

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.

Anonymous Referee #3

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This work describes the measurement of stable ^{127}I and the long-lived radioisotope ^{129}I in aerosol samples collected in Denmark. By chemical treatment of the filter samples, different iodine species were investigated separately in order to study sources and formation mechanisms of iodide, iodate, NaOH-soluble iodine and residual insoluble iodine (RII). Due to the emerging interest in halogen chemistry in aerosol research, the different origins of the two iodine isotopes, which may allow the differentiation of individual sources, and the long experience of the group of Dr. Hou with this type of analysis, this work is relevant and I recommend publication in ACP. Substantial revisions will be necessary, however, before the manuscript can be accepted, mainly because of too

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speculative interpretation of the data, as already was pointed out by Reviewer 1.

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.
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.
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

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not be included in any kind of further interpretation.

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.

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

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may initiate a nucleophilic 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.

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.

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.

Technical comments:

8. "Atoms" is not a SI unit. ^{129}I concentrations should be given in units as $(11.3-97.0) \times 10^5 \text{ m}^{-3}$ (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 ^{129}I atom concentration of $97.00 \times 10^5 \text{ m}^{-3}$ was about..." (example from 25144, line 19).

9. 25140, line 16: "heavily ^{129}I -contaminated seawater" is overstated and "heavily" should be removed.

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)."

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

12. Table 2: As far as I understand, results of samples AE11-5 and 7 were already

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published earlier by Zhang et al., 2015. This needs to be indicated in the table caption.

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.

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

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

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