Reply to Nicholson’s comment on “Consistent calculation of aquatic gross production from oxygen triple isotope measurements” by Kaiser (2011)

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Abstract

The comment by Nicholson (2011a) questions the “consistency” of the “definition” of the “biological end-member” used by Kaiser (2011a) in the calculation of oxygen gross production. “Biological end-member” refers to the relative oxygen isotope ratio difference between photosynthetic oxygen and Air-O\textsubscript{2} (abbreviated $^{17}\delta_{P}$ and $^{18}\delta_{P}$ for $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O, respectively).

This comment has no merit for the following reasons: (a) the isotopic composition of photosynthetic oxygen cannot be “defined”, it can only be measured, modelled or calculated based on other data; (b) the isotopic composition of photosynthetic oxygen was not “defined” in Kaiser (2011a), but derived from published measurements; (c) the published measurements themselves were inconsistent and no single result could be identified as best; (d) since no best value could be identified, a hypothetical base case was constructed in a way that was consistent with previous publications; (e) the values of $^{17}\delta_{P} = -11.646 \, \text{‰}$ and $^{18}\delta_{P} = -22.835 \, \text{‰}$ assumed for the base case are compatible with the experimental evidence published before the paper of Kaiser (2011a); (f) even if the “biological end-member” was based on a definition, there could be no argument about the “consistency” of this definition – as per its nature, a definition is arbitrary.

The qualification of base case gross production values as being “30 % too high” must therefore also be rejected. Even though recently revised measurements of the relative $^{17}$O/$^{16}$O isotope ratio difference between VSMOW and Air-O\textsubscript{2}, $^{17}\delta_{\text{VSMOW}}$ (Barkan and Luz, 2011), do support lower estimates of gross production, our own measurements disagree with these revised $^{17}\delta_{\text{VSMOW}}$ values. If scaled for differences in $^{18}\delta_{\text{VSMOW}}$, they are actually in good agreement with the original data (Barkan and Luz, 2005). Moreover, species-dependent differences in photosynthetic isotope fractionation (Eisenstadt et al., 2010) correspond to an uncertainty of at least 15 % around the central estimate for the inferred gross production.

Nicholson (2011a) also suggests that approximated calculations of gross production should be performed with a triple isotope excess defined as $^{17}\Delta^# \equiv \ln(1 + ^{17}\delta)$ –
1 Introduction

Kaiser (2011a) introduced an improved method to calculate aquatic gross production from oxygen triple isotope measurements, dubbed the “dual-delta method”. This method uses the \( ^{17}\delta \) and \( ^{18}\delta \) measurements of dissolved O\(_2\) relative to Air-O\(_2\) directly, rather than computing the triple isotope excess (\( ^{17}\Delta \)) and using an approximation (Luz and Barkan, 2000). The calculation uses the following equation:

\[
g = \frac{(1 + 17\varepsilon_E)^{^{17}\delta - ^{18}\delta_{\text{sat}}}_{1+^{17}\delta}}{1 + ^{17}\delta} - \gamma_R (1 + 18\varepsilon_E)^{^{18}\delta - ^{19}\delta_{\text{sat}}}_{1+^{18}\delta} + s (17\varepsilon_E - \gamma_R 18\varepsilon_E) \]

Equation (1) is based on Eqs. (48) and (49) in Kaiser (2011a), but takes into account that measurements of the kinetic isotope fractionation during O\(_2\) gas exchange refer to evasion from the dissolved phase to the gas phase (Kaiser, 2011b; Knox et al., 1992). The symbols have the following meaning:

- \( g = P/(k c_{\text{sat}}) \): ratio of gross oxygen production to gross Air-O\(_2\) invasion
- \( ^{17}\delta, ^{18}\delta \): relative \( ^{17}\text{O}/^{16}\text{O} \) and \( ^{18}\text{O}/^{16}\text{O} \) ratio differences between dissolved O\(_2\) and Air-O\(_2\)
- \( ^{17}\delta_{\text{sat}}, ^{18}\delta_{\text{sat}} \): relative \( ^{17}\text{O}/^{16}\text{O} \) and \( ^{18}\text{O}/^{16}\text{O} \) ratio differences between dissolved O\(_2\) at saturation and Air-O\(_2\)
- \( ^{17}\delta_p, ^{18}\delta_p \): relative \( ^{17}\text{O}/^{16}\text{O} \) and \( ^{18}\text{O}/^{16}\text{O} \) ratio differences between photosynthetic O\(_2\) and Air-O\(_2\)
\[ \gamma_R = \frac{17 \varepsilon_R}{18 \varepsilon_R} : \text{ratio of respiratory } 17 \text{O}/16 \text{O} \text{ fractionation and } 18 \text{O}/16 \text{O} \text{ fractionation} \]

\[ s = \frac{c}{c_{sat}} - 1 : \text{relative supersaturation of dissolved } \text{O}_2 \]

The same method was developed independently by Prokopenko et al. (2011), without the inclusion of isotope fractionation during gas transfer. This resulted in the simplified solution

\[ g = \frac{17 \delta - 17 \delta_{sat}}{1 + 17 \delta} - \gamma_R \frac{18 \delta - 18 \delta_{sat}}{1 + 18 \delta} \]

The comment by Nicholson (2011a) does not question the validity of the dual-delta method. In contrast to the claim that the dual-isotope method requires knowledge of \(17 \varepsilon_R\) and \(18 \varepsilon_R\) (Nicholson, 2011b), the above equations clearly show that only \(\gamma_R\) is required, which is better constrained than \(17 \varepsilon_R\) and \(18 \varepsilon_R\) (Luz and Barkan, 2005).

The comment paper and the reviews it has received (Luz, 2011; Prokopenko, 2011) demonstrate that the definition and use of triple isotope excess values can be very confusing, even for experts in the field. The use of different \(17 \Delta\) definitions with different coefficients causes significant delays and misunderstandings during scientific communication, which can be avoided if the dual-delta method is adopted. In this paper, \(17 \Delta\) values are always reported in conjunction with the underlying \(17 \delta\) and \(18 \delta\) values and the definition of \(17 \Delta\) is indicated by the indices introduced in Kaiser (2011a), to avoid any further confusion.

In contrast to the approximated solution by Luz and Barkan (2000), the dual-delta does not require the assumption of steady state for the \(\text{O}_2\) concentration and can therefore be expected to be more universally applicable. Only the assumption of isotopic steady state is required for the dual-delta method.

In Sect. 2, we discuss the merits of Nicholson’s comment in view of actual measurements of the isotopic composition of photosynthetic \(\text{O}_2\). In Sect. 3, we evaluate
his suggested approximated solution to the calculation of $g$ from oxygen triple isotope measurements.

2 Isotopic composition of photosynthetic $O_2$ ($\delta_P$)

In his comment, Nicholson (2011a) questions the “consistency” of the “definition” of the isotopic composition of the “biological end-member” (i.e. photosynthetic $O_2$) in Kaiser (2011a). Specifically, he remarks that the triple isotope excess ($^{17}\Delta$) adopted for the base case is “too low” and therefore also $^{17}\delta_P$. He does not question the value of $-22.835 \text{%}$ assumed for $^{18}\delta_P$.

Firstly, the isotopic composition of photosynthetic $O_2$ cannot be “defined”; it can only be measured, modelled or calculated based on other data. Clearly, Sect. 5 in Kaiser (2011a) did not make any attempt to “define” $^{17}\delta_P$ or $^{18}\delta_P$.

Instead, data from the literature were used to derive $^{17}\delta_P$ following two different approaches: one was based on the measured isotopic composition of VSMOW and oceanic waters with respect to Air-$O_2$ (Barkan and Luz, 2005; Luz and Barkan, 2010), combined with the measured photosynthetic isotope fractionation by the cyanobacterium strain Synechocystis sp. PCC 6803 (Helman et al., 2005); the other was based on dark-light incubations of the coral Acropora (with its symbiotic algae) in airtight flasks (Luz and Barkan, 2000). The first approach was also used to derive $^{18}\delta_P = -22.835 \text{%}$.

To dispel any confusion about how the isotopic composition of photosynthetic $O_2$ (including the triple isotope excess) was calculated in Kaiser (2011a), we show the corresponding equations and results in the following subsections and include data that were previously omitted or not yet published. The resulting $^{17}\delta_P$ and $^{18}\delta_P$ values are shown in Table 1.
2.1 Calculation of $\delta_P$ based on the isotopic composition of source water ($\delta_W$) and the photosynthetic isotope fractionation ($\varepsilon_P$)

The isotopic composition of photosynthetic O$_2$ $\delta_P$ is calculated via

$$\delta_P = (1 + \delta_W)(1 + \varepsilon_P) - 1 \quad (3)$$

where $\delta_W$ is the isotopic composition of source water and $\varepsilon_P$ is the photosynthetic isotope fractionation.

The corresponding triple isotope excess is

$$^{17}\Delta^\dagger_P = 17 \delta_W - \kappa 18 \delta_P$$
$$= 17 \delta_W + 17 \varepsilon_P + 17 \delta_W 18 \varepsilon_P - \kappa (18 \delta_W + 18 \varepsilon_P + 18 \delta_W 18 \varepsilon_P)$$
$$= 17 \Delta^\dagger_W + (\gamma_P - \kappa) 18 \varepsilon_P - [\kappa (1 - \gamma_P) 18 \delta_W - \gamma_P 17 \Delta^\dagger_W] 18 \varepsilon_P \quad (4)$$

where $\gamma_P = 17 \varepsilon_P / 18 \varepsilon_P$ and

$$^{17}\Delta^\#_P = \ln(1 + 17 \delta_P) - \ln(1 + 18 \delta_P)$$
$$= \ln(1 + 17 \delta_W) + \ln(1 + 17 \varepsilon_P) - \lambda \ln(1 + 18 \delta_W) - \lambda \ln(1 + 18 \varepsilon_P)$$
$$= 17 \Delta^\#_W + (\theta_P - \lambda) \ln(1 + 18 \varepsilon_P) \quad (5)$$

where $\theta_P = \ln(1 + 17 \varepsilon_P) / \ln(1 + 18 \varepsilon_P)$.

Note that the respiratory isotope fractionation $\varepsilon_R$ does not enter these equations. $\varepsilon_R$ is only needed if the isotopic composition of O$_2$ in steady state between photosynthesis and respiration ($\delta_S$) was required. $\delta_S$ can be calculated using Eq. (31) in Kaiser (2011a). For comparison with the calculation in Sect. 2.2, the corresponding $\delta_{S0}$ values for a net to gross production ratio of $f = 0$ are also shown in Table 1.

Kaiser (2011a) chose $\delta_W$ to correspond to the isotopic composition of seawater. $^{18}\delta_W$ was set equal to $^{18}\delta_{VSMOW} = (-23.323 \pm 0.02) \%^{\circ}$ (Barkan and Luz, 2005). $^{17}\delta_W$ was calculated as $^{17}\delta_W = (1^{17}\delta_{VSMOW})e^{-5^{\text{ppm}}} - 1 = (1 - 11.936^{\%})e^{-5^{\text{ppm}}} - 1 = (-11.941 \pm 0.01) ^{\%}$ (Luz and Barkan, 2010) (Table 1, row 5).
Only a cyanobacterium strain that lacked the gene for photorespiration (Synechocystis sp. PCC 6803) was considered with $^{18}\varepsilon_P = (0.5 \pm 0.5)\%$ and $\theta_P = 0.5354 \pm 0.0020$ (Helman et al., 2005; Kaiser, 2011a). This gave $^{18}\delta_P = (-22.835 \pm 0.50)\%$, $^{17}\delta_P = (-11.676 \pm 0.26)\%$ and $^{17}\Delta_P^\dagger(0.5179) = (150 \pm 13) \text{ppm}$ (Table 1, row 5a). The propagated error in $^{17}\Delta_P^\dagger$ is smaller than for $^{17}\delta_P$ because the uncertainties in $^{17}\delta_P$ and $^{18}\delta_P$ are correlated in a mass-dependent way.

Eisenstadt et al. (2010) report on $^{18}\varepsilon_P$ and $\theta_P$ values for four additional phytoplankton species: Nannochloropsis oculata (a eustigmatophyte), Phaeodactylum tricornutum (a diatom), Emiliania huxleyi (a coccolithophore) and Chlamydomonas reinhardtii (a green alga). The $^{18}\varepsilon_P$ values are significantly larger than for Synechocystis and range from (2.85 ± 0.05)\% for N. oculata to (7.04 ± 0.10)\% for C. reinhardtii. The $\theta_P$ values are lower than for Synechocystis and range from 0.5198 ± 0.0001 for C. reinhardtii to 0.5253 ± 0.0004 for N. oculata and E. huxleyi. The resulting $^{17}\Delta_P^\dagger(0.5179)$ values range from (175 ± 9) ppm for N. oculata to (211 ± 10) ppm for E. huxleyi (Table 1, rows 5b–e).

### 2.2 Calculation of $\delta_P$ based on flask cultures in steady state between photosynthesis and respiration

Following Sect. 3.4 in Kaiser (2011a), the isotopic composition of oxygen in concentration steady state (net to gross production ratio $f = 0$) is given by

$$\delta_{S0} = \frac{1 + \delta_P}{1 + \varepsilon_R} - 1 = \frac{\delta_P - \varepsilon_R}{1 + \varepsilon_R} \tag{6}$$

To derive $\delta_P$, Eq. (6) is rearranged to

$$\delta_P = (1 + \delta_{S0})(1 + \varepsilon_R) - 1 \tag{7}$$

In addition to $\delta_{S0}$, this calculation also requires $\varepsilon_R$.

Luz and Barkan (2000) have performed incubations of a Nannochloropsis species and a hermatypic Acropora coral species in airtight flasks. These incubations are
supposed to correspond to steady state. No values were reported for \( \delta_{S0} \), only
\[ 17\Delta_P(0.521) = (244 \pm 20) \text{ ppm for } Nannochloropsis \text{ and } (252 \pm 5) \text{ ppm for } Acropora. \]

For Acropora, Luz and Barkan (2005) reported \( 18\varepsilon_R = (-13.8 \pm 0.5)\% \) and \( \gamma_R = 0.519 \pm 0.001 \). Assuming \( 18\delta_P = (-22.835 \pm 0.5)\% \) as for Synechocystis, this gives
\[ 18\delta_{S0} = (-9.16 \pm 0.71)\% \] (Kaiser, 2011a, b). With
\[ 17\delta_{S0} = 17\Delta_P(0.521) + 0.521 18\delta_{S0} \quad (8) \]
this gives \( 17\delta_{S0} = (-4.52 \pm 0.37)\% \) and, using Eq. (7), \( 17\delta_P = (-11.651 \pm 0.26)\% \) (Table 1, row 3). The resulting \( 17\Delta(0.5179) \) value is \( (175 \pm 15) \) ppm (note that the value \( 17\Delta_P(\gamma_R) \) in Table 1 corresponds to \( \gamma_R = 0.519 \)).

Kaiser (2011a) mentioned that no corresponding calculation could be performed for Nannochloropsis because \( 18\varepsilon_R \) and \( \gamma_R \) values have not been reported for this species. In Sect. 4 of Nicholson (2011a), this calculation is performed nonetheless, assuming \( 18\varepsilon_R = -20\% \) (without uncertainty) and \( \gamma_R = 0.5179 \) (without uncertainty). Just as for Acropora and Synechocystis above \( 18\delta_P \) was assumed to be \( (-22.835 \pm 0.5)\% \).

Here, we repeat this calculation, assuming more realistic uncertainty estimates of \( 18\varepsilon_R = (-20 \pm 4)\% \) and \( \gamma_R = 0.5179 \pm 0.0006 \). This gives \( 17\delta_P = (-11.608 \pm 0.26)\% \) and \( 17\Delta(0.5179) = (218 \pm 38) \) ppm (Table 1, row 4a). If instead \( 18\varepsilon_P = (2.85 \pm 0.05)\% \) (Eisenstadt et al., 2010) is used, then \( 17\delta_P = (-10.400 \pm 0.047)\% \) and \( 17\Delta_P(0.5179) = (237 \pm 39) \) ppm (Table 1, row 4a). Both values clearly differ from \( 17\Delta_P(0.5179) = (175 \pm 9) \) ppm derived for \( N. oculata \) based on \( \delta_W \) and \( \varepsilon_P \) (Sect. 2.2; Table 1, row 5b). The increased uncertainty estimates compared to Acropora are due to the higher uncertainty in \( 17\Delta_{S0}(0.521) \) of 20 ppm and the higher uncertainty in \( 18\varepsilon_R \) of 4\%. 

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Interactive Discussion
2.3 Hypothetical base case values for the isotopic composition of photosynthetic O\textsubscript{2}

Based on the discrepancy between $^{17}\delta_P = -11.676$‰ for *Synechocystis* (Table 1, row 5a) and $^{17}\delta_P = -11.651$‰ for *Acropora* (Table 1, row 3), Kaiser (2011a) found it impossible to assign a best value for $^{17}\delta_P$.

Instead a hypothetical base case was constructed in a way that was consistent with previous studies (Hendricks et al., 2004; Reuer et al., 2007; Juranek and Quay, 2010). The base case adopted a triple isotope excess of $^{17}\Delta^\#_P(0.5179) = (249 \pm 15$) ppm (Table 1, row 1). This is the same numerical value for the triple isotope excess used in previous studies, although $\lambda$ values of 0.516 (Hendricks et al., 2004; Reuer et al., 2007) and 0.518 were used elsewhere (Juranek and Quay, 2010). $^{17}\Delta^\#_P(0.5179) = (249 \pm 15$) ppm results in $^{17}\delta_P = -11.646$‰ which is slightly higher than the corresponding values for *Synechocystis* and *Acropora*. The resulting value of $^{17}\Delta^{\dagger}_P(0.5179) = (180 \pm 15$) ppm is compatible with the $^{17}\Delta^{\dagger}_P(0.5179)$ values based on the $^{18}\varepsilon_P$ measurements of Eisenstadt et al. (2010) (Table 1, rows 5b,c,e) except for *E. huxleyi* (Table 1, row 5d).

Nicholson (2011a) questions the validity of this base case and suggests that $\lambda$ should be chosen such that $^{17}\Delta^\#_{S0} = ^{17}\Delta^\#_P$ and these values should equal $(249 \pm 15$) ppm. This “tuned” $\lambda$ value, denoted $\lambda_{BSS}$ (for biological steady state) by Nicholson (2011a), is actually identical to the triple isotope fractionation coefficient for respiration ($\theta_R$) and calculated as

\[
\lambda_{BSS} = \theta_R = \frac{\ln(1 + ^{17}\varepsilon_R)}{\ln(1 + ^{18}\varepsilon_R)} = \frac{\ln(1 + Y_R^{18}\varepsilon_R)}{\ln(1 + ^{18}\varepsilon_R)} \quad (9)
\]

This leads to an alternative hypothetical base case with $^{17}\delta_P = -11.588$‰ and $^{17}\Delta^{\dagger}_P(0.5179) = (238 \pm 35$) ppm (Table 1, row 2). Within error, this Nicholson (2011a) base case agrees with the *Nannochloropsis* flask experiments if the assumptions of...
\( \gamma_R = 0.5179 \pm 0.0006 \) and \( \varepsilon_R = (-20 \pm 4) \%_o \) for these experiments are correct. However, it differs substantially from the corresponding values for the *Acropora* flask experiments (Table 1, row 3) and the results for all species based on the isotopic composition of seawater and the photosynthetic isotope fractionation (Table 1, rows 5a–e).

In Sect. 4, Nicholson (2011a) comments that \( \Delta^\#_{\text{P}}(\theta_R) = 231 \text{ ppm} \) for the *Nannochloropsis* flask experiments are very close to \( \Delta^\#_{\text{P}}(\theta_R) = 234 \text{ ppm} \) for the *Acropora* flask experiments. Notwithstanding that our own calculations give an identical result of \( \Delta^\#_{\text{P}}(\theta_R) = 229 \text{ ppm} \) in both cases (Table 1, rows 3 and 4a), this is not a fair comparison because \( \theta_R \) is equal to 0.5173 for *Acropora* and 0.5154 for *Nannochloropsis*. Clearly, the \( \delta_{\text{P}} \) values differ in both cases (for the same \( \delta_{\text{P}} \) value) and calculations of gross production using the accurate dual-delta method would lead to different results. This illustrates the perils associated with using \( \Delta^\# \) values in isolation.

Both the base cases used by Kaiser (2011a) and by Nicholson (2011a) are hypothetical. On their own, they should therefore not be used to draw definitive conclusions on the quantitative accuracy of the resulting values for \( g \). Specifically, the agreement or disagreement of \( g \) values based on one base case or another with parameterisations used in previous studies (Hendricks et al., 2004; Reuer et al., 2007; Juranek and Quay, 2010) should not be used to single out one base case as superior to the other. Kaiser (2011a) did not make such a claim and rather used the disagreement between different estimates of the isotopic composition of photosynthetic O\(_2\) to highlight the need for additional measurements of the required parameters, especially \( \delta_{\text{P}} \). The claim by Nicholson (2011a) that the \( g \) values calculated using the base case of Kaiser (2011a) were 30% too high was therefore premature.

### 2.4 New measurements of \( \delta_{\text{VSMOW}} \) and \( \delta_{\text{VSMOW}} \)

Four days after publication of Kaiser (2011a) and three days before publication of Nicholson (2011a), new measurements of \( \delta_{\text{VSMOW}} \) and \( \delta_{\text{VSMOW}} \) were published (Barkan and Luz, 2011). The authors of this paper found that they could not reproduce
their earlier results for $^{17}\delta_{VSMOW}$ (Barkan and Luz, 2005). Their new results gave $^{17}\delta_{VSMOW} = (-11.883 \pm 0.012) \%$. The resulting $^{17}\delta_{W}$ value is $(-11.888 \pm 0.012) \%$ (Table 1, row 6) when accounting for the 5 ppm depletion of ocean water relative to VSMOW (Luz and Barkan, 2010). This value is 0.053\% or more than five standard deviations higher than the original value of $(-11.941 \pm 0.01) \%$ (Barkan and Luz, 2005). The corresponding $^{18}\delta_{VSMOW}$ value of $(-23.324 \pm 0.017) \%$ remained virtually unchanged compared to the original value of $(-23.32 \pm 0.02) \%$.

In terms of $^{17}\Delta^\dagger_{W}(0.5179)$, this amounts to a change from $(138 \pm 9)$ ppm to $(191 \pm 4)$ ppm. The authors do not give an explanation for this change, other than that the “experimental system and measurement procedures were somewhat improved” (Barkan and Luz, 2011).

The revised measurements allow recalculating $\delta_p$ based on $\delta_W$ and $\varepsilon_p$ (Sect. 2.1). $^{18}\delta_p$ remains virtually unchanged, but the corresponding $^{17}\delta_p$ and $^{17}\Delta^\dagger_p(0.5179)$ values increase by 53 ppm (Table 1, rows 6a–e). The revised $^{17}\Delta^\dagger_p(0.5179)$ values are in agreement with those estimated for Nannochloropsis flask cultures and the base case used by Nicholson (2011a). They are in disagreement with the Acropora flask cultures and the base case used by Kaiser (2011a).

Our own measurements of VSMOW relative to Air-O$_2$ give $^{18}\delta_{VSMOW} = (-23.647 \pm 0.04) \%$ and $^{17}\delta_{VSMOW} = (-12.102 \pm 0.03) \%$. Taking into account the $^{17}O/^{16}O$ depletion of ocean water with respect to VSMOW, this gives $^{17}\delta_{W} = (-12.107 \pm 0.03) \%$ and $^{17}\Delta^\dagger_{W}(0.5179) = (140 \pm 6)$ ppm. The uncertainty of the latter values is lower than for $^{17}\delta_{W}$ because the errors in $^{18}\delta$ and $^{17}\delta$ are correlated in a mass-dependent way.

Our $^{17}\Delta^\dagger_{W}(0.5179)$ value is in good agreement with the original measurements of Barkan and Luz (2005), but disagrees with their revised results (Barkan and Luz, 2011). Just as the results of Barkan and Luz, our data have been obtained on a Finnigan MAT Delta Plus isotope ratio mass spectrometer. However, our results have been corrected for a 0.8 % scale contraction, based on gravimetrically calibrated mixtures of 99.7 % pure H$_2^{18}$O with tap water. The scale correction affected $^{17}\Delta^\dagger_{W}(0.5179)$ by a 2 ppm
increase only. It actually brings $^{18}\delta_{\text{VSMOW}}$ into closer agreement with independent estimates of $(−23.781\pm 0.06)\%$ (Kaiser, 2008), based on isotope measurements in CO$_2$. Barkan and Luz (2005, 2011) did not perform a scale correction, even though their measured SLAP-VSMOW difference of $(−55.11\pm 0.05)\%$ (Barkan and Luz, 2005) differs from the internationally accepted value of $−55.5\%$ (Gonfiantini, 1977, 1978). If the value of $−55.5\%$ were accurate, the corresponding scale contraction would amount to 0.7%. A scale contraction of 0.7 to 0.8% may be typical for this particular type of mass spectrometer.

The varying results for the relative isotope ratio differences between VSMOW and Air-O$_2$ within a single laboratory and between laboratories warrant further measurements of this important parameter and perhaps inter-laboratory comparisons.

For comparison purposes, we construct a new base case here based on the measurements of Barkan and Luz (2011) and Eisenstadt et al. (2010). We adopt $^{18}\delta_{W} = −23.324\%$ and $^{17}\delta_{W} = −11.883\%$, as discussed above (Table 1, row 6). For the photosynthetic isotope fractionation, we adopt the arithmetic average of the corresponding values based on Eisenstadt et al. (2010), i.e. $^{18}\varepsilon_{P} = (4.126\pm 2.6)\%$ and $^{17}\varepsilon_{P} = (2.156\pm 1.3)\%$. This $^{18}\varepsilon_{P}$ value is in good agreement with the global average of $^{18}\varepsilon_{P} = 4\%$ derived by Luz and Barkan (2011). With Eq. (3), this results in $^{18}\delta_{P} = −19.294\%$ and $^{17}\delta_{P} = −9.757\%$. (Table 1, row 7). It would not be appropriate to take the arithmetic average of $\theta_{P}$ reported for various organisms to derive $^{17}\varepsilon_{P}$ because $^{17}\varepsilon_{P}$ is essentially linearly related to $^{17}\delta_{P}$ whereas $\theta_{P}$ is not.

Just as shown in Sect. 2.1 for previous $\delta_{W}$ measurements (Barkan and Luz, 2005), there is a large species-dependent range in $^{17}\Delta_{P}^\dagger(0.5179)$, from 203 ppm (for the cyanobacterium Synechocystis) to 264 ppm (for the coccolithophore E. huxleyi). In the next section, we will show the systematic impact of different $\delta_{P}$ values on $g$. 

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3 Dependence of $g$ on the assumed isotopic composition of photosynthetic O$_2$

3.1 Accurate calculation of $g$ using the dual-delta method

Since the interaction between the parameters $^{17}\delta_P$, $^{18}\delta_P$ and $\gamma_R$ is not straightforward to predict based on Eq. (1), their impact on $g$ is best illustrated through example calculations (Kaiser, 2011a). Results for $g$ based on $^{17}\delta_P$ and $^{18}\delta_P$ derived in Sects. 2.1–2.3, including the base case suggested by Nicholson (2011a), are compared with the base case “Kaiser (2011a)” (Fig. 1a,b) and the new base case constructed here (Fig. 1c, d). The same scenarios as in Kaiser (2011a) were used, i.e. $g = 0.4$ with $-1.0 \leq f \leq +1.0$ (Fig. 1a,c) and $f = 0.1$ with $0.01 \leq g \leq 10$ (Fig. 1b and d). Parameters related to gas exchange were left unchanged at $^{17}\delta_{sat} = 0.382 \%o$, $^{18}\delta_{sat} = 0.707 \%o$, $^{17}\varepsilon_E = -1.463 \%o$, $^{18}\varepsilon_E = -2.800 \%o$ (Kaiser, 2011a,b).

In Fig. 1b ($f = 0.1$), there is a variation of at least $\pm 24 \%$ around the $g$ values derived for the base case “Kaiser (2011a)”, with $g$ values based on Synechocystis parameters deviating $\geq +24 \%$ and “Nicholson (2011a)” deviating $\leq -27 \%$ from the base case “Kaiser (2011a)”. $g$ values based on other species-specific parameters and Acropora or Nannochloropsis flask incubations are in between. For $f < 0.1$ or $g > 0.01$, these relative deviations are higher (Fig. 1a, b). The relative deviations of $g$ for the E. huxleyi parameters are $\leq -16 \%$ from the base case for $f = 0.1$, which means the $g$ values deviate $\leq -32 \%$ from the $g$ values based on Synechocystis parameters, a significant species-related uncertainty.

For the new base case constructed here (Table 1, row 7), the relative deviations from the base case are $\geq +35 \%$ for “Kaiser (2011a)” and $\leq -12 \%$ for the E. huxleyi parameters (Fig. 1d, $f = 0.1$). Again, for $f < 0.1$ or $g > 0.01$, these deviations tend to be even higher (Fig. 1c,d). The relative deviations of $g$ for the Synechocystis parameters are $\geq +18 \%$ from the base case, which means the $g$ values based on E. huxleyi parameters deviate $\leq -26 \%$ from the $g$ values based on Synechocystis parameters. The span
between these two species is slightly smaller than in the previous paragraph because the different base case parameters lead to different $^{17}\delta$ and $^{18}\delta$ scenarios for the same two cohorts. Nevertheless, there is still a significant uncertainty in $g$ related to which species is assumed to have produced the $O_2$ and therefore which set of parameters $^{17}\delta_P, ^{18}\delta_P$ and $\gamma_R$ is adopted for the calculation.

3.2 Approximate calculation of $g$

Even though the development of the accurate dual-delta method makes use of approximations in the calculation of $g$ unnecessary, we will revisit the different approximations used in the past to address the corresponding comment by Nicholson (2011a).

Luz and Barkan (2000) suggested the following approximate calculation of oxygen gross production from oxygen triple isotope measurements

$$g = \frac{^{17}\Delta - ^{17}\Delta_{sat}}{^{17}\Delta_P - ^{17}\Delta}$$

with the triple isotope excess defined as $^{17}\Delta^\dagger(0.521) \equiv ^{17}\delta - 0.521^{18}\delta$, i.e. using a linear definition.

The same authors later revised this method and stated that the triple isotope excess should be defined using the natural logarithm (ln) as $^{17}\Delta^\#(\gamma_R) \equiv \ln(1 + ^{17}\delta) - \gamma_R \ln(1 + ^{18}\delta)$ with $\gamma_R = 0.5179$ (Luz and Barkan, 2005), but that this definition shall not apply to $^{17}\Delta_P$. Instead, the photosynthetic end-member should be set equal to $^{17}\Delta^\#(\theta_R)$, with $\theta_R = 0.5154$ for $\gamma_R = 0.5179$ and $^{18}\epsilon_R = -20$‰ (Sect. 2.3). As evidenced by its use in Luz and Barkan (2009), a coefficient of $\gamma_R$ is also meant to apply to $^{17}\Delta_{sat}^\#$.

The use of different coefficients for the triple isotope excess is confusing, especially for the non-expert reader. Moreover, $\theta_R$ can only be computed if $^{18}\epsilon_R$ is also known. Even though the influence of the uncertainty in $^{18}\epsilon_R$ is not as severe as when $^{18}\delta$ were used for the calculation directly (Quay et al., 1993), this goes somewhat against the rationale behind the triple oxygen isotope technique (i.e. the absence of the need for
to know $^{18}\epsilon_R$). Finally, the suggested approximations are mathematically inconsistent with Eqs. (1) and (2).

Instead, Kaiser (2011a) suggested that Eq. (10) is used with the triple isotope excess defined as $^{17}\Delta^\dagger(y_R) \equiv ^{17}\delta - y_R^{18}\delta$. This definition is consistent with the asymptotic behaviour of Eq. (2) for $^{17}\delta$, $^{18}\delta \to 0$. However, it was shown that this approximated calculation can lead to systematic biases from the accurate solution calculated using the dual-delta method and the use of this approximation was not recommended.

Nicholson (2011a) comments that the approximations of Kaiser (2011a) and, by implication, Luz and Barkan (2005) can be improved if a definition of the triple isotope excess as $^{17}\Delta^\#(\theta_R)$ is adopted. The corresponding $^{17}\Delta^\#P(\theta_R)$ value is named $^{17}\Delta^{BSS}$ for “biological steady state” because it is identical to the $^{17}\Delta^\#S_0(\theta_R)$ value under concentration steady state ($f = 0$). However, as shown in Sect. 3.4 and the uncorrected Fig. 1 of Kaiser (2011a), isotopic steady state can also be achieved for $f \neq 0$ and in this case, $^{17}\Delta^\#S(\theta_R) \neq ^{17}\Delta^\#P(\theta_R)$. It is therefore not clear a priori whether the approximation suggested by Nicholson (2011a) performs better than the other approximations.

Just as in Sect. 3.1, we therefore compare the different approximations to the accurate solution using a range of scenarios. The scenarios correspond to $0.01 \leq g \leq 10$ and $-1 \leq f \leq 1$ (in steps of 0.2). The underlying parameters $^{17}\delta_P$, $^{18}\delta_P$ and $\gamma_R$ correspond to the base case in Kaiser (2011a) (Table 1, row 1; Fig. 2); the new base case constructed here (Table 1, row 7; Fig. 3), which is similar to the base case adopted by Nicholson (2011a); and the parameters derived from the Acropora flask experiments (Table 1, row 3; Fig. 4).

The approximate solutions are calculated using Eq. (10) with the triple isotope excess defined as (a) $^{17}\Delta^\dagger(y_R)$ (Kaiser, 2011a; Figs. 2a, 3a, 4a); (b) $^{17}\Delta^\#(y_R)$ in general, but $^{17}\Delta^\#P(\theta_R)$ for photosynthetic $O_2$ (Luz and Barkan, 2005; Figs. 2b, 3b, 4b); (c) $^{17}\Delta^\#(y_R)$ (shown for completeness; Fig. 2c, 3c, 4c) and (d) $^{17}\Delta^\#(\theta_R)$ (Nicholson, 2011a; Figs. 2d, 3d, 4d). In the following, we refer to these definitions as methods (a) to (d).
None of the approximations deliver unbiased results for \( g > 1 \). Of course, such conditions rarely occur in the environment (except for intense blooms or very low wind speeds). However, even for \( g < 1 \) significant biases can occur in all cases under certain conditions.

For all scenarios, method (c) performs worst. However, \( ^{17}\Delta^\#(\gamma_R) \) on its own has actually never been used together with Eq. (10), as far as we know, so this has no consequence for already published data.

For the base case adopted by Kaiser (2011a), method (a) returns nearly unbiased results for \( f = 0 \) and \( g < 0.1 \). For \( g < 1 \) and \(-0.4 \leq f \leq 0.2\), the relative deviation from the accurate solution does not exceed \( \pm 22\% \) (Fig. 1a). \( g \) values based on method (d) are biased 10\% low for \( f = 0 \), but the relative deviation from the base case is at most \(-21\% \) for \( g \leq 0.4 \) (Fig. 1d). Method (b) is biased only 7\% low for \( f = 0 \) (Fig. 1b), but otherwise the derived \( g \) values have larger deviations from the accurate solution than those for method (d), more similar to method (a).

For the new base case constructed in this paper, methods (a), (b) and (d) give nearly unbiased results for \( f = 0 \) and the entire range of \( g \) values explored. Method (d) has the least bias for \( g < 1 \), where as methods (a) and (b) perform similarly.

For the scenario based on the Acropora parameters, method (a) gives the least bias for \( f = 0 \). In this case, methods (b) and (d) are biased low by 19\% and 12\%, respectively. Interestingly, method (d) does not show any significant variation in this bias for \( g < 0.1 \) and the entire range in \( f \).

In summary, none of the calculation methods is free from bias under all conditions and scenarios. The value Nicholson (2011a) attributed to method (d) may be due to the particular hypothetical scenario he has chosen, which is very similar to that of the new base case constructed here (Fig. 1c,d). However, if other \( ^{17}\delta_P \) and \( ^{18}\delta_P \) parameters were adopted such as those of the Acropora flask experiments, then significant biases from the accurate solution would occur.
4 Conclusions

With the development of the dual-delta method (Kaiser, 2011a; Prokopenko et al., 2011), it is time to abandon approximated solutions based on the triple isotope excess ($^{17}\Delta$). The end of the discussion about what the appropriate definition is for $^{17}\Delta$, which is the right coefficient and whether it should be defined in terms of $\delta$ or $\ln(1+\delta)$, will also help alleviate the confusion that newcomers and students feel when they first enter this field of research.

Even though the methodological bias due to the use of Eq. (10) may often be smaller than the uncertainty due to wind speed-gas exchange parameterisations, there is no reason for such bias to exist at all if the dual-delta method is adopted.

However, considerable systematic uncertainty remains in the calculation of $g$ due to the uncertainty in the isotopic composition of photosynthetic $O_2$, $^{17}\delta_P$ and $^{18}\delta_P$. Part of this uncertainty is due to conflicting results for the $^{17}O/^{16}O$ isotope ratio of seawater relative to Air-$O_2$ (Sect. 2.4). Moreover, the experiments by Eisenstadt et al. (2010) and the results in Fig. 1 show that there is considerable interspecies variability in the photosynthetic isotope fractionation and the inferred gross production $g$, depending on what species is assumed to have produced the oxygen. Independent measurements and perhaps laboratory comparison exercises should be performed to establish the reproducibility of $^{17}O/^{16}O$ isotope ratio measurements in water. Further experiments with cultures under steady-state conditions would help to verify the calculations based on the isotopic composition of water and the photosynthetic isotope fractionation.

The comment by Nicholson (2011a) on “Consistent calculation of aquatic gross production from oxygen triple isotope measurements” by Kaiser (2011a) centred on the appropriate choice of $^{17}\delta_P$ and $^{18}\delta_P$. At the moment, however, it seems to be more important to emphasise the differences that result from different parameters and calculation methods. The demand for the “correct” choice is premature and besides the main topic of the original paper.
Acknowledgements. Jan Kaiser thanks the Royal Society (Wolfson Research Merit Award WMO052632) and the Natural Environment Research Council (NERC NE/H012532/1) for support. Osamu Abe was supported during a sabbatical year at UEA by the JSPS “Institutional Program for Young Researcher Overseas Visits”.

References


Kaiser, J.: Technical note: Consistent calculation of aquatic gross production from oxygen


Table 1. Isotopic composition of photosynthetic O$_2$ (\(^{17}\delta_p\), \(^{18}\delta_p\), \(^{17}\Delta_p\)) and O$_2$ at steady state between photosynthesis and respiration with a net to gross production ratio of \(f = 0\) (\(^{17}\delta_{SO}\), \(^{18}\delta_{SO}\), \(^{17}\Delta_{SO}\)), calculated as per Sect. 2. All values have been adjusted to the same decimal for clarity, irrespective of their actual uncertainty. The following assumptions were made: \(\gamma_R = 0.5179 \pm 0.0006\), \(^{18}\varepsilon_R = (-20 \pm 4)\%\), \(\theta_R = 0.5154\); except for Acropora where \(\gamma_R = 0.519 \pm 0.001\), \(^{18}\varepsilon_R = (-13.8 \pm 0.5)\%\), \(\theta_R = 0.5173\); for “base case, Kaiser (2011a)”, \(^{17}\Delta_p(0.5179) = (249 \pm 15)\) ppm; for “base case, Nicholson (2011a)”, \(^{17}\Delta_p(\theta_R) = (249 \pm 15)\) ppm; for “Acropora (flask)”, \(^{17}\Delta_{SO}(0.521) = (252 \pm 5)\) ppm. For “Nannochloropsis (flask)”, \(^{17}\Delta_{SO}(0.521) = (244 \pm 20)\) ppm. The \(\delta_p\) and \(^{17}\Delta_p\) values in rows 5 and 6 correspond to \(\delta_W\) and \(^{17}\Delta_W\); for rows 1 to 5, \(^{18}\delta_W = (-23.323 \pm 0.02)\%\) and \(^{17}\delta_W = (-11.941 \pm 0.01)\%\) (Barkan and Luz, 2005; Luz and Barkan, 2010); for rows 6 to 7, \(^{18}\delta_W = (-23.324 \pm 0.017)\%\) and \(^{17}\delta_W = (-11.888 \pm 0.012)\%\) (Barkan and Luz, 2011; Luz and Barkan, 2010), abbreviated B & L (2011).

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<th>Row</th>
<th>Description</th>
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*a = k = \(\gamma_R = 0.519\). The \(^{17}\Delta\) values for \(\lambda = k = 0.5179\) are \(^{17}\Delta_p = (175 \pm 15)\) ppm, \(^{17}\Delta_p = (224 \pm 15)\) ppm, \(^{17}\Delta_{SO} = 224\) ppm and \(^{17}\Delta_{SO} = 235\) ppm.*
Fig. 1. Relative deviation of $g$ from the base case adopted by Kaiser (2011a) (a and b) and from the base case constructed in this paper (c and d). The value of $g$ is calculated using Eq. (1) for different sets of $^{17}\delta P$, $^{18}\delta P$ and $\gamma_R$ (Table 1). (a) and (c) correspond to $g = 0.4$ and $-1.0 \leq f \leq +1.0$. (b) and (d) correspond to $f = 0.1$ and range of $0.01 \leq g \leq 10$ (logarithmic axis). The red curves correspond to rows 5a to 5e (a) and 6a to 6e (b) in Table 1. “Nicholson (2011a)”, “Acropora, flask”, “Nannochl., flask” and “Kaiser (2011a)” correspond to rows 2, 3, 4a and 1, respectively, in Table 1.
**Fig. 2.** Relative deviation of the approximated solution for $g$ (Eq. 10) from the accurate solution (Eq. 1) for the base case adopted in Kaiser (2011a) (Table 1, row 1). (a) linear definition of $^{17}\Delta$ with $\kappa = \gamma_R$: $^{17}\Delta_p(0.5179) = 180$ ppm, $^{17}\Delta_{sat}(0.5179) = 16$ ppm. (b) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$ except for $^{17}\Delta_{sat}^h$: $^{17}\Delta_p(0.5154) = 191$ ppm, $^{17}\Delta_{sat}(0.5179) = 16$ ppm. (c) ln-definition of $^{17}\Delta$ with $\lambda = \theta_R$: $^{17}\Delta_p'(0.5179) = 249$ ppm, $^{17}\Delta_{sat}'(0.5179) = 16$ ppm. (d) ln-definition of $^{17}\Delta$ with $\lambda = \theta_R$: $^{17}\Delta_p'(0.5154) = 191$ ppm, $^{17}\Delta_{sat}'(0.5154) = 18$ ppm.
Fig. 3. Relative deviation of the approximated solution for \( g \) (Eq. 10) from the accurate solution (Eq. 1) for the new base case constructed in this paper (Table 1, row 7). (a) Linear definition of \( ^{17}\Delta \) with \( \kappa = \gamma_R \): \( ^{17}\Delta_p(0.5179) = 235 \text{ ppm}, \) \( ^{17}\Delta_{\text{sat}}(0.5179) = 16 \text{ ppm} \). (b) In-definition of \( ^{17}\Delta \) with \( \lambda = \gamma_R \) except for \( ^{17}\Delta_{\#} \): \( ^{17}\Delta_p(0.5154) = 236 \text{ ppm}, \) \( ^{17}\Delta_{\text{sat}}(0.5179) = 16 \text{ ppm} \). (c) In-definition of \( ^{17}\Delta \) with \( \lambda = \gamma_R \): \( ^{17}\Delta_p(0.5179) = 285 \text{ ppm}, \) \( ^{17}\Delta_{\text{sat}}(0.5179) = 16 \text{ ppm} \). (d) In-definition of \( ^{17}\Delta \) with \( \lambda = \theta_R \): \( ^{17}\Delta_p(0.5154) = 236 \text{ ppm}, \) \( ^{17}\Delta_{\text{sat}}(0.5154) = 18 \text{ ppm} \).
Fig. 4. Relative deviation of the approximated solution for $g$ (Eq. 10) from the accurate solution (Eq. 1) for *Acropora* (flask) (Table 1, row 3). (a) linear definition of $^{17}\Delta$ with $\kappa = \gamma_R$: $^{17}\Delta^\dagger_{P}(0.519) = 200$ ppm, $^{17}\Delta^\dagger_{sat}(0.519) = 15$ ppm. (b) In-definition of $^{17}\Delta$ with $\lambda = \gamma_R$ except for $^{17}\Delta^\#_{P}$: $^{17}\Delta^\#_{P}(0.5173) = 229$ ppm, $^{17}\Delta^\#_{sat}(0.519) = 15$ ppm. (c) In-definition of $^{17}\Delta$ with $\lambda = \gamma_R$: $^{17}\Delta^\#_{P}(0.519) = 269$ ppm, $^{17}\Delta^\#_{sat}(0.519) = 15$ ppm. (d) In-definition of $^{17}\Delta$ with $\lambda = \theta_R$: $^{17}\Delta^\#_{P}(0.5173) = 229$ ppm, $^{17}\Delta^\#_{sat}(0.5173) = 17$ ppm.