

# 1 **Commentary on: Consistent calculation of aquatic gross** 2 **production from oxygen triple isotope measurements**

3 **D. P. Nicholson<sup>1</sup>**

4 [1]{Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic  
5 Institution, Woods Hole, Massachusetts}

6 Correspondence to: D.P. Nicholson (dnicholson@whoi.edu)

## 7 8 **Abstract**

9 Kaiser (2011) has introduced an improved method for calculating gross productivity from the  
10 triple isotopic composition of dissolved oxygen in aquatic systems. His equation avoids  
11 approximations of previous methodologies, and also accounts for additional physical  
12 processes such as kinetic fractionation during invasion and evasion at the air-sea interface.  
13 However, when comparing his new approach to previous methods, Kaiser inconsistently  
14 defines the biological end-member with the result of overestimating the degree to which the  
15 various approaches of previous studies diverge. In particular, for his base case, Kaiser assigns  
16 a <sup>17</sup>O excess to the product of photosynthesis that is too low, resulting in his result being  
17 ~30% too high when compared to previous equations. When this is corrected, I find that  
18 Kaiser's equations are consistent with all previous study methodologies within about ± 20%  
19 for realistic conditions of metabolic balance (*f*) and gross productivity (*g*). A methodological  
20 bias of ± 20% is of similar magnitude to current uncertainty in the wind-speed dependence of  
21 the air-sea gas transfer velocity, *k*, which directly impacts calculated gross productivity rates  
22 as well. While previous results could and should be revisited and corrected using the  
23 proposed improved equations, the magnitude of such corrections may be much less than  
24 implied by Kaiser.

## 25 **1 Introduction**

26 In the manuscript "Consistent calculation of aquatic gross production from oxygen  
27 triple isotope measurements" Kaiser derives exact equations for calculating gross oxygen  
28 production (GOP) from the triple oxygen isotopic composition of dissolved oxygen (<sup>17</sup>Δ).  
29 The derived equations improve upon previous methods of calculating GOP in that they avoid  
30 approximations and account for additional processes such as kinetic fractionation during air-

1 sea evasion and invasion of oxygen. These new equations and similar results of Prokopenko  
2 et al. (in press), provide improved methodology that should be applied to future studies that  
3 interpret triple oxygen isotopic composition of dissolved oxygen in seawater.

4 However, in comparing the results of these new equations to previous methods of  
5 calculating GOP, I believe Kaiser has misinterpreted previous results with the consequence of  
6 overstating the difference between various previous methods of calculating GOP (e.g.  
7 Kaiser's Fig 3). Since differing definitions of  $^{17}\text{O}$  excess are used, I repeat here definitions 4  
8 and 7 from Kaiser (2011)

$$9 \quad {}^{17}\Delta^\dagger = {}^{17}\delta - \kappa {}^{18}\delta \quad (1)$$

$$10 \quad {}^{17}\Delta^\# = \ln(1 + {}^{17}\delta) - \lambda \ln(1 + {}^{18}\delta) \quad (2)$$

11 where  $\kappa$  and  $\lambda$  are mass dependent fractionation slopes. For Kaiser's 'base case', both are  
12 assigned the observed slope for a  $\ln(1+{}^{18}\delta)$  vs  $\ln(1+{}^{17}\delta)$  plot for dark respiration of  $\gamma_R =$   
13 0.5179 (Luz and Barkan, 2005).

14 The crux of the discrepancy is in the assumptions Kaiser uses to calculate the relation  
15 between  ${}^{17}\delta_P$  and  ${}^{18}\delta_P$ , where the subscript 'P' refers to dissolved oxygen produced by  
16 photosynthesis. In his 'base case' used for comparison of methods, Kaiser uses Eqn. (2) by  
17 assuming a  ${}^{17}\Delta_P^\# (\lambda = 0.518) = 249$  ppm where 249 ppm is the biological end-member value  
18 reported by Luz and Barkan (2000). I will argue that the 249 must be applied instead to  
19 oxygen in biological steady state with seawater ( ${}^{17}\Delta_{S0}$ ) which is influenced by photosynthesis  
20 and respiration, rather than  ${}^{17}\Delta_P$  in order for consistent comparison between calculation  
21 methods. I introduce the notation  ${}^{17}\Delta_{S0}$  to refer specifically to the biological steady-state  
22 condition in which  $P = R$  (and thus  $f = 0$ , where  $f$  is the net to gross production ratio).  ${}^{17}\Delta_{S0}$  is  
23 distinctly different than  ${}^{17}\Delta_P$  as noted by Kaiser, because  ${}^{17}\Delta_P$  is the pure photosynthetic  
24 product, while  ${}^{17}\Delta_{S0}$  is a balance of  $P$  and  $R$ . The 249 ppm value published by Luz and  
25 Barkan (2000) was a measure of  ${}^{17}\Delta_{S0}$  and not  ${}^{17}\Delta_P$  because the original experiment measured  
26 dissolved oxygen in a terrarium experiment which was in biological steady state ( $P \approx R$ ). For  
27 a system in biological steady state, it has been demonstrated that the appropriate slope ( $\lambda_{BSS}$ )  
28 for relating the composition of  ${}^{17}\Delta_{S0}$  and  ${}^{17}\Delta_P$  is systematically less than  $\gamma_R$  (Angert et al.,  
29 2003). In the following sections I will describe how  ${}^{17}\delta_P$  and  ${}^{18}\delta_P$  should have been defined  
30 using a slope of  $\lambda_{BSS} = 0.5154$  instead of  $\gamma_R$ . With this correction, Kaiser's 'base case' value

1 can be corrected from  $^{17}\Delta_P^\dagger=180$  to  $^{17}\Delta_P^\dagger = 238$  ppm (see Section 3) and the discrepancy  
2 between the calculation methods of earlier studies and the new method proposed by Kaiser  
3 becomes much smaller.

4 I will focus my comments on this aspect of the manuscript and stress that I am not  
5 questioning the validity of the equations derived by Kaiser et al., but rather how he has  
6 interpreted previous results and measurements in order to fairly compare GOP from previous  
7 calculation methods to the proposed new equations. To communicate the difference between  
8 previous methodology and the proposed method, it is important to clarify the relative roles of  
9 (1) Measured physical parameters used in calculations, such as  $^{17}\delta$  and  $^{18}\delta$  and fractionation  
10 factors  $^{18}\epsilon_R$  and (2) The accuracy of various equations under varying conditions of metabolic  
11 balance ( $f$ ) and productivity ( $g$ ) when the same physical parameters are used.

## 12 **2 Biological steady state**

13 Understanding the distinction between composition of photosynthetic oxygen (P) and  
14 oxygen in biological steady-state (S) and is essential to the following discussion.  
15 Photosynthetic oxygen is produced from seawater with only a very small fractionation  
16 ( $\sim 0.5\%$ ) and thus has a  $^{18}\delta_P$  near that of VSMOW (Kaiser's base case is  $^{18}\delta_P = -22.835\%$ )  
17 (Eisenstadt et al., 2010). Biological steady-state refers to the composition of oxygen reached  
18 with a constant rate of photosynthesis and respiration (see Kaiser Sect. 3.4). For the special  
19 case where  $P = R$ , I use the subscript 'S0'. Angert et al. (2003) described the relationship  
20 between  $^*\delta_P$  and  $^*\delta_{S0}$  using the mass balance equation

$$21 \quad P(1 + ^*\delta_P) = ^*\alpha_R R(1 + ^*\delta_{S0}) \quad \text{where } P = R \quad (3)$$

22 where '\*' indicates 17 or 18 and  $\alpha_R$  is the fractionation factor for respiration. Since average  
23 ocean  $\alpha_R$  is 0.980 ( $^{18}\alpha_R = 1 + ^{18}\epsilon_R = -20\%$ ) (Kidson et al., 1993),  $^*\delta_{S0}$  is much closer to 0‰  
24 (with air as the standard) than to  $^*\delta_{VSMOW}$ .

25 Inferring  $^{17}\Delta_P$  from an observed  $^{17}\Delta_{S0}$  involves extrapolating across a large difference  
26 in  $^{18}\delta$  and thus large error can be introduced if an incorrect mass dependent slope is used (Luz  
27 and Barkan, 2005) causing  $^{17}\Delta_P$  and  $^{17}\Delta_{S0}$  to differ significantly unless an appropriate 'tuned'  
28 definition is used. Angert et al. (2003) demonstrated that  $^{17}\Delta_P$  equals  $^{17}\Delta_{S0}$  when the  
29 following definition is used

$${}^{17}\Delta^{BSS} = \ln(1 + {}^{17}\delta) - \lambda_{BSS} \ln(1 + {}^{18}\delta) \quad (4)$$

The slope ( $\lambda_{BSS}$ ) that satisfies the criteria that  ${}^{17}\Delta_P^{BSS} = {}^{17}\Delta_{S0}^{BSS}$  depends on the magnitude of fractionation during respiration such that

$$\lambda_{BSS} = \frac{\ln({}^{17}\alpha_R)}{\ln({}^{18}\alpha_R)} = \frac{\ln(1 + \gamma_R {}^{18}\epsilon_R)}{\ln({}^{18}\epsilon_R)} \quad (5)$$

Thus, for  ${}^{18}\epsilon_R = -20\text{‰}$  and  $\gamma_R = 0.5179$  I calculate  $\lambda_{BSS} = 0.5154$ . Additionally, assuming an error in  ${}^{18}\epsilon_R$  of  $\pm 2\text{‰}$  the *difference* between  $\gamma_R$  and  $\lambda_{BSS}$  is very well constrained ( $\gamma_R - \lambda_{BSS} = 2.5 \times 10^{-3} \pm 2.5 \times 10^{-4}$ ).

For the above definition, the same  ${}^{17}\Delta^{BSS}$  should be acquired whether measuring the direct product of photosynthesis or a system in biological steady-state ( ${}^{17}\Delta_{S0}^{BSS} = {}^{17}\Delta_P^{BSS}$ ). The experimental determination of the biological end-member by Luz and Barkan (2000), ( ${}^{17}\Delta_{bio} = 249 \pm 15$  ppm) was a measurement of dissolved oxygen in biological steady-state with seawater ( $P \approx R$ ) and thus its composition relative to seawater should be governed by Eqn. (4). (Angert et al., 2003; Luz and Barkan, 2000). A more precise definition of the original approximate equation for calculating  $g$  (Luz and Barkan, 2000) should then be

$$g = \frac{P}{kC_{sat}} = \frac{{}^{17}\Delta^{\#} - {}^{17}\Delta_{sat}^{\#}}{{}^{17}\Delta^{BSS} - {}^{17}\Delta^{\#}} \quad (6)$$

### 3 Consistent comparison of equations used to calculate $g$

Equation (6) for calculating  $g$  uses  ${}^{17}\Delta^{BSS}$  as the biological end member, while both the iterative equation (Hendricks et al., 2004) and Kaiser's equation use  ${}^{17}\delta_P$  and  ${}^{18}\delta_P$ . To consistently compare the skill of such equations relative to each other, Eqn. (4) and  $\lambda_{BSS}$  must be used to relate  ${}^{17}\delta_P$  to  ${}^{17}\Delta^{BSS}$ . However for the default case, Kaiser calculates values for  ${}^{17}\delta_P = -11.646\text{‰}$  and  ${}^{18}\delta_P = -22.835\text{‰}$  (Kaiser Table 2) by applying the equation for  ${}^{17}\Delta^{\#}$  (Eqn. 2) rather than  ${}^{17}\Delta^{BSS}$  (Eqn. 4), effectively underestimating the  ${}^{17}\text{O}$  excess of photosynthetically produced oxygen. The implied  ${}^{17}\Delta^{BSS}$  from Kaiser's 'base case' scenario using Eqn. (4) is 191 ppm rather than 249 ppm.

Using Eqns. (4) and (5) instead with values of  ${}^{17}\Delta^{BSS} = 249$  ppm,  ${}^{18}\delta_P = -22.835\text{‰}$ ,  $\gamma_R = 0.5179$  and  ${}^{18}\epsilon_R = -20\text{‰}$ , I calculate  ${}^{17}\delta_P = -11.588\text{‰}$ . Using  ${}^{17}\delta_P = -11.588\text{‰}$  in Eqn. (1)

1 yields  $^{17}\Delta^{\dagger}(\kappa = 0.5179) = 238$  ppm rather than 180 ppm as reported by Kaiser. Thus if the  
2 value of 249 ppm is used for  $^{17}\Delta^{BSS}$  in Eqn. (5), then the comparable  $^{17}\delta_P$  for an equivalent  
3 calculation using Kaiser's Eqn. 48 should be  $-11.588\%$  not  $-11.646\%$ . This correction has a  
4 significant impact when comparing various equations (Hendricks et al., 2004; Luz and  
5 Barkan, 2000, 2005; Miller, 2002) that have previously been used to calculate  $g$  and  $^{17}\Delta$  to  
6 the equation derived by Kaiser.

7 Based on the changes I describe, I illustrate the importance of the suggested correction  
8 by recalculating figures 3a and 3b from Kaiser (2011). In addition to the results presented by  
9 Kaiser, I have added two green lines to the plot that show the error induced by the choice of  
10 equation form alone (Fig 1). For these two cases,  $^{17}\text{O}$  excess is calculated using the 'base  
11 case' values from Kaiser except with  $^{17}\delta_P = -11.588\%$  as described above. Using the  
12 approximate Eqn. (6) results in an error no greater than about  $-25\%$  at the extremely  
13 heterotrophic conditions (Fig 1a) and  $40\%$  at very high production rates (Fig 1b). Under more  
14 typical conditions ( $-0.1 < f < 0.4$  and  $0.01 < g < 1$ ) the error is less than  $\sim 10\%$ . Using the  
15 iterative method of Hendricks et al. (2004), the bias is much less still, overestimating  $g$  by less  
16 than  $5\%$  under all conditions. The  $\sim 5\%$  overestimate is caused primarily by the kinetic  
17 fractionating effects during gas exchange (i.e.  $\varepsilon_I$  and  $\varepsilon_E$ ) which are accounted for by Kaiser  
18 but not by earlier equations.

19 The red and black lines are calculated from Kaiser Table 3 data except for one  
20 correction: In column 6 showing results of Juranek and Quay (2010) the  $\gamma_R$  value should be  
21  $0.5205$  (not  $0.518$ ) because the relationship  $^{17}\alpha_R = (^{18}\alpha_R)^{\lambda}$  was used, similarly to Hendricks et  
22 al. (2004) and Reuer et. al. (2007). In Kaiser's Figure 3, relative error for many of the  
23 methods clusters around  $-30\%$  for  $f \sim 0$  (Kaiser Fig 3a) and  $g \sim 0.5$ . Although notation varied,  
24 each study using an iterative approach defined the composition of  $^{17}\delta_P$  using a  $\lambda_{BSS}$  slope  $\approx 2.5$   
25  $\times 10^{-3}$  less than the implied respiratory fractionation slope ( $\gamma_R$ ) as described by Eqn 4. Thus,  
26 despite taking various approaches, each previous study has calculated  $g$  in a manner that is  
27 accurate to within about  $20\%$  for the relevant environmental conditions. The more precise  
28 equation introduced by Kaiser and Prokopenko is superior to previous methods and should be  
29 applied to future studies, however much care should be taken in any attempt to 'reinterpret'  
30 previous results.

1 Effectively, Kaiser has compared previous equations with a  $^{17}\Delta^{BSS} = 249$  ppm to his  
2 equation using  $^{17}\Delta^{BSS} = 191$  ppm (the  $^{17}\Delta^{BSS}$  value for Kaiser's 'base case' values). This  
3 difference is responsible for the majority of the apparent discrepancy between methods. The  
4 significantly lower  $^{17}\Delta^{BSS}$  of 191 ppm is why Kaiser's calculations yield  $g \sim 30\%$  higher than  
5 most other calculation methods (Kaiser Fig. 3). After correcting Kaiser's 'base case' with  
6  $^{17}\delta_p = -11.588\text{‰}$  (and thus  $^{17}\Delta^{BSS} = 249$  ppm), the remaining differences have clear  
7 explanations. Variations in the slope  $\lambda$  from the base case cause an error dependent on  $f$  where  
8 slopes greater than the base case causing an overestimate under strongly autotrophic  
9 conditions ( $f > 0$ ) and underestimate for heterotrophic conditions ( $f < 0$ ) (Fig 1a). If a lower  
10 gas exchange end-member ( $^{17}\Delta_{sat}$ ) is used,  $g$  is overestimated, particularly for low values of  $g$   
11 (Fig 1b). Neglecting kinetic fractionation during gas exchange causes iterative methods to be  
12 slightly too high. When regressing the results of Reuer et al. (2007), Kaiser arrives at a result  
13  $\sim 40\%$  higher than Reuer (Kaiser Fig. 4). I find that about 30% of the discrepancy is due to  
14 the difference in implied  $^{17}\Delta^{BSS}$  while the remaining difference is due to how the gas exchange  
15 end member was parameterized.

#### 16 **4 Inconsistent estimates of the biological end member**

17 In the above section, I argue that  $^{17}\Delta^{BSS} = 249$  ppm is consistent with  $^{17}\delta_p = -11.588$   
18 and  $^{18}\delta_p = -22.835$ . However, as noted by Kaiser, previous studies provide results that often  
19 imply conflicting values for the biological end member of photosynthetically produced  
20 dissolved oxygen. Both the biological end member and atmospheric equilibrium end member  
21 should be redetermined. An important point is that a new value for  $^{17}\Delta^{BSS}$  would effect all  
22 equations almost equally without changing the *relative* error between equations or  
23 significantly altering the results shown in Fig 1.

24 While the  $^{18}\delta$  and  $^{17}\delta$  associated with  $249 \pm 15$  ppm were not reported by Luz and  
25 Barkan (2000), it is possible to reinterpret these results using some reasonable guesses. The  
26 commonly used value of  $249 \pm 15$  ppm (Luz and Barkan, 2000) was determined by measuring  
27 dissolved oxygen in biological steady state with seawater for *Nannochloropsis* ( $244 \pm 20$  ppm)  
28 and the coral *Acropora* with its symbiotic algae ( $252 \pm 5$  ppm). However as Kaiser points out,  
29 these values were calculated using an outdated definition of  $^{17}\text{O}$  excess ( $^{17}\Delta^+ (\kappa = 0.521)$ ). I  
30 recalculate the  $^{17}\text{O}$  excess assuming the values of  $^{18}\epsilon_R = -20\text{‰}$  and  $\lambda_R = 0.5179$  for

1 *Nannochloropsis* and  $^{18}\epsilon_R = -13.8\text{‰}$  and  $\lambda_R = 0.519$  for *Acropa* (Luz and Barkan, 2005).  
 2 Values for *Acropa* were measured, while we assign the ‘base case’ values for  
 3 *Nannochloropsis*. The bio-steady state  $^{18}\delta_{S0}$  for each case is estimated from Eqn. (3). When  
 4 recalculated using Eqn. (4) these values are equivalent to  $^{17}\Delta^{BSS} = 231$  ppm and  $^{17}\Delta^{BSS} = 234$   
 5 ppm for *Nannochloropsis* and *Acropa*, respectively. The true  $^{17}\Delta^{BSS}$  therefore is likely  
 6 somewhat lower than the commonly used value of 249 ppm but significantly higher than the  
 7  $^{17}\Delta^{BSS} = 191$  ppm implied by Kaiser’s base case values.

## 8 **5 Conclusions**

9 Since the introduction of the triple isotopic composition of dissolved oxygen was  
 10 introduced as a tracer of gross oxygen production by Luz and Barkan (2000), the  
 11 methodology for calculating  $g$  from measured isotopic ratios has evolved and improved.  
 12 While improved equations will better estimates of  $g$ , perhaps the greater cause of error is in  
 13 analytically determining what the accurate and appropriate photosynthetic and gas exchange  
 14 end members should be ( $^{17}\delta_P$ ,  $^{18}\delta_P$ ,  $^{17}\delta_{sat}$  and  $^{18}\delta_{sat}$ ).

15 When applying an equation to calculate  $g$  that requires  $^{17}\delta_P$  in the calculation, it is  
 16 essential to set  $^{17}\delta_P$  using the slope  $\lambda_{BSS}$  and Eqn. (4). If when remeasured 249 ppm turns out  
 17 to be the correct value for  $^{17}\Delta^{BSS}$  then the  $g$  calculated by Kaiser for the ‘base case’ scenario is  
 18 ~30% too high. If, as suggested in Section 4, the true  $^{17}\Delta^{BSS}$  falls somewhere between 191  
 19 ppm (as implied by Kaiser’s base case) and 249 ppm (as used by previous studies), the  
 20 estimates of  $g$  provided by Kaiser would need to be revised downward by somewhat less than  
 21 30% while  $g$  from previous studies would need to be revised slightly upwards.

## 22 **Appendix A: Derivation for biological steady-state**

23 The following derivation is adapted from Angert et al. (2003) and shows the relationship  
 24 between  $\lambda_{BSS}$  and  $\gamma_R$  for a  $P = R$  steady-state system.

25 The slope  $\lambda_{BSS}$  is defined as the slope for which  $^{17}\Delta_P^{BSS} = ^{17}\Delta_{S0}^{BSS}$  so that from Eqn (4),

$$26 \quad ^{17}\Delta^{BSS} = \ln(1 + ^{17}\delta_{S0}) - \lambda_{BSS} \ln(1 + ^{18}\delta_{S0}) = \ln(1 + ^{17}\delta_P) - \lambda_{BSS} \ln(1 + ^{18}\delta_P) \quad (A1)$$

27 Which can be rearranged to

$$1 \quad \lambda_{BSS} = \frac{\ln\left(\frac{1 + {}^{17}\delta_P}{1 + {}^{17}\delta_{S0}}\right)}{\ln\left(\frac{1 + {}^{18}\delta_P}{1 + {}^{18}\delta_{S0}}\right)} \quad (A2)$$

2 Noting that when  $P = R$ , Eqn. (3) simplifies to

$$3 \quad (1 + {}^*\delta_P) = {}^*\alpha_R (1 + {}^*\delta_{S0}) \quad (A3)$$

4 Substituting (A3) into (A2) and noting  ${}^{17}\varepsilon_R = \gamma_R {}^{18}\varepsilon_R$  and  $1 + {}^*\varepsilon_R = {}^*\alpha_R$  yields  $\lambda_{BSS}$  as  
 5 described in Eqn. (5)

$$6 \quad \lambda_{BSS} = \frac{\ln({}^{17}\alpha_R)}{\ln({}^{18}\alpha_R)} = \frac{\ln(1 + \gamma_R {}^{18}\varepsilon_R)}{\ln({}^{18}\varepsilon_R)} \quad (A4)$$

## 7 **Acknowledgements**

8 This work was funded by the NOAA Global Carbon Cycle Program (NA 100AR4310093).

9 The author would like to thank Rachel Stanley and Maria Prokopenko for helpful discussions.



## 1 **References**

- 2 Angert, A., Rachmilevitch, S., Barkan, E. and Luz, B.: Effects of photorespiration, the  
3 cytochrome pathway, and the alternative pathway on the triple isotopic composition of  
4 atmospheric O<sub>2</sub>, *Global Biogeochem. Cycles*, 17(1), 1030, doi:10.1029/2002GB001933,  
5 2003.
- 6 Eisenstadt, D., Barkan, E., Luz, B. and Kaplan, A.: Enrichment of oxygen heavy isotopes  
7 during photosynthesis in phytoplankton, *Photosynth. Res.*, 103(2), 97-103,  
8 doi:10.1007/s11120-009-9518-z, 2010.
- 9 Hendricks, M. B., Bender, M. L. and Barnett, B. A.: Net and gross O<sub>2</sub> production in the  
10 southern ocean from measurements of biological O<sub>2</sub> saturation and its triple isotope  
11 composition, *Deep-Sea Res., Part I*, 51(11), 1541-1561, 2004.
- 12 Juranek, L. W. and Quay, P. D.: In vitro and in situ gross primary and net community  
13 production in the North Pacific Subtropical Gyre using labeled and natural abundance  
14 isotopes of dissolved O<sub>2</sub>, *Global Biogeochem. Cycles*, 19, GB3009,  
15 doi:10.1029/2004GB002384, 2005.
- 16 Juranek, L. W. and Quay, P. D.: Basin-wide photosynthetic production rates in the subtropical  
17 and tropical Pacific Ocean determined from dissolved oxygen isotope ratio  
18 measurements, *Global Biogeochem. Cycles*, 24, GB2006, doi:201010.1029/2009GB003492,  
19 2010.
- 20 Kiddon, J., Bender, M. L., Orchardo, J., Caron, D. A., Goldman, J. C. and Dennett, M.:  
21 Isotopic fractionation of oxygen by respiring marine organisms, *Global Biogeochem. Cycles*,  
22 7(3), 679-694, 1993.
- 23 Luz, B. and Barkan, E.: Assessment of oceanic productivity with the triple-isotope  
24 composition of dissolved oxygen, *Science*, 288(5473), 2028-2031,  
25 doi:10.1126/science.288.5473.2028, 2000.
- 26 Luz, B. and Barkan, E.: The isotopic ratios <sup>17</sup>O/<sup>16</sup>O and <sup>18</sup>O/<sup>16</sup>O in molecular oxygen and their  
27 significance in biogeochemistry, *Geochim. Cosmochim. Acta*, 69(5), 1099-1110,  
28 doi:10.1016/j.gca.2004.09.001, 2005.
- 29 Miller, M. F.: Isotopic fractionation and the quantification of <sup>17</sup>O anomalies in the oxygen  
30 three-isotope system: an appraisal and geochemical significance, *Geochim. Cosmochim.*  
31 *Acta*, 66(11), 1881-1889, doi:10.1016/S0016-7037(02)00832-3, 2002.
- 32 Prokopenko, M. G., Pauluis, O. M., Granger, J. and Yeung, L. Y.: Exact evaluation of gross  
33 photosynthetic production from the oxygen triple-isotope composition of O<sub>2</sub>: implications for  
34 the net-to-gross primary production ratios, *Geophys. Res. Lett.*, doi:2011GL047652, 2011.
- 35 Quay, P. D., Karl, D. M., Peacock, C. and Bjorkman, K. M.: Measuring primary production  
36 rates in the ocean: differences between incubation, non-incubation and satellite based methods  
37 at Stn ALOHA, *Global Biogeochem. Cycles*, doi:10.1029/2009GB003665, 2010.

1 Reuer, M. K., Barnett, B. A., Bender, M. L., Falkowski, P. G. and Hendricks, M. B.: New  
2 estimates of Southern Ocean biological production rates from O<sub>2</sub>/Ar ratios and the triple  
3 isotope composition of O<sub>2</sub>, *Deep-Sea Res., Part I*, 54(6), 951-974,  
4 doi:10.1016/j.dsr.2007.02.007, 2007.

5 Sarma, V. V. S. S., Abe, O., Hashimoto, S., Hinuma, A. and Saino, T.: Seasonal variations in  
6 triple oxygen isotopes and gross oxygen production in the Sagami Bay, Central Japan,  
7 *Limnol. Oceanogr.*, 50(2), 544-552, 2005.

8

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21

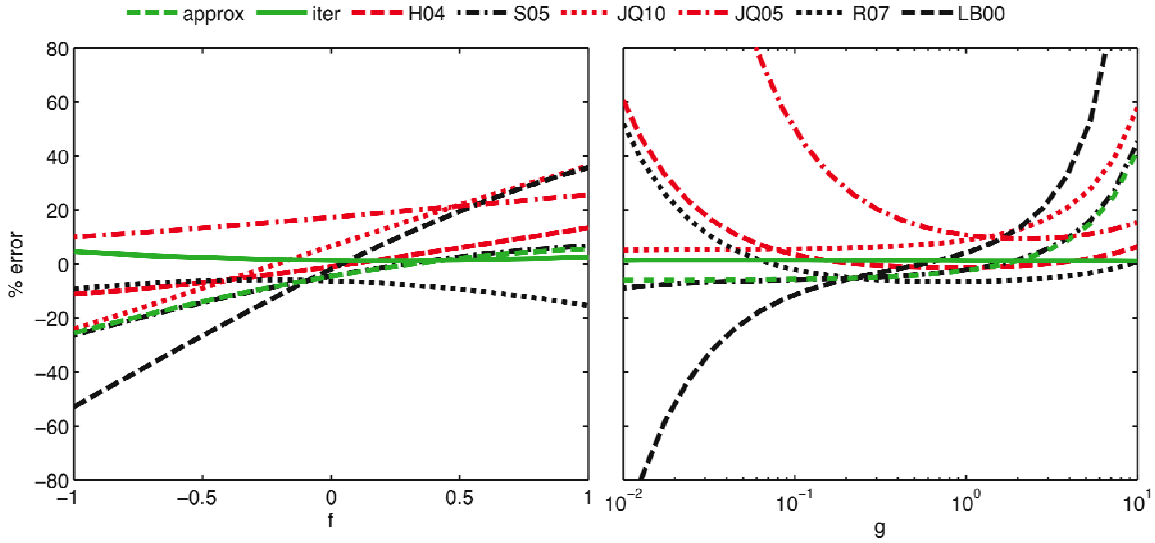


Figure 1: Relative deviation of  $g$  from the ‘corrected base case’ as calculated using the equation proposed by Kaiser. All values are the same as Kaiser’s base case except  $^{17}\delta_p = -11.588\%$  instead of  $^{17}\delta_p = -11.646\%$  as described in Section 3. The dashed green line ‘approx’ shows error when ‘modified base case’ values are used with the approximate equation from Luz and Barkan (2000) (Eqn. 5) and  $^{17}\Delta^\# (\lambda = 0.5179)$ . The solid green line ‘iter’ shows error due to using the corrected ‘base case’ values ( $^{17}\delta_p = -11.588\%$ ,  $^{18}\varepsilon_R = -20\%$  and  $\lambda = 0.5179$ ) with the iterative method from Hendricks et al. (2004). Red and black lines show deviation from base case using the parameters and approaches employed in previous studies (see Table 3 in Kaiser, 2011 for details). They are calculated from the same values as used by Kaiser, except now compared against the ‘corrected base case’ Within typical oceanic conditions ( $-0.1 < f < 0.4$  and  $0.01 < g < 1$ ), the methods generally agree with  $\pm 20\%$ . The following abbreviations are used to refer to previous studies: (H04 = Hendricks et al., 2004; JQ05, JQ10 = Juranek and Quay, 2005, 2010; LB00 = Luz and Barkan, 2005; R07 = Reuer et al., 2007; S05 = Sarma et al., 2005).