

## Response to Referee #2

I would like to thank the referee for the appraisal of the discussion paper and the useful comments. My reply (in black) to the comments (in blue) is given below.

This manuscript presents important insights into oxygen triple isotope calculations and should be published. However, the manuscript needs significant revision to clarify the message and strengthen the conclusions. In addition, I believe that there are important lessons presented in this paper that are relevant to the broader tracer community. However, as written, the manuscript is inaccessible to those outside of the oxygen isotope community. Therefore, I strongly suggest that the author consider clarifying and reorganizing the manuscript to make it more accessible.

Concerns: My primary concern is that the author attempts to present too many peripheral conclusions making the argument non-linear and difficult to follow. It is easy for the reader to get lost in the tangential arguments which are not relevant to the primary conclusions of the paper. I suggest that the author determine the 2 or 3 main points that he wishes to convey and lay out the manuscript so as to strongly and linearly convey these conclusions. For example, I would suggest that the author edit sections 3 and 4 to present a linear derivation of the most relevant equations.

I believe that the manuscript is organised in a logical fashion. It starts out with a general introduction (Sect. 1) and an explanation of terminology and units (Sect. 2), followed by a systematic (linear) development of the mathematical framework, going from "respiration only" to "production only", "production and respiration", "steady-state between production and respiration" and "production, respiration and gas exchange" (Sect. 3). This carries on in Sect. 4 where the mathematical framework is applied specifically to the calculation of gross production below the mixed layer and within the mixed layer, at steady-state conditions and at non-steady state conditions. In Sect. 5, the necessary input parameters for the calculation are reviewed and critically discussed. Finally, in Sect. 6, the systematic uncertainty in the calculation due to input parameters and calculation method are explored using synthetic data as well as an example taken from the literature (Reuer et al. 2007).

All of the arguments I am using are relevant for the paper, i.e. they all deal with the "Consistent calculation of aquatic gross production from oxygen triple isotope measurements". The referee does not identify any of the arguments deemed to be "tangential", so that I cannot be more specific in my reply.

Referee #1 agrees that the manuscript offers "valuable insights not only for the isotope experts in this field, but also for the beginner and/or non-isotope communities who require another on-site observation method to evaluate both net and gross productivities in aquatic ecosystems."

On page 4021, the author introduces four equations for  $17\Delta$ . One of the main points of the manuscript is that these equations are functionally different and that calculations must therefore be done in a consistent manner to avoid significant error. However, the author never directly compares all four of these equations. Furthermore, in the conclusions, the author writes: "It is not important which  $17\Delta$  definition is chosen – any single one will do, provided all calculations are performed consistently" While the last half of this statement is strongly supported in the manuscript, the author never demonstrates that the choice of  $17\Delta$  definition is not important. On the contrary, in several cases he shows one equation or another to be inadequate.

The statement that it is not important which  $^{17}\Delta$  definition is chosen as long all calculations are done consistently is correct. Where I am showing that one equation or another

are inadequate, this is always in the context of a calculation that is mathematically inconsistent, be it because different  $^{17}\Delta$  definitions were adopted or be it because approximations were made. It is important to realise that the definitions used for  $^{17}\Delta$  are not only different in their functional relationship between  $^{17}\delta$  and  $^{18}\delta$ , but also in the coefficients and the reference material used (Air-O<sub>2</sub>, VSMOW, VPDB-CO<sub>2</sub>, the so-called terrestrial fractionation line, etc.). It is therefore impossible to compare them all and, as the paper demonstrates, it is also irrelevant to compare them because all calculations can be done (more consistently) using  $^{17}\delta$  and  $^{18}\delta$  alone. However, the  $^{17}\Delta$  definitions are important when it comes to comparing of data from different studies that have used different definitions. This applies not only in the context of oxygen gross production calculations, but is a general problem in the field of triple isotope measurements. Because of the existing confusion, we have convened an IUPAC Task Group that is looking into the "Terminology and definition of quantities related to the isotope distribution in elements with more than two stable isotopes" (<http://www.iupac.org/web/ins/2009-046-2-200>).

The author presents a large range of  $f$  and  $g$  values in section 6 but focuses only on the oceanic range. The conclusions made in this section are only valid for the more limited oceanic range and providing the larger range is therefore confusing. If the author believes that a range of  $f = -0.1$  to  $+0.4$  and  $g = 0.01$  to  $0.1$  [sic] is the pertinent range, then this is what should be presented and the extended range can be given as a supplemental figure. If the entire range is of interest than the conclusions need to be modified.

As explained on p. 4037, l. 4, I focus on production in the marine mixed layer because this is the region where the oxygen triple isotope technique has found the widest application. Therefore, Sect. 6 also concentrates on this region and the range of  $f$  and  $g$  values commonly encountered here, but is not restricted to it (see, for example, p. 4043 and 4044). It would also appear to be rather inconvenient for the reader to split off part of the figure into a supplement when everything can be presented clearly in a single figure. Moreover, there may well be conditions that correspond to  $f$  and  $g$  values outside the identified oceanographically most relevant range, for example in coastal regions. This has been highlighted by the work of Prokopenko et al. who used the oxygen triple isotope technique to estimate oxygen gross production during a bloom in the coastal Bering Sea (*Geophys. Res. Lett.*, doi:10.1029/2011GL047652, in press, <http://www.agu.org/journals/pip/gl/2011GL047652-pip.pdf>). Prokopenko et al. found  $f$  values from 0 to 1 and  $g$  values  $> 1$ , outside the typical range of  $-0.4 < f < 0.4$  and  $0.01 < g < 1$  identified here. My conclusions clearly identify the range to which they pertain and therefore do not need to be modified.

I suggest adding a table with all of the variables and assumptions used throughout the paper that the reader could use as a guide.

An overview with the variables and parameters with their measured or assumed values is given in Tables 2 and 3. The Conclusions also summarise which parameters are needed for the calculation of gross production using oxygen triple isotopes.

Page 4018 line 13 "measurements to determine in production" should be "measurements in determining production"

This is correct.

On page 4018 lines 19 - 29: Here the author refers to the "different equations of  $^{17}\Delta$ " and "certain parameters". While these are discussed in detail later in the paper, it would be helpful to provide the reader more information in the Introduction.

I have chosen this vague language because the general reader does not have sufficient background knowledge at this point to fully understand the meaning of the different definitions and parameters. As the referee points out, these are discussed at the appropriate place later in the paper. For the purposes of the introduction, it is sufficient to say that there are different definitions in use and that certain parameters have to be chosen. The expert reader will know what these are. Introducing them at this place would make the introduction unnecessarily long.

Page 4020 lines 12 - 24: I suggest shortening this section to one sentence containing the relevant information.

This paper is also meant to serve as an introduction for novices and non-isotope experts to gross productivity calculation using oxygen triple isotopes. Referee #1 agrees that it is suitable for this purpose. Removing the relevant definitions would be counterproductive.

Page 4021 lines 17 – 22: If both  $\kappa$  and  $\lambda$  are the “expected mass-dependent isotope fractionation” then for simplicity and clarity in this paper I would suggest using the same symbol (ie standardize equations 4 -7 to use the same nomenclature).

For the reasons stated by the referee (simplicity and clarity) I have chosen to distinguish between the coefficient used in Eq. (4) ( $\kappa$ ) and the coefficient used in the other equations ( $\lambda$ ). Using the same symbol would make the discussion in the rest of the paper more difficult to follow. The use of different symbols also serves to remind the reader that they are only 'meant to reflect the “expected” mass-dependent isotope fractionation'. Actually, the choice of their values is entirely arbitrary. There is no single mass-dependent fractionation relationship and the corresponding equations merely represent definitions.

Section 2.3: The issue of “per meg” terminology is a non sequitur and tangential to the primary argument. I suggest removing it here and on page 4049 lines 8 – 11.

The paper deals with the "Consistent calculation of aquatic gross production from oxygen triple isotope measurements". "Consistent calculation" includes the use of symbols that are in agreement with international metrological recommendations. The symbol "per meg" used in the context of oxygen triple isotope measurements in H<sub>2</sub>O and O<sub>2</sub> is not agreement with these recommendations and I therefore favour the use of "ppm" to abbreviate the value 10<sup>-6</sup>. However, since "per meg" has been used in a number of prior publications, I think it is adequate to justify this decision.

Figure 1: I suggest adding the other  $^{17}\Delta$  equations to this figure.

It would be confusing to show the results for other  $^{17}\Delta$  definitions in this figure, since I am only discussing  $^{17}\Delta^\dagger$  and  $^{17}\Delta^\#$  with  $\kappa = \lambda = 0.5179$  in the main text (p. 4029 and p. 4039). There are an infinite number of  $^{17}\Delta$  definitions and I fail to see the point in showing more than the two that are actually relevant for the paper in this figure.

Page 4032 lines 8-9: state which equations are being referred to.

I am referring to Eq. (28), as stated two lines above (l. 6).

Equation 42 + 43: these equations appear to be missing a ‘c’ on the right hand side of the equation.

This is correct. Thank you pointing out this error, which was also mentioned by the other referee and which I failed to see in the galley proofs.

Page 4035 lines 6-8: It appears that the author is stating here that  $^{17}\Delta\#$  definition is not appropriate, this is in contradiction to pg 4049 line 2.

There is no contradiction here. The paragraph on p. 4035 refers to approximate calculations using only triple isotope excess values. If the calculations are done consistently and take the underlying  $^{17}\delta$  and  $^{18}\delta$  values into account, then it is indeed irrelevant which definition is chosen for the triple isotope excess, as correctly stated on p. 4049.

Page 4035 lines 16-17: Since the iterative approach has frequently been used to estimate gross oxygen production, it might be nice to demonstrate with a figure that the iterative approach and equation 48 give the same answer.

Iterative approach and Eq. (48) are mathematically identical, so the corresponding results would not show up on a figure. Besides the mathematical formulation, the choice of parameters is critically important. The iterative approach and Eq. (48) only agree for the same set of parameters. The red lines in Fig. 3 compare results from iterative calculations to the base case and show that the different iterative calculations give different answers and also differ from the base case because their underlying parameters differ (see Table 3 for the list of parameters used).

Page 4038 lines 10-12: I suggest that the author contact Helman et al to determine which definition of  $^{17}\text{O}$  they used.

The  $^{17}\epsilon_p$  value is actually not very sensitive to the assumed definition of the triple isotope excess during photosynthesis. Using  $\lambda = 0.501$  or  $\lambda = 0.531$  instead of  $\lambda = 0.518$  would change  $^{17}\epsilon_p$  by less 0.01 ‰. See also the response to the following comment.

Page 4039 lines 6-10: I suggest that the author contact Luz and Barkan for the  $^{17}\delta$  and  $^{18}\delta$  values presented in their paper.

Before submitting the Discussions paper, I contacted Boaz Luz about this and the preceding issue and learnt that I was not the only one asking these questions and that he decided to write a short paper on the subject, together with Eugeni Barkan. Their short paper will combine published information with new data. I would like to think that it might well resolve the systematic uncertainty of 30 ppm in the  $^{17}\Delta_p$  value.