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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Temporal variation of ^{129}I and ^{127}I in aerosols from Xi'an, China: influence of East Asian monsoon and heavy haze events" *by* Luyuan Zhang et al.

Anonymous Referee #2

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This manuscript reports the concentrations and ratios of 129-I and 127-I in aerosol samples collected over a period of approximately one year at Xi'an in China. The data are interpreted in terms of the dominant sources and transport pathways of these isotopes to the site, and the discussion considers the influence of the fluctuating modes of the East Asian Monsoon on the observed record. The subject matter is highly relevant for Atmospheric Chemistry and Physics and the authors have a track record of producing high quality data from the demanding measurements employed. However, the manuscript suffers from a number of shortcomings, including factual errors and subjective and unsupported interpretations. I think that this will be an excellent contribution once these have been addressed. There are many minor errors in the English used,

but the meaning of the manuscript is still clear.

Major comments There are numerous instances of inconsistent units being used for iodine concentrations for the Xi'an site in the Results section (line 77 onwards). In the text, the units are frequently given as micrograms per cubic metre, while in the figures and supplementary material the units are nanograms per cubic metre. Since the numbers in both cases are the same, one of the units must be incorrect. I assume that the units should actually be nanograms per cubic metre, but please check and correct.

On line 91 the authors state that "A weak correlation between 129I and 127I was found with a Pearson correlation coefficient of 0.34 (p=0.01) for the whole year data, while no significant correlation between the two iodine isotopes in each season at the level of 0.05 (Table 1 and Fig. S3)." This does not agree with the statement made in the caption to Fig S3: "Relationship between 127I and 129I, showing no significant correlation (R=0.265) between the two iodine isotopes". Why do these statements not agree? Since it is apparent from Fig S3 that the dataset is not normally distributed, I would suggest the authors use a non-parametric regression method (such as Spearman's Rank Correlation) instead of Pearson's for all regression analysis in the manuscript. This will give far more robust results. Perhaps Figure S3 might be more informative if plotted with different symbols for the time periods of interest.

I am not quite sure how the authors have used the values published in Saiz-Lopez et al., 2012 to compare to the results obtained at Xi'an. In Table 5 of Saiz-Lopez, aerosol iodine concentrations of up to 25 ng m-3 and >3.3 ng m-3 are quoted for open ocean and continental sites respectively. These do not seem to relate to the values for "terrestrial" (1 ng m-3) and "marine" (<10 ng m-3) air quoted in lines 100 & 101. The higher values in Saiz-Lopez et al. also do not give strong support to the statement in the last sentence of this paragraph (lines 102-103).

The statement about natural sources of iodine (lines 104-105) comes from a rather old source (Fuge & Johnson, 1986). While it is true that sea spray contributes iodine to the atmosphere, we now know that gas-phase emissions of iodine from the ocean are a much stronger source (see, for example, Carpenter et al., 2013 – which the authors cite later in the manuscript). Thus the study of He (2012) which apparently used sodium concentrations to estimate the seaspray contribution of iodine to precipitation at Zhouzhi county almost certainly greatly underestimated the "direct contribution of ocean". (The citation of He 2012 in the reference list does not give sufficient information for the source to be found).

In lines 114 - 118, the authors attempt to balance estimated emissions of iodine from terrestrial soil and vegetation (from Sive et al., 2007) against an estimate of iodine deposition flux. There is insufficient detail given of how this deposition flux calculation was done, but it appears to be based on "dust fall". Better explanation is required if this calculation is to be understood. Does "dust" here refer to mineral dust? If so, why should its deposition be specifically associated with the deposition of iodine? How exactly was the calculation done? The value given for the terrestrial emission flux (2.27 ug m-2 d-1) does not seem to agree with the value given by Sive et al. (2.7 ug m-2 d-1). How reliable is the comparison likely to be when the emission flux estimate is derived entirely from observations in North America, where vegetation types and land surfaces are different from the study region here?

Have the authors considered the influence of seasonal changes in boundary layer height on aerosol iodine concentrations? These could potentially be significant, and could cause changes in surface level concentrations even when emission fluxes are constant.

While I understand that the authors' estimate of the potential contribution of coal combustion to aerosol iodine loading at their study site is only intended as a first-order estimate, I do not think that they have sufficient information to attempt it. The assumption that surface iodine emissions are mixed through the entire troposphere (i.e. to 10 km) is certainly not realistic, since only a small proportion of emissions are likely to

leave the boundary layer ($\sim$1 km). This implies an order of magnitude greater iodine concentration derived from coal, which does not appear to be plausible.

Lines 221 – 222: "Two severe dust storm events occured in Xi'an in 17-18 April and 4-6 May, 2017, as shown by the peaks of air quality index (AQI) of 268 and 306, respectively (Fig. 2e)." There is only one peak in AQI visible in Fig 2e in this time period. Please explain or amend.

Please give further explanation of the significance of the "low-altitude air mass" mentioned on line 232.

On lines 250 – 254 (and later in the manuscript) the authors discuss the possibility that the aerosol iodine they observed might have formed through primary nucleation. While there are relationships between iodine concentration and those of other species associated with nucleation (e.g. SO2, Fig S6), it is also apparent that the concentration of SO2 is three orders of magnitude greater than that of aerosol iodine. There is no evidence available in this dataset that would make it possible to determine whether iodine is incorporated into aerosol in Xi'an via primary formation or secondary uptake onto existing particles. I therefore suggest that discussion of the iodine aerosol formation mechanism can only be speculation, and it would be better to remove it entirely.

In section 4.2.3 the authors make a convincing case for the influence of interactions with the East Asian Monsoon on long-range 129-I transport to the study site. I am not familiar with the EAWM index mentioned on line 303, but I wonder whether it is possible to make more use of this when exploring the variations in iodine isotope concentrations and their ratios during the study. Can it be plotted on Fig 2? The "z-score" approach discussed on lines 333 – 336 would be more convincing if it could be combined with some quantitative indicator of EAM strength.

On lines 301 – 302 it is stated that "In addition, the 129I level in March 2018 was much less than that in March 2017". This is certainly true, and in fact the 129-I concentration in March 2018 is very similar to that in the two LLP periods. Why did the authors choose to include these samples in the HLP period?

The statement on line 338 that the iodine isotope ratio shows “relatively weak fluctuation” seems rather subjective, and quite surprising given the relative standard deviation quoted for the parameter of >120%. There are strong variations in the ratio during the HLP 2 period, which do not appear to be consistent with the statement on line 339 about background levels.

Minor comments Line 61: replace “combing” with “combined”? Line 75: replace “ration” with “ratio” Line 178-179: Toyama et al. is cited both at the beginning and end of this sentence, but with different years. Please correct. Line 211: I think the correct units for ozone concentration here should be ppbv, not pptv.

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