

Supporting Information for “Revising estimates of aquatic gross oxygen production by the triple oxygen isotope method to incorporate the local isotopic composition of water”

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Code availability

The code for calculating gross oxygen production from triple oxygen isotope data is published as *Manning and Howard* [2017]:

Manning, C. C., & Howard, E. M. (2017). calcGOP: MATLAB functions for the calculation of gross oxygen production from triple oxygen isotope data used in Manning et al. (2017) *Geophysical Research Letters*, release 1.0. <http://github.com/caramanning/calcGOP>. <https://doi.org/10.5281/zenodo.376786>.

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Text S1. Method of estimating the local H₂O isotopic composition

For oceanic systems, we estimate $\delta^{18}\text{O-H}_2\text{O}$ using a published database [*Schmidt et al.*, 1999; *LeGrande and Schmidt*, 2006], and assume a ¹⁷O-excess of -5 (standard deviation 4) per meg, the average value for near-surface seawater (<5 m depth) reported in Table 1 of [*Luz and Barkan*, 2010]. For freshwater systems (precipitation-derived or meteoric water), we use published $\delta^{18}\text{O-H}_2\text{O}$ data for the study region, and a ¹⁷O-excess of 27 (standard deviation 20) per meg, or a value specific to the study region where data is available [*Luz and Barkan*, 2010; *Li et al.*, 2015]. The value of 27 per meg is the average of all published freshwater measurements compiled in *Li et al.* [2015], Tables 3 and S2.

For brackish systems (e.g., estuaries), we assume that the water represents a mixture of local seawater and local meteoric water. A common approach to evaluate mixing between different water types in estuaries is to plot salinity versus $\delta^{18}\text{O-H}_2\text{O}$. Both tracers tend to behave conservatively and mix as a function of the two endmembers: seawater and meteoric water [*Macdonald et al.*, 1995; *Surge and Lohmann*, 2002; *Wankel et al.*, 2006]. We define $\delta^{18}\text{O-H}_2\text{O}$ and salinity for the two endmembers and then estimate $\delta^{18}\text{O-H}_2\text{O}$ for each water sample as a linear function of the measured salinity. Specifically, given that the meteoric water endmember has salinity (S) = 0, then

$$\delta^{18}\text{O-H}_2\text{O}_{\text{samp}} = \frac{(\delta^{18}\text{O-H}_2\text{O}_{\text{sw}} - \delta^{18}\text{O-H}_2\text{O}_{\text{mw}})}{S_{\text{sw}}} S_{\text{samp}} + \delta^{18}\text{O-H}_2\text{O}_{\text{mw}}, \quad (1)$$

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where the subscripts *sw*, *mw*, and *samp* refer to seawater, meteoric water, and the sample, respectively. The value of $\delta^{17}\text{O-H}_2\text{O}$ for each endmember is estimated from $\delta^{18}\text{O-H}_2\text{O}$ and the ^{17}O -excess, and then we use equation 1 with $\delta^{17}\text{O-H}_2\text{O}$ to estimate $\delta^{17}\text{O-H}_2\text{O}$ for each sample. We use $\delta^{17}\text{O-H}_2\text{O}$ in the mixing calculation because $\delta^{17}\text{O-H}_2\text{O}$ behaves approximately conservatively during mixing and ^{17}O -excess does not.

The method of estimating the H_2O triple isotopic composition of each dataset in Table 1 is described below.

Plum Island Estuary (Section 3): For the chamber experiments, we used a freshwater endmember with $S = 0$, $\delta^{18}\text{O-H}_2\text{O} = -6.657\text{‰}$, and ^{17}O -excess = 13.5 per meg [Li *et al.*, 2015] and a seawater endmember with $S = 31.5$ PSS, $\delta^{18}\text{O-H}_2\text{O} = -1\text{‰}$, and ^{17}O -excess = -5 per meg [Schmidt *et al.*, 1999; LeGrande and Schmidt, 2006; Luz and Barkan, 2010]. We used the observed salinity in the chambers (24.9–28.6 PSS) and equation 1 to estimate the value of $^{17}\Delta_{\text{BSS}}$ for each sample. The local meteoric water endmember $\delta^{18}\text{O-H}_2\text{O}$ and ^{17}O -excess is based on measurements of tap water collected in Chicopee, MA and Lewiston, ME from Li *et al.* [2015]. The seawater endmember $\delta^{18}\text{O-H}_2\text{O}$ and salinity are based on measurements in nearby North Atlantic surface waters from Schmidt *et al.* [1999], and the ^{17}O -excess for seawater is the average value for surface waters from Luz and Barkan [2010]

Beaufort Sea (Section 4): Values of $\delta^{18}\text{O-H}_2\text{O}$ were measured and the ^{17}O -excess was set to -5 per meg for all samples, the average value for seawater from Luz and Barkan [2010]. As discussed in the main text, there is some uncertainty about the appropriate ^{17}O -excess to use in the Arctic Ocean because there are no published measurements in this region and because Arctic Ocean seawater is a mixture of three endmembers: ocean water, sea ice melt, and river/meteoric water.

Other ocean regions (Section 5, Bering Sea, California Coast, Northeast Pacific, South Atlantic and Bellingshausen Sea): Values of $\delta^{18}\text{O-H}_2\text{O}$ were estimated based on average values for the region from a published database and model [Schmidt *et al.*, 1999; LeGrande and Schmidt, 2006], and the ^{17}O -excess was set to -5 per meg for all samples [Luz and Barkan, 2010].

Bras d'Or Lake (Section 5): The values of $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^{17}\text{O-H}_2\text{O}$ were estimated using meteoric water and seawater endmembers with salinity of 0 and 31.25 PSS, $\delta^{18}\text{O-H}_2\text{O}$ of -9.3 and -1.68‰, and ^{17}O -excess of 27 and -5 per meg, respectively [Schmidt *et al.*, 1999; IAEA/WMO, 2016; Li *et al.*, 2015]. The local meteoric water isotopic composition is based on a multi-year precipitation record from Truro, Nova Scotia (for $\delta^{18}\text{O-H}_2\text{O}$) and the average ^{17}O -excess value for freshwater given by Li *et al.* [2015].

Waquoit Bay (Section 5): The values of $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^{17}\text{O-H}_2\text{O}$ were estimated using meteoric water and seawater endmembers with salinity of 0 and 31.5 PSS, $\delta^{18}\text{O-H}_2\text{O}$ of -6.657 and -1‰, and ^{17}O -excess of 13.5 and -5 per meg, respectively [Schmidt *et al.*, 1999; Luz and Barkan, 2010; Li *et al.*, 2015]. The local meteoric water endmembers are based on measurements of tap water collected in Chicopee, MA and Lewiston, ME from Li *et al.* [2015].

Text S2. Estimating the ^{17}O -excess in other systems and incorporating it into the GOP calculation

The ^{17}O -excess in near-surface oceanic waters varies over a relatively small range, from -15–1 per meg, according to the only published dataset we are aware of, Luz and Barkan [2010]. However, data coverage is sparse and no data has been published for the Arctic Ocean, which has a significant freshwater influence.

The ^{17}O -excess of published freshwater measurements varies over a wider range, from -35 to 76 per meg [Li *et al.*, 2015]. For $\delta^{18}\text{O-H}_2\text{O}$, there are multi-year records of precipi-

tation in many regions, whereas published ^{17}O -excess measurements are almost exclusively single time point measurements [Li *et al.*, 2015; IAEA/WMO, 2016]. Given the limited ^{17}O -excess data currently available, we recommend that investigators measure the ^{17}O -excess in future studies whenever possible.

We concur with other authors that in TOI-based GOP studies, all data used to calculate productivity (e.g., $\delta^{17}\text{O-O}_2$, $\delta^{18}\text{O-O}_2$, $^{17}\Delta$, $[\text{O}_2]$, temperature, salinity, and depth, as well as the wind speed record used and/or gas transfer velocity, and information on the H_2O isotopic composition if applicable) should be archived and openly available, so that productivity can be recalculated in the future based on new consensus and information about the most accurate equations and values to use in these calculations [Hamme *et al.*, 2012; Juranek and Quay, 2013].

Text S3. Choice of λ in GOP calculations

We contend that it is most appropriate to use $\lambda = \gamma_R = 0.5179$ rather than λ_{BSS} when calculating the rate of gross photosynthetic production in equation 7 [Kaiser, 2011; Nicholson, 2011; Nicholson *et al.*, 2012; Hamme *et al.*, 2012; Juranek and Quay, 2013]. However, we acknowledge that some other works have advocated for the use of λ_{BSS} in GOP calculations [Luz and Barkan, 2011]. If λ_{BSS} is used in equation 7, the calculated GOP is even more sensitive to the H_2O isotopic composition than presented in this work.

Text S4. Behaviour of $\delta^{18}\text{O-O}_2$ and $\delta^{17}\text{O-O}_2$ in chamber incubations

In the chamber experiments, $\delta^{18}\text{O-O}_2$ and $\delta^{17}\text{O-O}_2$ asymptote but do not reach the published photosynthetic endmember values, which are based on laboratory cultures of individual autotrophic species (Figure S1). For example, $\delta^{18}\text{O-O}_2$ at the end of each incubation ranged from -11 to -15.5‰ in the three chambers shown here, whereas the predicted value for photosynthetic O_2 derived from ‘average phytoplankton’ with the estimated isotopic composition of H_2O was \sim -22‰. We suspect that these differences occurred because we incubated a heterogeneous, intact microbial community (both autotrophs and heterotrophs), and also because of differences in biogeochemical conditions between chambers, and the short incubation period. The heterogeneous microbial community would affect the final value of $\delta^{18}\text{O-O}_2$ and $\delta^{17}\text{O-O}_2$ but not $^{17}\Delta_{BSS}$ because there are a wide range of respiratory fractionation factors ($^{18}\epsilon_R$) reported in the literature, whereas the value of γ_R (the ratio of $^{17}\epsilon_R/^{18}\epsilon_R$) is nearly universal for a wide range of organisms [Luz and Barkan, 2005].

Text S5. Method for O_2 isotope analysis

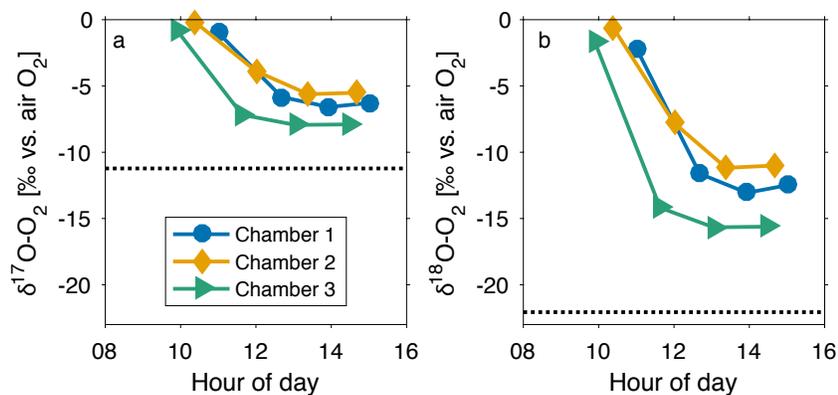
Samples for analysis of the triple oxygen isotopic composition of O_2 were collected from Plum Island Estuary (chamber incubations), the Canada Basin, South Atlantic Ocean, Bras d’Or Lake, and Waquoit Bay and analyzed at Woods Hole Oceanographic Institution with a Thermo Finnigan MAT 253 isotope ratio mass spectrometer. The analytical procedure followed published methods [Barkan and Luz, 2003] with modifications as described in Stanley *et al.* [2010, 2015]. All measurements are referenced to O_2 in air collected locally in Woods Hole, MA. Standards of air-equilibrated distilled water are run daily to check instrument performance and precision. For all data sets the value of $^{17}\Delta$ for these air-equilibrated samples was very close to 8 per meg, which is equivalent to the value reported in Stanley *et al.* [2010]. The standard deviation of replicate field samples as well as replicate equilibrated water standards was \sim 5 per meg for all data sets.

Other data sets shown in Table 1 and Figure 2 were analyzed by similar methods [Prokopenko *et al.*, 2011; Juranek *et al.*, 2012; Castro-Morales *et al.*, 2013; Munro *et al.*, 2013].

Text S6. Method for H₂O isotope analysis

Samples for analysis of $\delta^{18}\text{O}\text{-H}_2\text{O}$ were collected from the Arctic Ocean and analyzed at the Oregon State University College of Earth, Ocean and Atmospheric Sciences Stable Isotope Laboratory with a Thermo Finnigan DeltaPlus XL isotope ratio mass spectrometer, using the $\text{H}_2\text{O}/\text{CO}_2$ equilibration method [Epstein and Mayeda, 1953]. Replicate analyses had a precision of 0.05 ‰ or better.

Figure S1.



Caption for Figure S1: Chamber incubation measurements of (a) $\delta^{17}\text{O}\text{-H}_2\text{O}$, and (b) $\delta^{18}\text{O}\text{-H}_2\text{O}$. The samples are from the same dataset plotted in Figure 1. The dashed line on each figure shows the predicted isotopic composition of O_2 produced by “average phytoplankton” as reported in [Luz and Barkan, 2011], based on culture experiments, and derived from H_2O with the isotopic composition estimated as described in the main text.

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