Team Karl Highlight

Gross Oxygen Production by a Novel ^{18}O/MIMS Method

Submitted by: Sara Ferrón and David Karl

We have developed a method to measure aquatic gross primary production by the ^{18}O in vitro technique using shipboard or laboratory-based membrane inlet mass spectrometry (MIMS). The method was validated in the low-productivity oligotrophic North Pacific Subtropical Gyre, where the measured GPP ranged from 0.2 to 1.1 µmol O_2 L^{-1} d^{-1}. Compared to the more conventional method using isotope ratio mass spectrometry (IRMS) and head-space equilibration, this new approach has the advantages of simple water sample handling and analysis, accurate dissolved gas measurements, capability of analysis on board of a ship, and use of relatively inexpensive instrumentation.

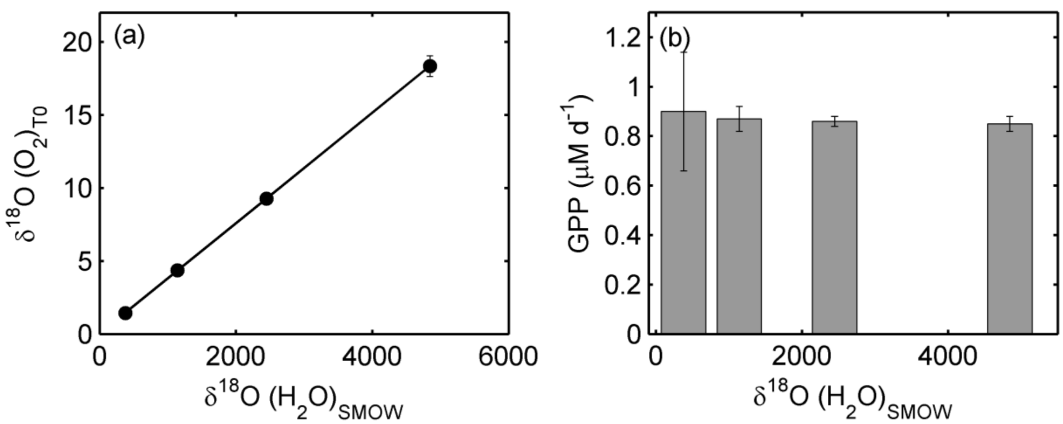

Figure 1. (a) Relationship between the isotopic water enrichment relative to VSMOW, $\delta^{18}O(H_2O)_{VSMOW}$, and the final enrichment of dissolved O_2 relative to time zero. The $\delta^{18}O$ values are in ‰. The black line is a linear regression to the data ($y = 0.0038x + 0.0163$; r^2=0.9999). Calculated (b) GPP. Error bars represent one SD of triplicate samples, except for the smallest enrichment in which we had only duplicates.

In order to decide the minimum initial ^{18}O-H_2O enrichment needed to obtain a measurable enrichment in dissolved O_2 at Station ALOHA and also to check the potential negative or positive effects of the addition of ^{18}O-H_2O due to accompanying contaminants or nutrients, we measured ^{18}O-GPP adding different volumes of labeled water (Figure 1). The results showed that even the smallest addition (~380‰ enrichment), resulted in a measurable enrichment of ^{18}O in dissolved O_2, and the calculated ^{18}O-GPP did not differ for the different enrichments (Figure 1b). Whereas the ^{18}O-GPP values did not differ between the treatments, the uncertainty in the calculated GPP value decreased when increasing the final $\delta^{18}(O_2)$, and therefore an initial enrichment of ~2500‰ was considered appropriate for surface waters at Station ALOHA, which resulted in an approximate uncertainty in GPP of ± 0.02 µmol O_2 L^{-1} d^{-1}. We also tested that the spike of ^{18}O-H_2O used at Station ALOHA for ^{18}O-GPP measurements did not affect primary production rates, measured by ^{14}C uptake technique.

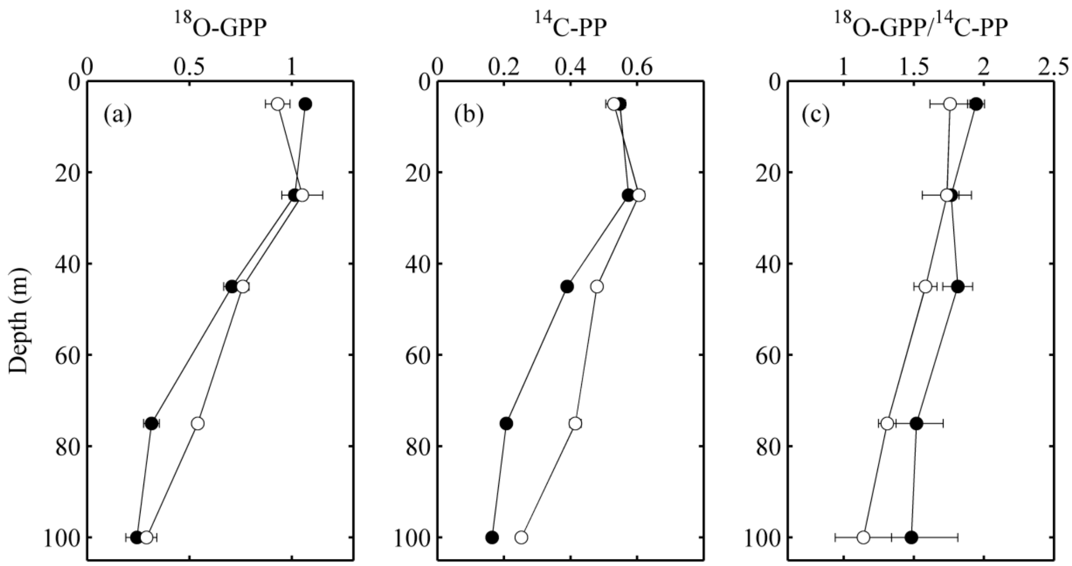

Figure 2. Two depth profiles of in situ primary production rates measured at Station ALOHA measured using: (a) ^{18}O in vitro method (units in µmol O_2 L^{-1} d^{-1}), and (b) ^{14}C uptake method (units in µmol C L^{-1} d^{-1}). Also shown (c) the ratio ^{18}O-GPP to ^{14}C-PP (mol O_2/mol C). Black and white circles represent profiles conducted on April 7, 2015 (HOE-Legacy 1) and May 23, 2015 (HOT 272), respectively. The error bars in (a) and (b) represent the SD of triplicate samples, whereas in (c) they represent the propagated error from (a) and (b).

Two depth profiles of ^{18}O-GPP and ^{14}C-PP rates measured at Station ALOHA are shown in Figure 2. As expected, elevated production rates were observed in the top 25 m of the water column, ranging from 0.7 to 1.1 µmol O_2 L^{-1} d^{-1} for ^{18}O-GPP, and from 0.4 to 0.6 µmol C L^{-1} d^{-1} for ^{14}C-PP. At or below 75 m, rates ranged from 0.2 to 0.5 µmol O_2 L^{-1} d^{-1} and 0.2 to 0.4 µmol C L^{-1} d^{-1}, respectively. Measured rates of ^{18}O-GPP and ^{14}C-PP were positively correlated ($r^2 = 0.942$), indicating that the ^{18}O-GPP measurements changes tracked the changes in primary productivity as determined by the ^{14}C uptake. The slope of a model II regression fit to the data was 2.2 ± 0.2 µmol O_2/ µmol C, indicating that ^{18}O-GPP decreased with depth approximately twice as fast as ^{14}C-PP, which is consistent with previous observations at Station ALOHA (Quay et al. 2010). The ^{18}O-GPP to ^{14}C-PP ratio averaged 1.8 ± 0.1 in surface waters (5-45m) and 1.3 ± 0.1 in the deeper section of the euphotic zone (75-100 m). The values and the decreasing pattern of GPP to ^{14}C-PP ratios are also consistent with previous observations at Station ALOHA (Corno et al. 2005; Juranek and Quay 2005; Quay et al. 2010). These profiles demonstrate that, even in a low productivity oceanic region such as the North Pacific Subtropical Gyre, it is possible to precisely measure ^{18}O-GPP throughout the top 100 m of the water column using MIMS.

Lastly, an inter-comparison exercise between IRMS and MIMS showed that ^{18}O-GPP values were comparable for the two methods and agreed to within ±4%, which clearly validates the MIMS approach to measure in vitro ^{18}O-GPP in the ocean.

References

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