

## ***Interactive comment on “A novel inter-comparison of nutrient analysis at sea: recommendations to enhance comparability of open ocean nutrient data” by Triona McGrath et al.***

### **Anonymous Referee #3**

Received and published: 9 June 2018

Review results of “A novel inter-comparison of nutrient analysis at sea: recommendations to enhance comparability of open ocean nutrient data” by McGrath et al.

In this paper, the authors reported the results, findings and lessons learned from a rare opportunity in which two independent nutrient analysis teams participated jointly in a deep ocean hydro graphic section A02. The reviewer completely agree with motivations of the authors to improve comparability of oceanic nutrients data and respect their effort as shown in this article. It is however that there are many issues which should be re-evaluated, re-calculated, re-check the fact about availability of CRMs, the treatment of certified values with uncertainty, comparison between measure value and certified

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value and way of Z-scor calculation as stated below, the reviewer judges and request the authors to do major revision.

The major points:

Line 226-224 An Z score of 2 from QUASIMEME criteria is “acceptable” (line 231) in this article but the reviewer think that this criteria is not for deep ocean and Z-scor should be calculated using uncertainty of certification stated as  $K=2$  for CRMs, not use Total error as the authors did in this article. In terms of SI tractability, we need to think about uncertainty of certified value. (Quasimeme criteria; the data is “satisfactory” if people do produce within a z of  $\pm 2$  at a taken proportional error of 6% and above that a constant error(offset) of e.g. 0.05umol/l for NO<sub>3</sub>) In coastal waters the variety can be large, like in the North Sea, it is however not at all comparable with open Ocean waters. If the reviewer calculates the max and minimum offset line within  $z=2$  from Quasimeme for e.g. TOxN at the level of CD 5.5uM with the 6% prop error and the extra 0.05uM constant error the reviewer get a total error of  $(5.5 \cdot 6\% / 100\%) + (0.5 \cdot 0.05) = 0.355uM$  multiplied with 2 becomes  $\pm 0.71uM$ . So the limits are  $5.5 \pm 0.71 = 4.79$  up to  $6.21uM$  which give the level of “acceptance” if we use equation 2 for open ocean waters. The reviewer thinks that “4.79 up to 6.21uM” range is too big to accept for research at open oceans. If we use 2% as proportional error the limits will be:  $(5.5 \cdot 2 / 100) + (0.5 \cdot 0.05) \cdot 2 = \pm 0.27uM$ . Therefore we need to discuss our “satisfactory” level based on reality of variability of nutrients concentration in open water environment and capability of reproducibility of nutrients measurements.. Therefore the reviewer asks the authors to revise this section to fit open water environment.

In addition, in line 231 z-score within 2 is mentioned as being “accepted” however Quasimeme use the term “satisfactory”, see attachment page 9.(Round AQ1 2014-1) (and for the errors used page 13 Round 70 data).

Line311-313, Table 3 The reviewer found serious mistake about the certified value treatment. The certified concentration of KANSO CRMs are stated in micro mol kg-1,

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not micro mol L<sup>-1</sup>, because in SI we need to use mol and kg. In Line 312 and table 3, Certified values are stated in micro mol L<sup>-1</sup> but the concentrations in table 3 are same as certified values stated in micro mol kg<sup>-1</sup>. This mistake leads the authors about 2.5 % differences when the authors convert micro mol L<sup>-1</sup> to micro mol kg<sup>-1</sup> or micro mol kg<sup>-1</sup> to micro mol L<sup>-1</sup> using density of sample seawater or CRMs as appropriately. Please be careful that density of seawater depends sea water temperature and salinity as stated in TEOS10 ([http://www.go-ship.org/Manual/TEOS-10\\_Manual\\_06Jul10.pdf](http://www.go-ship.org/Manual/TEOS-10_Manual_06Jul10.pdf)).

Line330-366 The conclusion of the discussion in this article is good stated as “This firmly supports the recommendations of Hydes et al. (2010) concerning the importance of understanding and evaluating the best fit for an individual CFA system.” It is however, the discussion here is not clear for the reviewer. Therefore the authors re-organize discussion here based on a view point of simple linearity/fitting method problem as discusses in current GO-SHIP nutrients manual.

Line 523-524 The authors stated that there is no low CRM available around the detection limit, but this is not true. Nutrients CRMs by KANSO, SCOR-JAMSTEC CRM and NMIJ CRMs all cover full range of nutrients concentration. There is batch BY(2015), SCOR-JAMSTC batch CE(2016, <http://www.jamstec.go.jp/scor/available.html>) and NMIJ CRM 7601a ( [https://www.nmij.jp/english/service/C/crmlist\\_E\\_20180418.pdf](https://www.nmij.jp/english/service/C/crmlist_E_20180418.pdf)) with all values close to detection.

Line 431-443 The authors stated that one of the key findings in this study is the need for using two (or more) reference materials for nutrient analysis that covers the range of the expected nutrients for the survey. Hydes et al. (2010) already recommends the use of CRMs to improve the comparability of the global ocean nutrient data set, and that a minimum of three reference material solutions (low, mid and top range) should be used at regular intervals during a cruise to detect non-linearity. It is obvious that we need to use at least three concentration levels CRMs from low, mid and high range. Theoretically two point CRM use is not enough as the authors faced in thier experiments. Therefore the authors reconsider this statement and should say more

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appropriately about use of CRM.

Line 486-496 The authors stated that we should mention a criteria for nutrients concentration in the GO-SHIP manual like other parameters. The reviewer agree with this, but before that all should state uncertainty with measured value using appropriate way and scientists need to study about magnitude of natural variability of nutrients concentration. After that our community can get good number of the criteria as appropriately.

Line 523-524 The authors stated that there is no low CRM available around the detection limit, but this is not true. Nutrients CRMs by KANSO, SCOR-JAMSTEC CRM and NMIJ CRMs all cover full range of nutrients concentration. There is batch BY(2015), SCOR-JAMSTEC batch CE(2016, <http://www.jamstec.go.jp/scor/available.html>) and NMIJ CRM 7601a ( [https://www.nmij.jp/english/service/C/crmlist\\_E\\_20180418.pdf](https://www.nmij.jp/english/service/C/crmlist_E_20180418.pdf)) with all values close to detection.

Line 524-535 The reviewer observes that this part is a kind of conclusion or recommendation, therefore it might better to put conclusion/recommendation section

Minor points:

Page21 Table 5 In table 5, actually measured values for CRM CD and BW are in general high compared with certified values and they will be more close to the certified values if divided by approximately a density of 1.024 to convert from micro mol L-1 to micro mol kg-1. Also look at comment above.

Line 202-241 Procedure to prepare daily standards and treatment of blank value are unclear for the reviewer. Therefore it might better to add schematic diagram how the authors prepare daily working standards.

End of review.

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