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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 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, I 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 μm) particles would be expected to have lifetimes shorter than 20 days.

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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, I 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, I 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, I 17 (and several other instances throughout the manuscript). Here the authors report average ^{129}I 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

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are not justified. We keep 2 significant figures and revised three values in the manuscript. In P25244 I16 and I17, the values “ 1.79 ± 0.52 ” is revised to “ 1.8 ± 0.5 ”, and “ 43.65 ± 18.88 ” to “ 44 ± 19 ”. In P25244 I16 and I17, 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 ^{129}I 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 phrase “Except for the Norwegian Sea” is revised to “Except for the Norwegian Sea and the North Sea” in the revised version.

P25148, I 4-7. Here the authors cite the relatively low terrestrial emissions of iodine as the cause of the relatively low ^{129}I 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 ^{127}I concentrations, but this does not appear to be the case. Probably more important is the low $^{129}\text{I}:^{127}\text{I}$ ratio of the terrestrial emissions, due to their distance from the western (marine) ^{129}I 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 $^{129}\text{I}/^{127}\text{I}$ 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 ^{129}I concentrations.” is revised to “Terrestrial emissions of iodine occur through vegetation and terrestrial microorganisms (Bewers and Haysom, 1974).

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Low $^{129}\text{I}/^{127}\text{I}$ 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, I 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, I 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, I 18-21. I am conññAđent that the authors' statement regarding the relative strengths of direct atmospheric and secondary marine emissions of ^{129}I 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 ^{129}I concentrations with known emissions from Le Hague and SellaññAeld, 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

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can therefore be concluded" has been deleted.

P25148, I 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, I, 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 representative of the material at ground level. I do not understand the point the authors wish to make regarding back trajectory analysis in the īñAñal 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 I23-P25149 I8).

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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 north-west 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 SO₂ source in the revised version.

P25150, l 21. “We note that relatively low WSI 129I and 127I was measured in marine sourced aerosols from the North Sea”. I agree that this appears to be the case for 127I, 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 129I and 127I 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-129I (decades) and Fukushima 129I (days), incorporation degree of 129I 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 ba-



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sis that little (<10%) ^{129}I remains after NaOH leaching. They later state that the RII fraction might be associated with “metal oxides that originated by suspension of inorganic particles”. What might these 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 have happened, 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 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 iodine with oxides, minerals."

P25152, I 20 – p25153, I 3. I struggle to understand the authors' interpretation of the relationships they found between iodine species concentrations and ^{7}Be . Although the iodide/iodate ratios of ^{127}I and ^{129}I 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 ^{129}I , then this must also be the case for ^{127}I .

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, I 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, I 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.

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P25155, I 22-24. This statement appears to be worded a little too strongly. The difference in ^{127}I 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.

Regards

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