

RESEARCH LETTER

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Key Points:

- Systematic errors in gross oxygen production (GOP) estimates can occur due to incorrect assumptions about the water isotopic composition
- We present a method for estimating the local oxygen isotopic composition of water and incorporating it into GOP calculations
- Oxygen and water triple isotope measurements should be paired in GOP studies when the isotopic composition of water differs from VSMOW

Supporting Information:

- Supporting Information S1

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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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Abstract Measurement of the triple oxygen isotope (TOI) composition of O₂ is an established method for quantifying gross oxygen production (GOP) in natural waters. A standard assumption to this method is that the isotopic composition of H₂O, the substrate for photosynthetic O₂, is equivalent to Vienna standard mean ocean water (VSMOW). We present and validate a method for estimating the TOI composition of H₂O based on mixing of local meteoric water and seawater H₂O end-members, and incorporating the TOI composition of H₂O into GOP estimates. In the ocean, GOP estimates based on assuming the H₂O is equivalent to VSMOW can have systematic errors of up to 48% and in low-salinity systems, errors can be a factor of 2 or greater. In future TOI-based GOP studies, TOI measurements of O₂ and H₂O should be paired when the H₂O isotopic composition is expected to differ from VSMOW.

1. Introduction

The triple oxygen isotope (TOI) composition of O₂ (i.e., the relative abundance of ¹⁶O, ¹⁷O, and ¹⁸O) is a tracer of gross oxygen production (GOP) that has been used in marine environments globally over the past two decades (Juraneck & Quay, 2013; Luz & Barkan, 2000, 2005). GOP is the gross rate of photosynthetic O₂ production by the ecosystem, prior to any respiratory O₂ consumption. Furthermore, the analytical method generally also involves the measurement of O₂/Ar gas ratios, which are used to quantify net oxygen production (NOP), that is, GOP minus community respiration from autotrophs and heterotrophs (Juraneck & Quay, 2013). The approach enables simultaneous in situ estimation of GOP, NOP, and community respiration averaged over a time scale of days to weeks. The TOI approach exploits the unique TOI signatures of the two sources of dissolved O₂: photosynthetic O₂, which is derived from H₂O, and atmospheric O₂, which is added to surface waters via air-water gas exchange and has a small mass-independent isotope signature (Barkan & Luz, 2011; Luz & Barkan, 2005). Although the method is O₂-based, GOP and NOP can be converted from O₂ to carbon (C) units (to gross primary production and net community production) using published stoichiometric ratios (Juraneck & Quay, 2013; Laws, 1991).

The TOI approach has some advantages over other techniques for simultaneously estimating oxygen production and respiration. For example, incubation-based techniques typically require assuming light respiration and dark respiration rates are equal and can be biased by “bottle effects,” and in situ measurements of dual oxygen isotopes (¹⁸O and ¹⁶O only) are sensitive to the choice of respiratory fractionation factor and cannot be used in the open ocean as the rate of change in the tracers is too low (Hotchkiss et al., 2014; Staehr et al., 2012; Tobias et al., 2007).

Since the TOI approach was first published in 1999, there have been frequent revisions to the calculations to improve the accuracy of the GOP estimates (Kaiser, 2011; Luz and Barkan, 2005, 2011; Luz et al., 1999; Nicholson, 2011; Nicholson et al., 2014; Prokopenko et al., 2011). Here we demonstrate that the local relative abundance of ¹⁶O, ¹⁷O, and ¹⁸O in H₂O is an important variable affecting GOP calculations that is not typically taken into account in field-based studies of GOP. We present and validate a method for estimating the local

TOI composition of H₂O (when paired measurements of O₂ and H₂O triple oxygen isotopes are not available) and incorporating the local H₂O isotopic composition into GOP calculations. We demonstrate that this approach can be applied to accurately estimate GOP in environments where the isotopic composition of H₂O differs from standard mean ocean water. This approach is crucial to extending the application of the TOI tracer from the open ocean, where it has been frequently used, to systems influenced by precipitation-derived water which has a highly variable isotopic composition (Juraneck & Quay, 2013; Jurikova et al., 2016; Luz et al., 2002; Yeung et al., 2012).

2. Calculations

In this section we provide background on TOI calculations and describe our method of estimating the local TOI composition of H₂O and incorporating the TOI composition of H₂O into the GOP calculation. MATLAB code used for performing these calculations is available on GitHub (<http://github.com/caramanning/calcGOP>).

The oxygen isotopic composition of a chemical species is characterized using

$$\delta^{18}\text{O} = \frac{X^{18}}{X_{\text{std}}^{18}} - 1, \quad (1)$$

and expressed in ‰ by multiplying by 1,000. Here X^{18} is the measured ¹⁸O/¹⁶O ratio determined relative to X_{std}^{18} , the ¹⁸O/¹⁶O ratio of a known standard. The term $\delta^{17}\text{O}$ is defined similarly, using ¹⁷O/¹⁶O ratios. Typically, O₂ in air is the standard for isotopic measurements of O₂ (Juraneck & Quay, 2013; Luz & Barkan, 2000). The current best practice is to normalize H₂O isotope measurements using two standards: VSMOW (Vienna standard mean ocean water) and SLAP (standard light Antarctic precipitation) (Li et al., 2015; Schoenemann et al., 2013). On the VSMOW-SLAP scale, VSMOW has a $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of 0‰. Hereafter, all O₂ isotopic compositions are referenced to air O₂ and all H₂O isotopic compositions are referenced to VSMOW-SLAP. In this paper, we distinguish between the isotopic composition of the two substrates (O₂ and H₂O) as $\delta^{18}\text{O-O}_2$ and $\delta^{18}\text{O-H}_2\text{O}$.

The typical assumption in GOP studies is that the water isotopic composition is equivalent to VSMOW, a standard based on deep open ocean water (Barkan & Luz, 2011; Hamme et al., 2012; Nicholson, 2011). However, surface ocean water differs from VSMOW by up to 7‰ for $\delta^{18}\text{O-H}_2\text{O}$, though is most commonly within 2‰ of VSMOW (LeGrande & Schmidt, 2006). Furthermore, in brackish and freshwater systems the isotopic composition of H₂O can be substantially different from VSMOW (by up to ~40‰ for $\delta^{18}\text{O-H}_2\text{O}$) because the isotopic composition of meteoric (precipitation derived) water has substantial regional and seasonal variability (Craig, 1961; Epstein & Mayeda, 1953; Feng et al., 2009; Jasechko et al., 2013; Vachon et al., 2007).

The term $^{17}\Delta$ quantifies the TOI composition of dissolved O₂:

$$^{17}\Delta = \ln(\delta^{17}\text{O-O}_2 + 1) - \lambda \ln(\delta^{18}\text{O-O}_2 + 1). \quad (2)$$

Here we report $^{17}\Delta$ with $\lambda = \gamma_R$, where

$$\gamma_R = \frac{^{17}\epsilon_R}{^{18}\epsilon_R} = 0.5179. \quad (3)$$

In this equation, ϵ_R is the respiratory O₂ consumption isotope effect (Luz & Barkan, 2005). When $\lambda = \gamma_R$, $^{17}\Delta$ reflects the proportion of O₂ that is derived from photosynthesis relative to air-water gas exchange (Hendricks et al., 2005; Juraneck & Quay, 2013; Nicholson et al., 2014).

We use λ_{BSS} to refer to the isotopic behavior of a system at biological steady state, in which the rates of photosynthesis and respiration are approximately constant and within the same order of magnitude (Luz & Barkan, 2005; Kaiser, 2011; Nicholson, 2011). The term γ_R describes the kinetic fractionation that occurs during respiratory O₂ consumption and λ_{BSS} is an approximation of the trend in bulk O₂ isotopic composition that arises from respiratory fractionation and subsequent mixing between newly generated photosynthetic O₂ and the residual pool of O₂ (e.g., see Figure 2 of Luz and Barkan (2005)). We calculate

$$\lambda_{\text{BSS}} = \frac{\ln(^{17}\alpha_R)}{\ln(^{18}\alpha_R)} = \frac{\ln(1 + \gamma_R^{18}\epsilon_R)}{\ln(1 + ^{18}\epsilon_R)}. \quad (4)$$

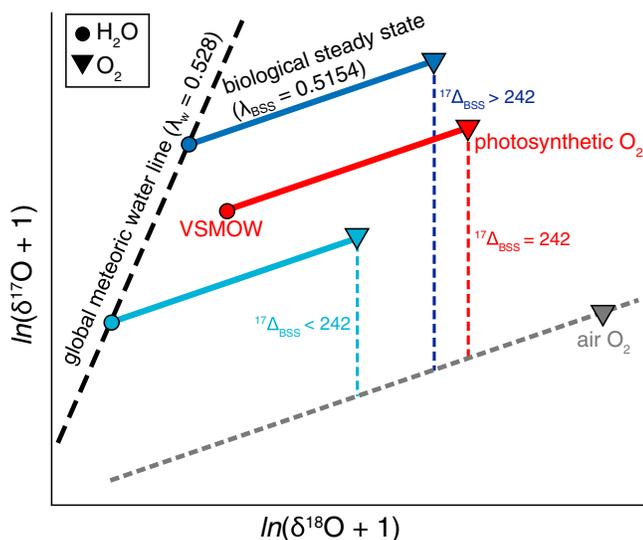


Figure 1. Schematic (not to scale), adapted from Luz and Barkan (2000), showing how the oxygen triple isotopic composition is modified as H_2O is converted to biological O_2 in a steady state system with production, respiration, and no air-water gas exchange. The red line shows the oxygen isotopic fractionation as H_2O with $\delta^{18}\text{O}\text{-H}_2\text{O} = 0\text{‰}$ and $^{17}\text{O}\text{-excess} = 0$ per meg versus VSMOW-SLAP (red circle) is converted to biological O_2 (red triangle) with $^{17}\Delta = 242$ per meg versus air O_2 . The light and dark blue lines show the oxygen isotopic fractionation of meteoric H_2O , with a higher (dark blue) or lower (light blue) $\delta^{18}\text{O}\text{-H}_2\text{O}$ than VSMOW, and a $^{17}\text{O}\text{-excess}$ of ~ 30 per meg (Li et al., 2015; Luz & Barkan, 2000). The slope λ_{BSS} is independent of the H_2O isotopic composition whereas the value of $^{17}\Delta_{\text{BSS}}$ differs for each starting H_2O isotopic composition.

Assuming $^{18}\epsilon_R = -20\text{‰}$ (Kiddon et al., 1993) and $\gamma_R = 0.5179$, $\lambda_{\text{BSS}} = 0.5154$ (Nicholson, 2011). Then we can calculate $^{17}\Delta_{\text{BSS}}$ using λ_{BSS}

$$^{17}\Delta_{\text{BSS}} = \ln(\delta^{17}\text{O}\text{-O}_2 + 1) - \lambda_{\text{BSS}} \ln(\delta^{18}\text{O}\text{-O}_2 + 1). \quad (5)$$

Other authors have shown that $^{17}\Delta_{\text{BSS}}$ is equivalent for pure photosynthetic O_2 and for the bulk O_2 isotopic composition after respiratory consumption and mixing (Angert et al., 2003; Nicholson, 2011).

Using the isotopic composition of photosynthetic O_2 generated by “average phytoplankton” from VSMOW reported in Luz and Barkan (2011), the $^{17}\Delta$ of biological O_2 produced in a steady state system with production, respiration and no air-water gas exchange is ~ 242 per meg (Figure 1). The $^{17}\Delta$ value for air-equilibrated water is ~ 8 per meg (Reuer et al., 2007; Stanley et al., 2010). In natural waters, $^{17}\Delta$ of dissolved O_2 will typically fall between these two end-members (Kaiser, 2011; Luz & Barkan, 2005; Nicholson, 2011).

The term $^{17}\text{O}\text{-excess}$ quantifies TOI composition of H_2O :

$$^{17}\text{O}\text{-excess} = \ln(\delta^{17}\text{O}\text{-H}_2\text{O} + 1) - \lambda_w \ln(\delta^{18}\text{O}\text{-H}_2\text{O} + 1) \quad (6)$$

with $\lambda_w = 0.528$ and all isotopic compositions normalized to VSMOW-SLAP. Equation (6) has a similar form to equation (5); however, the H_2O isotope community has traditionally used the $^{17}\text{O}\text{-excess}$ terminology, whereas the O_2 isotope community has preferred the $^{17}\Delta$ notation (Luz & Barkan, 2010). The value of $\lambda_w = 0.528$ is well established for globally distributed measurements of meteoric waters and seawater (Landais et al., 2008; Luz & Barkan, 2010; Meijer & Li, 1998). Spatial variability in the $^{17}\text{O}\text{-excess}$ of natural waters is less well understood relative to variability in $\delta^{18}\text{O}\text{-O}_2$ due

to the currently limited observations at sufficient accuracy to resolve the small excess (Barkan & Luz, 2005; Landais et al., 2008; Li et al., 2015; Luz & Barkan, 2010).

In this paper, we quantify the effect of using the water isotopic composition in GOP calculations by combining measured $^{17}\Delta$ with previously published estimates of the local isotopic composition of H_2O . We also present a data set from the Arctic Ocean where $^{17}\Delta$ and $\delta^{18}\text{O}\text{-H}_2\text{O}$ were measured simultaneously, and we estimate the $^{17}\text{O}\text{-excess}$. The approach used to estimate the isotopic composition of H_2O for different locations is based on the best available published data (LeGrande & Schmidt, 2006; Li et al., 2015; Luz & Barkan, 2010; Schmidt et al., 1999). For brackish systems, we assume that the water sampled represents a mixture of two end-members, seawater, and meteoric water, and use the sample salinity to estimate the fraction of each end-member (supporting information Text S1 and S2, Macdonald et al., 1995; Surge and Lohmann, 2002; Wankel et al., 2006).

We calculate GOP using equation S8 from Prokopenko et al. (2011)

$$\text{GOP} = k_{\text{O}_2} [\text{O}_2]_{\text{eq}} \left[\frac{X^{17} - X_{\text{eq}}^{17}}{X^{17}} - \lambda \frac{X^{18} - X_{\text{eq}}^{18}}{X^{18}} \right] + \frac{h[\text{O}_2] \frac{\partial^{17}\Delta}{\partial t}}{\left[\frac{X_p^{17} - X^{17}}{X^{17}} - \lambda \frac{X_p^{18} - X^{18}}{X^{18}} \right]}. \quad (7)$$

Here k_{O_2} is the gas transfer velocity for O_2 (m d^{-1}), $[\text{O}_2]$ is the O_2 concentration (mol m^{-3}), h is the mixed layer depth (m), X^{17} is the $^{17}\text{O}/^{16}\text{O}$ ratio of O_2 , and the subscripts *eq* and *P* refer to O_2 at air-water equilibrium and O_2 produced by photosynthesis, respectively. Oxygen terms without a subscript (O_2 , X^{17} , and $^{17}\Delta$) are the measured mixed layer values. We calculate X_{eq}^{18} based on Benson & Krause (1980, 1984) and then derive X_{eq}^{17} using $^{17}\Delta_{\text{eq}} = 8$ per meg (Reuer et al., 2007; Stanley et al., 2010). We calculate X_p^{18} and X_p^{17} using the isotopic composition of H_2O estimated as described above, and isotopic fractionation factors for photosynthetic O_2 with respect to H_2O based on the average of four different types of phytoplankton, using data in Table 1

of Luz and Barkan (2011), specifically $^{18}\epsilon_p = 3.389\text{‰}$ and $^{17}\epsilon_p = 1.778\text{‰}$. We use $\lambda = \gamma_R = 0.5179$ in equation (7) (supporting information Text S3, Hamme et al., 2012; Juranek and Quay, 2013; Kaiser, 2011; Nicholson, 2011; Nicholson et al., 2012). The triple isotopic composition of photosynthetic O_2 can be easily modified in equation (7) and our software for calculating GOP. Such modifications could be required due to ongoing revisions in the isotopic composition of atmospheric O_2 with respect to VSMOW (Barkan & Luz, 2011; Pack et al., 2016; Young et al., 2014) or changes in the photosynthetic fractionation factors to reflect a different community composition (section 3) and/or new experimental data (Angert et al., 2003; Eisenstadt et al., 2010; Luz & Barkan, 2011).

The first term on the right side of equation (7) is the steady state GOP term, and the second term is the non-steady state GOP term. If there is no change in $^{17}\Delta$ with time (steady state with respect to $^{17}\Delta$), then the second term on the right side of equation (7) equals zero. The relative (percent) error in GOP associated with the local H_2O isotopic composition is independent of the magnitude of the nonsteady state term. Additional terms to correct for physical transport and mixing processes can also be included in the GOP calculation (Munro et al., 2013; Nicholson et al., 2014; Wurgaft et al., 2013), but we omit further discussion of these corrections here and instead focus on the sensitivity of the GOP calculations to the H_2O isotopic composition.

3. Chamber Experiments

We conducted field-based incubation experiments which demonstrate that the TOI composition of O_2 in a system approximating biological steady state agreed with the value predicted from the local isotopic composition of water, rather than the typically used VSMOW value. These experiments used benthic flux chambers (Stanley & Howard, 2013) in tidal creeks in the Plum Island Estuary, Massachusetts. The chambers were inserted into the water-sediment interface and sealed to limit exchange with surrounding creek water (Howard, 2017). Over the ~ 4 h daytime incubation period, the concentration of O_2 in each chamber increased due to photosynthetic production exceeding respiration, and the fraction of O_2 derived from photosynthesis also increased (Figure 2). Based on the initial O_2 isotopic composition, observed O_2 concentrations in the chambers, and estimates of ecosystem production and respiration, it is likely that by the end of the incubation $>90\%$ of the O_2 in each chamber was biological in origin (Howard, 2017), and therefore $^{17}\Delta$ of the dissolved O_2 approached the biological steady state value (Luz & Barkan, 2000). By the end of each incubation, the value of $^{17}\Delta$ (calculated with $\lambda = 0.5179$) stabilized at a value near 210 per meg, rather than continuing to increase toward the value of ~ 242 per meg predicted for a steady state system where photosynthetic O_2 is derived from VSMOW (Figure 2).

Using an estimated local isotopic composition of H_2O based on published data and the salinity in the chambers (supporting information Text S1), we predict $^{17}\Delta_{\text{BSS}}$ (calculated with $\lambda_{\text{BSS}} = 0.5154$) to be 215 per meg assuming the isotopic fractionation factor for “average phytoplankton” (average of diatoms, cyanobacteria, coccolithophores, and green algae) defined in Luz and Barkan (2011) or 206 per meg assuming a 1:1 mixture of diatoms and cyanobacteria only (based on microbial cultures from water sampled in the creeks). These predicted values are consistent with the observed $^{17}\Delta$ of ~ 210 per meg.

If the incubations were extended for a longer duration, all of the atmospheric O_2 should eventually be removed by respiration and the O_2 within the chamber should become essentially 100% biological in origin and have a composition equivalent to $^{17}\Delta_{\text{BSS}}$ (206–215 per meg) (Luz & Barkan, 2011; Nicholson, 2011). If 90% of the O_2 in the chamber were biological in origin at the end of the incubation (and the rest derived from gas exchange), the expected $^{17}\Delta_{\text{BSS}}$ would be 194–205 per meg.

Because the measured $^{17}\Delta_{\text{BSS}}$ matched the predicted value with the estimated local isotopic composition of H_2O taken into account, we conclude that chamber incubations are an effective approach for determining $^{17}\Delta_{\text{BSS}}$ in coastal waters. There are several advantages to the chamber approach compared to published techniques for estimating $^{17}\Delta_{\text{BSS}}$ (Luz & Barkan, 2011; Luz et al., 1999). For example, the method measures the isotopic composition of dissolved O_2 directly, rather than the composition of gaseous O_2 in a headspace equilibrated with water (Luz et al., 1999; Luz & Barkan, 2000), the phytoplankton are grown in oxygenated water (not zero- O_2 conditions) (Barkan & Luz, 2011; Eisenstadt et al., 2010; Luz & Barkan, 2011), and we determine the isotopic composition for an intact microbial community in situ rather than a single autotrophic species in lab-based culture.

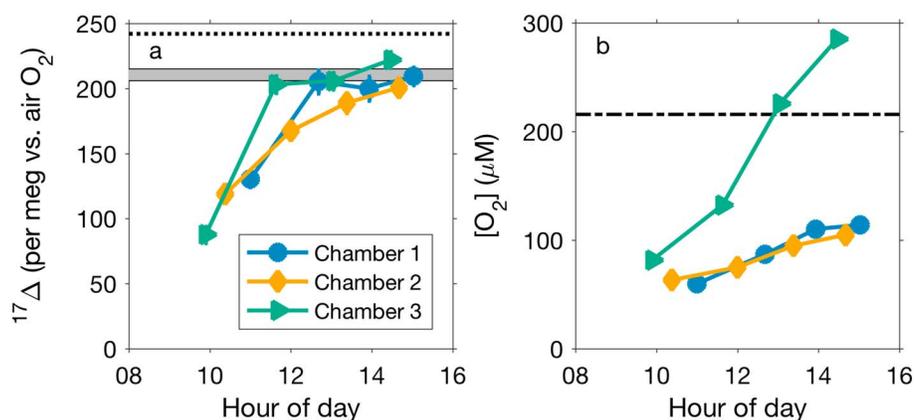


Figure 2. (a) Observed and predicted measurements of $^{17}\Delta$ during three chamber incubation experiments. The colored lines show measured values of $^{17}\Delta$ (calculated with $\lambda = \gamma_R = 0.5179$). The gray shaded region shows the predicted value of $^{17}\Delta_{BSS}$ (calculated with $\lambda = \lambda_{BSS} = 0.5154$) using the estimated local H_2O isotopic composition, and the dashed black line shows the $^{17}\Delta_{BSS}$ value for VSMOW water (see text). Error bars indicate uncertainty due to measurement and sampling. (b) Measured O_2 concentrations in each chamber. Dash-dotted black line shows the equilibrium O_2 concentration. Variability in $[O_2]$ between chambers is due to expected heterogeneity in benthic estuarine sediments.

Notably, $\delta^{18}O-O_2$ and $\delta^{17}O-O_2$ approached an asymptote in the same manner as $^{17}\Delta$ but differed between chambers and did not reach the published values for photosynthetic end-members (supporting information Text S4 and Figure S1). GOP calculations are much more sensitive to $^{17}\Delta_{BSS}$ than to the absolute value of $\delta^{18}O-O_{2p}$. For example, changing $\delta^{18}O-O_{2p}$ from -22‰ to -11‰ changes GOP by less than 5%, as long as $^{17}\Delta_{BSS}$ is held constant. Therefore, the fact that we estimated $^{17}\Delta_{BSS}$ but not $\delta^{18}O-O_{2p}$ does not significantly reduce the utility of the chamber incubation approach and does not affect our conclusion that the local TOI composition of H_2O should be incorporated into GOP calculations in systems where the H_2O isotopic composition differs from VSMOW.

4. Beaufort Sea, Arctic Ocean

In the Arctic Ocean, $\delta^{18}O-H_2O$ in the surface mixed layer can range from -7 to 0‰ (LeGrande & Schmidt, 2006). To quantify the effect of incorporating the local H_2O isotopic composition into Arctic Ocean GOP estimates, we use a data set of measurements of $^{17}\Delta$ from summer 2011 to 2012 in the Beaufort Sea region of the Canada Basin (Stanley et al., 2015) and incorporate measurements of $\delta^{18}O-H_2O$ from the same cruise. We assume a fixed ^{17}O -excess of -5 per meg, the average near-surface seawater value from Luz and Barkan (2010); however, this value is uncertain because no published observations are available in this region. For this data set, the calculated GOP assuming the isotopic composition of H_2O is VSMOW is on average 29% lower (range 48 to 19% lower) than the calculated GOP using the local isotopic composition of H_2O (Figures 3 and S2 and Table 1). Increasing or decreasing the ^{17}O -excess by 8 per meg for all samples (two standard deviations of the global seawater data set from Luz and Barkan (2010)) changes the calculated GOP by 5–6% on average. The systematic error in Beaufort Sea GOP calculations associated with assuming the H_2O isotopic composition is equivalent to VSMOW is larger in magnitude than most other sources of error in the calculation, such as the gas transfer velocity (10–15% error) (Ho et al., 2006). Given that the isotopic composition of H_2O differs from VSMOW throughout most of the Arctic Ocean, we expect that GOP estimates in other regions of the Arctic Ocean would have similarly large systematic errors if the isotopic composition of H_2O is not incorporated into the GOP calculation.

For future studies of GOP from $^{17}\Delta$ measurements in the Arctic Ocean, we strongly recommend investigators also measure $\delta^{18}O-H_2O$ and preferably the ^{17}O -excess and that they include these variables in the GOP calculation. Recently, in many regions of the Arctic Ocean the freshwater content has substantially increased and sea ice cover has substantially decreased, and therefore, it would likely be inaccurate to infer the TOI composition of H_2O using previously published, location-based measurements of $\delta^{18}O-H_2O$ (McPhee et al., 2009; Morison et al., 2012; Yamamoto-Kawai et al., 2009). Additionally, in the Arctic Ocean, there are three salinity and H_2O isotope end-members (seawater, meteoric water, and sea ice melt) (Eicken et al., 2002; Ekwurzel et al., 2001; Östlund & Hut, 1984; Yamamoto-Kawai et al., 2008). The ^{17}O -excess of these three end-members

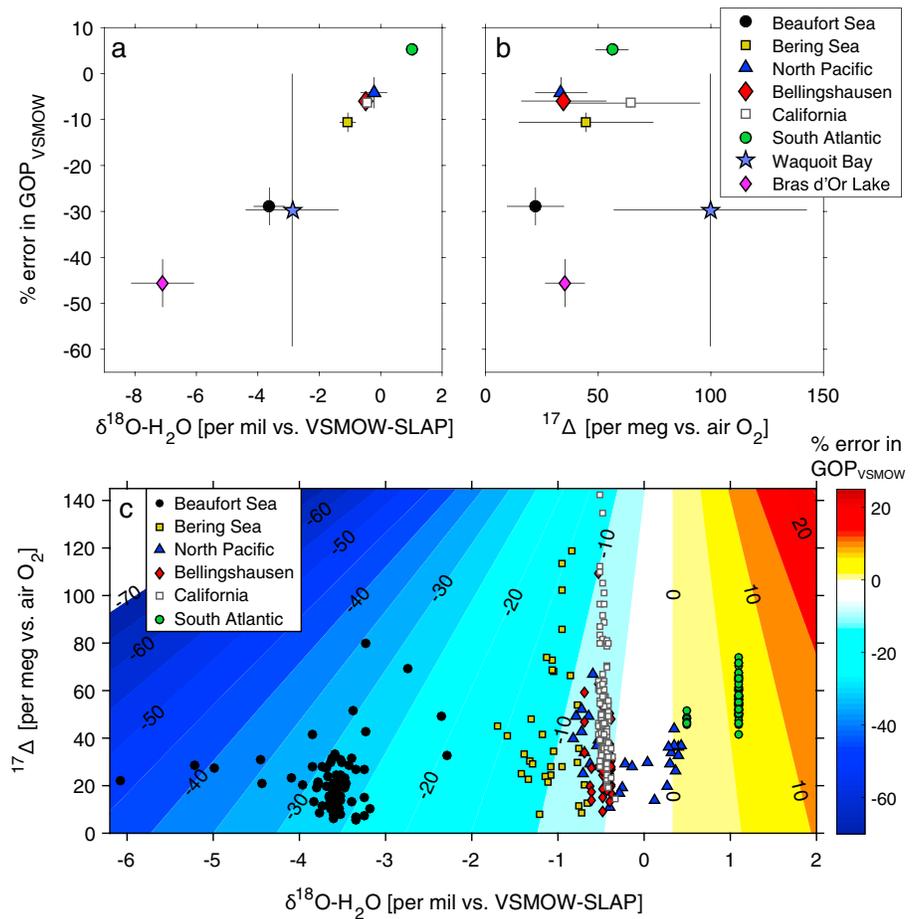


Figure 3. Error in GOP calculations caused by assuming the water isotopic composition is equivalent to VSMOW ($\text{GOP}_{\text{VSMOW}}$) compared to using the local H_2O isotopic composition. Percent error as a function of (a) $\delta^{18}\text{O-H}_2\text{O}$ and (b) $^{17}\Delta$ for all data sets shown in Table 1. Black lines indicate one standard deviation of the values for each region. (c) Contour plot showing % error in $\text{GOP}_{\text{VSMOW}}$ as a function of $^{17}\Delta$ and $\delta^{18}\text{O-H}_2\text{O}$, for a fixed ^{17}O -excess of -5 per meg (the average oceanic value), calculated using equation (7). Individual samples from each oceanic data set are shown.

Table 1

Globally Distributed Triple Oxygen Isotope Data and Errors in Calculated GOP Caused by Assuming the H_2O Isotopic Composition is Equivalent to VSMOW

Location	$\delta^{18}\text{O-H}_2\text{O}^a$ (‰ versus VSMOW-SLAP)	^{17}O -excess ^a (per meg versus VSMOW-SLAP)	$^{17}\Delta$ (per meg versus air O ₂)	% Error in GOP ^b	Reference
Beaufort Sea	-3.6 (-6.1, -2.3)	-5	22 (6, 80)	-29 (-48, -19)	Stanley et al. (2015)
Bering Sea	-1.1 (-1.7, -0.7)	-5	45 (8, 119)	-11 (-16, -7)	Prokopenko et al. (2011)
California Coast	-0.5 (-0.5, -0.3)	-5	64 (14, 170)	-6 (-11, -5)	Munro et al. (2013)
Northeast Pacific	-0.4 (-0.8, 0.4)	-5	34 (11, 67)	-4 (-9, 1)	Juranek et al. (2012)
South Atlantic	0.8 (0.3, 1.4)	-5	32 (17, 50)	5 (1, 6)	Howard (2017)
Bellingshausen Sea	-0.5 (-0.7, -0.4)	-5	35 (9, 109)	-6 (-10, -5)	Castro-Morales et al. (2013)
Bras d'Or Lake	-7.1 (-9.3, -4.8)	16 (6, 27)	35 (9, 54)	-46 (-56, -33)	Manning (2017)
Waquoit Bay	-2.9 (-6.1, -1.1)	1 (-5, 11)	100 (45, 236)	-30 (-234, -11)	This manuscript

Notes. Values are reported as mean (min, max). All tabulated data include only near-surface samples (depth <10 m). ^aDetails on the estimation of $\delta^{18}\text{O-H}_2\text{O}$ and ^{17}O -excess for each data set are provided in the supporting information Text S1. Analytical methods are described in supporting information Text S5 and S6 (Barkan and Luz, 2003; Epstein and Mayeda, 1953; Stanley et al., 2010, 2015). ^bPercent error in GOP is calculated as % error = $(\text{GOP}_{\text{VSMOW}} - \text{GOP})/\text{GOP} \times 100\%$ where $\text{GOP}_{\text{VSMOW}}$ is calculated assuming the H_2O is equivalent to VSMOW and GOP is calculated using the estimated local H_2O isotopic composition.

is currently unknown in this region. Therefore, it is not possible to use the two-end-member approach and estimate $\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta^{17}\text{O}\text{-H}_2\text{O}$ based on salinity alone, nor to estimate $\delta^{17}\text{O}\text{-H}_2\text{O}$ based on measured $\delta^{18}\text{O}\text{-H}_2\text{O}$ and salinity (supporting information Text S1). If the ^{17}O -excess of the three end-members were known, one could estimate the ^{17}O -excess using a water mass analysis based on measurements of $\delta^{18}\text{O}\text{-H}_2\text{O}$ and an additional freshwater source tracer such as total alkalinity (Yamamoto-Kawai et al., 2008). Concurrent measurements of both $\delta^{18}\text{O}\text{-H}_2\text{O}$ and ^{17}O -excess would avoid the uncertainties associated with the water mass analysis.

5. Implications for Oceanic and Estuarine Systems

We use a variety of TOI measurements in other oceanic regions and brackish waters to estimate the error in GOP estimates caused by assuming the water is equivalent to VSMOW (Table 1). In all data sets, the magnitude of the error in GOP estimates is strongly dependent on the magnitude of $\delta^{18}\text{O}\text{-H}_2\text{O}$ and more weakly dependent on the magnitude of $^{17}\Delta$ (Figure 3c). In the Bering Sea, GOP is up to 16% lower when calculated using VSMOW H_2O instead of the local H_2O isotopic composition, and in other oceanic regions outside the Arctic, the maximum error varies from 11% too low to 6% too high.

In freshwater and brackish regions, the magnitude of the errors in calculated GOP is significantly larger, up to 56% in an estuary in Nova Scotia, Canada, and over 200% in an estuary in Massachusetts (Table 1). These larger errors occur primarily due to the large influence of meteoric water in estuaries, which has a $\delta^{18}\text{O}\text{-H}_2\text{O}$ of -6 to -9‰ in these regions, and in the Massachusetts estuary the errors are exacerbated by high values of $^{17}\Delta$ in some samples (Figure 3b). Notably, there are somewhat large uncertainties in the appropriate ^{17}O -excess to use for brackish systems because published data are limited and the range of observed values is large (supporting information Text S2). In future studies, we recommend that authors applying the TOI approach to estimate GOP in regions influenced by meteoric water should measure the ^{17}O -excess of H_2O in addition to $^{17}\Delta$ of O_2 .

6. Conclusions and Future Outlook

We have shown that the local TOI composition of H_2O is an important variable to include in GOP calculations in systems where the isotopic composition of H_2O differs from VSMOW. We have presented a quantitative approach for estimating the local TOI composition of H_2O and incorporating this variable into GOP calculations. Chamber incubation data in an estuary validated this approach and suggest that the TOI approach could be used to estimate GOP in estuarine and freshwater systems, which could greatly expand its utility (Staeher et al., 2012).

New analytical methods could enable the routine measurement of $\delta^{18}\text{O}\text{-H}_2\text{O}$ and ^{17}O -excess as a part of future TOI-based GOP studies and promise to increase scientific understanding of spatial trends in H_2O isotopes. Until the past couple of years, analytical methods with sufficient precision to resolve the ^{17}O -excess of H_2O were mass spectrometer-based, required a specialized front end and the generation of hazardous chemicals, and did not permit the simultaneous measurement of $\delta^{17}\text{O}$ and $\delta^2\text{H}$ (Luz & Barkan, 2005). The recent development of commercially available laser-based sensors that simultaneously measure the ^{17}O -excess and $\delta^2\text{H}$ of H_2O directly, without complicated sample processing (Berman et al., 2013; Steig et al., 2014), will greatly increase the number of laboratories making this measurement and reduce analytical costs (Schauer et al., 2016).

Openly accessible databases of ^{17}O -excess in natural waters, similar to existing databases for $\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta^2\text{H}\text{-H}_2\text{O}$ (Schmidt et al., 1999; IAEA/WMO, 2016), would be highly beneficial to the stable isotope geochemistry community. For example, these data could improve estimates of the ^{17}O -excess for data sets where TOI measurements of O_2 and H_2O were not collected simultaneously, including previously published data sets. Additionally, public archiving of all data used in TOI-based GOP studies will ensure that GOP can be recalculated in the future based on new consensus about the most appropriate way to perform these calculations (supporting information Text S2).

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