Toyama, C., Muramatsu, Y., Igarashi, Y., Aoyama, M., Matsuzaki, H. Atmospheric fallout of $^{129}$I in Japan before the Fukushima accident: regional and global contributions (1963-2005). *Environ. sci. Technol. 47*, 8383-8390, 2013**.**

Tölgyessy, J. (Ed.): Chemistry and Biology of Water, Air and Soil-Environmental Aspects, Studies in Environmental Science, Elsevier, Amsterdam-London-New York-Tokyo, 53, 1-858, 1993.

Tsukada, H., Hara, H., Iwashima, K. and Yamagata, N.: The iodine content of atmospheric aerosols as determined by the use of a fluoropore filter for collection, Bull. Chem. Soc. Jpn., 60, 3195-3198, 1987.

Vogt, R., Sander, R., von Glasow, R. and Crutzen, P.: Iodine Chemistry and its Role in Halogen Activation and Ozone Loss in the Marine Boundary Layer: A Model Study, J. Atmos. Chem., 32, 375-395, 1999.

Weather Wunderground: http://www.wunderground.com/, last access: 26 May 2015.

Wimschneider, A. and Heumann, K. G.: Iodine speciation in size fractionated atmospheric particles by isotope dilution mass spectrometry, Fresenius J. Anal. Chem., 353, 191-196, 1995.

Xu, S., Freeman, S. P. H. T., Hou, X., Watanabe, A., Yamaguchi, K. and Zhang, L.: Iodine Isotopes in Precipitation: Temporal Responses to $^{129}$I Emissions from the Fukushima Nuclear Accident, Environmental Science and Technology, 47, 2010851-10859, 2013.

Xu, S., Zhang, L., Freeman, S. P. H. T., Hou, X., Shibata, Y., Sanderson, D., Cresswell, A., Doi, T. and Tanaka, A.: Speciation of Radiocesium and Radioiodine in Aerosols from Tsukuba after the Fukushima Nuclear Accident, Environ. Sci. Technol., 49, 1017-1024, 2015.

Yi, P., Aldahan, A., Hansen, V., Possnert, G. and Hou, X.: Iodine Isotopes ($^{129}$I and $^{127}$I) in the Baltic Proper, Kattegat, and Skagerrak Basins, Environ. Sci. Technol., 43, 903-909, 2011.

Yi, P., Aldahan, A., Possnert, G., Hou, X., Hansen, V. and Wang, B.: $^{127}$I and $^{129}$I Species and Transformation in the Baltic Proper, Kattegat, and Skagerrak Basins, Environ. Sci. Technol., 46, 10948-10956, 2012.

Zhang, L., Hou, X. and Xu, S.: Speciation Analysis of $^{129}$I and $^{127}$I in Aerosols Using Sequential Extraction and Mass Spectrometry Detection, Anal. Chem., 87, 6937-6944, 2015.

Zhang, L.Y., Zhou, W.J., Hou, X.L., Chen, N., Liu, Q., He, C.H., Fan, Y.K., Luo, M.Y., Wang, Z.W., Fu, Y.C.: Level and source of $^{129}$I of environmental samples in Xi'an region, China. Sci. Total Environ. 409:3780-3788, 2011.

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

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

Table 2.Analytical results of chemical species of $^{127}$I and $^{129}$I in aerosols collected from Risø, Denmark during spring 2011 and winter 2014[a].

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

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

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

| Phase | Reactions | Equations | References |
|---|---|---|---|
| Gas | $DMS + OH \rightarrow SO_2$ | (1) | (Chatfield and Crutzen 1990) |
| | $DMS + NO_3 \rightarrow SO_2$ | | |
| Gas/Aerosol | $SO_2 + H_2O \rightarrow HSO_3^-$ | (2) | |
| | $SO_2 + H_2O \rightarrow SO_3^{2-}$ | | |
| Gas-Aerosol interface | $I + HSO_3^- \rightarrow I^- + SO_4^{2-}$ | (3) | |
| | $I + SO_3^{2-} \rightarrow I^- + SO_4^{2-}$ | | |
| Aerosol | $HOI + HSO_3^- / SO_3^{2-} \rightarrow I^- + SO_4^{2-}$ | (4) | (Saiz-Lopez et al., 2012) |
| | $HOI + SO_3^{2-} \rightarrow I^- + SO_4^{2-}$ | | |
| | $HOI_2 + HSO_3^- / SO_3^{2-} \rightarrow I^- + SO_4^{2-}$ | | |
| | $HOI_2 + SO_3^{2-} \rightarrow I^- + SO_4^{2-}$ | | |

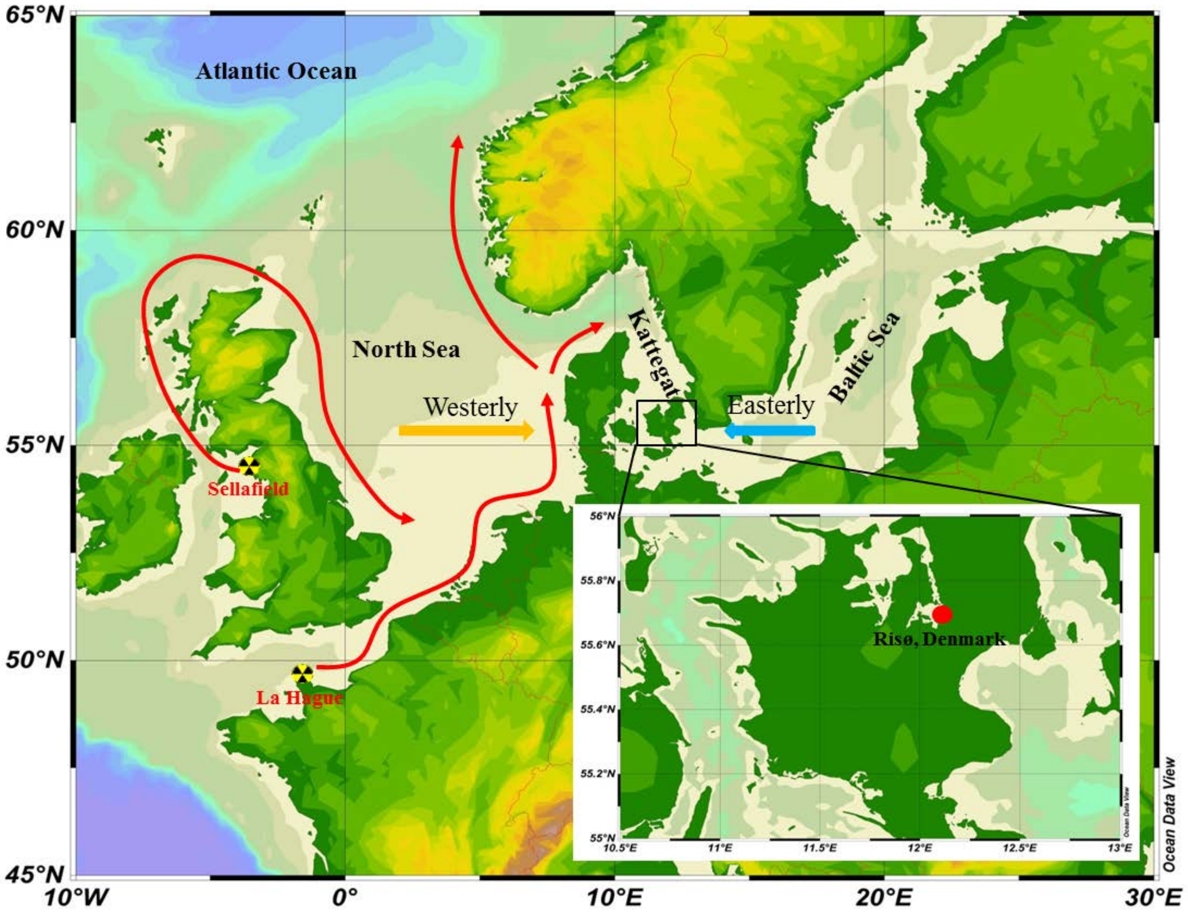

Figure 1. Map showing the sampling site (red dot in the inset) at Risø, Denmark for aerosol collection. The two nuclear reprocessing plants (radioactivity labels), Sellafield (United Kingdom) and La Hague (France) have released a large quantity of $^{129}$I to the marine and atmospheric environment.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

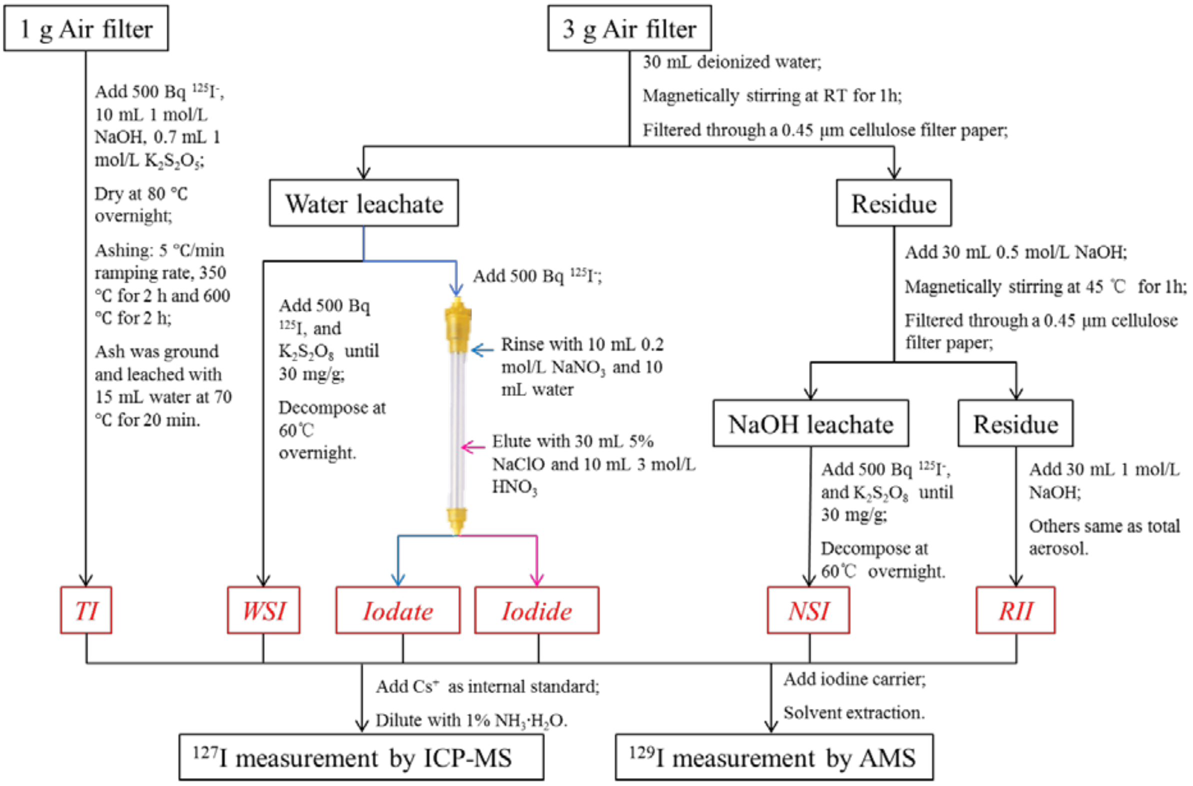

Figure 2. Schematic diagram of the analytical procedure for the determination of $^{127}$I and $^{129}$I species in aerosols (adapted from Zhang et al., 2015). TI for total iodine, WSI for water-soluble iodine, NSI for NaOH-soluble iodine and RII for residual-insoluble iodine.

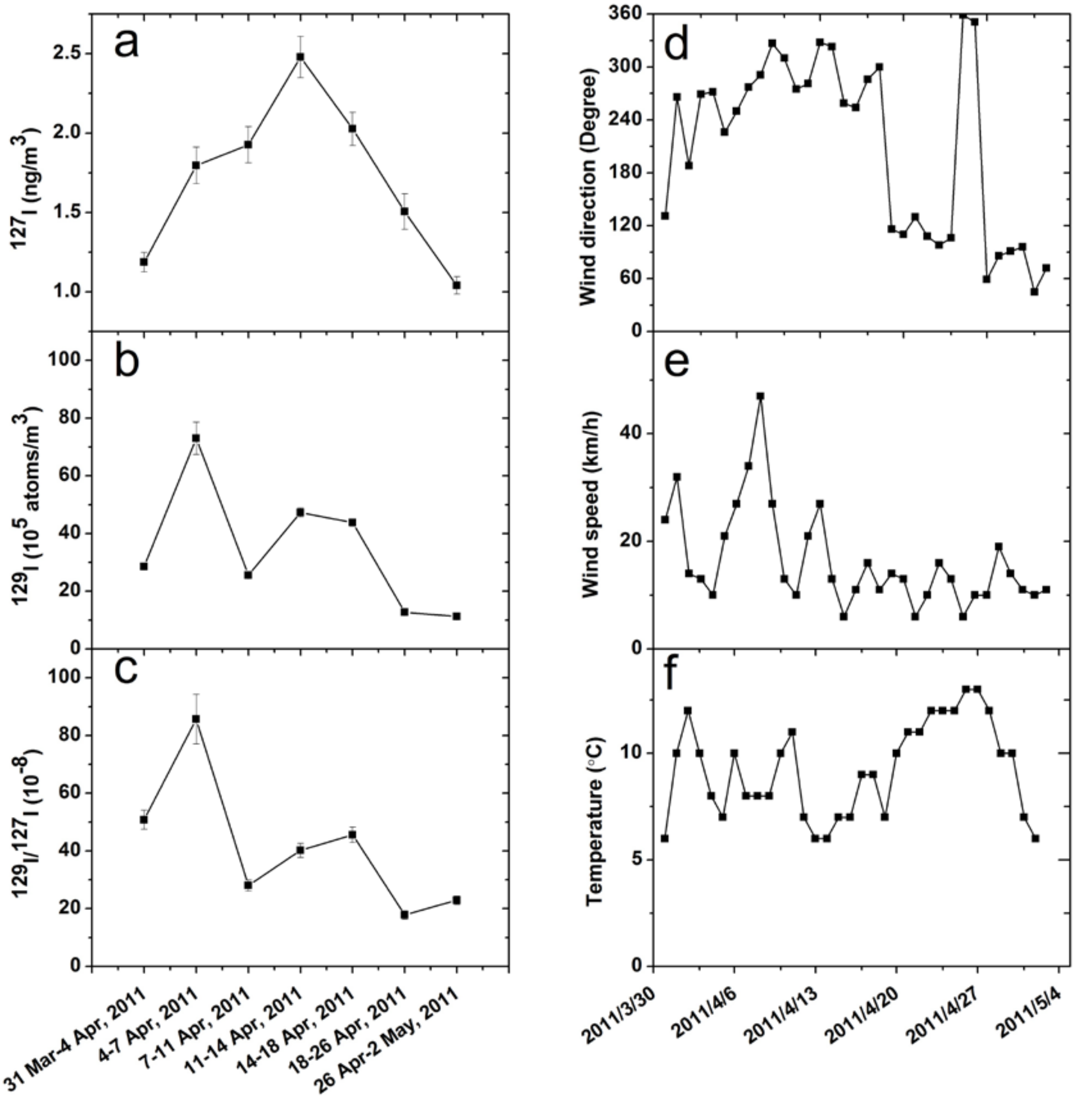

Figure 3. Variation of $^{127}$I concentrations (a), $^{129}$I concentrations (b), $^{129}$I/$^{127}$I ratios in aerosols (c), wind direction (d), wind speed (e) and temperature (f) during the sampling period. The historical meteorological data, including temperature, wind direction and wind speed were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

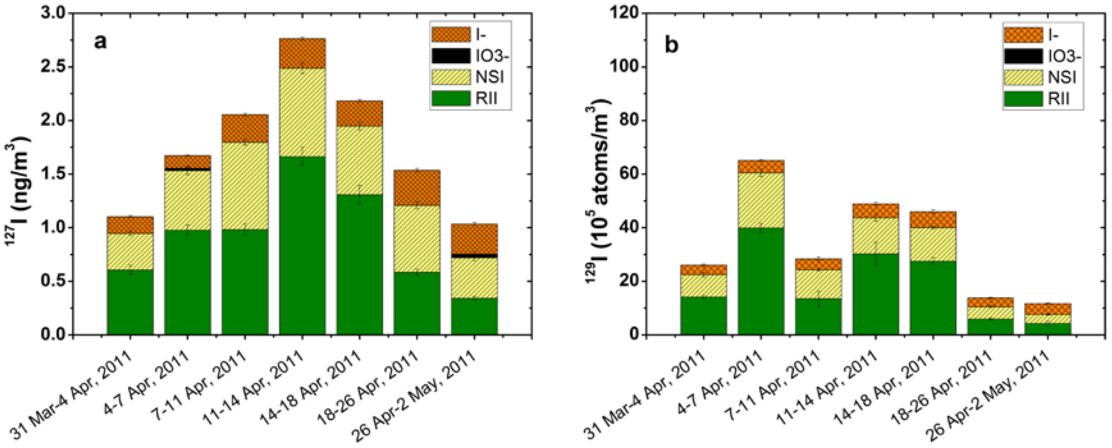

Figure 4. Concentrations of iodine species in the aerosol samples for $^{127}$I (a) and $^{129}$I (b), indicating that NSI and RII are major iodine species and that iodide is the dominant fraction of water-soluble iodine. Dot lines are same as those in Figure 3.

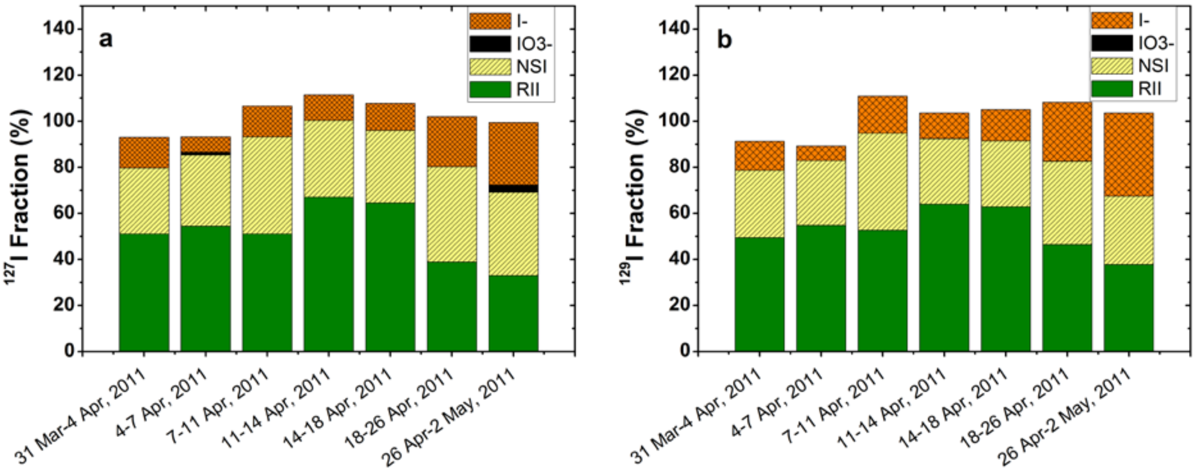

Figure 5. Distribution of iodine species in the aerosol samples for $^{127}$I (a) and $^{129}$I (b), compared with the measured concentrations of total $^{127}$I and $^{129}$I in bulk aerosols. Dot lines are same as those in Figure 3.

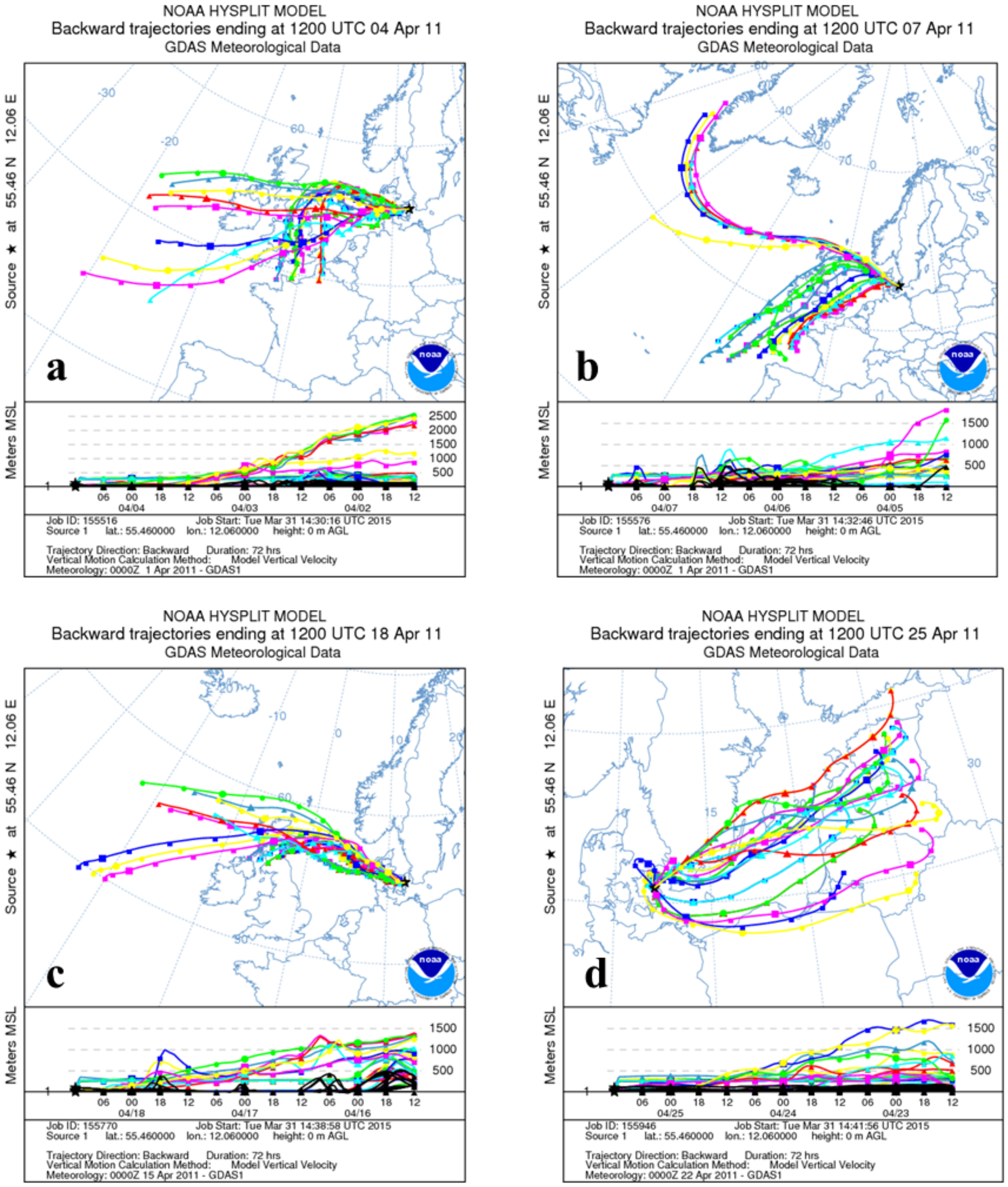

Figure 6. The 72 h (3 days) air mass back trajectories for starting altitudes of 0 m above ground level (AGL) calculated from the FNL database of the National Ocean and Atmospheric Administration (NOAA) and simulated by using the Hybrid Single-Particle Langrangian Integrated Trajectory (HY-SPLIT) model. 31 March-4 April (a), 4-7 April 2011 (b), 14-18 April (c) and 21-25 April 2011 (d).

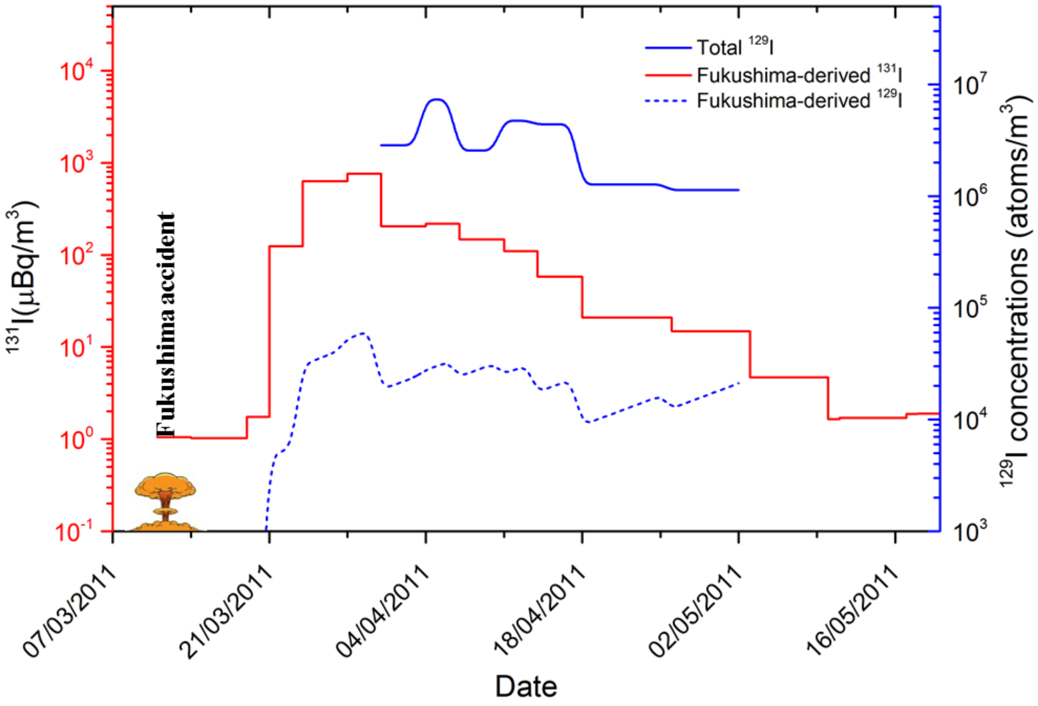

Figure 7. $^{131}$I radioactivity (red), $^{129}$I concentrations (blue) in aerosols from Risø, Denmark after the Fukushima accident (Nielsen et al., 2011). The Fukushima-derived $^{129}$I concentrations are calculated based on $^{129}$I/$^{131}$I atomic ratio of 16.0±2.2 deduced from Fukushima-affected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