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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.

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Interactive comment from Anonymous Referee #2: 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 iso- topes 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

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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.

Response: We thank the admirable reviewer for the positive evaluation and providing us these constructive comments. The reviewer has a very deep understanding and rich experience on iodine study area. It is also our honor to have such valuable suggestions and comments, which significantly improve the quality of this manuscript. We are in complete agreement that some interpretations are not fully supported by the current evidence, for instance, the associated mechanisms of locally released 127I and externally input 129I with particles in urban atmosphere, whether they are mainly involved into primary particle formation or scavenged by existing particles. To answer this, more research is needed in the future. Following the detailed comments, we have carefully checked throughout the content, made all English corrections and revised the manuscript. Below are our responses the comments item by item.

Major comments

1. 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.

Response: Sorry for the basic mistakes on the incorrect unit of 127I concentrations. As the reviewer commented, 127I concentrations in aerosols should be nanograms per cubic metre, not microgram per cubic metre. All the unit mistakes have been carefully checked and revised.

2. 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.

Response: According to the reviewer's comment, we use Spearman coefficient to discuss the correlation. Although 127I and 129I data are not normally distributed, Pearson and Spearman coefficients are typically identical. The inconsistency between Table 1 and Figure 3 is resulted from numbers of data used for calculation. The Pearson coefficient of 0.26 is used for all the 68 data points. It is a good idea to replot Figure S3 using different symbols. We have tried in this way as shown below. The Figure 1 below is plotted with different symbols and fitting trends for the four seasons, clearly showing the concentration distribution in different seasons. While no more information could be obtained because the previous Figure S1 and S2 (now move to the context as Figure 3 and 4, respectively) have clearly showed the information. Therefore, Figure S3 is kept as before only with a small revision by changing the Pearson correlation coefficient to Spearman coefficient.

Figure 1. Relation of 127I and 129I indicated by different symbols and trend lines for four seasons

3. 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

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"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).

Response: We agree with the reviewer that this statement and citation of Saiz-Lopez is vague. Therefore, we revise lines 100-104, and also add more data in China. This paragraph was modified as below. "The level of 127I concentrations, in particular in winter, is much higher than those in continental sites (below 0.61 ng m-3 in South Pole and 2.7-3.3 ng m-3 in the Eastern Transvaal), and comparable to those in coastal and ocean sites (typically below 20 ng m-3, and up to 24 ng m-3 in tropic marine aerosols) (Saiz-Lopez et al., 2012). A similar range of TSP 127I was observed to be 4.5-22 ng m-3 at coastal urban, Shanghai, China, showing lowest in summer and an increase occurred in fall and winter (Gao et al., 2010). Iodine associated with PM10 and PM2.5 were found to be 3.0-115 ng m-3 and 4-18 ng m-3, respectively, in urban and island sites of Shanghai, slightly lower than TSP iodine (Cheng et al., 2017; Gao et al., 2010). The maximum of marine aerosol iodine offshore China was found below 8.6 ng m-3 during the XueLong cruise from July to September 2008 (Xu et al., 2010). These results suggest a relatively high aerosol 127I level in both inland and coastal urbans in China."

4. 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).

Response: Accept. The reference "Carpenter et al., 2013" is added as "Natural iodine

is from marine emission through sea spray, weathering of base rock and continental release through vegetation and suspended soil particles (Carpenter et al., 2013; Fuge and Johnson, 1986)." Because of direct emission of gaseous iodine from sea surface, we agree that marine iodine contribution in the reference of He (2012) would be underestimated when using Na+ as reference element for calculation. In this reference, spatial distribution of iodine in rainwater and surface freshwater were also reported. Despite being underestimated, sea source contribution of iodine showed a decline trend with increasing distance from the sea until 100 km, over which no significant change of marine contribution could be found. Our study site, Xi'an, is an inland city about 900 km from the nearest sea. It is therefore not likely that marine source (including sea spray, direct volatilization and gaseous emission) is the major contribution of iodine.

5. 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?

Response: As commented by the reviewer, the dry deposition flux of 127I is not specific enough. In this manuscript, the dry deposition flux of 127I is calculated by 127I mass concentration in total suspension particles multiplying the average dust fall flux. Since it is hard to know the deposition velocity of total suspension particles, we use dustfall flux for approximate calculation. Dust in this manuscript refer to natural dust, not but

including mineral dust in air. The dustfall is collected by wet method, i.e. a 20 cm in diameter $\times$30 cm height container with enough deionized water. There are 14 sampling sites in Xi'an. The natural dustfall ranges within 4.5-47.8 t (km-1 30 d-1) with an annual mean of 13.2 t (km-1 30 d-1). According to the reference Yang et al., 2017 listed below, the annual dustfall flux in 2014 at Qujiang District, about 2km from our sampling site was 11.76$\pm$3.65 t (km-1 30 d-1). The uncertainty for the dustfall flux is 31%, and iodine concentration uncertainty is within 5%, resulting in a total uncertainty of 32%. We have given a more detailed description about this calculation in the context. Reference: Yang Wenjuan, Chen Ying, Zhao Jianqiang, et al. Spatial and temporal variation of atmospheric deposition pollution in Xi'an City. Environmental Science & Technology (in Chinese),2017,40(3):10-14. In reference Sive et al., 2007, 2.7 μg m-2 d-1 and 2.27 μg m-2 d-1 were presented in abstract and Section 5, respectively. The value of 2.7 μg m-2 d-1 just occurred in Abstract, lacking of calculation details. The average terrestrial emission flux (2.27 μg m-2 d-1) was estimated, on a global basis, over an active season of 240 days, together with biome areas for temperate forest and wood lands (28.5 $\times$1012 m2) and temperate grasslands (31.9$\times$1012 m2). Therefore, we cite the value of 2.27 μg m-2 d-1 because of its clear mathematical description. The terrestrial emission flux by Sive et al., 2007 should be much higher than that in urban environment, since a part of the urban land is covered by houses and roads without iodine emission.

6. 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.

Response: This is a very good point to consider the boundary layer height, which is closely related with air pollution, and can indicate the vertical dispersion scale of air pollutants by thermal turbulent mixing. Not only the boundary layer height (BLH), but also the atmospheric stability (AS) could directly affect the concentration and time-

space distribution of pollutants. And they might be important factors to control the variation of iodine isotopes. To be honest, at present, we have no idea about the impact. In future, we would like to make further investigation for 3-4 years to evaluate, to what extent the BLH and AS have influence on variation of iodine isotopes.

7. 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 (âĹij1 km). This implies an order of magnitude greater iodine concentration derived from coal, which does not appear to be plausible.

Response: We agree that this calculation of aerosol iodine from coal iodine is not plausible, so the following statement has been deleted. "The area of the Guanzhong Basin is 3.6×104 m2, and the height of troposphere is taking as 10 km. Then, 127I concentration in the air is about 250 ng m-3. The particle-associated iodine accounts for approximately 10%-20% (Hasegawa et al., 2017). Thus, 127I in aerosols can be estimated to be about 25-50 ng m-3. The estimated value is comparable with the 127I peak values in winter, but about ten times higher than the less polluted aerosol 127I concentrations (1.21-9.01 ng m-3)."

8. Lines 221 – 222: "Two severe dust storm events occurred 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.

Response: Thanks for pointing out this flaw. It is right that only the first dust storm in 17-18 April have been shown in Figure 2e, because no sample was analysed during the second sand storm in 4-6 May. Thus, we give the AQI values for the two events. Below is Figure 2 for the daily measurement of AQI, from which we can see two peaks

of the dust storm events. After careful thinking and for simplification, we decide to use AQI data on the days with iodine isotopes values. Thus, we have revised the statement as "Two severe dust storm events occurred in Xi'an in 17-18 April and 4-6 May, 2017, as indicated by the peaks of air quality index (AQI) of 268 and 306, respectively."

Figure 2. Temporal variation of 127I and AQI during March 2017 to March 2018, showing the correlation of 127I and AQI.

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

Response: Further explanation has been added as below. "Furthermore, the back trajectory analysis also showed that the low 129I level on April 18 can be partially attributed to an 129I-poor low-altitude air mass (< 900m) (Fig.S3a). This is because either the low-altitude air mass might be formed in 129I-poor inland areas, not from the 129I-rich European area, or long-range transported 129I in low-altitude air mass could be easily lost by the topographic countercheck (Dong et al., 2018)."

10. 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.

Response: We agree that the mechanism of iodine association with particle is not well understood on the basis of our data. Therefore, these corresponding statements in Section 4.2.2 has been removed as below. "Typically, new particle formation occurs in two distinct stages, i.e., nucleation to form a critical nucleus and subsequent growth of

the freshly nucleated particle to a larger size (Zhang et al., 2015). It is widely accepted that iodine is involved into the formation of fine particles, and increasing investigations have been carried out in coastal and open sea areas (Saiz-Lopez et al., 2012). However, in megacities with severe air pollution, the role of iodine on formation and development of heavy haze events is far not understood. Iodine-mediated particles were suggested to be formed from highly concentrated, localized pockets of iodine oxides as primary nucleation, and to rapidly grow by uptake of H2SO4, H2O, NO2, short chain dicarboxylic acids, gaseous iodine and other gaseous species (Saiz-Lopez et al., 2012). Winter urban air in Xi'an provides two requirements of sufficiently high iodine concentrations and the presence of high levels of aerosol nucleation precursors, such as SO2, NH3, amines, and anthropogenic VOCs." "In spring and summer, iodine is probably associated with primary matters and secondary organic aerosols due to low level of air iodine and greatly increased artificial and biogenic VOCs (Feng et al., 2016). In fall and winter when the key aerosol nucleation precursors are noticeably elevated, the significantly positive correlation between 127I and these precursors indicates that locally emitted iodine is likely involved into formation of secondary inorganic aerosols, while externally input 129I may not occur in the nucleation of secondary inorganic aerosols." "The minimum in ozone concentrations on 15 November and 14 December, 2017 may support iodine-containing aerosol nucleation process, in which ozone acted as oxidant and reactant to form iodine oxidizes, and aggregated into high valence iodine oxidizes (Saiz-Lopez et al., 2012). This study suggests iodine is closely related to aerosol formations, and high level of iodine likely facilitates the growth of fine particles along with major aerosol precursors particularly during haze episodes."

11. 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

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some quantitative indicator of EAM strength.

Response: When we prepare this manuscript, we have actually plotted the EAWM and EASM indexes with 129I variation as shown by Figure 3 below. It is quite interesting that the fluctuation of 129I concentrations have some close relation with these indexes. Whereas, this is our first try to link the monsoon strength with 129I variation, so that we could not understand it deeper at present. We also expect to do further work on this. Figure 3. Variation of 129I and EAWM (top) and EASM (bottom) indexes during 2017-2018 The "z-score" method gives clear indications for different monsoon stages, so Figure S8 has been moved into the manuscript as Figure 6, together with the statements.

12. 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 129I 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?

Response: We can find that the fluctuation of 129I is very large during the HLP periods, but with low concentrations down to the level same as LLP periods. In March 2018, only four data are available. Considering this period is under control of EAWM, these low values were likely as a consequence of fluctuation, and therefore categorized into the HLP period.

13. 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.

Response: Agree. The subjective statement "Both two iodine isotopes show apparently temporal changes in northwestern China, while 129I/127I ratios show relatively weak fluctuation (Fig.2c)." has been deleted.

14. 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.

Response: Line 61, “combing” has been revised to be “combined”; Line 75, “ration” has been revised to be “ratios”; Line 178-179: “Toyama et al. (2012)” at the beginning of this sentence has been revised to “Toyama et al. (2013)”, and the citation at the end of the sentence has been deleted. Line 211: We appreciate the reviewer for this unit mistake. After carefully checking the cited reference, ozone concentration here has been to revised to be ppbv.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-818/acp-2019-818-AC2-supplement.pdf

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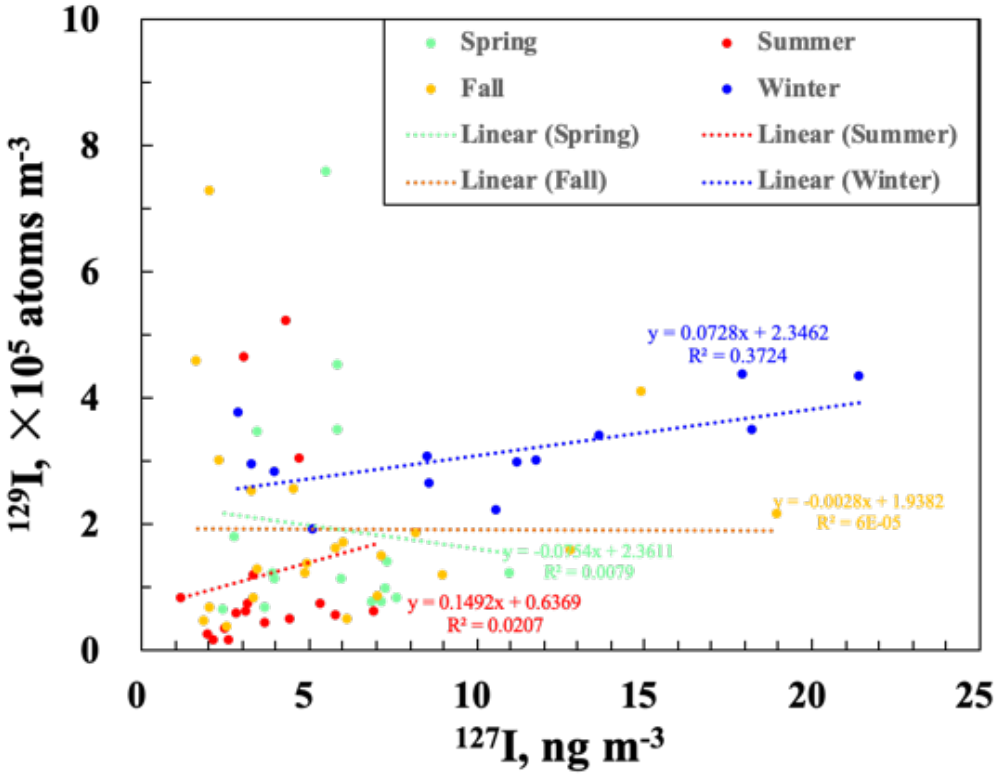

Fig. 1.

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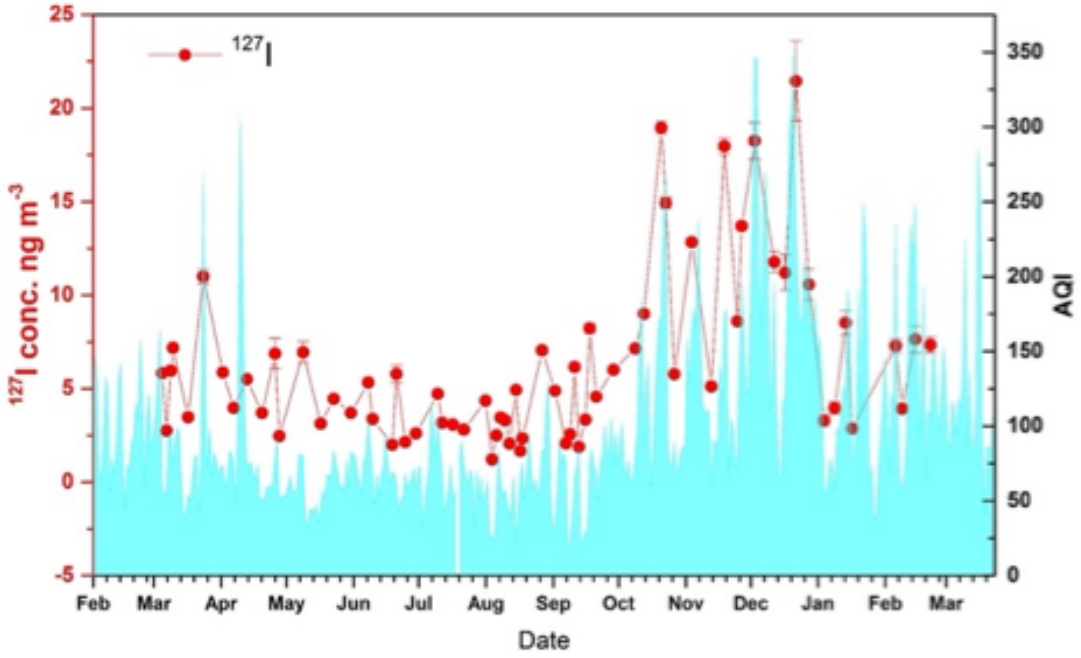

Fig. 2.

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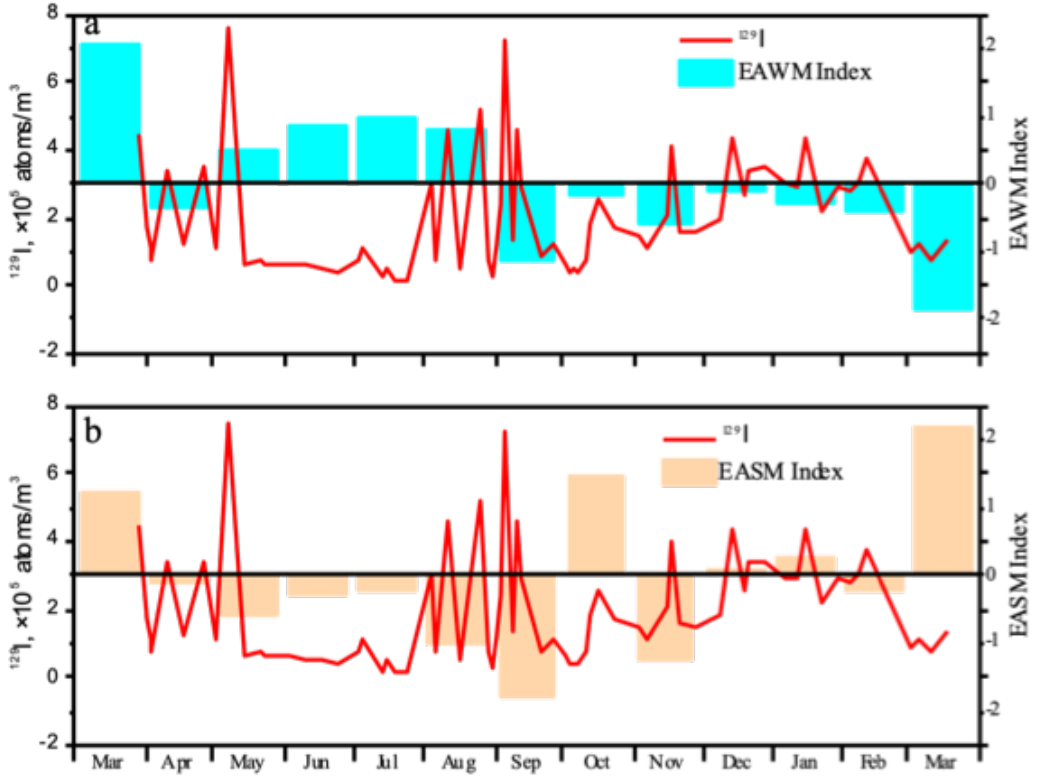

Fig. 3.

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