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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_2 (abbreviated $^{17}\delta_P$ and $^{18}\delta_P$ for $^{17}O/^{16}O$ and $^{18}O/^{16}O$, respectively). The comment claims that this leads to an overestimate of the discrepancy between previous studies and that the resulting gross production rates are "30 % too high".

Nicholson recognises the improved accuracy of Kaiser's direct calculation ("dual-delta") method compared to previous approximate approaches based on ^{17}O excess ($^{17}\Delta$) and its simplicity compared to previous iterative calculation methods. Although he correctly points out that differences in the normalised gross production rate (g) are largely due to different input parameters used in Kaiser's "base case" and previous studies, he does not acknowledge Kaiser's observation that iterative and dual-delta calculation methods give exactly the same g for the same input parameters (disregarding kinetic isotope fractionation during air-sea exchange). The comment is based on misunderstandings with respect to the "base case" $^{17}\delta_P$ and $^{18}\delta_P$ values. Since direct measurements of $^{17}\delta_P$ and $^{18}\delta_P$ do not exist or have been lost, Kaiser constructed the "base case" in a way that was consistent and compatible with literature data. Nicholson showed that an alternative reconstruction of $^{17}\delta_P$ gives g values closer to previous studies. However, unlike Nicholson, we refrain from interpreting either reconstruction as a benchmark for the accuracy of g.

A number of publications over the last 12 months have tried to establish which of these two reconstructions is more accurate. Nicholson draws on recently revised measurements of the relative $^{17}O/^{16}O$ difference between VSMOW and Air-O_2 ($^{17}\delta_{VSMOW}$; Barkan and Luz, 2011), together with new measurements of photosynthetic isotope fractionation, to support his comment. However, our own measurements disagree with these revised $^{17}\delta_{VSMOW}$ values. If scaled for differences in $^{18}\delta_{VSMOW}$, they are actually in good agreement with the original data (Barkan and Luz, 2005) and support Kaiser's "base case" g values. The statement that Kaiser's g values are "30 % too high" can therefore not be accepted, pending future work to reconcile different $^{17}\delta_{VSMOW}$ measurements.

Nicholson also suggests that approximated calculations of gross production should be performed with a triple isotope excess defined as $^{17}\Delta^{\#} \equiv \ln(1+^{17}\delta) - \lambda \ln(1+^{18}\delta)$, with $\lambda = \theta_R = \ln(1+^{17}\varepsilon_R)/\ln(1+^{18}\varepsilon_R)$. However, this only improves the approximation for certain $^{17}\delta_P$ and $^{18}\delta_P$ values, for certain net to gross production ratios (f) and for certain ratios of gross production to gross Air-O_2 invasion (g). In other cases, the approximated calculation based on $^{17}\Delta^{\dagger} \equiv ^{17}\delta - \kappa \, ^{18}\delta$ with $\kappa = \gamma_R = ^{17}\varepsilon_R/^{18}\varepsilon_R$ (Kaiser, 2011a) gives more accurate results.

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 $^{17}\delta$ and $^{18}\delta$ measurements of dissolved O_2 relative to Air-O_2 directly, rather than the ^{17}O excess ($^{17}\Delta$) and using an approximation (Luz and Barkan, 2000). The calculation uses the following equation:

$$g = \frac{(1+^{17}\varepsilon_E)\frac{^{17}\delta-^{17}\delta_{sat}}{1+^{17}\delta} - \gamma_R(1+^{18}\varepsilon_E)\frac{^{18}\delta-^{18}\delta_{sat}}{1+^{18}\delta} + s(^{17}\varepsilon_E - \gamma_R^{18}\varepsilon_E)}{\frac{^{17}\delta-^{17}\delta}{1+^{17}\delta} - \gamma_R\frac{^{18}\delta_P-^{18}\delta}{1+^{18}\delta}} \quad (1)$$

Equation (1) is based on Eq. (48) in Kaiser (2011a), but takes into account that previous measurements of the kinetic isotope fractionation during O_2 gas exchange refer to evasion from solution to gas phase (Kaiser, 2011b; Knox et al., 1992). The symbols have the following meaning:

$g = P / (kc_{sat})$: ratio of gross oxygen production to gross Air-O_2 invasion.

$^{17}\delta$, $^{18}\delta$: relative $^{17}O / ^{16}O$ and $^{18}O / ^{16}O$ differences between dissolved O_2 and Air-O_2.

$^{17}\delta_{sat}$, $^{18}\delta_{sat}$: relative $^{17}O / ^{16}O$ and $^{18}O / ^{16}O$ differences between dissolved O_2 at air saturation and Air-O_2.

$^{17}\delta_P$, $^{18}\delta_P$: relative $^{17}O / ^{16}O$ and $^{18}O / ^{16}O$ differences between photosynthetic O_2 and Air-O_2.

$^{17}\varepsilon_E$, $^{18}\varepsilon_E$: kinetic $^{17}O / ^{16}O$ and $^{18}O / ^{16}O$ fractionations during O_2 evasion from sea to air.

$\gamma_R =^{17}\varepsilon_R / ^{18}\varepsilon_R$: ratio of respiratory $^{17}O / ^{16}O$ fractionation and $^{18}O / ^{16}O$ fractionation.

$s = c/c_{sat} - 1$: relative supersaturation of dissolved O_2.

Prokopenko et al. (2011) developed virtually the same method, but did not include kinetic isotope fractionation during O_2 gas transfer. This resulted in the simplified solution

$$g = \frac{\frac{^{17}\delta-^{17}\delta_{sat}}{1+^{17}\delta} - \gamma_R\frac{^{18}\delta-^{18}\delta_{sat}}{1+^{18}\delta}}{\frac{^{17}\delta_P-^{17}\delta}{1+^{17}\delta} - \gamma_R\frac{^{18}\delta_P-^{18}\delta}{1+^{18}\delta}} \quad (2)$$

The comment by Nicholson (2011a) does not question the validity of the dual-delta method. Unlike the approximated calculation of Luz and Barkan (2000), it does not assume steady state for O_2 concentrations and can, therefore, be expected to be more universally applicable. Only the assumption of isotopic steady state is needed. In contrast to the claim that the dual-delta method requires $^{17}\varepsilon_R$ and $^{18}\varepsilon_R$ (Nicholson, 2011b), the above equations clearly show that only γ_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 delays and misunderstandings during scientific communication, which can be avoided with the dual-delta method. In this paper, $^{17}\Delta$ values are 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 Sect. 2, we discuss the merits of Nicholson's comment in view of different reconstructions of the isotopic composition of photosynthetic 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 (δ_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 ‰ assumed for $^{18}\delta_P$.

The "definition" of the base case $^{17}\delta_P$ or $^{18}\delta_P$ values in Sect. 5 of Kaiser (2011a) followed the approach of previous studies that used the measured ^{17}O excess of O_2 evolved in flask studies of $^{17}\Delta^{\dagger}(0.521) = (249 \pm 15)$ ppm (Luz and Barkan, 2000) and combined its numerical value with the inferred $^{18}\delta_P$ value and an entirely different ^{17}O excess definition, in this case $^{17}\Delta^{\#}(\gamma_R)$, where $\gamma_R = 0.5179$. Even though the reconstructed $^{17}\delta_P$ value of -11.646 ‰ must be considered hypothetical, it is consistent with $^{17}\delta_P$ values derived from actual literature data following two different approaches: one 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 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 $^{18}\delta_P = -22.835$ ‰ .

Nicholson suggests that $^{17}\Delta^{\#}(\theta_R)$ should be used to reconstruct $^{17}\delta_P$, where $\theta_R = \ln(1+^{17}\varepsilon_R)/\ln(1+^{18}\varepsilon_R) = 0.5154$ for $^{18}\varepsilon_R = -20$ ‰. This assumes concentration steady state in Luz and Barkan's flask experiments and near-zero steady-state $^{18}\delta$ values ($^{18}\delta_{S0}$). The resulting $^{17}\delta_P$ value of -11.588 ‰ (for $^{18}\delta_P = -22.835$ ‰) gives gross production rates that are about 30 % higher than for Kaiser's "base case".

To dispel any confusion about how the isotopic composition of photosynthetic O_2 (including the triple isotope excess) was calculated, 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 3. We also update any values in Kaiser (2011a) and Nicholson (2011a) to reflect recent publications by Luz and Barkan displaying them

with more decimals than previously; however, this does not significantly change any results or conclusions.

2.1 Calculation of δ_P based on the isotopic composition of source water (δ_W) and the photosynthetic isotope fractionation (ε_P)

The relative isotope ratio difference of photosynthetic O_2 to Air-O_2 (δ_P) can be calculated via

$$\delta_P = (1 + \delta_W)(1 + \varepsilon_P) - 1 \tag{3}$$

where δ_W is the relative isotope ratio difference of source water to Air-O_2 and ε_P is the photosynthetic isotope fractionation. The corresponding triple isotope excess is

$$\begin{aligned}
{}^{17}\Delta_P^\dagger &= {}^{17}\delta_P - \kappa\,{}^{18}\delta_P \\
&= {}^{17}\delta_W + {}^{17}\varepsilon_P + {}^{17}\delta_W\,{}^{17}\varepsilon_P \\
&\quad - \kappa({}^{18}\delta_W + {}^{18}\varepsilon_P + {}^{18}\delta_W\,{}^{18}\varepsilon_P) \\
&= {}^{17}\Delta_W^\dagger + (\gamma_P - \kappa)\,{}^{18}\varepsilon_P \\
&\quad - \left[\kappa(1 - \gamma_P)\,{}^{18}\delta_W - \gamma_P\,{}^{17}\Delta_W^\dagger\right]{}^{18}\varepsilon_P
\end{aligned} \tag{4}$$

where $\gamma_P = {}^{17}\varepsilon_P / {}^{18}\varepsilon_P$ and

$$\begin{aligned}
{}^{17}\Delta_P^\# &= \ln(1 + {}^{17}\delta_P) - \lambda\ln(1 + {}^{18}\delta_P) \\
&= \ln(1 + {}^{17}\delta_W) + \ln(1 + {}^{17}\varepsilon_P) - \lambda\ln(1 + {}^{18}\delta_W) \\
&\quad - \lambda\ln(1 + {}^{17}\delta_P) \\
&= {}^{17}\delta\Delta_W^\# + (\theta_P - \lambda)\ln(1 + {}^{18}\varepsilon_P)
\end{aligned} \tag{5}$$

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

Note that the respiratory isotope fractionation ε_R does not enter into these equations. ε_R is only needed if the isotopic composition of O_2 in steady state between photosynthesis and respiration (δ_S) was required. δ_S can be calculated using Eq. (31) in Kaiser (2011a). For comparison with Sect. 2.2, the corresponding δ_{S0} values for a net to gross production ratio of $f = 0$ are also shown in Table 3; see also Eq. (6) below.

Kaiser (2011a) chose δ_W to correspond to the isotopic composition of seawater. $^{18}\delta_W$ was set equal to $^{18}\delta_{VSMOW} = (-23.323 \pm 0.02)\,‰$ (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). Barkan and Luz (2011) reported more decimals and these values need to be corrected to $^{18}\delta_W = -23.320\,‰$ and $^{17}\delta_W = -11.936\,‰$ (Table 1, row 3; Table 3, row 5). Other measurements of $^{17}\delta_{VSMOW}$ were disregarded because they were less precise (Table 1, rows 1 and 2) or did not differ in terms of the ^{17}O excess (Table 1, row 4), which is critical for the magnitude of g; see Sect. 2.4 below for the impact of new $^{17}\delta_{VSMOW}$ measurements listed in Table 1, rows 5 and 6.

For ε_P, 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). The uncertainty of $^{18}\varepsilon_P$ was chosen to reflect the range of photosynthetic isotope fractionation in other systems (Guy et al., 1993). This gave $^{18}\delta_P = (-22.835 \pm 0.5)\,‰$, $^{17}\delta_P = (-11.676 \pm 0.26)\,‰$, $^{17}\Delta_P^\dagger(0.5179) = (150 \pm 13)\,\text{ppm}$; with the δ_W update referred to above, $^{18}\delta_P = (-22.832 \pm 0.5)\,‰$, $^{17}\delta_P = (-11.671 \pm 0.26)\,‰$, $^{17}\Delta_P^\dagger(0.5179) = (153 \pm 6)\,\text{ppm}$; with the actual $^{18}\varepsilon_P = (0.467 \pm 0.17)\,‰$ (Table 2), $^{18}\delta_P = (-22.864 \pm 0.17)\,‰$, $^{17}\delta_P = (-11.689 \pm 0.09)\,‰$, $^{17}\Delta_P^\dagger(0.5179) = (152 \pm 6)\,\text{ppm}$ (Table 3, row 5a). The propagated error in $^{17}\Delta$ 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) reported on $^{18}\varepsilon_P$ and θ_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 higher than for *Synechocystis* sp. PCC 6803 and range from $(2.850 \pm 0.05)\,‰$ for *N. oculata* to $(7.04 \pm 0.10)\,‰$ for *C. reinhardtii* (Table 2). The θ_P values are lower than for *Synechocystis* sp. PCC 6803 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 $(178 \pm 4)\,\text{ppm}$ for *N. oculata* to $(214 \pm 5)\,\text{ppm}$ for *E. huxleyi* (Table 3, rows 5b–5e). These high $^{18}\varepsilon_P$ values contradict the notion that water undergoes little isotopic fractionation during photosynthetic O_2 production, based on measurements (Guy et al., 1993; Helman et al., 2005) and theoretical considerations (Tcherkez and Farquhar, 2007). They might be explained by cell-internal O_2 consumption. However, discrepancies also appear between the $^{18}\varepsilon_P$ value of 0.62‰ reported for *P. tricornutum* by Guy et al. (1993) and the value of $(4.426 \pm 0.01)\,‰$ reported by Eisenstadt et al. (2010), although in both cases essentially the same experimental setup (helium-sparging of cell cultures) was used. Eisenstadt et al.'s attribution of this difference to improved methods for the measurement of the relative isotope ratio difference between the evolved O_2 and the source water is not in line with the small difference in measurements of the "Dole effect" (i.e., the $^{18}O / ^{16}O$ difference between Air-O_2 and VSMOW) by the same research group (Barkan and Luz, 2005), compared to independent estimates of $(23.8 \pm 0.1)\,‰$ (Coplen et al., 2002; Kroopnick and Craig, 1972) and $(24.36 \pm 0.06)\,‰$ (Kaiser, 2008). Despite these inconsistencies, we will consider the measurements of Eisenstadt et al. (2010) here to work out δ_P values; an approach that was also taken by Luz and Barkan (2011b).

Table 1. Historic and new measurements of the relative oxygen isotope ratio differences between Vienna Standard Mean Ocean Water (VS-MOW) and Air-O_2 ($^{17}\delta_{\text{VSMOW}}$, $^{18}\delta_{\text{VSMOW}}$, $^{17}\Delta_{\text{VSMOW}}$). For clarity, all values are shown with the same number of decimals, irrespective of their uncertainty.

Row	Reference	$^{18}\delta_{\text{VSMOW}}$/‰	$^{17}\delta_{\text{VSMOW}}$/‰	$^{17}\Delta_{\text{VSMOW}}^{\dagger}(0.5179)$/ppm	$^{17}\Delta_{\text{VSMOW}}^{\#}(0.5179)$/ppm
1	Thiemens et al. (1995)	-22.873 ± 0.04	-11.744 ± 0.08	102 ± 80[a]	170 ± 80[a]
2	Luz et al. (1999); based on Thiemens et al. (1995)	-22.960[b]	-11.778[b]	113[b]	182[b]
3	Barkan and Luz (2005)	-23.320 ± 0.02	-11.931 ± 0.01	146 ± 4	218 ± 4
4	Kaiser (2008); based on Barkan and Luz (2005)	-23.771 ± 0.06	-12.167 ± 0.04	144 ± 4	218 ± 4
5	Barkan and Luz (2011)	-23.324 ± 0.02	-11.883 ± 0.01	196 ± 4	268 ± 4
6	This paper	-23.647 ± 0.04	-12.102 ± 0.03	145 ± 6	218 ± 6

[a] Minimum error based on the uncertainty of the corresponding $^{17}\delta$ value.
[b] No error estimate was given.

Table 2. Photosynthetic oxygen isotope fractionation for different marine (rows 2 to 4) and freshwater (rows 1 and 5) species (Eisenstadt et al., 2010; Helman et al., 2005). The third decimal of $^{18}\varepsilon_{\text{P}}$ in rows 2 to 4 has been reconstructed from Luz and Barkan (2011b). The mean θ_{P} value has been calculated from a linear regression of the five species-dependent $\ln(1+^{17}\varepsilon_{\text{P}})$ and $\ln(1+^{18}\varepsilon_{\text{P}})$ values. It is useful for error propagation purposes. The resultant y-axis intercept of (0.012 ± 0.013)‰ is statistically indistinguishable from zero. For clarity, θ_{P} and $^{17}\varepsilon_{\text{P}}$ values are shown with the same number of decimals, irrespective of their uncertainty.

Row	Species	θ_{P}	$^{18}\varepsilon_{\text{P}}$/‰	$^{17}\varepsilon_{\text{P}}$/‰
1	*Synechocystis* sp. strain PCC 6803	0.5354 ± 0.0020	0.467 ± 0.17	0.250
2	*Nannochloropsis oculata*	0.5253 ± 0.0004	2.850 ± 0.05	1.496
3	*Phaeodactylum tricornutum*	0.5234 ± 0.0004	4.426 ± 0.01	2.314
4	*Emiliania huxleyi*	0.5253 ± 0.0004	5.814 ± 0.06	3.050
5	*Chlamydomonas reinhardtii*	0.5198 ± 0.0001	7.04 ± 0.10	3.653
	Mean	0.5203 ± 0.0027	4.119 ± 2.6	2.153

2.2 Calculation of δ_{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

$$\delta_{\text{S0}} = \frac{1+\delta_{\text{P}}}{1+\varepsilon_{\text{R}}} - 1 = \frac{\delta_{\text{P}} - \varepsilon_{\text{R}}}{1+\varepsilon_{\text{R}}} \tag{6}$$

To derive δ_{P}, Eq. (6) is rearranged to

$$\delta_{\text{P}} = (1+\delta_{\text{S0}})(1+\varepsilon_{\text{R}}) - 1 \tag{7}$$

In addition to δ_{S0}, this calculation also requires ε_{R}.

Luz and Barkan (2000) performed incubations of a *Nannochloropsis* species and the hermatypic coral *Acropora* in airtight flasks. These incubations are supposed to correspond to steady state. No values were reported for δ_{S0}, only $^{17}\Delta_{\text{S0}}^{\dagger}(0.521) = (244 \pm 20)$ ppm for *Nannochloropsis* and (252 ± 5) ppm for *Acropora*; anecdotal evidence suggests that δ_{S0} was close to 0 (Barkan and Luz, 2011).

For *Acropora*, Luz and Barkan (2005) reported $^{18}\varepsilon_{\text{R}} = (-13.8 \pm 0.5)$‰ and $\gamma_{\text{R}} = 0.519 \pm 0.001$. Assuming $^{18}\varepsilon_{\text{P}} = (0.5 \pm 0.5)$‰ and $^{18}\delta_{\text{W}} = -23.320$‰, this gives $^{18}\delta_{\text{P}} = (-22.832 \pm 0.5)$‰ and $^{18}\delta_{\text{S0}} = (-9.16 \pm 0.71)$‰ (Kaiser, 2011a, b). With

$$^{17}\delta_{\text{S0}} = {}^{17}\Delta_{\text{S0}}^{\dagger}(0.521) + 0.521\,^{18}\delta_{\text{S0}} \tag{8}$$

this gives $^{17}\delta_{\text{S0}} = (-4.52 \pm 0.37)$‰ and, using Eq. (7), $^{17}\delta_{\text{P}} = (-11.649 \pm 0.26)$‰ and $^{17}\Delta_{\text{P}}^{\dagger}(0.5179) = (175 \pm 15)$ ppm (Table 3, row 3a). The photosynthetic isotope fractionation for *Acropora* is not known; if we assume the highest value reported for a marine species (*E. huxleyi*), the resulting $^{17}\Delta_{\text{P}}^{\dagger}(0.5179)$ value is (210 ± 15) ppm (Table 3, row 3b).

Kaiser (2011a) mentioned that no corresponding calculation could be performed for *Nannochloropsis* because $^{18}\varepsilon_{\text{R}}$ and γ_{R} values have not been reported for this species. In Sect. 4 of Nicholson (2011a), this calculation is performed nonetheless, assuming $^{18}\varepsilon_{\text{R}} = -20$‰ and $\gamma_{\text{R}} = 0.5179$ (without uncertainties). Here, we repeat this calculation, assuming more realistic uncertainty estimates of 4‰ for $^{18}\varepsilon_{\text{R}}$ and 0.0006 for γ_{R}. This gives $^{18}\delta_{\text{P}} = (-22.832 \pm 0.5)$‰, $^{17}\delta_{\text{P}} = (-11.606 \pm 0.26)$‰ and $^{17}\Delta_{\text{P}}^{\dagger}(0.5179) = (218 \pm 38)$ ppm for $^{8}\varepsilon_{\text{P}} = (0.5 \pm 0.5)$‰ (Table 3, row 4a). If $^{18}\varepsilon_{\text{P}} = (2.850 \pm 0.05)$‰ (Eisenstadt et al., 2010) is used instead, $^{17}\delta_{\text{P}} = (-10.399 \pm 0.047)$‰ and $^{17}\Delta_{\text{P}}^{\dagger}(0.5179) = (237 \pm 39)$ ppm (Table 3, row 4b). Both values clearly differ from $^{17}\Delta_{\text{P}}^{\dagger}(0.5179) = (178 \pm 4)$ ppm derived for *N. oculata* based on δ_{W} and ε_{P} (Sect. 2.1; Table 3, row 5b). The increased uncertainty estimates compared to *Acropora* are due to the higher uncertainty in $^{17}\Delta_{\text{S0}}^{\dagger}(0.521)$ of 20 ppm and the higher uncertainty in $^{18}\varepsilon_{\text{R}}$ of 4‰.

Table 3. 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 $f = 0$ ($^{17}\delta_{S0}$, $^{18}\delta_{S0}$, $^{17}\Delta_{S0}$), calculated as per Sect. 2. For clarity, all values are shown with the same number of decimals, irrespective of their uncertainty. Directly measured values are in bold. Assumed values are in bold italics, i.e., for "Kaiser (2011a)" (row 1), $^{17}\Delta_P^{\#}(0.5179) = (249 \pm 15)$ ppm; for "Nicholson (2011a)" (row 2), $^{17}\Delta_{S0}^{\#}(0.5154) = (249 \pm 15)$ ppm. Other values were calculated using $\gamma_R = 0.5179 \pm 0.0006$, $^{18}\varepsilon_R = (-20 \pm 4)$ ‰, $\theta_R = 0.5154$, except for "Acropora (flask)" where $\gamma_R = 0.519 \pm 0.001$, $^{18}\varepsilon_R = (-13.8 \pm 0.5)$ ‰, $\theta_R = 0.5173$. For "Acropora (flask)" and "Nannochloropsis (flask)", $^{17}\Delta_{S0}^{\dagger}(0.521) = (252 \pm 5)$ ppm and (244 ± 20) ppm, respectively, were used (Luz and Barkan, 2000). δ_P values in rows 1 to 5m are based on the δ_{VSMOW} values in Table 1, row 3 (Barkan and Luz, 2005); rows 6 to 6m are based on Table 1, row 5 (Barkan and Luz, 2011); rows 7 to 7m are based on Table 1, row 6 (this paper); all account for the 5 ppm lower $^{17}O / ^{16}O$ ratio of ocean water compared to VSMOW (Luz and Barkan, 2010) and the photosynthetic isotope fractionations in Table 2.

Row	Description / Unit	$^{18}\delta_P$ ‰	$^{17}\delta_P$ ‰	$^{17}\Delta_P^{\dagger}(0.5179)$ ppm	$^{17}\Delta_P^{\#}(0.5179)$ ppm	$^{18}\delta_{S0}$ ‰	$^{17}\delta_{S0}$ ‰	$^{17}\Delta_{S0}^{\dagger}(0.5179)$ ppm	$^{17}\Delta_{S0}^{\#}(0.5179)$ ppm	$^{17}\Delta_{S0}^{\#}(0.5154)$ ppm
1	Kaiser (2011a), $^{18}\varepsilon_P = (0.50 \pm 0.50)$ ‰	−22.832	−11.644	180 ± 15	**_249 ± 15_**	−2.889	−1.300	197	198	191
2	Nicholson (2011a), $^{18}\varepsilon_P = (0.50 \pm 0.50)$ ‰	−22.832	−11.587	238 ± 35	307 ± 35	−2.889	−1.242	255	256	**_249 ± 15_**
3a	Acropora (flask), $^{18}\varepsilon_P = (0.50 \pm 0.50)$ ‰	−22.832	−11.649	175 ± 15[a]	244 ± 15[a]	−9.158	−4.519	224[a]	235[a]	−[a]
3b	Acropora (flask), $^{18}\varepsilon_P = (5.814 \pm 0.06)$ ‰	−22.832	−8.927	210 ± 15[b]	251 ± 15[b]	−3.895	−1.777	240[b]	242[b]	−[b]
4a	Nannochloropsis (flask), $^{18}\varepsilon_P = (0.50 \pm 0.50)$ ‰	−22.832	−11.606	218 ± 38	287 ± 38	−2.889	−1.261	235	236	229
4b	Nannochloropsis (flask), $^{18}\varepsilon_P = (2.85 \pm 0.05)$ ‰	−20.536	−10.399	237 ± 39	293 ± 40	−0.547	−0.041	242	242	241
5	δ_W based on Barkan and Luz (2005), $\varepsilon_P = 0$	**−23.320**	**−11.936**	141 ± 4	213 ± 4	−3.388	−1.594	160	162	153
5a	ε_P (Synechocystis, sp. strain PCC 6803)	−22.864	−11.689	152 ± 6	221 ± 5	−2.923	−1.345	169	170	163
5b	ε_P (Nannochloropsis oculata)	−20.536	−10.458	178 ± 4	234 ± 4	−0.547	−0.101	183	183	181
5c	ε_P (Phaeodactylum tricornutum)	−18.997	−9.649	189 ± 4	237 ± 4	1.023	0.716	186	186	189
5d	ε_P (Emiliania huxleyi)	−17.642	−8.922	214 ± 5	256 ± 5	2.407	1.451	204	205	211
5e	ε_P (Chlamydomonas reinhardtii)	−16.444	−8.326	190 ± 4	226 ± 4	3.628	2.053	174	175	184
5m	mean of rows 5a to 5e	−19.297	−9.809	185 ± 22	234 ± 13	0.718	0.555	183 ± 14	183 ± 14	185 ± 18
6	δ_W based on Barkan and Luz (2011), $\varepsilon_P = 0$	**−23.324**	**−11.888**	192 ± 4	263 ± 4	−3.392	−1.546	211	212	204
6a	ε_P (Synechocystis, sp. strain PCC 6803)	−22.868	−11.641	202 ± 6	272 ± 5	−2.927	−1.297	219	221	213
6b	ε_P (Nannochloropsis oculata)	−20.540	−10.410	228 ± 4	284 ± 4	−0.552	−0.052	233	234	232
6c	ε_P (Phaeodactylum tricornutum)	−19.001	−9.601	239 ± 4	288 ± 4	1.019	0.765	237	237	239
6d	ε_P (Emiliania huxleyi)	−17.646	−8.874	264 ± 5	306 ± 5	2.402	1.499	255	255	261
6e	ε_P (Chlamydomonas reinhardtii)	−16.448	−8.278	240 ± 4	277 ± 4	3.624	2.102	225	226	235
6m	mean of rows 6a to 6e	−19.301	−9.761	235 ± 22	285 ± 13	0.714	0.603	234 ± 14	234 ± 14	236 ± 18
7	δ_W based on this paper, $\varepsilon_P = 0$	**−23.647**	**−12.107**	140 ± 6	213 ± 6	−3.722	−1.767	160	163	153
7a	ε_P (Synechocystis, sp. strain PCC 6803)	−23.192	−11.860	151 ± 7	222 ± 7	−3.257	−1.518	169	171	162
7b	ε_P (Nannochloropsis oculata)	−20.865	−10.629	177 ± 6	235 ± 6	−0.882	−0.274	183	184	181
7c	ε_P (Phaeodactylum tricornutum)	−19.326	−9.821	188 ± 6	238 ± 6	0.688	0.543	187	187	189
7d	ε_P (Emiliania huxleyi)	−17.971	−9.094	213 ± 6	256 ± 7	2.071	1.278	205	205	211
7e	ε_P (Chlamydomonas reinhardtii)	−16.774	−8.498	189 ± 6	227 ± 6	3.292	1.880	175	176	184
7m	mean of rows 7a to 7e	−19.625	−9.980	184 ± 23	235 ± 14	0.382	0.382	184 ± 15	184 ± 15	185 ± 18

[a] The corresponding values for $\lambda = \kappa = 0.519$ are $^{17}\Delta_P^{\dagger}(0.5179) = (200 \pm 15)$ ppm, $^{17}\Delta_P^{\#}(0.5179) = (269 \pm 15)$ ppm, $^{17}\Delta_{S0}^{\dagger}(0.5179) = 245$ ppm and $^{17}\Delta_{S0}^{\#}(0.5179) = 229$ ppm.

[b] The corresponding values for $\lambda = \kappa = 0.519$ are $^{17}\Delta_P^{\dagger}(0.5179) = (229 \pm 15)$ ppm, $^{17}\Delta_P^{\#}(0.5179) = (271 \pm 15)$ ppm, $^{17}\Delta_{S0}^{\dagger}(0.5179) = 244$ ppm, $^{17}\Delta_{S0}^{\#}(0.5179) = 247$ ppm and $^{17}\Delta_{S0}^{\#}(0.5173) = 240$ ppm.

2.3 Hypothetical "base case" values for the isotopic composition of photosynthetic O_2

Based on the discrepancy between the ^{17}O excess for photosynthetic O_2 produced by *Synechocystis* and *Acropora*, Kaiser (2011a) found it impossible to assign a best value for $^{17}\delta_P$. The inclusion of *Nannochloropsis* with Nicholson's assumptions does not help to resolve this.

Instead, Kaiser (2011a) constructed a hypothetical base case in a way that was mathematically consistent with previous studies (Hendricks et al., 2004; Juranek and Quay, 2010; Reuer et al., 2007). The base case adopted a triple isotope excess of $^{17}\Delta_P^{\#}(0.5179) = (249 \pm 15)$ ppm (Table 3, row 1). This is the same numerical value for the triple isotope excess used in previous studies, although λ 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 $^{17}\delta_P = -11.646$ ‰ (-11.644 ‰ with the δ_W update referred to in Sect. 2.1; Table 3, row 1), which is slightly higher than the corresponding values of -11.671 ‰ for *Synechocystis* and -11.649 ‰ for *Acropora*. The resulting value of $^{17}\Delta_P^{\dagger}(0.5179) = (180 \pm 15)$ ppm is compatible with the $^{17}\Delta_P^{\dagger}(0.5179)$ values for other species based on the $^{18}\varepsilon_P$ measurements of Eisenstadt et al. (2010) (Table 3, rows 5b, 5c, 5e) except for *E. huxleyi* (Table 3, row 5d).

Nicholson (2011a) questions the validity of this base case and suggests that λ should be chosen such that $^{17}\Delta_{S0}^{\#}(\lambda_{BSS}) = {}^{17}\Delta_P^{\#}(\lambda_{BSS})$ and that these values should equal (249 ± 15) ppm. This "tuned" λ value, denoted λ_{BSS} (for biological steady state) by Nicholson (2011a), is actually identical to the triple isotope fractionation coefficient for respiration (θ_R) and calculated as

$$\lambda_{BSS} = \theta_R$$
$$= \frac{\ln(1 + {}^{17}\varepsilon_R)}{\ln(1 + {}^{18}\varepsilon_R)} = \frac{\ln(1 + \gamma_R {}^{18}\varepsilon_R)}{\ln(1 + {}^{18}\varepsilon_R)} \quad (9)$$

This leads to a set of calculation parameters with $^{18}\delta_P = -22.832$ ‰, $^{17}\delta_P = -11.587$ ‰ and $^{17}\Delta_P^{\dagger}(0.5179) = (238 \pm 35)$ ppm (Table 3, row 2). Within error, this agrees with the *Nannochloropsis* flask experiments if the assumptions of $\gamma_R = 0.5179 \pm 0.0006$ and $^{18}\varepsilon_R = (-20 \pm 4)$ ‰ for these experiments are correct. It differs substantially from the corresponding values for the *Acropora* flask experiments assuming $^{18}\varepsilon_P = 0.5$ ‰ (Table 3, row 3a) and the results for all species based on the isotopic composition of seawater and the photosynthetic isotope fractionation (Table 3, rows 5a–c, 5e) except for *E. huxleyi* (Table 3, row 5d). It may be reconciled with the *Acropora* flask experiments if $^{18}\varepsilon_P = 5.814$ ‰ is assumed (Table 3, row 3b).

In Sect. 4, Nicholson (2011a) comments that $^{17}\Delta_P^{\#}(\theta_R) = 231$ ppm for the *Nannochloropsis* flask experiments is very close to $^{17}\Delta_P^{\#}(\theta_R) = 234$ ppm for the *Acropora* flask experiments. Notwithstanding that our own calculations give identical results of $^{17}\Delta_P^{\#}(\theta_R) = 229$ ppm for both cases (Table 3, row 4a and footnote to row 3a), this is not a fair comparison because $\theta_R = 0.5173$ for *Acropora* and $\theta_R = 0.5154$ for *Nannochloropsis*. Clearly, the $^{17}\delta_P$ values differ in both cases (for the same $^{18}\delta_P$ value) and calculations of gross production using the accurate dual-delta method would lead to different results. This illustrates the perils associated with using $^{17}\Delta$ values in isolation.

2.4 New measurements of $^{18}\delta_{VSMOW}$ and $^{17}\delta_{VSMOW}$

Four days after publication of Kaiser (2011a) and three days before publication of Nicholson (2011a), new measurements of $^{18}\delta_{VSMOW}$ and $^{17}\delta_{VSMOW}$ 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 $^{17}\delta_{VSMOW} = (-11.883 \pm 0.012)$ ‰ (Table 1, row 5), which is 0.048 ‰ or five standard deviations higher than the original value of (-11.931 ± 0.01) ‰ (Barkan and Luz, 2005). The new $^{18}\delta_{VSMOW}$ value of (-23.324 ± 0.017) ‰ was virtually unchanged compared to the original value of (-23.320 ± 0.02) ‰. In terms of $^{17}\Delta_{VSMOW}^{\dagger}(0.5179)$, this amounts to a change from (146 ± 4) ppm to (196 ± 4) ppm. The authors do not give an explanation for this change, other than that "experimental system and measurement procedures were somewhat improved" (Barkan and Luz, 2011).

The revised measurements allow recalculating δ_P based on δ_W and ε_P (Sect. 2.1). $^{18}\delta_P$ remains virtually unchanged, but the corresponding $^{17}\delta_P$ and $^{17}\Delta_P^{\dagger}(0.5179)$ values increase by about 50 ppm (Table 3). Within error, the revised $^{17}\Delta_P^{\dagger}(0.5179)$ values agree with those estimated for *Nannochloropsis* (flask), *Acropora* (flask; assuming $^{18}\varepsilon_P = 5.814$ ‰) and Nicholson (2011a). They disagree with the *Acropora* (flask; assuming $^{18}\varepsilon_P = 0.5$ ‰) and Kaiser (2011a) values.

Our own measurements of VSMOW relative to Air-O_2 give $^{18}\delta_{VSMOW} = (-23.647 \pm 0.04)$ ‰ and $^{17}\delta_{VSMOW} = (-12.102 \pm 0.03)$ ‰ (Table 1, row 6). 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 $^{17}\Delta_W^{\dagger}(0.5179) = (140 \pm 6)$ ppm (Table 3, row 7). The uncertainty of $^{17}\Delta_W^{\dagger}$ is lower than for $^{17}\delta_W$ because the errors in $^{18}\delta$ and $^{17}\delta$ are correlated in a mass-dependent way.

Our $^{17}\Delta_W^{\dagger}(0.5179)$ 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 using CoF_3 fluorination on a Finnigan MAT Delta Plus isotope ratio mass spectrometer (University of Nagoya). 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 $^{17}\Delta_W^\dagger(0.5179)$ by a 2 ppm increase only. It actually brings $^{18}\delta_{VSMOW}$ into closer agreement with independent estimates of (-23.771 ± 0.06)‰ (Table 1, row 4), based on isotope measurements in CO_2 (Kaiser and Röckmann, 2008). Barkan and Luz (2005, 2011) did not perform a scale correction, even though their measured SLAP-VSMOW difference of (-55.11 ± 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 mean parameter sets from the species-dependent δ_P values (Table 3, rows 5m, 6m and 7m). For the photosynthetic isotope fractionation, we adopt the arithmetic average of the corresponding values based on Eisenstadt et al. (2010), i.e., $^{18}\varepsilon_P = (4.119 \pm 2.6)$‰ and $^{17}\varepsilon_P = (2.153 \pm 1.3)$‰ (Table 2). This $^{18}\varepsilon_P$ value is in good agreement with the global average $^{18}\varepsilon_P$ of 4‰ derived by Luz and Barkan (2011a). A similar approach was taken by Luz and Barkan (2011b), but they excluded *C. reinhardtii* from their mean δ_P values. It would not be appropriate to take the arithmetic average of θ_P reported for various organisms to derive $^{17}\varepsilon_P$ because $^{17}\varepsilon_P$ is essentially linearly related to $^{17}\delta_P$ whereas θ_P is not.

The good agreement between our own measurements of the isotopic composition of VSMOW relative to Air-O_2 and those of Barkan and Luz (2005) is also reflected by the closely matching species-dependent $^{17}\Delta_P(0.5179)$ values (Table 3, rows 5a–5e and 7a–7e). In the next section, we will illustrate the systematic impact of different δ_P values on g.

3 Dependence of g on the 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 γ_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 parameters suggested by Nicholson (2011a) and Kaiser (2011a) are compared with those using the mean δ_P values based on Barkan and Luz (2005; Table 3, row 5m; Fig. 1a and b) and based on Barkan and Luz (2011; Table 3, row 6m; Fig. 1c and d). The same scenarios as in Kaiser (2011a) were used, i.e., $g = 0.4$ with $-1.0 \le f \le +1.0$ (Fig. 1a

and c) and $f = 0.1$ with $0.01 \le g \le 10$ (Fig. 1b and d). Parameters related to gas exchange were left unchanged at $^{17}\delta_{sat} = 0.382$‰, $^{18}\delta_{sat} = 0.707$‰, $^{17}\varepsilon_E = -1.463$‰, $^{18}\varepsilon_E = -2.800$‰ (Kaiser, 2011a, b).

As may be expected from the corresponding $^{17}\Delta_P$ values, there is relative good agreement between g based on "Table 3, row 5m" (using VSMOW measurements reported by Barkan and Luz, 2005), "Table 3, row 7m" (using VSMOW measurements reported here), "Kaiser (2011a)", "*Acropora* (flask, $^{18}\varepsilon_P = 0.5$‰)" and the species-specific parameters for *N. oculata*, *C. reinhardtii* and *P. tricornutum* (Fig. 1a and b). However, g based on *Synechocystis* parameters is ≥ 24 % higher; g based on "Nicholson (2011a)", "*Nannochloropsis* (flask, 2.85‰)" and "Luz and Barkan, 2011b" is ≥ 27 % lower than "Table 3, row 5m". g values based on "*E. huxleyi*" and "*Acropora* (flask, 5.814‰)" and "*Nannochloropsis* (flask, 0.5‰)" are in between. For $f < 0.1$ or $g > 0.1$, these relative deviations are higher (Fig. 1a and b) The relative deviations of g for the *E. huxleyi* parameters are ≤ -16 % from the base case for $f = 0.1$, which means the g values deviate ≤ -32 % from the g values based on *Synechocystis* parameters, a significant species-related uncertainty.

For g based on "Table 3, row 6m" (using VSMOW measurements reported by Barkan and Luz, 2011), the species-specific parameters for *N. oculata*, *C. reinhardtii* and *P. tricornutum* again agree well with the mean δ_P set (Fig. 1c and d). There is also relative good agreement with "Nicholson (2011a)", "Luz and Barkan (2011b)", "*Acropora* (flask, 5.814‰)" and "*Nannochloroposis* (flask, 2.85‰)". However, the relative deviations are ≥ 35 % for "Kaiser (2011a)", "Table 3, row 5m" and "Table 3, row 7m" and ≤ -12 % for "*E. huxleyi*". Again, for $f < 0.1$ or $g > 0.1$, these deviations tend to be even higher (Fig. 1c and d). The relative deviations of g for the *Synechocystis* parameters are $\ge +18$ % from the base case, which means the g values based on *E. huxleyi* parameters deviate ≤ -26 % from the g values based on *Synechocystis* parameters. The span between these two species is slightly smaller than for "Table 3, row 5m" 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 γ_R is adopted for the calculation.

To summarise, the experimental evidence can accommodate both the δ_P parameters of Nicholson (2011a) as well as those of Kaiser (2011a). 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 conclusions on the quantitative accuracy of the resulting g values. While we agree with Nicholson's notion that different parameters used in Kaiser (2011a) can explain the lower g values based on parameters used in previous studies (e.g., Hendricks et al., 2004; Reuer et al., 2007; Juranek and Quay, 2010), this should not be used to single out one parameter set as superior to the other. Kaiser (2011a) did not make such
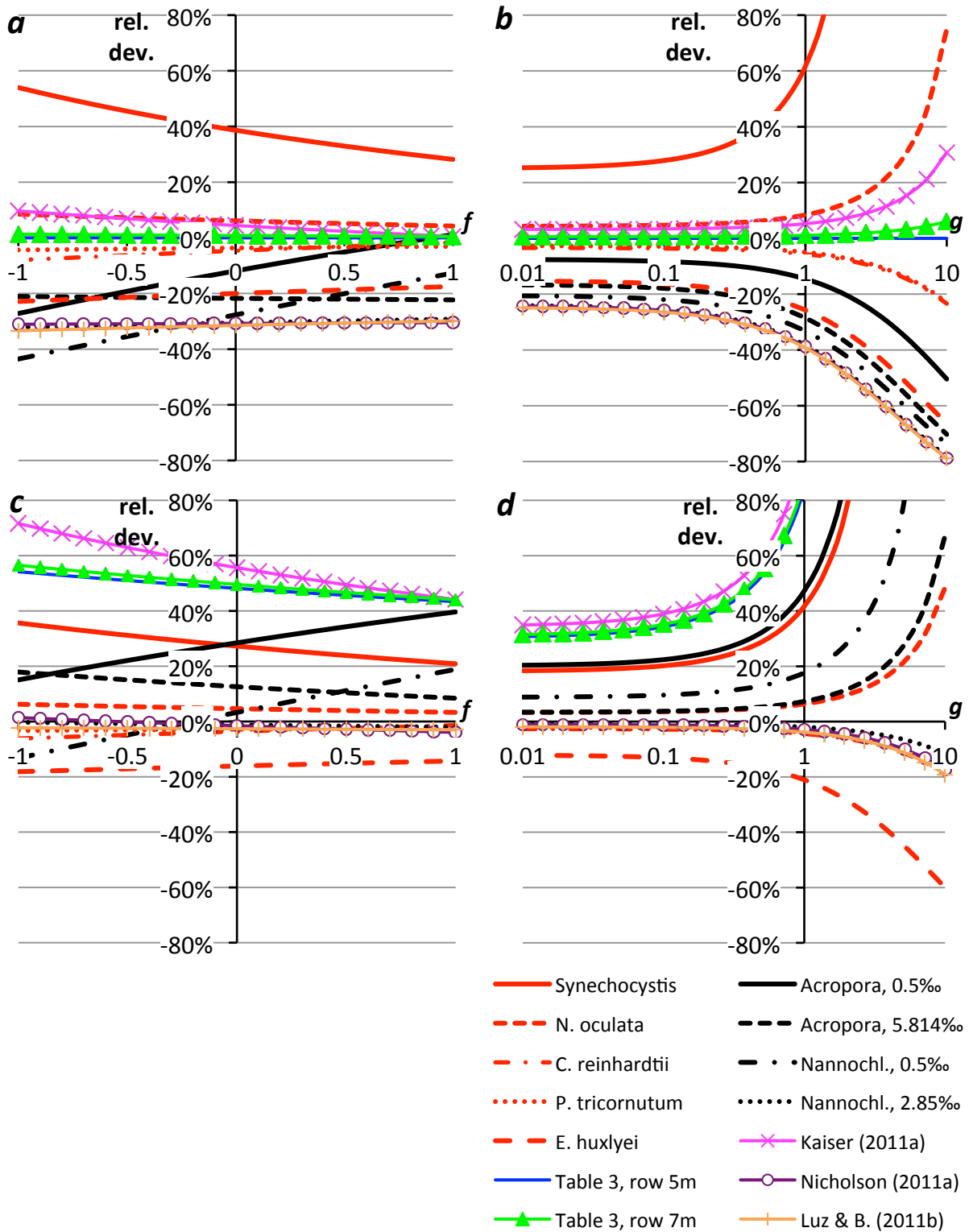
Fig. 1. Relative difference of g for different sets of $^{17}\delta_P$, $^{18}\delta_P$ and γ_R (Table 3) to g based on row 5m (**a**, **b**; Barkan and Luz, 2005) and row 6m (**c**, **d**; Barkan and Luz, 2011). (**a**, **c**) correspond to $g = 0.4$ and $-1.0 \le f \le 1.0$; (**b**, **d**) to $f = 0.1$ and $0.01 \le g \le 10$ (logarithmic axis). Red curves correspond to rows 5a–e (**a**, **b**) and 6a–e (**c**, **d**). "Kaiser (2011a)", "Nicholson (2011a)", "Acropora, 0.5 ‰", "Acropora, 5.814 ‰", "Nannochl., 0.5 ‰" and "Nannochl., 2.85 ‰" correspond to rows 1, 2, 3a, 3b, 4a and 4b. "Luz & B. (2011b)" uses $^{17}\delta_P = -10.126$ ‰ and $^{18}\delta_P = -20.014$ ‰ (Luz and Barkan, 2011b).

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 $^{17}\delta_P$. The claim by Nicholson (2011a) that the g values calculated using the base case of Kaiser (2011a) were 30 % too high is not justified.

Nicholson (2011a) also commented that Kaiser (2011a) overestimates the discrepancy of g based on different calculation methods/parameters, as seen in Fig. 3 of Kaiser (2011a) compared to Fig. 1 in Nicholson (2011a). However, this is largely due to how the results are presented (as relative deviations), and as we argue above, Kaiser's "base case" just provides a reference for comparison, not a benchmark for other studies.

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 Nicholson's comment that $^{17}\Delta$ should be defined as $^{17}\Delta^{\#}(\theta_R) \equiv \ln(1+{}^{17}\delta) - \theta_R \ln(1+{}^{18}\delta)$.

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

$$g = \frac{{}^{17}\Delta - {}^{17}\Delta_{sat}}{{}^{17}\Delta_P - {}^{17}\Delta} \qquad (10)$$

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 $^{17}\Delta_P^{\#}(\theta_R)$, with $\theta_R = 0.5154$ for $\gamma_R = 0.5179$ and $^{18}\varepsilon_R = -20\,‰$ (Sect. 2.3). As evidenced by its use in Luz and Barkan (2009), a coefficient of γ_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, θ_R can only be computed if $^{18}\varepsilon_R$ is also known. Even though the influence of the uncertainty in $^{18}\varepsilon_R$ is not as severe as when $^{18}\delta$ were used for the calculation directly (Quay et al., 1993), this goes against the rationale behind the triple oxygen isotope technique (i.e., the absence of the need to know $^{18}\varepsilon_R$). 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 $^{17}\Delta^{\dagger}(\gamma_R) \equiv {}^{17}\delta - \gamma_R\,{}^{18}\delta$. 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 $^{17}\Delta_{S0}^{\#}(\theta_R)$ 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 γ_R correspond to "Kaiser (2011a)" (Table 3, row 1; Fig. 2); the mean δ_P based on the VSMOW measurements of Barkan and Luz (2011) (Table 3, row 6m; Fig. 3), which is similar to "Nicholson (2011a)"; and the parameters derived from the *Acropora* flask experiments ($^{18}\varepsilon_P = 0.5\,‰$; Table 3, row 3a; Fig. 4).

The approximate solutions are calculated using Eq. (10) with the triple isotope excess defined as (a) $^{17}\Delta^{\dagger}(\gamma_R)$ (Kaiser, 2011a) (Figs. 2a, 3a, 4a); (b) $^{17}\Delta^{\#}(\gamma_R)$ in general, but $^{17}\Delta_P^{\#}(\theta_R)$ for photosynthetic O_2 (Luz and Barkan, 2005) (Figs. 2b, 3b, 4b); (c) $^{17}\Delta^{\#}(\gamma_R)$ (shown for completeness) (Figs. 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) (Table 3, row 1; Fig. 2), 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. 2a). g values based on Nicholson's 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. 2d). Luz and Barkan's method (b) is biased only 7 % low for $f = 0$ (Fig. 2b), 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 scenario using the mean δ_P value based on the VS-MOW measurements of Barkan and Luz (2011) (Table 3, row
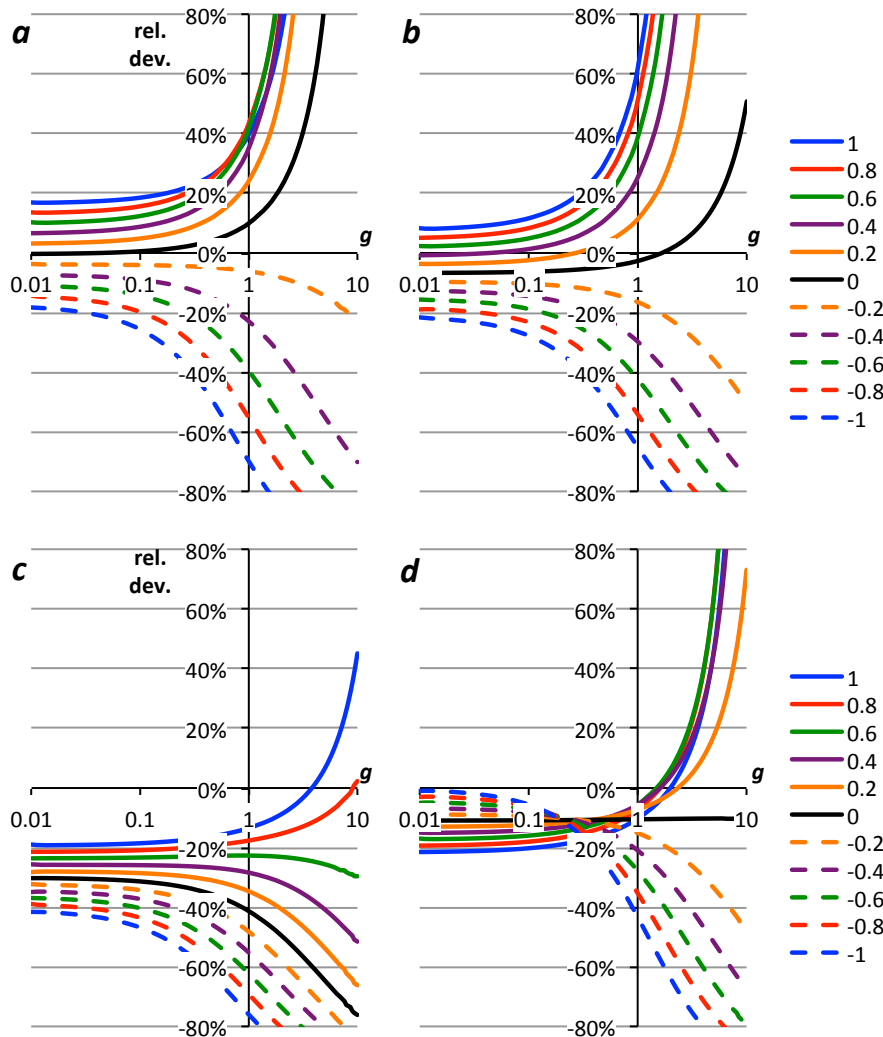
Fig. 2. Relative deviation of the approximated solution for g (Eq. 10) from the accurate solution (Eq. 1) for the parameters in Table 3, row 1 (Kaiser, 2011a).

(a) linear definition of $^{17}\Delta$ with $\kappa = \gamma_R$ (Kaiser, 2011a): $^{17}\Delta_P^\dagger(0.5179) = 180\,\text{ppm}$, $^{17}\Delta_{sat}^\dagger(0.5179) = 16\,\text{ppm}$.

(b) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$ except for $^{17}\Delta_P^\#$ (Luz and Barkan, 2005): $^{17}\Delta_P^\#(0.5154) = 191\,\text{ppm}$, $^{17}\Delta_{sat}^\#(0.5179) = 16\,\text{ppm}$.

(c) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$: $^{17}\Delta_P^\#(0.5179) = 249\,\text{ppm}$, $^{17}\Delta_{sat}^\#(0.5179) = 16\,\text{ppm}$.

(d) ln-definition of $^{17}\Delta$ with $\lambda = \theta_R$ (Nicholson, 2011a): $^{17}\Delta_P^\#(0.5154) = 191\,\text{ppm}$, $^{17}\Delta_{sat}^\#(0.5154) = 18\,\text{ppm}$.

6m; Fig. 3), 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 $g < 1$, whereas methods (a) and (b) perform similarly.

For the scenario based on the *Acropora* flask experiments ($^{18}\varepsilon_P = 0.5\,‰$; Table 3, row 3a; Fig. 4), 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 defined by "Table 3, row 6m" (Fig. 1c and d). However, if other $^{17}\delta_P$ and $^{18}\delta_P$ parameters were adopted such as those of the *Acropora* flask experiments (assuming $^{18}\varepsilon_P = 0.5\,‰$), then significant deviations from the accurate solution would occur.

4   Conclusions

It is important to make the distinction between different calculation methods (e.g., iterative versus dual-delta method; approximate based on $^{17}\Delta$ versus accurate based on $^{17}\delta$
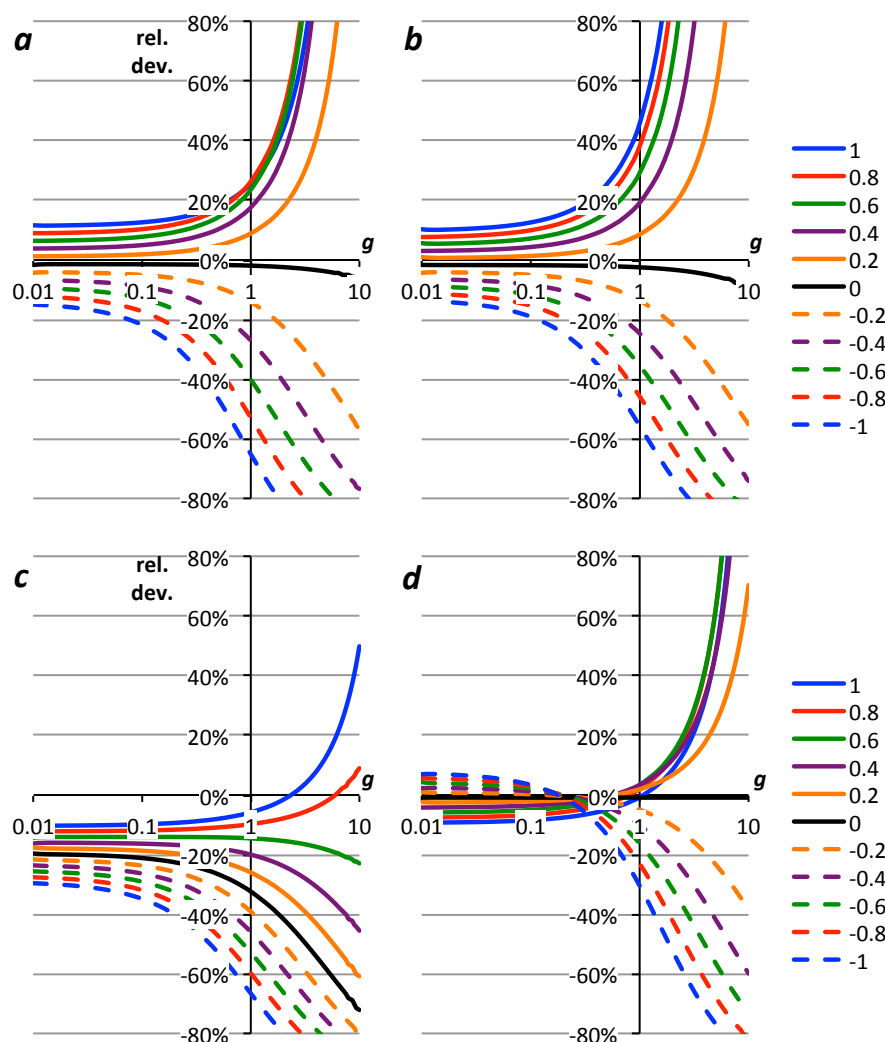
Fig. 3. Relative deviation of the approximated solution for g (Eq. 10) from the accurate solution (Eq. 1) for the parameters in Table 3, row 6m (δ_W based on Barkan and Luz, 2011).
(a) linear definition of $^{17}\Delta$ with $\kappa = \gamma_R$ (Kaiser, 2011a): $^{17}\Delta_P^\dagger(0.5179) = 235$ ppm, $^{17}\Delta_{sat}^\dagger(0.5179) = 16$ ppm.
(b) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$ except for $^{17}\Delta_P^\#$ (Luz and Barkan, 2005): $^{17}\Delta_P^\#(0.5154) = 236$ ppm, $^{17}\Delta_{sat}^\#(0.5179) = 16$ ppm.
(c) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$: $^{17}\Delta_P^\#(0.5179) = 285$ ppm, $^{17}\Delta_{sat}^\#(0.5179) = 16$ ppm.
(d) ln-definition of $^{17}\Delta$ with $\lambda = \theta_R$ (Nicholson, 2011a): $^{17}\Delta_P^\#(0.5154) = 236$ ppm, $^{17}\Delta_{sat}^\#(0.5154) = 18$ ppm.

and $^{18}\delta$ pairs) and different calculation parameters. 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 δ 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.

We agree with Nicholson (2011a) that different parameters are key to explaining the differences between Kaiser's base case and previous studies (e.g., Hendricks et al., 2004; Reuer et al., 2007; Juranek and Quay, 2010). 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
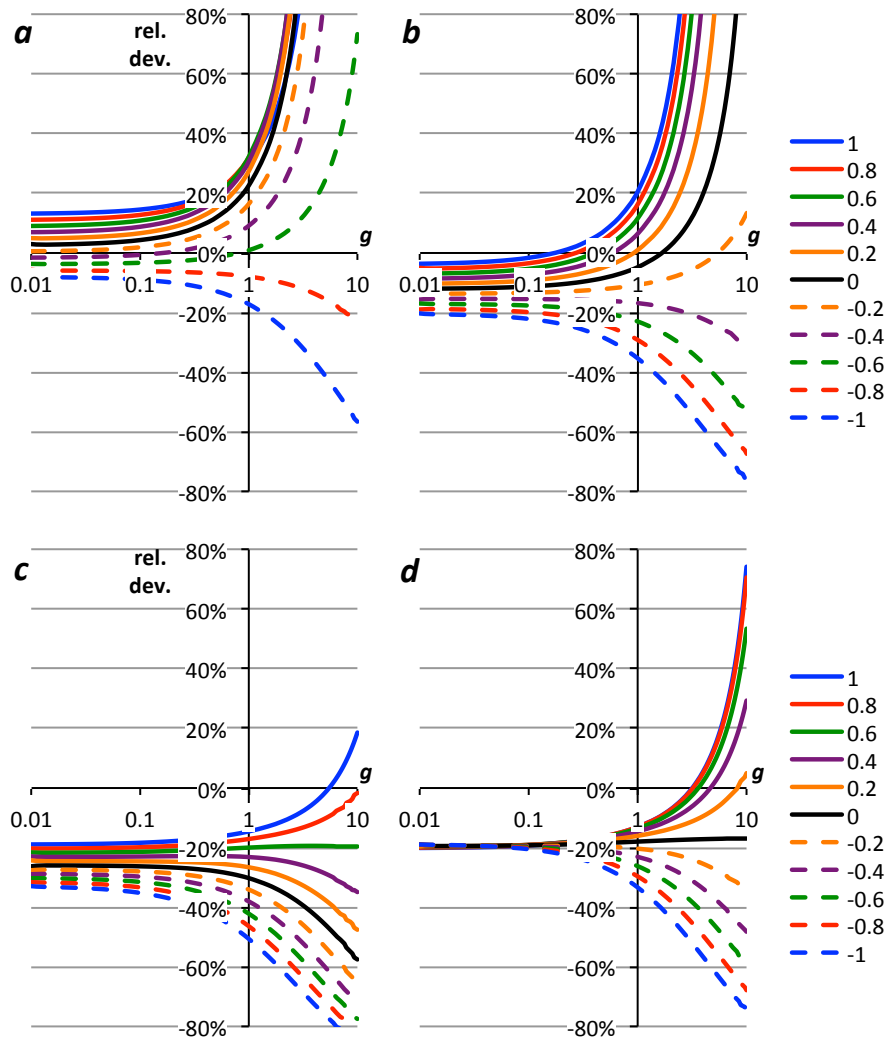
Fig. 4. Relative deviation of the approximated solution for g (Eq. 10) from the accurate solution (Eq. 1) for the parameters in Table 1, row 3a (*Acropora* (flask), $^{18}\varepsilon_P = 0.5$ ‰).

(a) linear definition of $^{17}\Delta$ with $\kappa = \gamma_R$ (Kaiser, 2011a): $^{17}\Delta_P^{\dagger}(0.519) = 200$ ppm, $^{17}\Delta_{sat}^{\dagger}(0.519) = 15$ ppm.

(b) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$ except for $^{17}\Delta_P^{\#}$ (Luz and Barkan, 2005): $^{17}\Delta_P^{\#}(0.5173) = 229$ ppm, $^{17}\Delta_{sat}^{\#}(0.519) = 15$ ppm.

(c) ln-definition of $^{17}\Delta$ with $\lambda = \gamma_R$: $^{17}\Delta_P^{\#}(0.519) = 269$ ppm, $^{17}\Delta_{sat}^{\#}(0.5179) = 15$ ppm.

(d) ln-definition of $^{17}\Delta$ with $\lambda = \theta_R$ (Nicholson, 2011a): $^{17}\Delta_P^{\#}(0.5173) = 229$ ppm, $^{17}\Delta_{sat}^{\#}(0.5173) = 17$ ppm.

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 Kaiser's original paper.

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