**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, between 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)$\times$10$^5$ atoms m$^{-3}$ for $^{129}$I, corresponding to $^{129}$/$^{127}$I atomic ratios of (17.8-86.8)$\times$10$^{-8}$. The contribution of Fukushima-derived $^{129}$I (peak value of 6.3$\times$10$^4$ atoms m$^{-3}$) is estimated to be negligible (less than 6%) compared to the total $^{129}$I concentration in 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 amounts of $^{129}$I than aerosols transported over the European continent. The high $^{129}$I concentrations of the marine aerosols are attributed to secondary emission
from $^{129}$I-contaminated seawater besides the primary gaseous release from the two European nuclear reprocessing plants. 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., 2013b; 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$_3$I, C$_2$H$_5$I) 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 December - 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$_3$·H$_2$O 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 1.138×10$^{-10}$, 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 5×10$^{-13}$, 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 11.3-72.9×10$^5$ atoms m$^{-3}$ (average of (44±19)×10$^5$ 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 \(^{129}\text{I}\) and \(^{127}\text{I}\) concentrations were observed during 18 April-2 May 2011 compared to those before 18 April (Fig. 3), but \(^{129}\text{I}\) levels didn’t show a synchronous variation with \(^{127}\text{I}\) concentrations. The results of \(^{127}\text{I}\) 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). \(^{129}\text{I}/^{127}\text{I}\) 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 \(^{129}\text{I}\) concentrations and \(^{129}\text{I}/^{127}\text{I}\) 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 \(^{127}\text{I}\), 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 \(^{127}\text{I}\) concentration (0.74 ng m^{-3}) was observed in aerosol collected in 2014, and there was no measurable water-soluble organic iodine. Water-soluble \(^{129}\text{I}\) shows a similar species pattern as water-soluble \(^{127}\text{I}\) except that iodate-129 was below the detection limit in all the analyzed samples. The concentrations of \(^{129}\text{I}\) varied in (3.26-5.91)×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 \(^{127}\text{I}\) and (13.64±10.1)×10^5 atoms m^{-3} for \(^{129}\text{I}\). RII is the dominant species in aerosol samples for both iodine isotopes, with concentration range of 0.34-1.66 ng m^{-3} for \(^{127}\text{I}\) and (4.27-39.9)×10^5 atoms m^{-3} for \(^{129}\text{I}\).

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 $^{127}\text{I}$ and $^{129}\text{I}$ 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 $^{129}\text{I}$ and $^{127}\text{I}$ 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 $^{129}\text{I}$ and $^{127}\text{I}$ 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 $^{127}\text{I}$ and 26.8% for $^{129}\text{I}$. 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 $^{127}\text{I}$, and no $^{129}\text{IO}_3^-$ was detectable in all aerosol samples investigated in this work.

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

4 Discussion

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

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

Marine emission of volatile iodine species is a major source of iodine in the atmosphere. 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, the sampled air mass was transported by westerly winds from a vast area over the northern Atlantic Ocean. This caused an elevated $^{127}$I concentration. Except for the Norwegian Sea and the North Sea, most areas of the northern Atlantic have low seawater $^{129}$I concentrations (He et al., 2013a), which is what we observed for the 11-14 April aerosol sample.

The highest measured $^{129}$I concentrations in spring 2011, $72.98 \times 10^5$ atoms m$^{-3}$, was observed in the aerosol sample collected in 4-7 April 2011. These samples reflect that air masses were transported from two directions, west/northwest and south/southwest (Fig. 6). The dominant south/southwesterly wind passed over regions of elevated $^{129}$I, including the North Sea and reprocessing sites at Sellafield and La Hague. In contrast to ocean source for $^{127}$I, more than 95% of environmental $^{129}$I originates from releases of Sellafield and La Hague reprocessing plants, located at west and southwest of Denmark, respectively (Fig. 1). A large fraction of $^{129}$I (200 -300 kg year$^{-1}$ since 1995) has been discharged to the sea as liquid form from these two reprocessing plants. After being introduced into the English Channel and Irish Sea, $^{129}$I follows surface ocean currents 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, $10^{9} - 10^{10}$ atoms L$^{-1}$ in Norwegian coastal waters and the Kattegat, 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). Only a small fraction of $^{129}$I (about 0.5 - 5 kg year$^{-1}$ in the past 20 years) has been released as gaseous form to the atmosphere from Sellafield and La Hague reprocessing plants, and it has dispersed over a large area, in particular in Europe (Ernst et al., 2003; Hou et al., 2007; Persson et al., 2007; Jabbar et al., 2012). Direct gaseous release of $^{129}$I is suggested as a major source of $^{129}$I in aerosols and precipitation in Zurich and Seville, Spain.
In this work, the results present a direct observation of $^{129}$I source in the Danish aerosol. The aerosol samples collected in 41 March-4 April and 4-7th April, which as air mass passed over Sellafield and La Hague, as well as the North Sea, but the air mass in the aerosol collected in 4-7th April were also passed through the English Channel where was highly contaminated by marine discharged $^{129}$I from La Hague reprocessing plant. A $^{129}$I concentration of $25.9 \times 10^5$ atoms m$^{-3}$ was observed in the aerosol sample in 31 March-4 April, 2.6 times lower than that in 4-7 April ($72.98 \times 10^5$ atoms m$^{-3}$). The aerosol in 7-11 April, when air mass didn't passed above Sellafield and La Hague, but over a narrow sea surface of the North Sea contained similar high level $^{129}$I concentration as that in 31 March - 4 April. In contrast, the two aerosols collected in 11-18 April, which the air mass did not passover Sellafield and La Hague, had relatively high $^{129}$I concentrations (($43.81-47.21) \times 10^5$ atoms m$^{-3}$) (Figs. 6 and S1). These results indicates that secondary emission from $^{129}$I-contaminated seawater, in particular in the North Sea, Kattegat and the Norwegian Sea, is a dominant source of $^{129}$I in the aerosols from Denmark, as well as part of north Europe. Emission process of volatile iodine from seawater can be facilitated by sea-spray and biological activity of macroalgae and microalgae (McFiggans, 2005; O'Dowd et al., 2002). This conclusion is also supported by $^{129}$I measurements in aerosols from high altitude European sites (Jabbar et al., 2012), as well as in precipitation from Denmark, Sweden and Germany (Buraglio et al., 2001; Hou et al., 2009a; Krupp and Aumann, 1999; Michel et al. 2012), as well as in two Irish lake waters influenced by precipitation (Atarashi-Andoh et al., 2007; Keogh et al., 2010).

The lowest $^{129}$I concentrations, $(11 -13) \times 10^5$ atomsm$^{-3}$, were observed in the aerosol samples collected in 18 -26 April and 26 April -2 May 2011. Back trajectory analysis (Fig. S1) 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. Terrestrial emissions of iodine occur through vegetation and terrestrial microorganisms (Bewers and Haysom, 1974). Low $^{129}$I/$^{127}$I ratio of terrestrial system can be observed in those areas distant from nuclear reprocessing plant and highly $^{129}$I-contaminated marine source (Jabbar, 2011 and 2012). This is reflected in these two aerosol samples by their relatively low $^{129}$I concentrations. An elevated $^{210}$Pb level
(249 -253 μ Bq m⁻³) (Table 1) for this period is also consistent with a continental origin
(²¹⁰Pb in the air is a decay product of ²²²Rn which is mainly released from the soil in the
continental area). The highest value of ¹²⁹I, 97.00×10⁵ atoms m⁻³, in 8-15 December 2014 is
also related with ¹²⁹I re-emission mainly from the North Sea, where the air masses passed
over (Fig. S2). Because of the possibilities, including probably increased releases from
Sellafield and La Hague and seasonal difference of iodine re-emission from seawater, the ¹²⁹I
concentration in winter 2014 is higher than that in spring 2011.

4.2 Species of ¹²⁹I and ¹²⁷I 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$_2$O, these reactions produce HSO$_3^-$ and SO$_3^{2-}$ (Eqs.s 1 and 2). Native iodine and other reactive species (not shown) can be reduced to I$^-$ on gas-aerosol interfaces (Eq. 3). Other iodine species in aerosols can also be reduced by reductive sulfur compounds to form iodide (Eq. 4). The electron-donors are not limited to sulfur compounds either, for example, nitrogen in the form of gaseous ammonia (NH$_3$→NO$_2$/NO$_3$) (McFiggans et al., 2000; Saiz-Lopez and Plane 2004) and elemental mercury (Hg$_0$→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 and winter of 2014 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 nucleophilic substitution or elimination of iodine-containing organic compounds, which releases iodine from the organic substances Therefore, NaOH-soluble iodine is 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 NRP-derived $^{129}$I in this study as compared to those from Fukushima. A significant difference is the timing of the $^{129}$I releases. NRP-derived $^{129}$I was released 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 and winter of 2014 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; Pittauеровá 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 $5 \times 10^8$ atoms m$^{-3}$ (Xu, et al. 2015). While the
Fukushima-derived $^{129}$I in environmental samples outside of Japan was less well-characterized. $^{131}$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±2.2 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 6.3×10$^4$ atoms m$^{-3}$ on 30-31 March 2011, which accounts for less than ~6% of total $^{129}$I (1.1-9.7×10$^6$ 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$\text{}_2$ 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 Atlantic Ocean contribute to high $^{129}$I concentrations compared to easterly air masses from the northeastern European continent. $^{129}$I in aerosols in Denmark is primarily derived from European nuclear
reprocessing plants. This includes secondary emission of $^{129}\text{I}$ from seawater in the North Sea, Norwegian coastal water and Kattegat, which has been contaminated by marine discharges of $^{129}\text{I}$ from NRPs.

3) Fukushima-derived $^{129}\text{I}$ contributed less than $\sim 6\%$ to the total $^{129}\text{I}$ in the European atmosphere immediately after the Fukushima accident, a negligible quantity when compared to $^{129}\text{I}$ 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.

Acknowledgement

L. Y. Zhang is grateful for the support from all colleagues in the Division of Radioecology (headed by Sven P. Nielsen), Center for Nuclear Technologies, Technical University of Denmark, for her PhD project. This work is partly supported by the projects of Innovation Methodology (No. 2012IM030200) and Fundamental Scientific Research (2015FY110800) from the Ministry of Science and Technology of China. We acknowledge Dr. Dr. George Burr for polishing English presentation.

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Yi, P., Aldahan, A., Hansen, V., Possnert, G. and Hou, X.: Iodine Isotopes ($^{129}$I and $^{127}$I) in
Yi, P., Aldahan, A., Possnert, G., Hou, X., Hansen, V. and Wang, B.: $^{127}$I and $^{129}$I Species and
Zhang, L., Hou, X. and Xu, S.: Speciation Analysis of $^{129}$I and $^{127}$I in Aerosols Using
Table 1. Sampling information of aerosols collected at Risø, Denmark in 2011 and 2014. Data of $^{131}$I and $^{210}$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.

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

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

3 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

<table>
<thead>
<tr>
<th>Phase</th>
<th>Reactions</th>
<th>Equations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>DMS + OH $\rightarrow$ SO$_2$</td>
<td>(1)</td>
<td>(Chatfield and Crutzen 1990)</td>
</tr>
<tr>
<td></td>
<td>DMS + NO$_3$ $\rightarrow$ SO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas/Aerosol</td>
<td>SO$_2$ + H$_2$O $\rightarrow$ HSO$_3^-$</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO$_2$ + H$_2$O $\rightarrow$ SO$_3^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-Aerosol</td>
<td>I + HSO$_3^-$ $\rightarrow$ I$^-$ + SO$_4^{2-}$</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td>interface</td>
<td>I + SO$_3^{2-}$ $\rightarrow$ I$^-$ + SO$_4^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol</td>
<td>HOI + HSO$_3^-$ / SO$_3^{2-}$ $\rightarrow$ I$^-$ + SO$_4^{2-}$</td>
<td>(4)</td>
<td>(Saiz-Lopez et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>HOI + SO$_3^{2-}$ $\rightarrow$ I$^-$ + SO$_4^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HOI$_2$ + HSO$_3^-$ / SO$_3^{2-}$ $\rightarrow$ I$^-$ + SO$_4^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HOI$_2$ + SO$_3^{2-}$ $\rightarrow$ I$^-$ + SO$_4^{2-}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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), $^{129}$/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. 4-7 April 2011 (left) and 21-25 April 2011 (right).
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).