Response to interactive comment on

"Speciation of 127I and 129I in atmospheric aerosols at Risø, Denmark: insight into sources of iodine isotopes and their species transformations"

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We appreciated to the comments from three anonymous referees, which are very useful for improving the quality of the manuscript. All these comments were fually considered and replied in the interactive discussion in the website, and listed below. According to these comments, the manuscript was carefully revised, and the revised manuscript with marked revision is attached.

Replies to Referee #1

Thanks a lot for the constructive comments, we appreciate it very much, these comments are very useful for improvement of the quality of the manuscript. The comments and questions from the referee are replied below item by item.

P25142, l 11. "Larger particles remained in the troposphere for about 20 days..." It would be helpful if the actual size range of the particles in question could be stated explicitly. Large (e.g. 20 um) particles would be expected to have lifetimes shorter than 20 days.

Answer: We agree with the reviewer's comment. The sentence "Larger particles remained in the troposphere for about 20 days before being deposited on the earth's surface" has changed to "From the troposphere, about one half of the radioactive particles is deposited onto the earth's surface within 20 days".

P25142, l 15. The expression "marine boundary layer" is very commonly used to describe the lowest levels of the troposphere in contact with, and directly influenced by, the ocean. From the context of the sentence I am not sure whether this is what the authors intend here. Do they actually mean the "sea surface"?

Answer: Thank you for giving the definition of marine boundary layer. Yes, it should be sea surface, hence in this sentence "the marine boundary layer" is revised to "sea surface" in the revised version.

P25143, l 22. I find the statement “diluted by a factor of 1-20” to be ambiguous. It implies that not all the samples were diluted by the same factor, which I don’t think was the case. Probably “diluted by a ratio of 1:20” would be more accurate.

Answer: Sorry for the confused description. In this experiment, the different iodine fractions were diluted by different factor from 1 to 20 depending on the concentrations of iodine and leaching solution. For example, water-soluble iodine fraction was diluted by a factor 1, while, NaOH-soluble iodine fraction was diluted by a factor of 20. In order to make clear, the sentence “diluted by a factor of 1–20 using ammonium” has been revised to “diluted by factors from 1 to 20 using ammonium depending on the iodine concentration in each fraction and the matrix of the leachate”.

P25144, l 17 (and several other instances throughout the manuscript). Here the authors report average 129I concentration and the standard deviation of that average to 4 significant figures. In my view this level of precision is not justified. Two significant figures would be quite enough in this case.

Answer: We agree that 4 significant figures of the average concentrations and SDs are not justified. We keep 2 significant figures and revised three values in the manuscript. In P25244 l16 and l17, the value “1.79±0.52” is revised to “1.8±0.5”, and “43.65±18.88” to “44±19”. In P25244 l16 and l17, the values “13.55±10.12” is revised to “14±10” in the revised version.

P25146, I 26. “Except for the Norwegian Sea.” the authors are implicitly excluding the North Sea (which has relatively high 129I seawater concentrations) from being part of the Atlantic Ocean. Perhaps it would be better to say “Except for the North Sea and Norwegian Sea..”.

Answer: We apologize for misleading the readers about this. The North Sea is also well known containing high concentration of ^{129}I. The phase “Except for the Norwegian Sea” is revised to “Except for the Norwegian Sea and the North Sea” in the revised version.

P25148, l 4-7. Here the authors cite the relatively low terrestrial emissions of iodine as the cause of the relatively low 129I concentrations in the aerosol concentrations observed in samples AE11-6 and AE11-7. If low terrestrial emission was the only factor involved then one would also expect these samples to have similarly low 127I concentrations, but this does not appear to be the case. Probably more important is the low 129I:127I ratio of the terrestrial emissions, due to their distance from the western (marine) 129I sources.

Answer: Thanks a lot for pointing out this unsuitable description. We agree the interpretation that the low ^{129}I concentration in the samples AE-6 and AE-7 is due to the low ^{129}I/^{127}I ratio of terrestrial emission, rather than the low terrestrial emission rate of iodine from earth’s surface. The sentence “Terrestrial emissions of iodine occur through vegetation and terrestrial microorganisms, and are much lower than marine emissions (Bewers and Haysom, 1974). This is reflected in these two aerosol samples by their relatively low 129I concentrations." is revised to "Terrestrial emissions of iodine occur through vegetation and terrestrial microorganisms (Bewers and Haysom, 1974). Low $^{129}I/^{127}I$ ratios of terrestrial system have been observed in those areas distant from nuclear reprocessing plant and highly ^{129}I-contaminated marine source (Jabbar, 2011 and 2012)."

P25148, l 15. "dominant air masses during the sampling periods were westerly". Please specify exactly which time periods are referred to here, as several different time periods are discussed in the preceding sentences.

Answer: The sentence has been specified exactly to "the dominant air masses during the sampling period of 11-18 April 2011 were westerly".

P25148, l 16. I do not understand what the authors intend by the word "secondarily" in this sentence.

Answer: Sorry for the ambiguous expression. The "secondarily high" is intended to express the "second highest". The phase "The secondarily high ^{129}I concentrations" has been revised to "The intermediate ^{129}I level". Under overall consideration, this paragraph has been deleted, please refer to the following answer.

P25148, l 18-21. I am confident that the authors' statement regarding the relative strengths of direct atmospheric and secondary marine emissions of 129I is correct, but I don't see how the data presented in this manuscript can allow one to draw that conclusion. I suggest that the words "It can therefore be concluded" be removed and the authors cite one or more of the studies that have compared atmospheric 129I concentrations with known emissions from Le Hague and Sellafield, as these do demonstrate this. ?

Answer: Thanks for the comment. We admit that such an expression is not very logical, therefore this sentence is moved up to the paragraph above in the revised version, where we discussed the source of ^{129}I in the aerosol with the highest ^{129}I level. In addition, we have cited some references to show the atmospheric ^{129}I level affected by nuclear facilities, especially nuclear reprocessing plants. Finally, the sentence "It can therefore be concluded" has been deleted.

P25148, l 29. "Hence, iodine in marine aerosols directly participates in aerosol formation." I think there is something incorrect here. If the iodine is already in marine aerosols how can it participate in aerosol formation? Is this intended to mean that iodine nano-particles nucleate particle growth?

Answer: We appreciate this comment. Yes, we intended to express the role of iodine on particle growth progress. The sentence "Hence, iodine in marine aerosols directly participates in aerosol formation." should be revised to "Hence, iodine directly participates in the formation of marine aerosols." Under the overall consideration, we have deleted this paragraph.

P25149, l, 1-8. Previous studies have shown that the speciation of iodine in rainfall and aerosol samples are rather different, even when the samples were collected at the same location over the same time periods (Gilfedder et al., ACP, 8, 6069-6084, 2008). One other factor contributing to this difference may be that the iodine present in the rainwater samples can originate from iodine present in the source cloud, as well as from material acquired during droplet descent, whereas the aerosol iodine is only representativeof thematerialat groundlevel. Idonot understandthepoint theauthors wish to make regarding back trajectory analysis in the final sentence here.

Answer: We agree with the referee that the difference of iodine speciation in rainfall and aerosol is caused not only by the different incorporation progress of iodine into rain and aerosol, but also by the sources of iodine (cloud or soil). This paragraph is intended to explain the correlation of iodine isotopes concentration in rain and aerosol with wind direction (i.e. origin and direction of air masses). However, we found back trajectory analysis showed that variation of iodine concentration in both rain and aerosol is associated with origin of air masses. Considering this, we think there is no necessary to discuss the difference that iodine incorporates into rain and aerosol. Therefore, we deleted this paragraph (P25148 l23-P25149 l8).

P25150, l 4. "alternative primary pathways". Alternative to what?

Answer: The phase "alternative primary pathways" is revised to "other primary pathways".

P25150, l 11-12. Gaseous SO2 can be formed by the oxidation of DMS, but in northwest Europe direct emission of SO2 from anthropogenic sources is more significant.

Answer: We appreciate for this clue that is valuable for interpreting the formation of iodide in aerosol. We have added one sentence and one reference to state the anthropogenic SO_2source in the revised version.

P25150, l 21. "We note that relatively low WSI 129I and 127I was measured in marinesourcedaerosolsfromtheNorthSea". Iagreethatthisappearstobethecasefor127I, but I am not so convinced for 129I (from looking at the concentrations listed in Table 2).

Answer: Sorry, this sentence is not clear, we want to express that "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." This sentence is updated in the revised version.

P25151, l 29 – p25152, l4. While there is no question that the environmental lifetime of NRP 129I is far longer than that of Fukushima 129I, their atmospheric lifetimes are short and probably rather similar. Might it therefore be possible that RII is formed over longer time periods in some other compartment (the sea surface?) and enters the atmosphere through primary emission?

Answer: Yes, It's possible that RII is formed in other compartments, such as sea surface and earth surface. Due to the lifetime of NRP-^{129}I (decades) and Fukushima ^{129}I (days), incorporation degree of ^{129}I into the insoluble matter is different, more into the insoluble part of Danish aerosol in this work and less into that of Fukushima aerosol.

P25152, l 5-19. I find this paragraph to be contradictory and poorly argued. Initially the authors appear to discount soil as being a significant source of RII on the basis that little (<10%) 129I remains after NaOH leaching. They later state that the RII fraction might be associated with "metal oxides that originated by suspension of fine inorganic particles". What might these fine inorganic particles be, if they are not of soil origin? They then state that a "relatively large fraction of iodine in soil and sediment has been observed in metal oxides associated form". Does this not contradict the earlier statement, or does it indicate that the latter fraction is not RII? There is no evidence presented at all to support the final statement regarding the association of gaseous iodine with inorganic particles.

Answer: We apologize for the poor statement in this paragraph. In this work, iodine in aerosol is fractionated into three fractions, water-soluble, NaOH leachable (i.e. organic associated iodine) and residue insoluble iodine (RII). The RII includes metal oxides and minerals; they are not soluble in water and NaOH. The source of RII might be suspension of particles including soil particles and dusts. Because a large fraction of iodine in soil and sediment has been observed to be associated with metal oxides (leached with reductive reagents), it is supposed that the part of RII in aerosol might be associated with metal oxides. Conversion of iodine species during the formation and dispersion of aerosol might happen, i.e. water soluble iodine was associated with metal oxides in the aerosol. We agree that association of gaseous iodine with inorganic particles is indeed unknown. This paragraph has been updated in the revised version (see below)

"The origin of the RII fraction is not well understood at present. It's possible that part of 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 oxides). 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 account 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 iodine with oxides, minerals."

P25152, l 20 – p25153, l 3. I struggle to understand the authors' interpretation of the relationships they found between iodine species concentrations and 7Be. Although the iodide/iodate ratios of 127I and 129I in the North Sea are different (Hou et al., EST, 41, 5993-5999, 2007), it is difficult to see how this could cause the speciation of emissions of the two isotopes from the sea surface to be significantly different. If emissions from the sea surface dominate behavior of 129I, then this must also be the case for 127I.

Answer: This paragraph aims to interpret the different distribution of ^{127}I and ^{129}I in iodide form using the correlations of them with ^{7}Be in the aerosol. ^{129}I re-emitted from the North Sea water might be one of major source of ^{129}I in the aerosol collected in Denmark, while ^{127}I in the aerosol might have multi-sources including those released from the land and large area of ocean. The iodide/iodate ratios of ^{129}I and ^{127}I are not related to this interpretation.

We agree with the referee that this interpretation is not easy to be understood, or might be inadequate. Therefore this paragraph is deleted in the revised version.

P25155, l 6. Why should the calculated dry deposition estimate from this work be consistent with the wet deposition? These are different deposition mechanisms.

Answer: Sorry for the inadequate description. We agree with the referee that dry and wet depositions are different mechanisms. The corresponding sentence is changed to " the wet deposition of …., which is comparable to our calculated deposition flux of ^{129}I,.."

P25155, l 16. I recommend changing this to read "... of the water-soluble iodine in the aerosols measured in this study", since other studies has found different results.

Answer: Thanks! This sentence is revised in the revised version.

P25155, l 22-24. This statement appears to be worded a little too strongly. The difference in 127I concentrations referred to here is only a factor of 2.

Answer: We apologize for mistyping. It should be ^{129}I concentrations.

Technical comments

Thanks a lot for the detailed and useful comments and suggestions. We corrected or revised the corresponding descriptions or sentences.

Replies to referee #2

Thanks a lot for the constructive comments. We have considered all comments and carefully revised the MS according to these comments. The comments and questions from the referee are answered below item by item.

1. The investigation has utilized a sample collection procedure of aerosols that provide all sizes of aerosols (including dust). It is understandable that as the first study, the procedure was reasonable, but in future investigations it will be vital to have the dust and aerosols sizes separated to properly estimate resuspension and other material size effects.

Answer: We agree with the referee. The size effect is important on the distribution and dispersion of iodine and its species, which should be well investigated in the future. Resuspension of the deposited iodine is one very interesting topic, which will help to understand the atmospheric behaviors of iodine, especially radioactive iodine released from accident.

2. It will be good to have a definition of atmospheric aerosols and dust in the beginning of the introduction in order to focus the reader on what is analyzed.

Answer: Thanks for the comment. We added one sentence to give the definition of atmospheric aerosol in the beginning of the introduction.

3. I agree with the authors that lack of international standards for the atmospheric aerosols when it comes to iodine makes the comparison rather floating, but this issue can be an excellent inter-laboratory exercise for the future.

Answer: We agree that it will greatly improve the analysis of ^{129}I, not only for speciation but also total ^{129}I, if some inter-laboratory exercises are organized in the future. We will be happy to participate in such an intercompariosn if such one is organized in the future.

4. Although not directly pertinent to subject of the investigation, it will have been interesting to obtain visual images (using SEM) of the aerosols particles to get some idea about size distribution and forms.

Answer: Thanks for this suggestion, we agree with the referee. Using more advanced technologies, such as SEM and TEM for aerosol morphology, XRF and ICP-MS for trace elements, IC for inorganic ions, will provide more ideas for interpreting the atmospheric iodine behavior. Therefore, our future may combine these techniques with speciation analysis of 129I and 127I in aerosols.

5. It is not clear what was the effect of temperature and wind speed on the iodine species distribution and may be this part needs further elaboration.

Answer: We appreciate for this comment. In this paper, we didn’t find any significant effect of temperature and wind speed on iodine species due to the limited aerosol samples and iodine species data points. A systematic investigation on time-series aerosols is needed to elucidate the effect. This might be carried out in our future work.

6. It was interesting that the authors used a correlation with 7Be isotope, but I am sure they know that these two isotopes have rather different atmospheric chemistry and physical behavior. The correlation between 127I and 7Be is rather interesting (although not many data points) and most likely point out iodide as possible adsorption site for 7Be. However, the authors did not mention the chemical procedure or the measurement technique used for 7Be. As with iodine, 7Be can also fractionate differently between water soluble and insoluble. A reference at the end of line 23 on page 25152 is needed.

Answer: Thanks for the comment. The significant correlation between 127Iodide and 7Be and no correlation between 129Iodide and 7Be were observed in this investigation, which is rather interesting. We agree that iodine and beryllium have different chemical and physical properties and distinct behaviors in the atmosphere. We tried to explore the formation process of iodide using these informations, but it seems a big challenge due to lack of sufficient evidence (more data points). Therefore, we have to delete the discussion of this part.

7. The paper provides interesting information about iodine isotopes and species, and some improvement can be achieved through consideration of the comments.

Answer: Thanks a lot for all of the comments. We have considered all of the comments, and the manuscript is revised and improved according to these comments.

Replies to referee #3

Thanks a lot for the constructive comments. We have considered all comments and carefully revised the MS according to these comments. The comments and questions from the referee are answered below item by item.

Major comments

1. 25142: In the first paragraph, only particulate iodine transport is discussed, but no gas transport. However, there are many relevant inorganic and organic gaseous compounds for atmospheric transport and transformation. This is also acknowledged by the authors in the second paragraph, as here “gas-aerosol exchange processes” are mentioned. So, gaseous emissions and transport should be discussed on this page as well.

Answer: We agree with the reviewer’s comment that gaseous iodine compounds are important in the atmosphere, which was considered inadequately in the introduction part. According to the comment, several sentences are added in the first paragraph of page 25142 to address the gas-aerosol relationship for discussion of transportation and transformation below.

2. 25145, lines 6-8; 25146, line 2; Tab. 2; Fig. 4: The values for iodate shown in Tab. 2 are below the detection limit (assuming the given uncertainties represent one standard deviation), as the measured concentration is smaller than two sigma. As a consequence, iodate has to be regarded as not significant for all samples throughout the whole paper and removed from the figures.

Answer: Thank you for the comment. We also have considered if these values of iodate should be removed from the paper due to its proximity to the detection limit, resulting in large uncertainties. The detection limit of iodine in our method is calculated to be 0.007 ng m^{-3} on the basis of three times of standard deviation of five blank samples (Zhang et al, Speciation Analysis of ^{129}I and ^{127}I in Aerosols Using Sequential Extraction and Mass Spectrometry Detection. *Analytical Chemistry*, 2015). The values, 0.022 and 0.033, are 3-4 times of the detection limit, therefore, the iodate in these two samples are detectable. But if we consider the quantitative detection limit, ten times of standard deviation of blank samples, these iodate concentrations are not significant. For better discussion in the context, therefore, we prefer to keep the values with large uncertainties as reference for readers. Asterisks are added to the iodate concentrations to note the case.

3. 25147, lines 3-10: The analysis of the sample from December 2014 cannot be used for discussion of general trends, as it is done in this passage and also at a few other locations (e.g., 25146, lines 5-7). All other samples span a coherent episode from end of March to beginning of

May 2011, which allows, for example, a distinction of ^{129}I transport to Denmark from western vs. eastern directions. This is only valid with the implicit assumption that a) the gross emissions are constant during this episode and b) temporal/seasonal variations are minor, which can be accepted for the 6 weeks in spring 2011, but not for the comparison of spring 2011 with winter 2014. First, the emissions from Sellafield and La Hague cannot a priori be supposed to have been constant over these >3 years and the seasonal difference is obvious (e.g. on the primary vs. secondary mechanisms of iodine aerosol formation). The authors should have investigated a similar episode in winter 2014 (i.e., 6 weekly samples) so that this data may have been used for deeper discussions. Therefore, the measurement result of the samples AE14-1 may be shown in Tables 1 and 2, but not in Figs. 3-5 and should also not be included in any kind of further interpretation.

Answer: We appreciate this comment and agree with the referee #3 that data and interpretation of episode December 2014 should be treated cautiously, and we fully accept the arrangement as the referee suggested. Therefore, we separate the episode December 2014 from the other high ^{129}I episode, and interpret the high values of December 2014 as possibilities, including probably increased emissions from Sellafield and La Hague, seasonal difference of iodine re-emission from seawater. We still keep the result of the sample AE14-1 in Figs. 3-5 in order to compare the data between spring 2011 and winter 2014 in the context after revision.

We agree that it would be better to have a similar episode investigation in winter 2014. Since this work is an attempt practice using ^{129}I and ^{127}I species to study aerosol iodine source and species transformation, we just give one datum to see if there is seasonal effect on iodine species distribution. Further investigation could be done on a long time series to see the seasonal variation of iodine species.

4. 25147, lines 8-28: The formation of iodine-containing aerosols is described from volatile precursors that have been emitted by sea-spray and biological activity of macroalgae and microalgae and defined as secondary source. According to lab and field studies (e.g., McFiggans, 2005; O'Dowd et al., 2002), this formation process has been identified for stable iodine (^{127}I) as source of so-called particle bursts of ultrafine aerosols particles in coastal regions. By implicit transferring the knowledge of ^{127}I to ^{129}I, the authors concluded from this that "this secondary iodine source is known to significantly increase atmospheric ^{129}I concentrations and may be expected to contribute to the iodine measured in our aerosol samples". This statement does not base on previous studies. Although Schnabel et al., 2001 (Radiochim. Acta 89, 815-822) and Jabbar et al., 2012 discuss the relative relevance of gaseous vs. liquid discharges from Sellafield and La Hague for sites directly influenced by these reprocessing plants (Zurich, Vienna, Zugspitze), both papers conclude that the data clearly depict that the ^{129}I inventory at these sites in air had more influence from direct gaseous emissions than from secondary formation. Only for Sonnblick, which is partially influenced from the Mediterranean and is therefore not comparable to the Danish site, this result was not so clear. Consequently, the statement on the dominance of

secondary iodine for ^{129}I aerosol observations in this study should be removed and later discussions on the sources (25148, lines 14 to 25149, line 8), the abstract (25140, lines 15-17) and the conclusions should be adapted. The trajectory analysis enables the separation of western vs. eastern air masses for the measurement site and the importance of both directions for the ^{129}I levels, but it does not give evidence for secondary vs. primary formation of radioactive aerosols.

Answer: Thanks for the comment. We also noticed the investigation of the source of ^{129}I in southern and middle Europe (Zurich, Vienna, and Seville), which showed that air release of 129I from the European nuclear reprocessing plants (NRPs) is the dominant source of ^{129}I in the air. However, it is not the case in North Europe. Investigation of ^{129}I in air and precipitation collected in Germany, Sweden and Denmark clearly showed that re-emission (secondary emission) of ^{129}I in the North Sea, Kattegat and Norwegian Seas is an important source of 129I in the North Europe. Meanwhile, ^{129}I/^{127}I ratio measured in atmosphere (air and precipitation) in the North Europe is also higher than those observed the south Europe, although a far distance from North Europe to the reprocessing plants in La Hague and Sellafield compared to the location at Middle and South Europe （Zurich, Vienna, Seville）. Some more evidences and interpretations are added in the revised version to support our conclusion that secondary emission from seawater is a major source of ^{129}I in the Danish aerosol, including 1) Combination of ^{129}I results in this work with air mass pathways as denoted by back trajectory analysis suggests that high ^{129}I concentration in the Danish aerosol is related to the North Sea originated air mass, rather than the NRPs originated air mass; 2) more previous ^{129}I studies on atmospheric samples (aerosol, precipitation and rainfall-influenced lake water) from different locations are added, in order to explain the contribution of air releases of ^{129}I from reprocessing plant and secondary emission from the seawater in different location in the Europe.

In order to make this interpretation clearer, the two paragraphs in lines 3-29 on page 25147 and lines 1-23 on page 25148 are rewritten in the revised version.

5. 25151, lines 15-16: This is possibly the major reason for the solubility of iodine containing aerosols by NaOH, but not the only one. On the one hand, elemental iodine (I_2) is much better soluble in alkaline solution than in water, because the disproportionation into iodide and iodate is than favored. On the other hand, the hydroxide anion may initiate a nuclephilic substitution or elimination of iodine-containing organic compounds, which releases iodide as leaving group. These alternative processes should be explained and mentioned in the discussion.

Answer: Thanks for providing these interpretation on the NaOH-soluble iodine, we carefully considered the comments:

1) Elemental iodine is not stable in aerosol, which is not comparable with other relatively stable iodine species, iodide, iodate, NaOH-soluble iodine and insoluble residual iodine, and thus can be negaligible.
2) It is possible nucleophilic substitution or decomposition of iodine-containing organic compounds occur during NaOH leaching, which can be used as a mechanism explanation.

According to the referee’s comments, some more interpretation are added in the revised version.

6. 25152, line 20 - 25153, line 3: This paragraph was already criticized by two other referees and the authors declared that this passage will be removed in the revised version. I totally agree with this.

Answer: Thanks for this comment. This paragraph is removed in the revised version including the corresponding figure.

7. Chapter 4.4: This discussion is inappropriate and should be removed completely. It is not acceptable to determine an average dry deposition flux in Denmark for 2011-2014 from 8 individual short-term samples collected at one specific site in that country, as the authors also admit at the end of the section. Moreover, the application of parameters of Duce et al., 1991 and Gabler and Heumann, 1993 are far too simple to achieve the mission of dry deposition fluxes.

Answer: We agree with the reviewer’s comment. The uncertainty of this estimation of ^{129}I dry deposition is too large to accept due to the limited data. This chapter is removed in the revised version.

Technical comments:

8. “Atoms” is not a SI unit. ^{129}I concentrations should be given in units as (11.3-97.0) ×10^5 m^{-3} (example from the abstract) throughout the whole paper including all tables and figures. If you want to underline that atoms were counted, you can emphasize it this way: “while 129I atom concentration of 97.00 _ 105 m□3 was about: : :” (example from 25144, line 19).

Answer: We agree with the referee that atom is not a SI unit, but a mass unit. ^{129}I mass concentration can be expressed as atoms/m^3, in which atoms is a mass unit, the corresponding SI unit is kg. Here the atom/m3 is used because of very low mass concentration of ^{129}I in aerosol. In the literatures, ^{129}I concentration in air samples has been expressed as atoms/m^3, Bq/m^3 or g/m^3, but most frequently expressed as atoms/m3.

9. 25140, line 16: “heavily 129I-contaminated seawater” is overstated and “heavily” should be removed.

Answer: The word “heavily” is removed in the revised version.

10. 25149, line 28 to 25150, line 2: It should read: “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).”

Answer: Thanks for suggestion; this sentence is revised in the revised version

11. 2516, line 14: I assume, it should read “Nielsen”.

Answer: Thanks a lot. We apologize for the mistyping. It is corrected in the revised version.

12. Table 2: As far as I understand, results of samples AE11-5 and 7 were already published earlier by Zhang et al., 2015. This needs to be indicated in the table caption.

Answer: The two data are indicated in the table caption in the revised version.

13. Figure 2: This Figure is reproduced from Zhang et al., 2015, which should be mentioned in the caption. Furthermore, the quality should be improved.

Answer: The reference is added in the figure caption. The high quality figure is uploaded.

14. Figures 3-5: Vertical lines should be used to separate episodes of westerly and easterly winds.

Answer: Dot lines are added to Figures 3-5 to separate the episodes.

15. Figure 7 should be removed, as the corresponding paragraph will also be removed.

Answer: Figure 7 and the corresponding are removed.

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, 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 $(11.3\text{-}97.0)\times10^{5}$ atoms m^{-3} for ^{129}I, ~~and~~ corresponding to ^{129}I/^{127}I atomic ratios of $(17.8\text{-}86.8)\times10^{-8}$. 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 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 ~~ocean~~seas ~~,~~ ~~contained~~ 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 ~~heavily~~ ^{129}I-contaminated seawater ~~rather than~~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~~s~~ an important role for iodine transportation from ocean to land. In particular, speciation analysis of iodine in aerosols is ~~expected~~ one of critical issue to understand~~speculate~~ 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 ~~in aerosols~~ 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~~s~~ 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 ~~considered~~ addressed water-insoluble iodine in aerosols (Gilfedder et al., 2010; Tsukada et al., 1987), which might be not easily ~~hardly be~~ converted to gaseous iodine before being deposited on the Earth's surface. ~~Existing~~ 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 ~~globe~~ world in water, atmosphere and terrestrial systems (Hou et al., 2009b). Above-ground nuclear explosions also produced ^{129}I, injecting it into ~~both~~ 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 ~~Larger particles remained in the troposphere for about 20 days before being deposited on the earth's surface~~ (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~~the marine boundary layer~~ 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. O3, NOx) 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 ~~travels~~ 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 ~~. Our goal is~~ 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

~~BulkThe a~~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 ~~is~~ 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. ~~Sample~~ 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~~diluted by a factor of 1-20 using ammonium to 1% $NH_3\cdot H_2O$~~. Cesium was added as internal standard to a final concentration of 2 ng g^{-1} to ~~monitor the ionization~~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~~National Institute of Standards and Technology - NIST~~, 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~~n~~ ^{129}I/^{127}I ratio of 1.138×10^{-10}, prepared from a ^{129}I standard solution (NIST 4949C) ~~standard~~

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~~are~~ 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.~~79~~8±0.5~~2~~ ng m^{-3}) for ^{127}I and 11.3~~1~~-~~73.0~~72.9~~8~~×10^5 atoms m^{-3} (average of (4~~3.65~~4±1~~8.88~~9)×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~~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~~4~~-86.8~~4~~)×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 ~~in~~ 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~~s~~ 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 ~~of~~ the analyzed samples. The concentrations of ^{129}I^{-} varied in ~~the range of~~ (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 ~~(30.12×10^{5} atoms m^{-3})~~ 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~~3.55~~4±10.1~~.12~~)×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 (4.27-39.94)×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~~ed~~ in all aerosol samples investigated in this work.

~~An range of~~ ^{129}I/^{127}I atomic ratios of (15.~~5~~6-102.~~36~~0)×10^{-8} ~~was~~ 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 ~~Concentration variations~~ of ^{127}I and ^{129}I concentration in aerosols against meteorological parameters (i.e. wind direction, wind speed and temperature) during the sampling period shows~~s~~ that wind direction has a dominant influence (Fig. 3). Back trajectory model analysis shows that ^{127}I and ^{129}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}I and ^{129}I concentrations was observed in ~~in~~ the aerosols collected early April 2011 and December 2014, when the air mass was mainly transported from the Atlantic Ocean ~~and~~ 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, (73-97)×10^{5} atoms m^{-3}, were observed in the aerosol samples collected in 4-7 April 2011 and 8-15 December 2014. These samples reflect that air masses were transported from two directions, west/northwest and south/southwest (Fig. 6, Figs. S-1 and S-2). The dominant south/southwesterly wind passed over regions of elevated ^{129}I, including the North Sea and reprocessing sites at Cap de La Hague and Sellafield. In contrast to the marine-derived ^{127}I, more than 95% of environmental ^{129}I is discharged from Sellafield and La Hague, west and southwest of Denmark, respectively (Fig. 1). Only a small fraction of ^{129}I in gaseous form (about 2-5 kg year^{-1} in the past 20 years) has~~

~~been released to the atmosphere from two reprocessing plants at La Hague and Sellafield, and this has become diluted over a large area, including southern Europe (Ernst et al., 2003; Hou et al., 2007). However, a large fraction of ^{129}I (200-300 kg year^{-1} since 1995) has been discharged directly to the sea in liquid form from these two reprocessing plants. After being introduced into the English Channel and Irish Sea, the ^{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., 2004b; 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., 2004a; He et al., 2014; Hou et al., 2007; Michel et al., 2012; Yi et al., 2011). In addition to direct releases to the atmosphere from the two reprocessing plants, volatile iodine is also emitted from seawater, especially in the North Sea and Kattegat. This process is facilitated by sea spray and biological activity of macroalgae and microalgae (McFiggans 2005; O'Dowd et al., 2002). This secondary iodine source is known to significantly increase atmospheric ^{129}I concentrations and may be expected to contribute to the iodine measured in our aerosol samples.~~

The highest measured ^{129}I concentrations in spring 2011, 72.98×10^{5} atomsm^{-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 ~~directly~~ 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 (Schnabel et al. 2001, Lopez-Gutierrez et al., 2004). In this work, ~~however,~~ 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 ~~Similar~~ as air mass ~~pathway in 4-7 April that~~ 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.~~87~~9×10^{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 (72.98×10^{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, ~~without~~which the air mass did not pass~~ing~~ over Sellafield and La Hague, had relatively high ^{129}I concentrations ((43.81-47.21)×10^{5} atoms m^{-3}) (Figs. 6 and S1). ~~Integrated analysis of t~~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 Den~~amrk~~mark, Sweden and~~,~~ Germany ~~and~~ (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)×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 (^{210}Pb in the air is a decay product of ^{222}Rn which is mainly released from the soil in the continental area). The highest value of ^{129}I, 97.00×10^{5} atoms m^{-3}, in 8-15 December 2014 is also related with ^{129}I re-emmission 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 ^{129}I concentration in winter 2014 is higher than that in spring 2011.

~~The lowest measured ^{129}I concentrations, (11-13)×10^{5} atoms m^{-3}, were observed in aerosol samples collected in 18-26 April and 26 April-2 May 2011. Back trajectory analysis (Fig. S-1) shows that in this period the air masses at the sampling site were mainly transported by easterly or northwesterly winds. Terrestrial emissions of iodine occur through vegetation and terrestrial microorganisms, and are much lower than marine emissions (Bewers and Haysom 1974). 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). The ^{129}I concentrations of aerosol samples collected in 11-14 and 14-18 April 2011 ranged of (43-47)×10^{5} atoms m^{-3}, which is lower than the 7 April sample (73×10^{5} atoms m^{-3}) by a factor of 1.6, but about 4 times higher than the aerosol~~

~~samples that passed over the European continent from 18 April to 2 May 2011. A back trajectory analysis clearly shows that the dominant air masses during the sampling periods were westerly, i.e. from the Atlantic Ocean but cross a narrow area of the northern North Sea (Fig. 6 and Fig. S-1). The secondarily high~~ ^{129}~~I concentrations in these aerosol samples should be attributed to the re-emission of~~ ^{129}~~I from the highly contaminated seawater in the North Sea. It can therefore be concluded that besides the direct air releases of~~ ^{129}~~I from the two European reprocessing plants, secondary emission of~~ ^{129}~~I from the highly contaminated North Sea water is the dominant source of~~ ^{129}~~I in the aerosols collected in Denmark. This is also supported by~~ ^{129}~~I measurements in aerosols from high altitude European sites (Jabbar et al., 2012).~~

~~It should be noted that such a result was not be observed for precipitation samples collected in central Sweden during 1998-1999 (Buraglio et al., 2001). This might be attributed to different mechanisms that iodine incorporates into particles and precipitation. Gaseous iodine species, e.g.~~ I_2 ~~and~~ CH_2I_2 ~~emitted by iodine-rich seaweed are important precursors for the formation of new particles, due to their relatively rapid photolysis to active iodine oxides (e.g. IO, OIO) (McFiggans 2005; O'Dowd et al., 2002; Saiz-Lopez et al., 2012). Hence, iodine in marine aerosols directly participates in aerosol formation. In contrast, iodine in precipitation originates from washout process of gaseous iodine and air-borne particulate iodine, primarily in the form of polar iodine compounds (e.g. HI, HOI, IO,~~ I^-, IO_3^-, I_2 ~~and unidentified organic iodine species) in~~ H_2O ~~molecules during precipitation events (Buraglio et al., 2001; Gilfedder et al., 2007). In addition, aerosol samples were collected over a relatively long time scale (3-7 days), reflecting an accumulated signal during the sampling period, while precipitation events are normally much shorter. Therefore, the source terms of iodine isotopes in precipitation might not necessarily follow back trajectory analysis.~~

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~~ phase~~, 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. ~~Current~~ Early models predicted a negligible iodide concentration in particle phases based on ~~an~~ 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 ~~other~~ the previous ~~results~~ reports (Baker 2004; Xu et al., 2015) suggests that there must be ~~alternative~~ 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~~ (Eqns. 1-1)~~. 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.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 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 ($NH_3 \rightarrow NO_2/NO_3$) (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~~We note that relatively low WSI ^{129}I and ^{127}I was measured in marine-sourced aerosols from the North Sea~~, 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). ~~Other possible NaOH-soluble iodine might be~~

~~derived from elemental iodine. Although the solubility of elemental iodine (I_2) in NaOH solution is much higher than that in water due to disproportionated reaction, it is volatile and unstable in aerosol, and the content of I_2 is negligible compared to the other relatively stable iodine species.~~ 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 Therefore, NaOH-soluble iodine is suggested to be likely associated with ~~HULIS~~ organic substances in aerosols.

RII in aerosols has received less attention than WSI ~~and NSI~~ (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~~s~~ 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 ~~been~~ releasing ^{129}I into the European environment for about 50 years, allowing ~~it~~ ^{129}I to follow geochemical pathways on timescales ranging from days to decades. In contrast, RII ~~from~~ 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.

~~The origin of the RII fraction is not well understood at present. It's possible that the RII fraction is derived from suspended soil particles (Xu et al., 2013). However, speciation analysis of ^{129}I in soils show that residual iodine after NaOH leaching accounts for less than 10% of the total, and this minor component is assumed to be associated with minerals (Hou et al., 2003; Qiao et al., 2012). Another possibility is a connection with soot and black carbon from combustion processes, found in anthropogenic aerosols (Kondratyev et al., 2006; Rose et al., 2006), However, the aerosols collected for this study in early April 2011 and winter of 2014 were mainly marine aerosols, with high RII. Alternatively, the RII fraction in aerosols might be associated with metal oxides that originated by suspension of fine inorganic particles. A relatively large fraction of iodine in soil and sediment has been observed in metal oxides associated form (Hou et al., 2003). Gaseous iodine in the atmosphere could interact with these inorganic particles and become firmly bound. The relatively high RII in the marine aerosols (Figs. 4 and 5) suggests that some marine component facilitates the association of gaseous iodine with inorganic particles.~~

~~A significant positive correlation between ^{127}Iodide and ^{7}Be in aerosol samples (R=0.76, p=0.05) is observed (Fig. 7). ^{7}Be ($t_{1/2}$ =54 days) is produced in the stratosphere by cosmic ray reactions with oxygen and nitrogen and rapidly transported to the troposphere by vertical mixing processes to be finally deposited onto the earth. The production of ^{7}Be decreases with decreasing altitude in the troposphere because of the attenuation of cosmic rays by~~

~~interactions with atomic targets in the atmosphere (Turekian et al., 1983). This positive correlation might indicate that the formation of iodide occurs in air masses at higher altitude. However, no significant correlation between ^{129}I^{-} and ^{7}Be is observed (Fig. 7). This is consistent with the process of secondary emission of ^{129}I from contaminated seawater, which would only increase ^{129}I in the troposphere. The significant negative correlation of NSI of ^{129}I with ^{7}Be (R=0.73, p=0.06) likely reflects the association of iodine with organic matter at low altitude, where organic matter is liberated by biological activity in the ocean and on land.~~

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 ~~offshore~~ Fukushima offshore seawater, the released ^{129}I ~~amount~~ from this accident was estimated to be 1.2 kg (Hou et al., 2013). ~~Gaseous ^{129}I~~Radioactive iodine in the air ~~travelled~~ dispersed across the Pacific Ocean, American continent and Atlantic Ocean, and some fraction arrived ~~o~~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 Fuk~~m~~ushima Dai-ichi NPP, reached 5×10^{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 ~~and other gamma emitters such as ^{134}Cs~~ in the aerosol samples collected at Risø, Denmark, 10 days after the Fukushima accident have been observed (Fig. ~~8~~7) (Nielsen et al., 2011). The radioactivity ~~peak~~ of ^{131}I ~~(763 µBq m^{-3} in aerosol)~~ 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 ~~expected~~ Fukushima-derived ^{129}I signal in Denmark can be reconstructed (Fig. ~~8~~7). The highest ^{129}I concentration in the aerosols in Denmark from the Fukushima accident is~~are~~ 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 ~~in~~ 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.

~~4.4 Dry deposition flux of iodine isotopes~~

~~Dry deposition fluxes of iodine can be estimated as $F_d = C_d \cdot v_d$ (Baker et al., 2001), where F_d is the flux (μg m^{-2} yr^{-1} for ^{127}I and atoms m^{-2} yr^{-1} for ^{129}I), C_d is the aerosol iodine concentration in the atmosphere (ng m^{-3} for ^{127}I and atoms m^{-3} for ^{129}I), and v_d is the deposition velocity (cm s^{-1}). The deposition velocities are size-dependent, at 0.1 cm s^{-1} for fine particles (Aerodynamic diameter < 1 μm) and 1.5 cm s^{-1} for larger particles (Duce et al., 1991). The aerosol samples in this work were collected on a PP filter with a pore size of approximately 0.45 μm. According to the particle size distribution at Spieka-Neufeld, Germany, whose atmospheric input of iodine is also from the North Sea, as in this study, 67% of aerosol iodine accumulated in particles larger than 1 μm and 33% in 0.45~1 μm particles (Gabler and Heumann 1993). Employing these parameters, dry deposition fluxes of iodine in Denmark can be estimated to be 342-815 μg m^{-2} yr^{-1} for ^{127}I, and (0.4-3.2)×10^{12} atoms m^{-2} yr^{-1} for ^{129}I during 2011-2014. If the average values of 1.8 ng m^{-3} and 43.7×10^5 atoms m^{-3} are used as the representative concentrations of ^{127}I and ^{129}I in aerosol, respectively for 2011, average dry deposition fluxes of iodine in 2011 would be 591 μg m^{-2} yr^{-1} and 1.4×10^{12} atoms m^{-2} yr^{-1} for ^{127}I and ^{129}I, respectively. The ^{127}I deposition flux falls within the range of natural stable iodine deposition, at 460-830 μg m^{-2} yr^{-1}, observed at Norfolk, on the north coast of the United Kingdom (Baker et al., 2001). It is also comparable with measured values from southern Sweden, but higher than northern Sweden (Englund et al., 2010b). The dry deposition flux of ^{129}I for aerosol samples collected in Sweden between 1983 and 2008 shows a range of 0.33-6.6×10^{11} atoms m^{-2} yr^{-1} in southern Sweden, and 0.008-1.6×10^{11} atoms m^{-2} yr^{-1}~~

~~in northern Sweden (Englund et al., 2010b), which are 1-3 orders of magnitude lower than the deposition fluxes determined here. This is attributed to the distant sampling locations in the Swedish study, much further away from the major point sources of aerosol ^{129}I than Denmark. The wet deposition of ^{129}I at the Risø site was calculated to be (1.25±0.30)×10^{12} atoms m^{-2} yr^{-1} during 2001-2006 (Hou et al., 2009a), which is consistent with our calculated dry deposition flux of ^{129}I, indicating that subequal contributions of ^{129}I by dry and wet deposition. It should be noted, however, that the estimated dry deposition flux was based on only one month of data in the spring and on a modeled deposition velocity, which could potentially introduce significant uncertainty due to temporal variations of ^{129}I in aerosols and particulate size dependent velocity.~~

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 ~~form~~ species (>97%) of the water-soluble iodine in the aerosols of this study~~in aerosol~~, its formation might be related to atmospheric reductants, such as reductive ~~SO_3~~ 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 Atlantic Ocean contribute to high $^{12\cancel{7}9}$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}I from seawater in the North Sea, Norwegian coastal water and Kattegat, which has been ~~heavily~~ contaminated by marine discharges of ^{129}I from NRPs.

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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Table 1. Sampling information of aerosols collected at Risø, Denmark in 2011 and 2014. Data of ^{131}I~~, ^{7}Be~~ 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 ~~^{7}Be and~~ ^{210}Pb).

Sample No	Sampling date	Air flux, m^3	Air flux, $m^3\ h^{-1}$	Weight, g	^{131}I, μBq m^{-3}	^{210}Pb, μBq 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 are 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)
	$HOI + SO_3^{2-} \rightarrow I^- + SO_4^{2-}$		
	$HOI_2 + HSO_3^- / SO_3^{2-} \rightarrow I^- + SO_4^{2-}$		
	$HOI_2 + SO_3^{2-} \rightarrow I^- + SO_4^{2-}$		

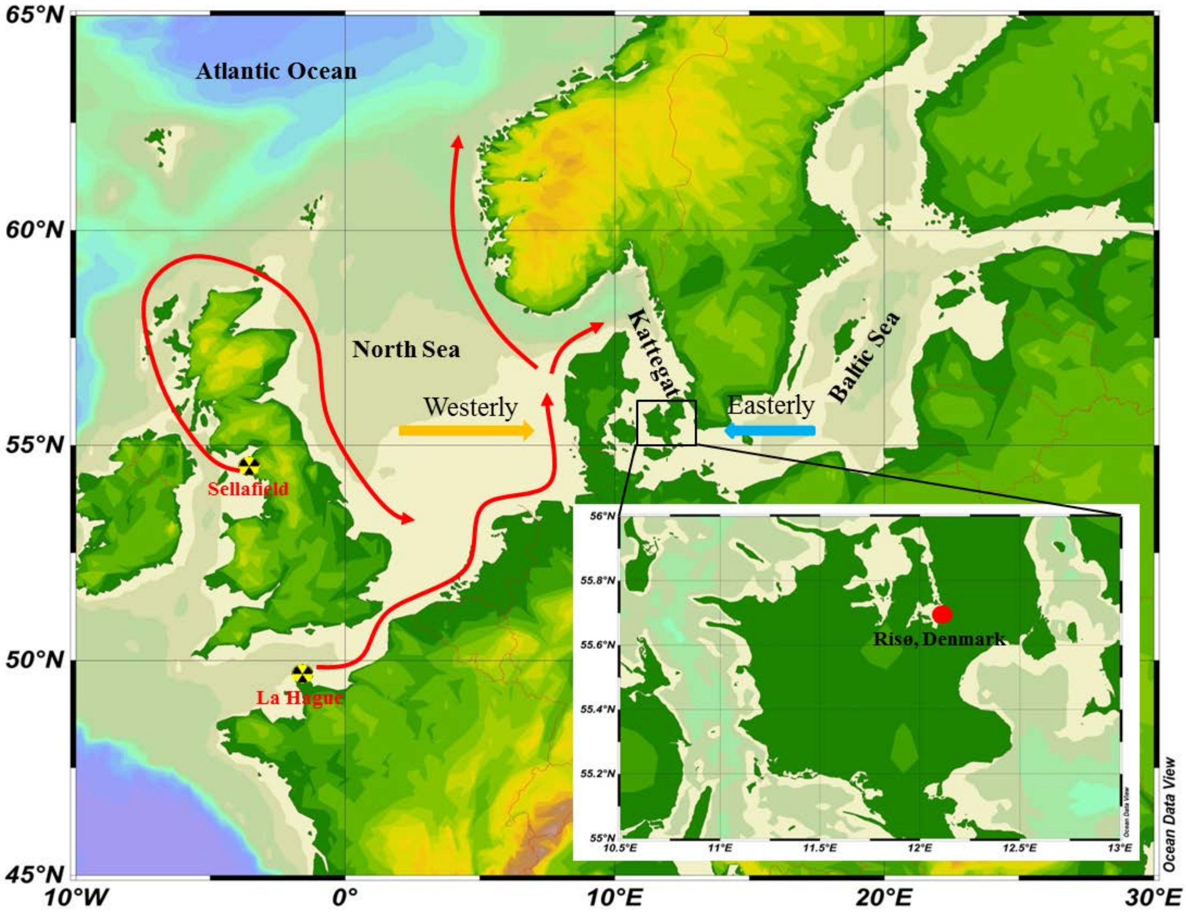


Figure 1. Map showing the sampling site (red dot in the inset) at Risø, Denmark for aerosol collection. The two nuclear reprocessing plants (radioactivity labels), Sellafield (United Kingdom) and La Hague (France) have released a large quantity of ^{129}I to the marine and atmospheric environment. This 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.

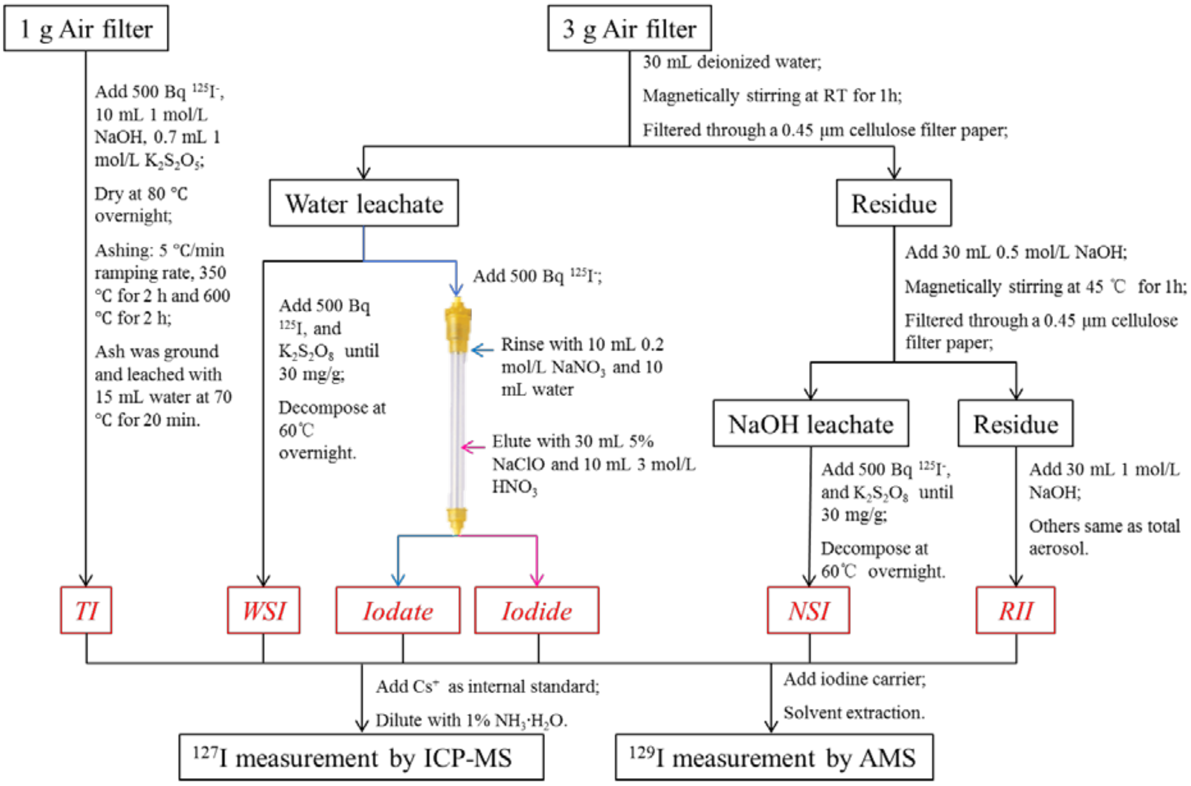
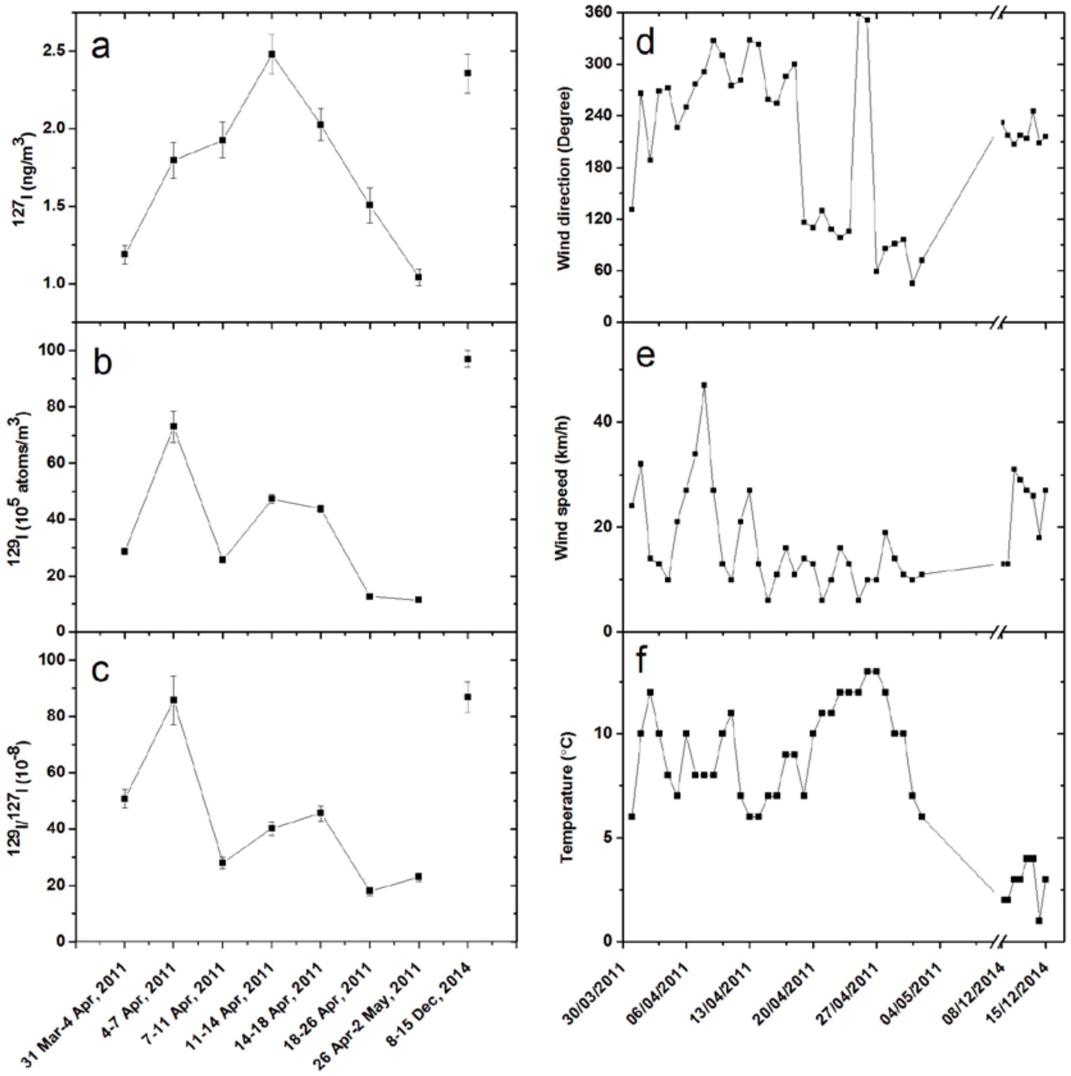


Figure 2. Schematic diagram of the analytical procedure for the determination of ^{127}I and ^{129}I species in aerosols (adapted from Zhang et al., 2015). TI for total iodine, WSI for water-soluble iodine, NSI for NaOH-soluble iodine and RII for residual-insoluble iodine.


a
^{127}I (ng/m^3)
1.0
1.5
2.0
2.5
b
^{129}I (10^5 atoms/m^3)
0
20
40
60
80
100
c
^{129}I/^{127}I (10^{-8})
0
20
40
60
80
100
31 Mar-4 Apr, 2011
4-7 Apr, 2011
7-11 Apr, 2011
11-14 Apr, 2011
14-18 Apr, 2011
18-26 Apr, 2011
26 Apr-2 May, 2011
8-15 Dec, 2014
d
Wind direction (Degree)
0
60
120
180
240
300
360
e
Wind speed (km/h)
0
20
40
f
Temperature (°C)
0
5
10
30/03/2011
06/04/2011
13/04/2011
20/04/2011
27/04/2011
04/05/2011
08/12/2014
15/12/2014

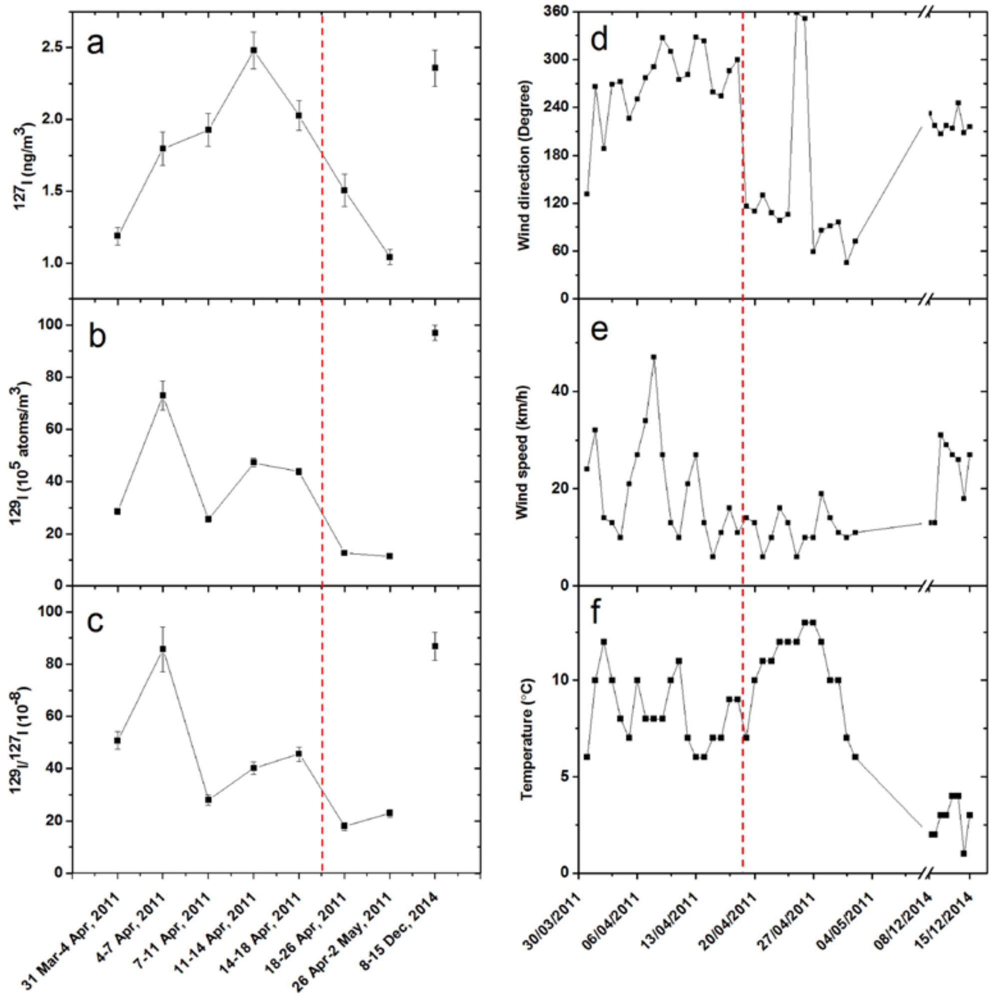
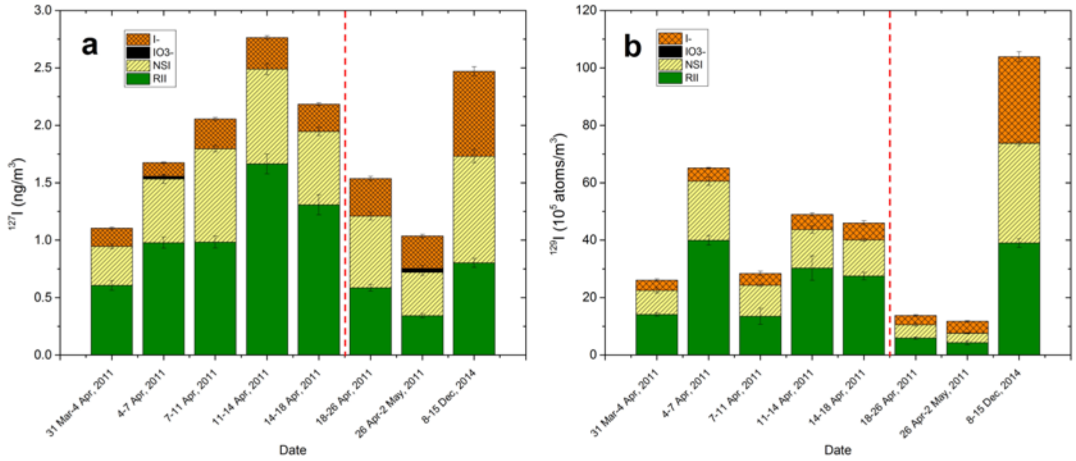


Figure 3. Variation of ^{127}I concentrations (a), ^{129}I concentrations (b), ^{129}I/^{127}I ratios in aerosols (c), wind direction (d), wind speed (e) and temperature (f) during the sampling period. The historical meteorological data, including temperature, wind direction and wind speed were obtained 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.



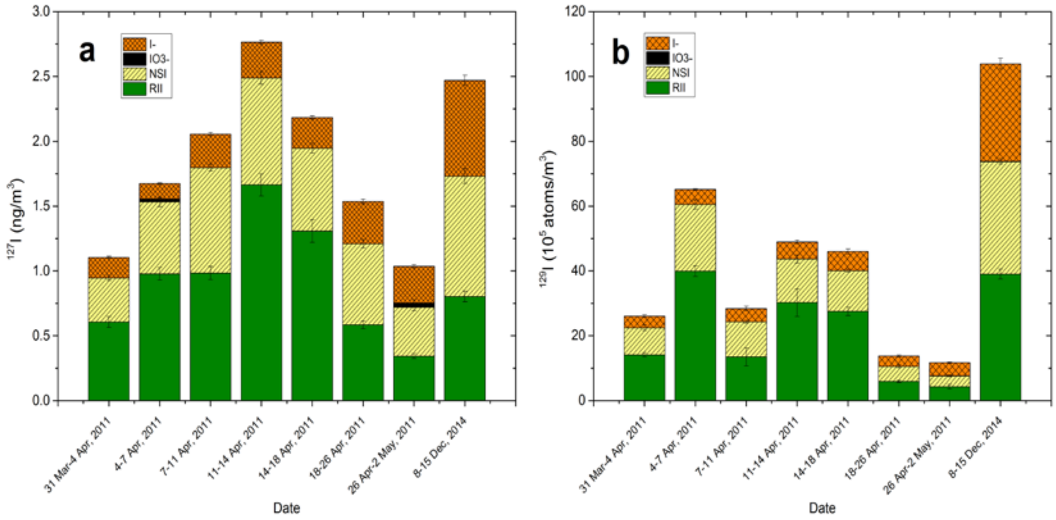
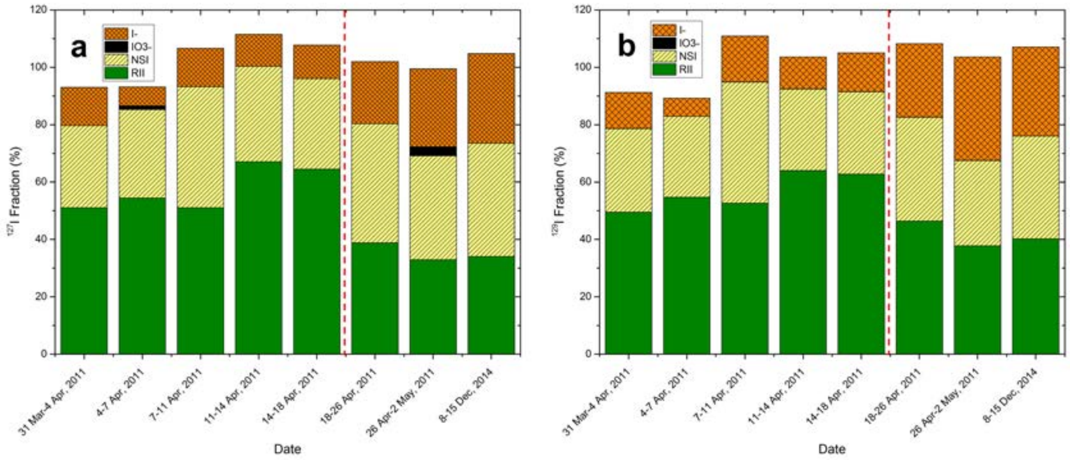


Figure 4. Concentrations of iodine species in the aerosol samples for ^{127}I (a) and ^{129}I (b), indicating that NSI and RII are major iodine species and that iodide is the dominant fraction of water-soluble iodine. Dot lines are same as those in Figure 3.



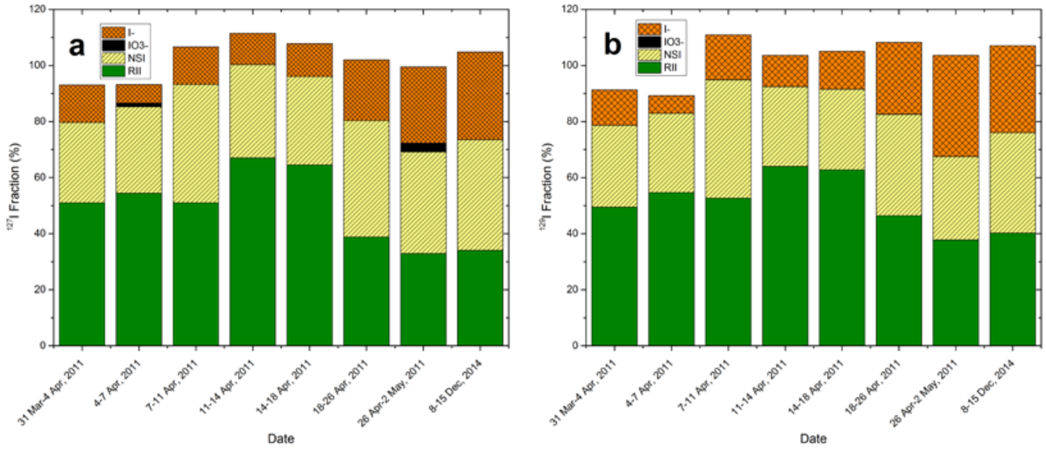


Figure 5. Distribution of iodine species in the aerosol samples for ^{127}I (a) and ^{129}I (b), compared with the measured concentrations of total ^{127}I and ^{129}I in ~~the whole~~ bulk aerosols. Dot lines are same as those in Figure 3.

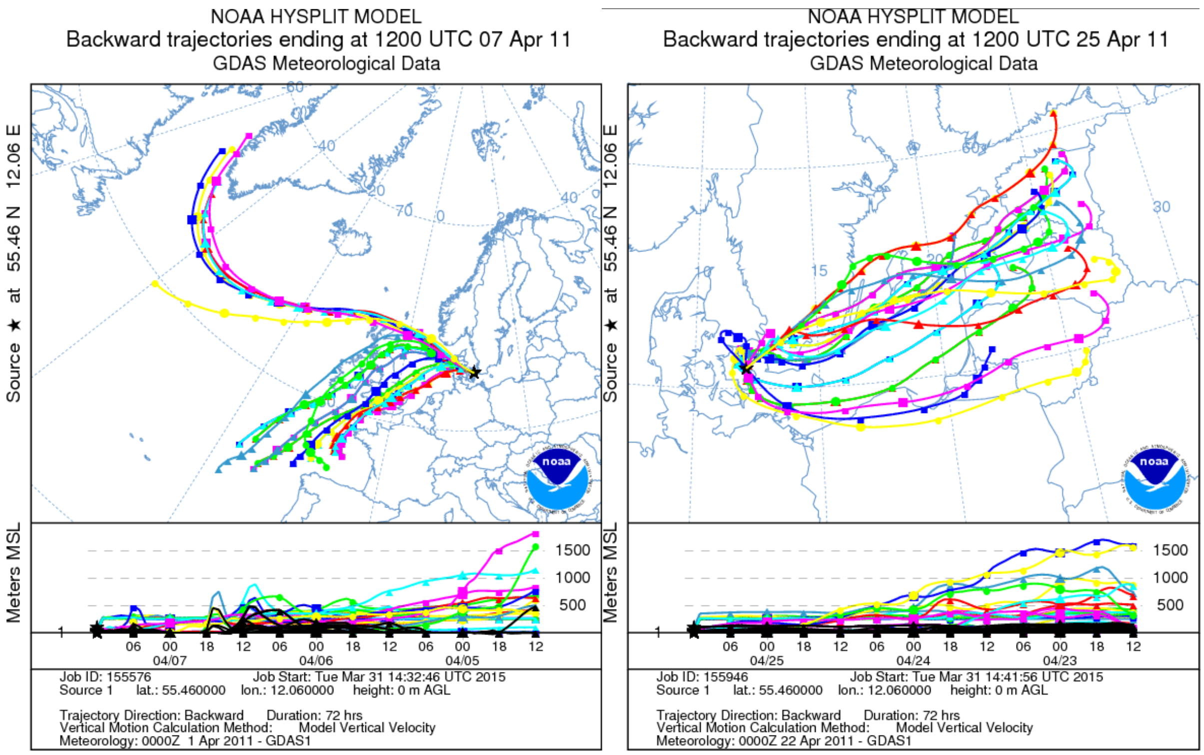
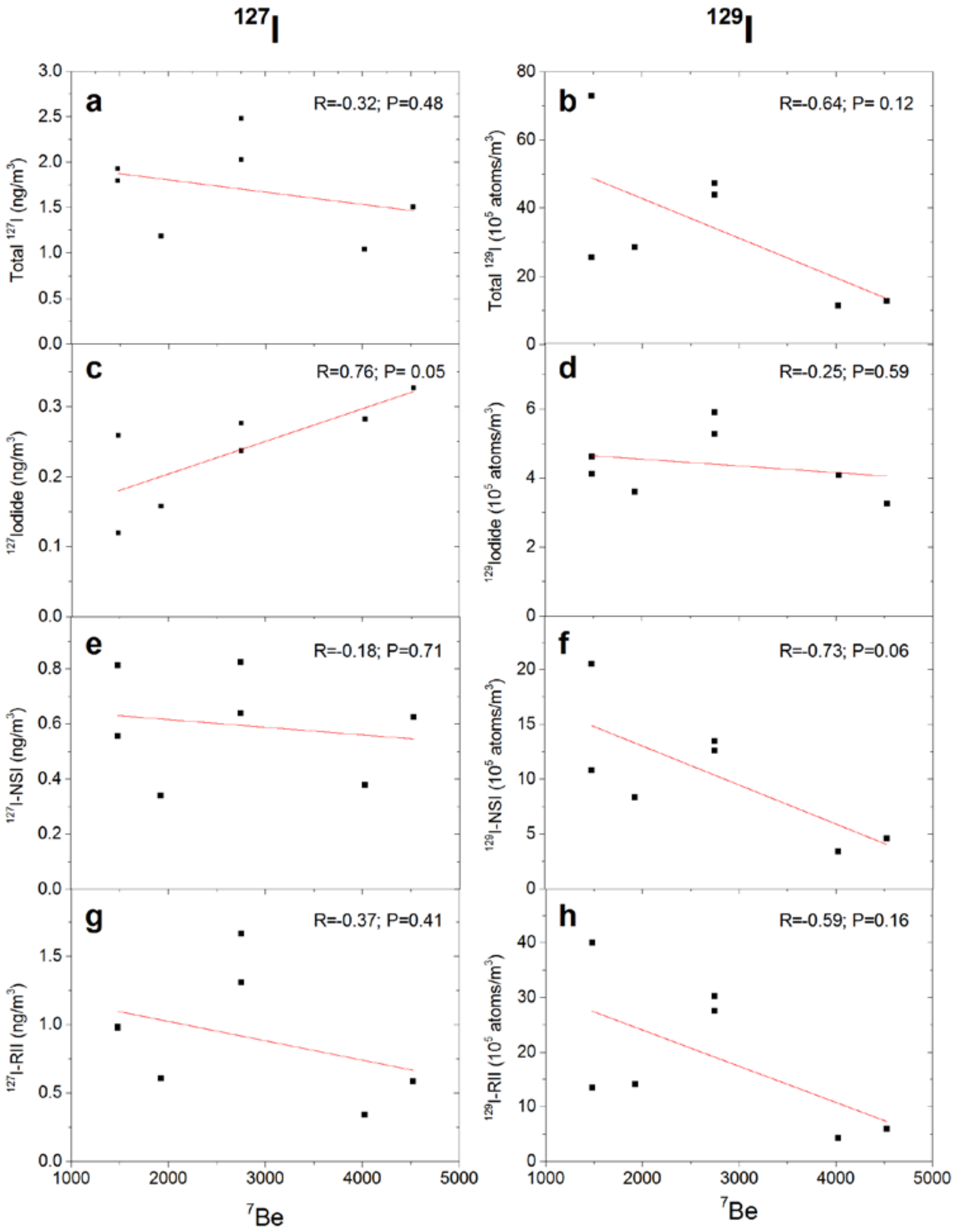


Figure 6. The 72 h (3 days) air mass back trajectories for starting altitudes of 0 m above ground level (AGL) calculated from the FNL database of the National Ocean and Atmospheric Administration (NOAA) and simulated by using the Hybrid Single-Particle Langrangian Integrated Trajectory (HY-SPLIT) model.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



~~Figure 7. Correlation of aerosol ^{7}Be with iodine species including total ^{127}I (a) and ^{129}I (b), ^{127}I^{-} (c), ^{129}I^{-} (d), NSI for ^{127}I (e) and ^{129}I (f), as well as RII for ^{127}I (g) and ^{129}I (h).~~

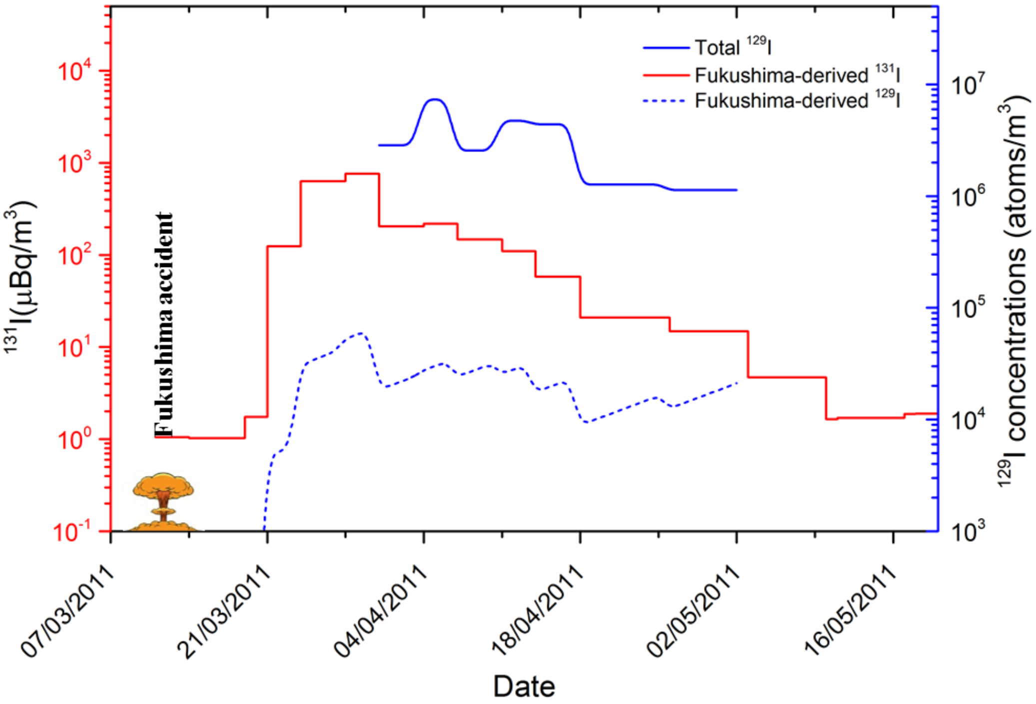


Figure ~~8~~7. ^{131}I radioactivity (red), ^{129}I concentrations (blue) in aerosols from Risø, Denmark after the Fukushima accident (Nielsen et al., 2011). The Fukushima-derived ^{129}I concentrations are calculated based on ~~an~~ ^{129}I/^{131}I atomic ratio of 16.0±2.2 deduced from Fukushima-affected aerosol samples (Xu et al., 2015).