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Technical note: The effect of vertical turbulent mixing on gross O_2 production assessments by the triple isotopic composition of dissolved O_2

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Abstract

The ^{17}O-excess ($^{17}\Delta$) of dissolved O_2 has been used, for over a decade, to estimate gross O_2 production (G^{17}OP) rates in the mixed layer (ML) in many regions of the ocean. This estimate relies on a steady-state balance of O_2 fluxes, which include air-sea gas exchange, photosynthesis and respiration but notably, not turbulent mixing with O_2 from the thermocline. In light of recent publications, which showed that neglecting the turbulent flux may lead to inaccurate G^{17}OP estimations, we present a simple correction for the effect of turbulent flux of O_2 from the thermocline on ML G^{17}OP. The correction is based on a turbulent-flux term between the thermocline and the ML, and use the difference between the ML $^{17}\Delta$ and that of a single data-point below the ML base. Using a numerical model and measured data we compared turbulence-corrected G^{17}OP rates to those calculated without it. The corrected G^{17}OP rates were 10–90 % lower than the uncorrected rates, which implies that a large fraction of the photosynthetic O_2 in the ML is actually produced in the thermocline.

1 Introduction

Gross O_2 production (GOP) in the ocean is a fundamental factor in the global cycling of O_2. As such, accurate estimates of GOP rates are essential in order to understand and model the global cycles of oxygen and carbon. During the past decade, the application of the triple isotope composition (^{16}O, ^{17}O, and ^{18}O) of dissolved O_2 as a tracer for GOP (G^{17}OP), which was first presented by Luz and Barkan (2000), has become widespread and has been used to estimate GOP rates in many regions of the ocean (Juranek and Quay, 2013).

1.1 GOP from $^{17}\Delta$

Estimating GOP rates from the isotopic composition of dissolved O_2 is based on the ^{17}O-excess ($^{17}\Delta$) that photosynthetically produced O_2 has in comparison to atmospheric O_2 (Luz et al. 1999). The $^{17}\Delta$ has been defined in several ways (Kaiser, 2011). A common definition (Miller, 2002; Luz and Barkan, 2005), which we use here is:

$$^{17}\Delta = \ln(\delta^{17}O + 1) - \lambda \ln(\delta^{18}O + 1), \tag{1}$$

where $\delta^{*}O = (^{*}R_{sample}/^{*}R_{ref} - 1)$; $^{*}R_{sample}$ and $^{*}R_{ref}$ are the $^{*}O/^{16}O$ in the sample and the reference, respectively. λ is the slope of a reference line on a $\ln(\delta^{17}O + 1)$ versus $\ln(\delta^{18}O + 1)$ plot, which represents the expected slope of the relevant processes. Following Luz and Barkan (2005), most studies use $\lambda = 0.518$ for the calculation of $^{17}\Delta$ and atmospheric O_2 as a standard for the isotopic measurements. To derive a steady-state expression for GOP in the mixed layer (ML), Luz and Barkan (2000) used an O_2 and $^{17}\Delta$ 1-box model. Their derivation yielded the following equation:

$$G^{17}OP = K\,[O_2]_{eq}\,\frac{\left(^{17}\Delta_{dis} - {}^{17}\Delta_{eq}\right)}{\left(^{17}\Delta_{p} - {}^{17}\Delta_{dis}\right)}, \tag{2}$$

where K is the air-sea gas exchange coefficient, $[O_2]_{eq}$ is the equilibrium concentration of O_2, $^{17}\Delta_{dis}$ is the $^{17}\Delta$ value of dissolved O_2, $^{17}\Delta_{eq}$ is the equilibrium $^{17}\Delta$, and $^{17}\Delta_{p}$ is $^{17}\Delta$ at steady state between photosynthesis and respiration. Recently, Luz and Barkan (2000) method for ML GOP estimation (hereafter $G^{17}OP_{LB}$) was revised by Prokopenko et al. (2011) and Kaiser (2011), who derived equations for $G^{17}OP$ that use measured $\delta^{17}O$ and $\delta^{18}O$, the isotopic composition of dissolved O_2 in air-seawater equilibrium ($\delta^{17}O_{eq}$ and $\delta^{18}O_{eq}$), and the isotopic composition of photosynthetic O_2 ($\delta^{17}O_{p}$ and $\delta^{18}O_{p}$). Unlike Eq. (2), their equations were not approximated. They did,

however, rely on $\delta^{17}O_p$ and $\delta^{17}O_{eq}$ which are still subject to disagreement among researchers in the field (e.g. Kaiser and Abe, 2012). However, Luz and Barkan (2011a, b) and Nicholson (2011) showed that if proper $\delta^{17}O_p$ and $\delta^{18}O_p$ are assigned, the differences between $G^{17}OP_{LB}$ and $G^{17}OP$ estimated from revised versions are small.

1.2 The effect of turbulent mixing on $G^{17}OP$ estimation

As in Luz and Barkan (2000), the ML $G^{17}OP$ equations that were presented by Prokopenko et al. (2011) and Kaiser (2011) were derived with a 1-box representation of the ML in which a balance exists between the O_2 fluxes of GOP, respiration and air-sea gas exchange, but without accounting for the flux of turbulent mixing with O_2 from the thermocline. This was, in spite of the fact that vertical $^{17}\Delta$ profiles often show a pronounced increase below the ML base (Fig. 1; Luz and Barkan, 2000; Juranek and Quay, 2005; Quay et al., 2010). Juranek and Quay (2005) estimated that vertical turbulence had a negligible affect over $G^{17}OP$. However, Nicholson et al. (2012) showed that mixing of ML O_2 with high $^{17}\Delta$ O_2 from the thermocline into the ML (by either entrainment due to ML deepening, or by turbulent flux) may result in an overestimation of up to 80 % in ML $G^{17}OP$. Nicholson et al. (2012) further suggested that this overestimation was the likely explanation for the higher ratio of $G^{17}OP$ to ^{14}C based net productivity ($G^{17}OP : N^{14}CP$; Marra, 2002; Quay et al., 2005, 2010), compared to the ratio of GOP estimated from ^{18}O-incubations to the same net productivity estimate ($G^{18}OP : N^{14}CP$). In addition, Jonsson et al. (2013) found that the turbulent mixing had a considerable effect on estimation of net O_2 production, using O_2/Ar measurements.

As noted above, high $^{17}\Delta$ O_2 from the thermocline can mix into the ML either by entrainment of water from the thermocline into the ML, which takes place as the ML base deepens, or by vertical turbulence of O_2 from the thermocline. The latter process takes place when the ML depth is constant (Fig. 1). Nicholson et al. (2012) did not consider these two process separately; however, their findings showed that $G^{17}OP$

overestimated GOP even when the ML depth was relatively constant, which indicates that vertical turbulence also affects $G^{17}OP$.

While Sarma et al. (2006) and Quay et al. (2010) discussed the effect of entrainment on $G^{17}OP$ and suggested non steady-state corrections, and Castro-Morales et al. (2013) suggested a correction for the vertical flux of O_2 into the ML, the effect of turbulence on the triple isotopic composition and the resulting effect on ML $G^{17}OP$ estimations has not been explicitly examined. In light of Nicholson et al. (2012) and Jonsson et al. (2013) results, it is clear that to accurately estimate $G^{17}OP$ rates, the magnitude of the turbulent mixing effect should be evaluated, and if large, corrected for. The aims of this work were to evaluate the magnitude of the effect of turbulent mixing on ML $G^{17}OP$ estimation, and to derive an analytical correction for this effect.

2 Derivation of a GOP equation with a turbulent mixing term

Prokopenko et al. (2011) presented a new equation for $G^{17}OP$ ($G^{17}OP_{PRO}$), which was obtained by rigorous derivation of time variations of O_2 isotopologues. We added a turbulent flux term to Eq. (4) and 5 in Prokopenko et al. (2011). The turbulent flux was calculated between the base of the ML and a single point along the $^{17}\Delta$ gradient below the ML, which was assigned as "deep" (Fig. 1). Consequently, the $^{17}\Delta$ gradient below the ML was assumed to be linear with depth (we will go back to this assumption in the discussion section). The resulting equation for the rate of change in $^{17}\Delta$ in the ML was (full derivation of the equation can be found in Appendix A):

$$
h[O_2]\frac{\partial\left(^{17}\Delta\right)}{\partial t} = G^{17}OP_C \left[\left(\frac{x_p^{17}-x^{17}}{x^{17}}\right) - \lambda\left(\frac{x_p^{18}-x^{18}}{x^{18}}\right)\right] - K[O_2]_{eq}\left[\left(\frac{x^{17}-x_{eq}^{17}}{x^{17}}\right) - \lambda\left(\frac{x^{18}-x_{eq}^{18}}{x^{18}}\right)\right] \\
- \frac{\kappa}{Z}[O_2]_{deep}\left[\left(\frac{x^{17}-x_{deep}^{17}}{x^{17}}\right) - \lambda\left(\frac{x^{18}-x_{deep}^{18}}{x^{18}}\right)\right], \quad (3)
$$

where h is the ML depth, $[O_2]$ is the dissolved O_2 concentration in the ML, κ is the eddy-diffusivity coefficient, and Z is the vertical distance between the base of the ML and the

depth assigned as "deep" (we use $D = \kappa / Z$ hereafter). X* represents the ratio $^*O / {}^{16}O$ and α^* is the fractionation factor associated with respiration for each isotopologue. The subscripts "p" and "eq" denote "photosynthetic" and "equilibrium", respectively. Note that as was shown by Luz and Barkan (2009) and Prokopenko et al. (2011), the rate of change of $^{17}\Delta$ is independent of respiration. When steady-state conditions in the ML are assumed, the resulting term for turbulent flux corrected $G^{17}OP$ is:

$$G^{17}OP_C = K[O_2]_{eq} \frac{\left(\frac{X^{17} - X_{eq}^{17}}{X^{17}} \right) - \lambda \left(\frac{X^{18} - X_{eq}^{18}}{X^{18}} \right)}{\left(\frac{X_p^{17} - X^{17}}{X^{17}} \right) - \lambda \left(\frac{X_p^{18} - X^{18}}{X^{18}} \right)} + D[O_2]_{deep} \frac{\left(\frac{X^{17} - X_{deep}^{17}}{X^{17}} \right) - \lambda \left(\frac{X^{18} - X_{deep}^{18}}{X^{18}} \right)}{\left(\frac{X_p^{17} - X^{17}}{X^{17}} \right) - \lambda \left(\frac{X_p^{18} - X^{18}}{X^{18}} \right)}, \quad (4)$$

where $G^{17}OP_C$ is the $G^{17}OP$ corrected for turbulence. The numerator of the second term on the right-hand side in Eq. 4 represents the contribution of the turbulent flux to the GOP estimated from ^{17}O-excess in the ML.

3 Simulations by a 1-D numerical model

We used a simple 1-D model, which simulated the effects of GOP, respiration, gas exchange and turbulence on each O_2 isotopologue, to compare the $G^{17}OP$ rates obtained by Eq. (4) with those obtained without applying corrections for the turbulent flux. Briefly, the model simulated the water column up to a depth of 300 m, which was divided into 30 layers of 10 m each, and calculated the fluxes of each O_2 isotopologue in each layer produced by photosynthesis, respiration, and turbulent mixing (model equations, parameters and MATLAB files are given in supplementary material). An additional layer at the top of the water column, represented the ocean surface. In this layer, $[O_2]$ and its isotopic composition were kept in air-sea equilibrium. The eddy diffusivity coefficient in the ML was assigned so that $[O_2]$ would remain fully mixed. For the seasonal thermocline, we used $\kappa = 10^{-4}\,\mathrm{m}^2\,\mathrm{s}^{-1}$. While this value is almost an order of magnitude

higher than the value estimated from SF_6 release experiments in the permanent thermocline (~ 300 m, Ledwell et al. 1993), using lower values did not yield realistic $^{17}\Delta$ profiles. Moreover, Nicholson et al. (2012) used similar values ($8–9 \times 10^{-5}$ m^2 s^{-1}) to reproduce the physical conditions (ML depth, heat content and sea-surface temperature) in the upper 1000 m in the Bermuda Atlantic Time-Series (BATS) station and in Hawaii Ocean Time-Series (HOT). Apparently, κ values near the interface between the ML and the thermocline are higher than those which characterize the thermocline at greater depths where SF_6 release experiments were conducted.

We ran two simulations to examine the effect of turbulent mixing on ML G^{17}OP. In the "fixed mixing depth" simulation (Table 1) we ran the model with a constant ML depth of 35 m. The layer directly below the ML base, at 45 m, was assigned as the "deep" data point for turbulence correction. At the end of each month, ML δ^{17}O, δ^{18}O and $^{17}\Delta$ values were calculated. In the first month of the simulation, G^{17}OP$_{LB}$ and G^{17}OP$_{PRO}$ slightly overestimated (by 7 %) the GOP assigned in the model (GOP$_M$). In the following months, the overestimation of both G^{17}OP$_{LB}$ and G^{17}OP$_{PRO}$ increased, reaching ~ 40 % after 5 months. As shown in Fig. 2, the increase in GOP overestimation was closely related to the increase in $^{17}\Delta$ in the seasonal thermocline. However, G^{17}OP$_C$, which corrects for the turbulent mixing flux, remained constant with a slight underestimation of ~ 7 % throughout the entire simulation period. When we effectively shut down turbulent mixing in the model by reducing κ within the thermocline to 10^{-6} m^2 s^{-1}, G^{17}OP$_{LB}$ and G^{17}OP$_{PRO}$ were in good agreement with GOP$_M$. This indicates that turbulent flux was indeed the cause of the overestimation.

In the "varying mixing depth" simulation, ML depths were allowed to change, roughly according to the typical seasonal changes in BATS station (Table 2). When ML depth underwent rapid changes (January–March and August–December), the steady state assumption was not valid, and neither G^{17}OP$_{LB}$ and G^{17}OP$_{PRO}$, nor G^{17}OP$_C$ yielded GOP rates comparable to GOP$_M$. On the other hand, when the ML depth experienced small variations (April–August), the turbulent mixing corrected G^{17}OP$_C$ rates

were close to GOP_M, while $G^{17}OP_{LB}$ and $G^{17}OP_{PRO}$ were about 60–90 % greater than GOP_M.

4   The effect of turbulent mixing on measured GOP rates

To estimate the effect of turbulent mixing on $G^{17}OP$ estimations in the ocean, we compared previously published GOP rates from BATS (Luz and Barkan, 2009) with equivalent $G^{17}OP_C$ rates. In addition, we used published data (Nicholson et al., 2012) to calculate and compare between $G^{17}OP_{LB}$ and $G^{17}OP_C$ in Hawaii Ocean Time-Series (HOT). To use Eq. (4), we chose months in which vertical profiles of $^{17}\Delta$ and O_2 were measured and published (Nicholson et al., 2012). Following our conclusions from the 1-D model simulations, we compared months in which there were no major changes in ML depth. The κ values for BATS and HOT were both taken from Nicholson et al. (2012)

ML depth was determined as the depth in which a difference of 0.5 % in O_2 concentration relative to the sea-surface was observed (Castro-Morales and Kaiser, 2012). The "deep" reference point was assigned as the depth nearest to the ML base in which $^{17}\Delta$ was at least 14 per meg larger than $^{17}\Delta$ in the ML. Wind speed data from ~ 10 days before the cruise were obtained from QuickScat database, and K was estimated according to Wannikhof (1992). The results (Table 3) showed that $G^{17}OP_C$ rates were 65–100 % lower than $G^{17}OP_{LB}$ in BATS, and 10–40 % lower in HOT. These results are in agreement with Nicholson et al. (2012), who estimated the effect of mixing as 60–90 % of $G^{17}OP$. Notably, using more recent parameterization for air-sea gas exchange (Ho et al., 2006; Sweeny et al., 2007), which gives lower estimate of gas-exchange rates, would result in an even greater contribution of the turbulent flux.

5   Discussion

Our results show that vertical turbulence of O_2 from the thermocline, affects ML $G^{17}OP$ estimations, such that corrected $G^{17}OP$ rates are considerably lower than the uncorrected rates. This indicates that a large fraction of the ML photosynthetic O_2 is not produced in the ML itself, but rather in the thermocline below it. However, our results also show that the turbulent contribution to the ML $^{17}\Delta$ can be corrected in a rather simple manner. Below, we discuss the technical aspects and the implications of these findings.

5.1   Applying turbulence correction

Our results showed that when the ML depth does not change considerably, the effect of turbulence on ML GOP estimation can be corrected by a simple correction. However, to apply this correction, at least one point of data, which includes $[O_2]$ and its isotopic composition below the ML is necessary. Such data points are easy to obtain in time-series study sites such as BATS and HOT, but can complicate basin-wide $G^{17}OP$ estimations, which usually rely on underway seawater systems installed on ship of opportunity for sampling (Juranek and Quay, 2010; Juranek et al., 2012). In the future, such studies would need to either collect several representative "deep" samples from the thermocline along the cruise route, or use existing data if available to correct for turbulence effects. Such corrections could also be applied to existing data.

5.2   Choice of "deep" reference point

The choice of the depth that would represent the "deep" point can affect the resulting GOP (Fig.1). Since the actual $^{17}\Delta$ gradient is not necessarily linear, the closer the point to the ML base, the better it would represent the actual flux between the ML and the thermocline (Fig. 1). On the other hand, the difference in the isotopic composition between the deep data point and the ML has to be considerably larger than the ana-

lytical error associated with $^{17}\Delta$ measurements ($\sim$ 6 per meg; e.g. Ruer et al., 2007). Previous knowledge of $^{17}\Delta$ dynamics for the study site would help with choosing the optimal depth to collect the "deep" sample. For example, Juranek and Quay (2005) and Quay et al. (2010) have shown that during summer months in HOT, differences greater than 60 per meg (an order of magnitude higher than the analytical error) between the ML and thermocline $^{17}\Delta$ could be found within 20–40 m below the ML base. In BATS, $^{17}\Delta$ gradients tend to be smaller, and a difference of 60 per meg can usually be found 40–60 m below the ML depth (Nicholson et al., 2012).

5.3 Parameterization of gas-exchange and eddy diffusivity

$G^{17}OP_C$ is sensitive to the accuracy of estimating both K and κ. While the sensitivity to K characterizes $G^{17}OP$ in general, a combination of errors on K and κ may yield inaccurate $G^{17}OP_C$ rates. We assume that the negative $G^{17}OP_C$ rates that we obtained in some months (Table 3) were the result of inaccurate choice of K and κ. The main aims of this work were to show the importance of turbulence effects and suggest a correction, rather than to perform accurate GOP estimations, therefore we used crude estimations of K and κ.

Since ^{18}O-incubations are not affected by turbulence, it is likely that provided that K and κ are accurately parameterized, $G^{17}OP_C : N^{14}CP$ would agree with $G^{18}OP : N^{14}CP$ (Marra, 2002). Moreover, the fact that $^{17}\Delta$ in the ML depends upon GOP, gas-exchange and turbulent flux from the thermocline, means that in future studies any one of these three parameters could be estimated by performing simultaneous measurements of the other two parameters. For example, if GOP is estimated by ^{18}O-incubations and gas exchange is estimated from wind speed measurements, $^{17}\Delta$ profiles could be used to estimate κ in the seasonal thermocline.

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6 Conclusions

1. Turbulent fluxes of O_2 isotopologues from the thermocline have a pronounced effect over $^{17}\Delta$ values in the ML, and consequently, over the accuracy of $G^{17}OP$ estimations.

2. An accurate $G^{17}OP$ estimate can be obtained by using a simple correction for the effect of the turbulent fluxes.

3. This correction is applicable when the mixed layer depth does not change sharply, and requires measurements of O_2 and its isotopic composition in a single point below the mixed layer, in addition to the standard measurements of these values in the mixed layer.

Appendix A

Derivation of the term for correcting mixed-layer gross O_2 production to turbulent flux from the thermocline

Like Prokopenko et al. (2011), we consider a surface mixed layer subject to respiration, photosynthesis and gas exchange with the atmosphere, but which also exchanges water with the underlying "deep" layer via turbulent diffusion. In the current box model framework, we parameterize the turbulent O_2 flux with the deep layer as $\kappa \left([O_2] - [O_2]_{\text{deep}} \right) / Z$, where $[O_2]$ and $[O_2]_{\text{deep}}$ are the dissolved O_2 concentrations in the mixed and deep layers, respectively. κ is the eddy diffusion coefficient and Z is the vertical distance between the base of the ML and the depth assigned as "deep". For convenience, we use $D = \kappa/Z$ hereafter. Likewise, turbulent fluxes of O_2 isotopes are parameterized as $-D \left([O_2]X^* - [O_2]_{\text{deep}} X^*_{\text{deep}} \right)$, where X^* represents the ratio $^*O/^{16}O$.

The mass balances for O_2 and its isotopes are given by:

$$h\frac{\partial\left([O_2]\right)}{\partial t} = GOP - R - K\left([O_2] - [O_2]_{eq}\right) - D\left([O_2] - [O_2]_{deep}\right),$$ (A1)

$$h\frac{\partial\left([O_2]X^*\right)}{\partial t} = GOP X_p^* - R\alpha^* X^* - K\left([O_2]X^* - [O_2]_{eq}X_{eq}^*\right) - D\left([O_2]X^* - [O_2]_{deep}X_{deep}^*\right),$$ (A2)

5 where h is the mixed layer depth, t is time, GOP is the gross O_2 production, R is the respiration rate and K is the piston velocity. α^* is the fractionation factor associated with respiration for each isotopologue. The subscripts "p" and "eq" denote "photosynthetic" and "equilibrium", respectively.

The remainder of the derivation is carried out by straightforward applications of the
10 steps outlined in Prokopenko et al. (2011), and repeated here for the sake of completion. The left-hand side of Eq. (A2) can be written explicitly as:

$$h\frac{\partial\left([O_2]X^*\right)}{\partial t} = hX^*\frac{\partial\left([O_2]\right)}{\partial t} + h[O_2]\frac{\partial\left(X^*\right)}{\partial t}.$$ (A3)

Upon substituting the left-hand side and the first term on the right-hand of Eq. (A3) with Eq. (A2) and (A1), respectively, rearranging and dividing by X^* one gets:

$$h[O_2]\frac{1}{X^*}\frac{\partial\left(X^*\right)}{\partial t} = GOP\left(\frac{X_p^*-X^*}{X^*}\right) + R\left(1-\alpha^*\right) + K[O_2]_{eq}\left(\frac{X_{eq}^*-X^*}{X^*}\right)$$
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$$+ D[O_2]_{deep}\left(\frac{X_{deep}^*-X^*}{X^*}\right).$$ (A4)

Note that the left-hand side of Eq. (A4) is equal to: $h[O_2]\frac{\partial\left(\ln X^*\right)}{\partial t}$. On the other hand, ^{17}O-excess is defined as:

$$^{17}\Delta = \ln(\delta^{17}O + 1) - \lambda\ln(\delta^{18}O + 1).$$ (A5)

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Taking the derivative of Eq. (A5) with respect to time and multiplying by $h[O_2]$ yields:

$$h[O_2]\frac{\partial\left({}^{17}\Delta\right)}{\partial t} = h[O_2]\left(\frac{\partial\left(\ln X^{17}\right)}{\partial t} - \lambda\frac{\partial\left(\ln X^{18}\right)}{\partial t}\right) \tag{A6}$$

Substituting Eq. (A4) into Eq. (A6) yields:

$$h[O_2]\frac{\partial\left({}^{17}\Delta\right)}{\partial t} = G^{17}OP_C\left[\left(\frac{X_p^{17}-X^{17}}{X^{17}}\right)-\lambda\left(\frac{X_p^{18}-X^{18}}{X^{18}}\right)\right]-K[O_2]_{eq}\left[\left(\frac{X^{17}-X_{eq}^{17}}{X^{17}}\right)-\lambda\left(\frac{X^{18}-X_{eq}^{18}}{X^{18}}\right)\right],$$
$$-D[O_2]_{deep}\left[\left(\frac{X^{17}-X_{deep}^{17}}{X^{17}}\right)-\lambda\left(\frac{X^{18}-X_{deep}^{18}}{X^{18}}\right)\right] \tag{A7}$$

where $G^{17}OP_C$ is the turbulence-corrected $G^{17}OP$. Note, the respiration term is not affected by the addition of the turbulent flux term and is cancelled out in the expression for the changes in ^{17}O-excess, as expected.

Finally, for a mixed layer in steady-state we obtain the following expression for GOP corrected for turbulent diffusion:

$$G^{17}OP_C = K[O_2]_{eq}\frac{\left(\frac{X^{17}-X_{eq}^{17}}{X^{17}}\right)-\lambda\left(\frac{X^{18}-X_{eq}^{18}}{X^{18}}\right)}{\left(\frac{X_p^{17}-X^{17}}{X^{17}}\right)-\lambda\left(\frac{X_p^{18}-X^{18}}{X^{18}}\right)} + D[O_2]_{deep}\frac{\left(\frac{X^{17}-X_{deep}^{17}}{X^{17}}\right)-\lambda\left(\frac{X^{18}-X_{deep}^{18}}{X^{18}}\right)}{\left(\frac{X_p^{17}-X^{17}}{X^{17}}\right)-\lambda\left(\frac{X_p^{18}-X^{18}}{X^{18}}\right)}. \tag{A8}$$

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/10/14239/2013/ bgd-10-14239-2013-supplement.zip.

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Table 1. Model simulations of GOP with a constant mixed layer depth.

time step (day)	ML depth (m)	GOP-M^t	G^{17}OP$^t_{LB}$	G^{17}OP$^t_{PRO}$	G^{17}OP^t_C	G^{17}OP$^{nt}_{LB}$	G^{17}OP$^{nt}_{PRO}$
30			112	117	98	100	104
60			126	132	101	102	106
90			134	140	101	102	107
120			139	146	101	102	107
150			143	149	101	103	107
180	35	107	146	152	100	103	108
210			148	155	100	103	108
240			150	156	100	103	108
270			151	158	100	104	108
300			152	159	100	104	109
330			153	160	100	104	109
360			154	161	99	104	109

ML – mixed layer, GOP-M – input GOP rate, G^{17}OP$_{LB}$ –Luz and Barkan (2000), G^{17}OP$_{PRO}$ – Prokopenko et al. (2011), G^{17}OP$_C$ – this work, includes a correction for turbulent mixing. All GOP rates are in mmol m^{-2} day^{-1}. In the columns marked with t, $\kappa = 10^{-4}$ m^2 s^{-1}, whereas in the columns marked with nt, $\kappa = 10^{-6}$ m^2 s^{-1}.

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The effect of vertical turbulent mixing on gross O$_2$ production assessments

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Table 2. Model simulations of GOP with varying mixed layer depth.

time step (day)	ML depth (m)	GOP-M^t	G^{17}OP$^t_{LB}$	G^{17}OP$^t_{PRO}$	G^{17}OP$^t_{C}$	G^{17}OP$^{nt}_{LB}$	G^{17}OP$^{nt}_{PRO}$
30	195	226	111	115	132	112	116
60	245	226	136	142	162	137	142
90	5	30	87	91	82	84	88
120	15	58	91	95	54	58	61
150	15	58	97	102	51	55	58
180	15	58	103	108	51	56	58
210	15	58	107	112	50	56	59
240	35	107	204	212	129	228	237
270	75	180	332	341	258	410	418
300	85	193	264	273	224	262	271
330	95	204	249	257	220	253	262
360	135	226	273	281	262	305	313

ML – mixed layer, GOP-M – input GOP rate, G^{17}OP$_{LB}$ –Luz and Barkan (2000), G^{17}OP$_{PRO}$ – Prokopenko et al. (2011), G^{17}OP$_{C}$ – this work, includes a correction for turbulent mixing. All GOP rates are in mmol m^{-2} day^{-1}. In the columns marked with t, $\kappa = 10^{-4}$ m^2 s^{-1}, whereas in the columns marked with nt, $\kappa = 10^{-6}$ m^2 s^{-1}.

Table 3. Comparison of G^{17}OP rates from BATS and HOT

Location	Date	κ (m^2 s^{-1})	ML depth (m)	"deep" (m)	G^{17}OP$_{LB}$	G^{17}OP$_{C}$
					(mmol m^{-2} day^{-1})	
BATS	May 2000	9×10^{-5}	20	40	29	9
	Jul 2000		20	80	45	16
	Sep 2000		20	40	50	−4
HOT	May 2007	8×10^{-5}	100	125	150	134
	Aug 2007		45	100	42	25

All the parameters used for the calulatios made in BATS were taken from Luz and Barkan (2009). κ values and the raw data used for the calculation of G^{17}OP$_{LB}$ and G^{17}OP$_{C}$, and the parameters used for the calculations in HOTS were taken from Nicholson et al. (2012). ML depth was determined as the depth in which a difference of 0.5 % in O$_2$ concentration relative to the sea-surface was observed. Gas exchange rates were calculated according to Wannikhof (1992) from wind speed data obtained from QuickSCAT.
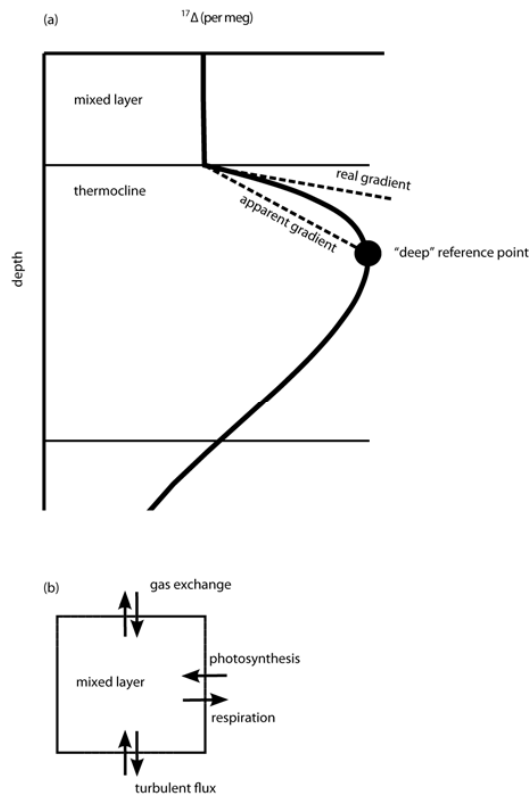
Fig. 1. **(a)** A schematic illustration of a typical mid-ocean $^{17}\Delta$ vertical profile. The dashed lines, which extend below the mixed-layer base define the $^{17}\Delta$ gradient, which in turn, is correlated with the $^{17}\Delta$ "flux" into the mixed layer. Depending on the profile shape, the choice of a "deep" reference point at some depth below the mixed layer depth, results in a $^{17}\Delta$ gradient which is different than the real $^{17}\Delta$ gradient. **(b)** A conceptual model of the O$_2$ isotopologues fluxes in and out of the ML.
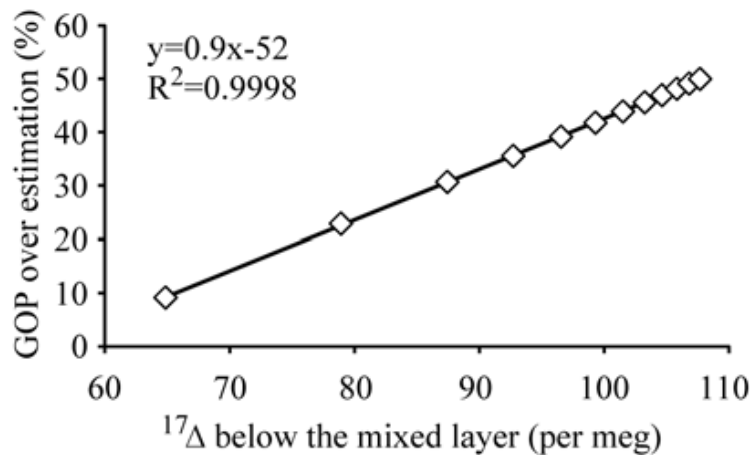
Fig. 2. Linear regression analysis of model simulation results, showing the increase in mixed layer GOP overestimation (($G^{17}OP_{PRO}$ / GOP_M -1) × 100) vs. ^{17}O-excess below the mixed layer.