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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Speciation of ^{127}I and ^{129}I in atmospheric aerosols at Risø, Denmark: insight into sources of iodine isotopes and their species transformations" *by* L. Y. Zhang et al.

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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 129I and 127I 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 129I 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 129I 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 129I and 127I 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 (127I) as source of so-called particle bursts of ultrafine aerosols particles in coastal regions. By implicit transferring the knowledge of 127I to 129I, the authors concluded from this that "this secondary iodine source is known to significantly increase atmospheric 129I 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 129I 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 129I 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 129I 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 129I 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 129I in the air. However, it is not the case in North Europe. Investigation of 129I in air and precipitation collected in Germany, Sweden and Denmark clearly showed that re-emission (secondary emission) of 129I in the North Sea, Kattegat and Norwegian Seas is an important source of 129I in the North Europe. Meanwhile, 129I/127I 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 ïijĹZurich, Vienna, SevilleïijĽ. 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 129I in the Danish aerosol, including 1) Combination of 129I results in this work with air mass pathways as denoted by back trajectory analysis suggests that high 129I concentration in the Danish aerosol is related to the North Sea originated air mass, rather than the NRPs originated air mass; 2) more previous 129I studies on atmospheric samples (aerosol, precipitation) from different locations are discussed, in order to explain the contribution of air releases of 129I 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 (I2) 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 129I 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. 129I concentrations should be given in units as (11.3-97.0) ×105 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 môĂĂĂ3 was about: : :" (example from 25144, line 19).

Answer: We agree with the referee that atom is not a SI unit, but a mass unit. 129I mass concentration can be expressed as atoms/m3, 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 129I in aerosol. In the literatures, 129I concentration in air samples has been expressed as atoms/m3, Bq/m3 or g/m3, 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.

Yours sincerely,

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 25139, 2015.