Biogeosciences Discuss., 10, C8342–C8348, 2014
www.biogeosciences-discuss.net/10/C8342/2014/

Interactive comment on "The 129-Iodine content of subtropical Pacific waters: impact of Fukushima and other anthropogenic ^{129}I sources" *by* T. P. Guilderson et al.

X. Hou

xiho@risoe.dtu.dk

Received and published: 29 January 2014

Page 19946, the first paragraph. The authors described that " Similar penetration depths are inferred from two 129I hydrographic profiles from April 2011: KT11-06 station A: 140.83° E, 38.4°N; and B: 143.47° E, 38.28° N (Suzuki et al., 2013). Contrary to these independent methodologies and tracer data, the 129I data of Hou et al. (2013), which were obtained from a sub-set of KOK samples, indicate penetration of 129I to densities approaching 1026.9 kgm−3 or approximately 400m (Fig. 8). Given the consistency between the Buesseler et al. (2012) cesium data and our 129I results from the same cruise, and the consistency between our 129I data and that of Suzuki et

al. (2013) we infer that there are unresolved issues with the Hou et al. (2013) 129I data at all depths." First of all, the coordinates of the cited sampling sites of reference (Suzuki 2013) is incorrect, the coordinate of sample site KT11-06 A should be 142°50'E 38°24'N. Secondly it is quite surprise that the authors compared their data with only selected two datasets out of 9 datasets of depth water profiles collected after Fukushima in Suzuki (2013), and concluded that "the consistency between our 129I data and that of Suzuki et al. (2013)" and "we infer that there are unresolved issues with the Hou et al. (2013) 129I data at all depths" without consideration of the agreement of the 129I data reported by Hou et al. (2013) with all reported ones in the surface water, and with the data at 3 sites (KH-11-07 FS1, ES2, FS2) reported in Suzuki (2013) for deep water (250-400 m). If these 3 datasets reported by Suzuki (2013) were plotted in the Fig. 8, the conclusion of <250 m penetration of Fukushima might become unsupported by the data of Suzuki (2013). The conclusion obtained in this article from such selective comparison and citation of the published data might be questionable.

Further comments:

1. The exactly same sets of data presented in this article have been reported by the same authors in JRNC (Tumey et al. 2013). The BGD article seems to be a republication of the same data set from the previous publication. This fact should be mentioned, and the focus of the present paper should be clearly identified.

2. Page 19938, Method section. A chemical procedure for separation of inorganic iodine from seawater was presented in this article, which is based on the conversion of iodide and iodate to molecular iodine and extract it to chloroform. This procedure has also been reported and used in another paper published by the same group of authors in JRNC (Tumey et al. 2013). The results from the applied procedure might be ok, but the description of the procedure might mislead the readers. The authors described that after 0.5 mg of iodine carrier was added to a 250 mL aliquot of each seawater sample. "through the addition of sodium sulfite and hydroxylamine hydrochloride, inorganic iodine was reduce to iodide." "the resulting iodide was oxidized to molecular

iodine by the addition of nitric acid and sodium nitrite." "Molecular iodine was extracted into chloroform and then back extracted into an aqueous solution of sodium sulfite and potassium hydroxide." "129I analyses were made on silver iodide precipitated by addition of silver nitrate." First of all, at pH>3, e.g. natural seawater (pH>6.5), sodium sulfite plus hydroxylamine hydrochloride could not reduce iodate to iodide. Although sodium sulfite can reduce molecular iodine to iodide at neutral pH and acidic solution, it could not reduce iodate to iodide or to molecular iodine at pH>3. Hydroxylamine hydrochloride can reduce iodate to molecular iodine at pH<3, but no at pH>3. In natural seawater, no reduction reaction of iodate will happen even both of sulfite and hydroxylamine are added. When HNO3 was first added to the solution to adjust pH<3, iodate in the seawater will be reduce to iodide by sodium sulfite, no matter if hydroxylamine hydrochloride was added. Then the addition of sodium nitrite will oxidize the formed iodide to molecular iodine at pH<2. However, if sodium nitrite was first added, which will react with sodium sulfite and hydroxylamine at pH<3, if excessive amount of sodium nitrite was added compared to sodium sulfite plus hydroxylamine hydrochloride , no reduction of iodate will occur, because sulfite and hydroxylamine will be consumed by excessive amount of nitrite. In addition, reduction of molecular iodine to iodide using sulfite to back extract iodine to aqueous phase can happen at neutral pH, i.e. addition of NaOH is not necessary. Of course for keeping iodide in the aqueous solution for a longer time after solvent extraction, addition of NaOH or ammonium might be helpful. However, the pH of the separated iodide solution has to be adjusted to pH<8 before precipitation of iodide as AgI, otherwise, when AgNO3 is added to an alkaline solution, AgOH will form, instead of AgI. If NaOH was added to the back-extraction solution, HNO3 has to be added to adjust pH<8 before AgNO3 solution is added.

3. Page 19940, line 4. "4.5E-5 Bq/m3" should be "4.5E-4 Bq/m3".

4. No 127I concentration in the investigated seawater was determined by the authors, while 129I/127I ratios in all samples were estimated, and used for comparison and discussed through the whole article. This was just based on a simple hypothesis of

homogeneous distribution of 127I in these sea water samples, no matter the sampling location and depth. Actually there are lots of reports on the 127I concentrations of seawater, including the reports cited in this article (Suzuki et al. 2013, 2019, Hou et al. 2013). All these reports showed a large variation of 127I concentrations up to 20% or even high for nearshore seawater. For simple comparison of the analytical results with others, it might be reasonable to assume a constant 127I concentration in the open seawater with similar salinity, but an incorrect conclusion might be drawn out if all discussion and conclusion of an article were based on such a simple hypothesis. If 129I analytical uncertainties are also taken into account (typically $\pm$10% at 1 sigma), the interpretation of results should be carried out with great precaution.

5. It is well known that the distribution of fallout radionuclides is not homogeneous all over the world. In general higher concentrations of weapons fallout radionuclides were observed in the middle of North Hemisphere and the lowest ones were observed in the equator and Antarctic. However, this article aims to compare the 129I data in seawater from very large areas in the Pacific from low latitude of about 20° N to middle latitude of about 45° N, and no consideration of the inhomogeneous distribution/deposition of global fallout source. In addition, it is well known that the nuclear spent fuel reprocessing plants in Europe, as well as other location have releases huge amount of 129I to the environment compared to the weapons tests and accidents in Fukushima and Chernobyl, while the authors did not consider this contribution in their estimation and discussion of the sources and origin of 129I in the Pacific Ocean. This might induce a high uncertainty on the conclusion of this article.

6. In section 4.2. 129I/137Cs and 129I/134Cs ratios of 3.9E-7 and 4.1E-7 off Fukushima were estimated using WHOI cesium data, and the estimated value was used to estimate the 129I budget. It is not clear how this was done. Which 129I data were used? Were 137Cs, 134Cs and 129I measured in the same water samples? How the contribution of the background values before Fukushima accident was subtracted?

7. Page 19944, line 13-14. The author described that "transfer times for the conversion

of volatile iodine to particulate is on the order of several weeks", but no evidence was given. How did the author get this number? Iodine chemistry in the atmosphere is very complicated, and the conversion among different species of iodine is a dynamic process, i.e. gaseous iodine might associate to particulates, but iodine associated to particulate might also release as gas form. Does any evidence show that the particulate associated iodine-131 is increased with the time when 131I was released to atmosphere as gas form?

8. Page 19944, line 18 to page 19945 Line 2. The authors estimated a 129I/134Cs activity ratio of 2.1E-6 released to the atmosphere from the Fukushima accident, which was later used to estimate the 129I budget in Section 4.4. This estimation is based on the reported average activity ratio of 131I/137Cs of 66.7 in post event aerosol and particulate data measured in Europe, and a measured atomic ratio of 129I/131I of 22.4 (11st March 2011) in Japanese soil were used. However, it has been described by the authors that most of 131I in the atmosphere (>75%) is in gas form, if only aerosol was analyzed, the 129I/134Cs ratio will be significantly underestimated by a factor of 3-4. Meanwhile, many measurements of 137Cs, 134Cs and 131I in environmental samples related to Fukushima accident have been reported, and these data were summarized in a recent published article (Thakur et al. Sci. Total Environ. 2013, 458-460, 577-613.), it showed that the reported 131I/137Cs activity ratios vary significantly from 3.3 to 350, and higher ratio from the remote locations comparing to those in the local area because of long distance dispersion of gaseous form iodine-131 compared to particulate associated radiocesium. Therefore the 129I/134Cs value estimated based on the measured average 131I/137Cs data in the Europe (far from the release site) might be unreasonable, and the induced excessive 129I level, 129I budget as well as the further discussion and conclusion on the sources and inventory of 129I in the seawater offshore Fukushima might be questionable.

9. In Figure 9a, the authors tried to construct average 129I profile from the nearshore and offshore regions of the KOK cruise. From the Fig.9, it can be seen that the con-

centrations of 129I in seawater at the same depth vary significantly from location to location, especially for the nearshore seawater profiles, it is therefore no sense to create such an average 129I profile, especially considering that only limited number of sampling sites were investigated. The further estimation of the excessive inventory of 129I based on this average distribution becomes meaningless.

10. Page 19946, Line 14. A 129I/127I atomic ratio of 2.4E-11 and 129I concentration of 0.9E-5 Bq/m3 was deduced using the 134Cs zero intercept for 134Cs data > 1.5 Bq/m3 as pre-Fukushima data of 129I in the investigated area. Numbers of pre-Fukushima samples in the investigated area have been reported including the datasets of the authors published in JRNC2013, all these data show a 129I/127I ratios higher than 3E-11 (3-6.5E-11) in most of the upper 250 m water. What is the sense to use this lower value induced from an indirect calculation?

11. Page 19947, Line 20. "Fig. 7" should be "Fig. 3b".

12. The contribution of a point source through the Columbia river to the 129I level in the seawater in the Pacific ocean along south California was estimated based on a few data of 129I in water of Columbia river collected at the site of the big Hanford nuclear reprocessing plant nearby, and the flow rate at the sampling site. The similar situation of the selective citation and use of the reported data of 129I in the river water occurred here. The reported 129I concentrations in the river water (Patton 2009) have a very large variation, (2.5+-2.1)E-6 Bq/L for 2004 and (1.6+-1.5)E-6 Bq/L for 2005 because of very high inhomogeneous distribution of 129I in the contaminated river water (See the original figure (Fig.8.4.8) in the cited reference of Patten 2009). The authors selected the highest value for their estimation, and amplified the effect of this point source. However, the other sources such as the releases from other nuclear reprocessing plants in the north hemisphere was excluded in their discussion, the conclusion from such a discussion might mislead the reader.

13. Page 19949, Line 17-21. The authors described that "The pre-anthropogenic

129I/127I of the ocean has, via the analysis of sediments and archived macrophytes, been estimated to be 1.5E-12 (Moran et al., 1998). This estimate is consistent with the deep water (sigma-t > 1027.6) results of Suzuki et al. (2013) who report ratios equivalent to 1.2E-12 (±100%) to as low as 3.5E-13 (±1000%). " It is interesting that how a value of 1.5E-12 was considered to be consistent with the value of (0.35-1.2)E-12. It is also interesting that the reported values of 129I/127I with 1000% uncertainty were used to discuss and made conclusion in this article, are such high uncertain values suitable to be used to draw a reliable conclusion?

Interactive comment on Biogeosciences Discuss., 10, 19935, 2013.