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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.

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1) Page 19951, bottom - the authors mentioned that "samples passing through Monaco since at least 1997 and continuing to present have inadvertently picked up 129I from the more common "environmental" samples with high 129I that are handled by the IAEA. Such inadvertent 129I contamination is not unprecedented (Szidat et al., 2000)." There has not been handling in the past in Monaco of any "high" 129I content samples that could make contamination problems. All samples were of environmental 129I levels, and actually an intercomparison of AMS laboratories on 129I analysis was organized in Monaco, which did not show any contamination problems (Pham et al., 2010

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– this reference is omitted in the paper of Guilderson et al.).

PHAM, M.K., BETTI, M., POVINEC, P.P., ALFIMOV, V., BIDDULPH, D., GASTAUD, J., KIESSER, W.E., LOPEZ GUTIERREZ, J.M., POSSNERT, G., SANCHEZ-CABEZA, J.A., SUZUKI, T. Certified reference material IAEA-418: 129I in Mediterranean Sea Water. Journal of Radioanalytical and Nuclear Chemistry, 286 (2010) pp. 121-127

Another possibility could be a contamination with surface water during sampling. During the IAEA'97 cruise (as well as during other cruises) 129I samples were collected from Rosette bottles, 1L for 129I and 1L for 3H analyses, well closed in glass bottles. A comparison of 3H and 129I results (see e.g., Povinec et al., 2010) did not show any inconsistencies, therefore we can rule out surface water contamination problems. Another possibility, of course, could be a contamination during sample preparation and AMS analysis. All the 129I analyses (until Fukushima samples, which were analyzed by the Tucson and Vienna AMS laboratories, for which targets were prepared by Riso lab) were done by the Isotrace laboratory of the Toronto University, which did not have any contamination problems, regularly checking for blank samples, and participating in intercomparisons. The background 129I levels were 1-2 orders of magnitude lower than the measured bottom water samples.

Therefore, if there are inconsistencies between the results discussed by Guilderson et al. and Povinec et al., 2010, they must have another origin than a contamination.

Reply to comment 1: We appreciate Dr. Povinec's comments and criticisms. The inconsistencies between the 129I data sets do pose an interpretational challenge. As we noted, the challenge with the IAEA 97 cruise 129I data is not (strictly) surface values; the 129I values across the whole of the water column appear to be anomalous. Integration of the putative excess 129I burden observed in all four profiles, relative to an estimated pre-anthropogenic background of $\sim$1.5x10-12, requires 20-30 kg of 129I (page 19951, lines 1-14). Although possible, it is difficult, given the available data in the literature, to square this anomaly with what is known regarding the production of

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129I from weapons test history.

In addition, the data sets of Povinec et al. (2000; 2010; IAEA 97) and Hou et al. (2013) for the North Pacific appear to be being used as a part of the basis for a characterization in the literature of 129I abundances in deep ocean waters; i.e., "No seawater from uncontaminated deep ocean with 129I/127I close to pre-anthropogenic level of 2 $\times$ 10$-$12 in marine environment has yet been analyzed" (Hou et al., 2013). This statement is inconsistent with the data sets presented by Suzuki et al. (2010, 2013) and our own data, which indicate low-level ($\leq$ 5x10-12) 129I at potential densities greater than 27.3 kg/m3 in the far western subtropical Pacific.

In this regard we also note that in the context of the currently available cesium data and our own 129I data, the Hou et al. (2013) data stand out as having elevated 129I values at density surfaces which do not appear to have been influenced by Fukushima-derived radionuclides at the time of the R/V KOK sampling. Visually comparing our figure 7 (cesium data of Buesseler et al., 2012) and our figure 8 clearly supports this statement.

In considering possible causes for the anomalous 129I burden implied by the IAEA 97 cruise data and the disagreements between the data sets of Povinec et al. (2000; 2010; IAEA 97) and Hou et al. (2013) and those of Suzuki et al. (2010; 2013) and our work, the following reasons lead us to hypothesize that 129I contamination of sample containers and/or the laboratory in Monaco, were common causes for the results obtained for Dr. Povinec's IAEA 97 samples and those for Hou et al.'s (2013) samples:

a) The results presented by Povinec et al. (2000; 2010) were obtained from samples that were collected for the group at Monaco. The results presented by Hou et al. (2013) were also obtained from samples that were initially collected for the group at Monaco.

b) Given the information in their respective papers, the iodine extractions from sea water and preparation of targets for Povinec et al. (2010) and Hou et al. (2013) were not done in the same locations, and were analyzed at various different AMS laboratories

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(this is supported by the Dr. Povinec's submitted comments).

c) In his comment, Dr. Povinec noted: "the background 129I levels were 1-2 orders of magnitude lower than the measured bottom water samples."

Firstly, we infer that this 'background' is distinct from the "machine background" which is reported as $\leq$2x10-14 (as described in Povinec et al., 2012), and which we infer to be simple direct precipitation of Woodward iodide. We caution that, although useful for other aspects of understanding the AMS system, a machine background is not an appropriate means to characterize matrix specific sample handling.

More importantly, as the measured bottom water samples 129I levels appear to have been $\sim$5x10-11 (figure 10 of Povinec et al., 2000), the implied backgrounds (what we interpret to be process blanks) were as high as $\sim$5x10-12, clearly indicating some source of contamination that raised the process blank 129I level to more than two orders of magnitude above the "machine background". The source and nature of this contamination is not discussed by Povinec et al. (e.g., 2000 or 2010), but we do note that many of the IAEA 97 samples appear to have been processed in Monaco.

Significantly, we note that given the relatively high process-blank background levels it is clear that the processing used by Povinec et al. (e.g., 2000; 2010) would not allow reliable measurements of deep sea water samples with 129I close to the $\sim$1.5x10-12 pre-anthropogenic levels.

d) Hou et al. (2013) reported a machine background of "around (2-4) x 10-14" and a "procedure blank" as high as 2.8 x 10-13. At about an order of magnitude above the machine background, Hou et al.'s procedure blank does indicate some level of 129I contamination, but at a level that is more than an order of magnitude below that encountered by Povinec et al. While Hou et al.'s procedure blank is sufficiently low to allow measurements at levels close to $\sim$1.5x10-12 pre-anthropogenic levels, the samples measured by Hou et al. were all from densities <1027.0, and hence would not be expected to be at levels $\leq$ 3x10-11. Thus, Hou et al.'s procedure blanks indicate

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that the processing of samples in Risø was likely not the source of the contamination that resulted in the Hou et al. samples having elevated 129I values at density surfaces which do not appear to have been influenced by Fukushima-derived radionuclides at the time of the R/V KOK sampling.

e) Since process blanks and/or instrument backgrounds do not exclude the possibility that samples were contaminated prior to extraction and analysis (i.e., during collection (sample containers), handling (splitting and subsampling), etc.), we hypothesized that there is a common original source of the 129I contamination that is upstream of the extraction labs; in this case, it would appear that the IAEA-MEL is a viable candidate for the source of the contamination. Additionally, we note that figure 9 of Povinec et al. (2000) indicates that seawater samples having 129I/127I ratios on the order of 10-8 have been handled and processed in Monaco.

f) With regards to handling elevated 129I in environmental samples, we point out that the MEL has handled significant volumes of acidified Irish Sea Water [IAEA-443, http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Radionuclides/IAEA-443/index.htm] with 129I/127I ∼10-6, six orders of magnitude above pre-anthropogenic seawater. It is common practice within the AMS community to segregate handling and preparation of high-level anthropogenic samples from low-level environmental samples. For example, most radiocarbon laboratories separate sample preparation into "natural" (14C/12C 1E-15 to 1E-12) and "tracer" (14C/12C 1E-12 to 1E-09) spaces that are completely isolated from each other. Given this, it seems reasonable to hypothesize that the IAEA-1997 and KOK data sets in Povinec [2000;2010] and Hou [2013] were compromised by contamination during handling in the IAEA-MEL.

g) We note that the Mediterranean seawater sample (IAEA-418) with a 129I content of 2.3x108 (atoms/L), 3.2x10-7 (Bq/L), or an estimated 129I/127I ratio of ∼8.1x10-10 is neither proof nor exoneration of contamination of samples that would otherwise be <1x10-11. As such the Pham et al. reference is not germane to this manuscript.

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A few suggestions:

2) The Guilderson et al. paper is treating the Pacific Ocean as a single box, not paying attention to spatial (a figure showing sampling stations is missing) and depth distribution of 129I – discussion on different water masses present in the Pacific is missing as well, generally, the oceanographic description is weak.

Reply to comment 2: Although the purpose and the focus of the paper was on the Fukushima release and not a classic tracer-oceanographic study, we agree that an expansion of the general circulation of the Pacific is useful and will be helpful for readers with less of an oceanographic background. We will rectify this by adding a separate section in Methods containing a brief overview of the circulation of the North Pacific. In this section we will also include a figure that shows the location of the other stations/data that we discuss (e.g., Suzuki et al., 2010; 2013; Povinec et al., 2010). See below figure a for an example.

3) 129I/127I ratio is sensitive on the content of stable 127I in seawater (which was not measured, and may be a source of irregularities), therefore we preferred to present results as atoms/L.

Reply to comment 3: While it is clear that iodine concentration can be quite variable in specific coastal/near-shore environments, it is also essentially certain that this is not the case for the offshore regions sampled by the R/V KOK. To the level that iodine is mostly conservative and would behave as a passive tracer (e.g., more like salinity), the salinities encountered in the sample suite from the KOK average 34.16 with a total range of 33.51 to 34.78, which would imply a limited range of iodine concentrations. Indeed, this is reflected in the iodine concentration data of Hou et al. (2013) for samples from the R/V KOK where the average concentration is 58 $\pm$ 2.6 (1-sigma sd) μg-L-1 (range of 54-62 μg-L-1). As described in our section 2, we propagated the uncertainty in the assumed iodine concentration through to the reported uncertainty of the 129I/127I. As stated at the beginning of the Results section, we have reported results

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as both activity per m3 and 129I/127I (19939 line 21-22); the 129I activity (Bq/m3) is explicitly synonymous with atoms/m3, which can be converted to atoms/L. Below, we provide a plot (figure b) consistent with figure 10 as atoms (x10E7)/L.

4) The 129I data well correlated with 3H data, except for the Bikini/Enewetak stations, where possible impact could be expected. When we look on the 3H and 129I profiles at these stations (Povinec et al., 2010) we see a fast decrease to bottom concentrations at depths of around 500 m (compared to 1000 m at other stations).

Reply to comment 4: We completely agree that the IAEA-97 cruise 3H data are consistent with other available 3H profiles from the near equatorial North West Pacific as well as other transient tracers such as CFCs (eg. WOCE P10, P04, P13). Be that as it may, the 129I results appear to be anomalous.

We present P13 (1993) tritium data as a function of potential density for a section along 165E (6N-39N) which, although collected four years prior to the IAEA 97 samples, will capture similar deep/interior large scale variability (figure c). In the interior/deep ocean currents are much slower (1-2 cm/s) than at the surface (10s of cm/s or more) and where isopycnal diffusion plays an important role in moving tracers/nutrients into the interior. The results indicate that stations between 6 and 10N the bomb-transient is confined to depths <750m (sigma_t < 27.0), stations between 10 and 20N confined to sigma t<27.2 and further north < 1500m (sigma_t < 27.5). The tracer data reinforce the sense (ie., the physical processes) of slower penetration into the waters below the gyre and underneath the equatorial thermocline. The IAEA 97 station 129I data imply bomb-transient 129I to all depths that were measured (to as deep as 5000m) and sigma_t approaching 28.

5) The relative uncertainties of 129I measurements in bottom waters are around ∼10%, sometimes even bigger. However, these are only statistical uncertainties associated with the analysis. The total uncertainties (including other sources, e.g. sampling) should be at least by a factor of 2 bigger, therefore if we take 3 sigma level as a

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meaningful value for any deviations, the uncertainties could go easily to ∼60%, what should be taken into consideration when interpreting 129I data. Generally we should have in mind that deviations in the oceanographic data which are within a factor of two do not represent any meaningful basis for specific interpretation.

Reply to comment 5: We whole-heartedly agree that representation error of samples is critical and should be considered when one has large gradients in tracer or concentration fields; e.g., in surface waters where a surface point source exists, at fronts or current boundaries, or where transport is rapid. In the interior ocean the concentration gradient of most constituents/tracers is low and the velocities are low. This is one of the reasons why comparisons of, e.g., deep-water Δ14C usually are very similar except for regions where deep ocean convection occurs. With regards to the west/central low latitude Pacific, given the pathways and timescale of deep/interior ventilation we should expect that the gradients would be low. See for example the tritium profiles composited in our discussions figure 10 and the additional figure included below, for P13 data.

6) Fig. 11:"Note that regardless of location: western subtropical North Pacific (stations 2, 3: squares) or low latitudes near Bikini/Enewetak (stations 6, 7: diamonds) that the IAEA 97 data imply a significant 129I excess at all depths". As already mentioned - St. 6 and 7 (the stations with the highest bottom 129I levels) had very specific 129I water profiles, see Povinec et al. 2010 (which cannot be seen in logarithmic scale in Fig. 11). As we can rule out possible contamination of samples, our hypothesis was that the enhanced levels could be due to the Bikini/Enewetak impact.

Reply to comment 6: We can and do believe that there could be local sources of anthropogenic/weapons-testing 129I. The challenge is that the implied excess 129I (several 10s of kg), although not impossible within the scope of uncertainty of weapons test produced 129I, is difficult to reconcile.

7) We also prefer to show 129I levels in atoms/L, and not by the 129I/127I ratio, which could be influenced by variations in the 127I content (not measured in all these sam-

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ples). Another point is that all the results should be presented with error bars, and only data outside of 3 sigma should be taken as possible deviations (having in mind again that the error bars represent only statistical uncertainties, but not the total uncertainties).

Reply to comment 7: The reviewer makes a valid point regarding the representation of error bars in the figures. For the revised manuscript we will include error bars on the figures. We reiterate the point that the (1-sigma sd) uncertainty in the assumed iodine concentration is included in the error analysis.

8) Text: The authors make several times a reference to the paper Povinec et al., 2012, however this reference is absent in the reference list. P.P. Povinec, R. Breier, L. Coppola, M. Groening, C. Jeandel, A.J.T. Jull, W.E. Kieser, S.-H. Lee, L. Liong Wee Kwong, U. Morgenstern, Y.-H. Park, Z. Top. Tracing of water masses using a multi isotope approach in the southern Indian Ocean. Earth and Planetary Science Letters, Volume 302, Issues 1–2, 1 February 2011, Pages 14-26. This paper is also important as it shows much lower 129I levels in the southern Pacific Ocean than in the northern one (thus ruling out possible "contamination problems in the Monaco laboratory"), and also because it discusses 129I levels in subsurface waters influenced by different water currents.

Reply to comment 8: We thank the reviewer for pointing out this inconsistency; 2012 is not the correct year for the paper being cited. The citations in the manuscript should refer to Povinec et al. (2010), in which IAEA-97 Stations 2, 3, 6, and 7 data were graphically presented together. We note that IAEA-97 stations 6 and 7 were initially graphically presented in Povinec et al., 2000 (figure 10, NIM-B, 172, 672-678) and the four stations (2, 3, 6 and 7) were published together in the 2010 reference. We will update the reference list to include this first presentation of the IAEA-97 station data.

The data presented in Povinec et al. (2011), from a 1999 cruise in the Crozet Basin of the South Indian Ocean, are interesting. However, the values reported do not ef-

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fectively support or deny the possibility of 129I contamination during collection or subsequent handling of the IAEA-97 samples (collected two years prior). While 129I distributions in regions remote from sources other than atmospheric weapons testing are expected to be similar to bomb tritium distributions (e.g., our figure 10), we note that the results reported by Povinec et al. (2011) imply waters in the Crozet Basin which do not contain measurable amounts of tritium (stations 3 and 7) have elevated 129I levels; ∼3.9x106 atoms/L (∼1x10-11), which is about an order of magnitude higher than the pre-anthropogenic level of ∼1.5 x 10-12.

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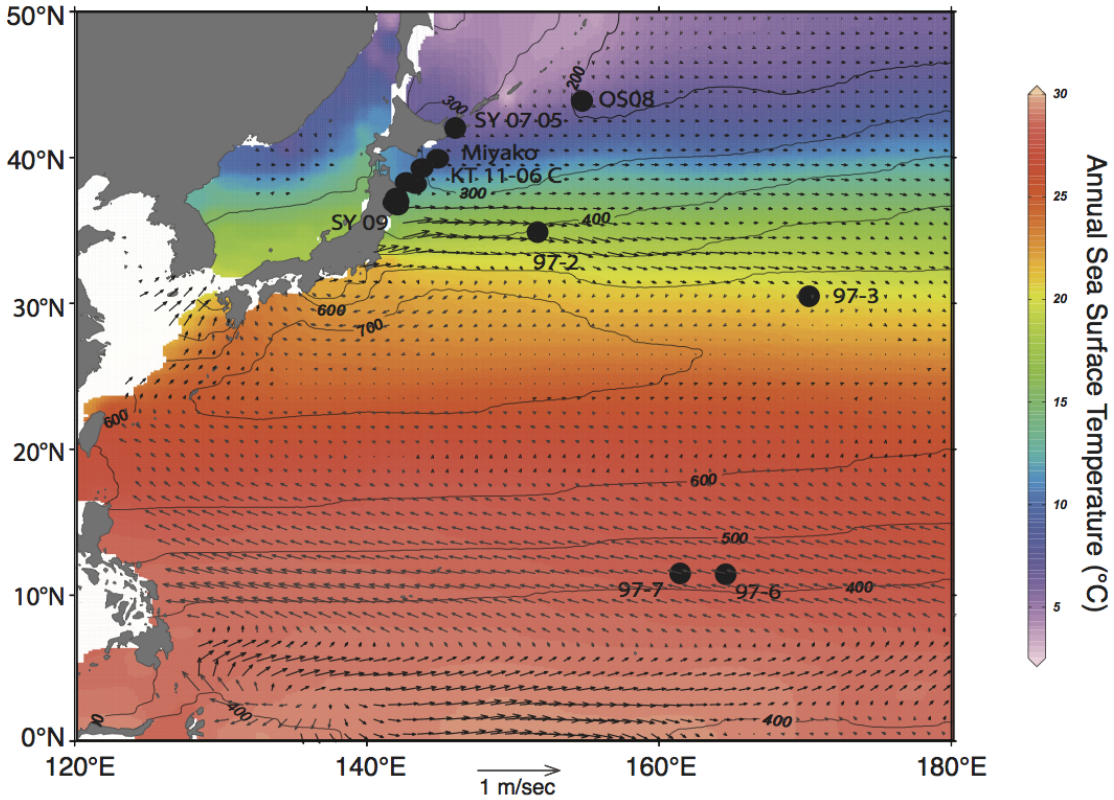

Fig. 1.

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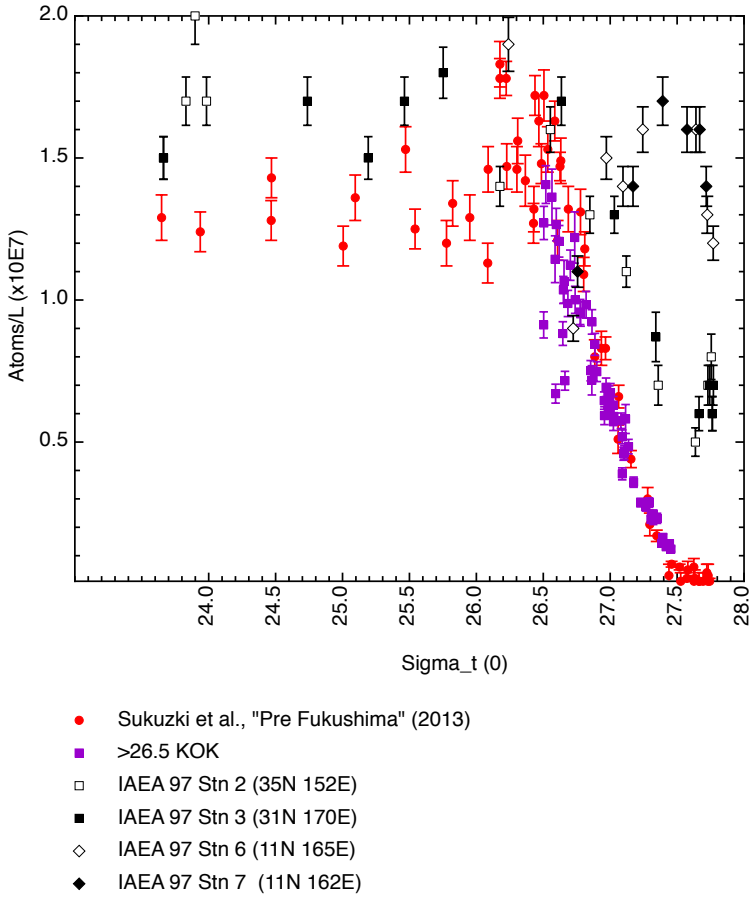

Fig. 2.

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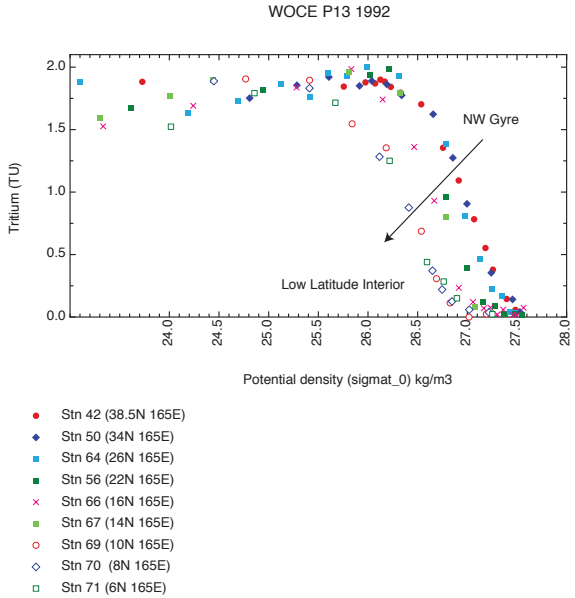

Fig. 3.

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