Geophysical Research Letters

Supporting Information for

Recent Increases in Water Column Denitrification in the Seasonally Suboxic Bottom Waters of the Santa Barbara Basin

Margot E. White[1], Patrick A. Rafter[2], and Brandon M. Stephens[3], Scott D. Wankel[4], Lihini I. Aluwihare[1]

[1]Scripps Institution of Oceanography, University of California, San Diego.

[2]University of California, Irvine.

[3]University of California, Santa Barbara.

[4]Woods Hole Oceanographic Institution.

Contents of this file

Text S1
Tables S1 to S2
Figure S1

Introduction

Presented here is the isotope fractionation factor ($^{15}\varepsilon$) mass balance used to interpret observed temporal variations in the apparent fractionation (ε_{app}) factor for denitrification in our dataset. We also include the nitrite isotope data (Table S1) and the calculated ε_{app} for closed system nitrate reduction between consecutive flushing events (Table S2; see body of paper for method description). Finally, we provide a timeseries demonstrating the secular decrease in oxygen concentrations at 450 m depth in the Santa Barbara Basin (Figure S1), which we use as an index for decreasing oxygen concentrations in intermediate waters of the North Pacific Ocean.

Text S1: Isotope Mass Balance

After estimating $^{15}\varepsilon_{app}$ as described in the paper, we used the following isotope mass balance equation to apportion N loss via denitrification between the sediments and the water column. If we assume that the apparent fractionation factor is a combination of sedimentary and water column denitrification processes, then:

$$^{15}\varepsilon_{app} = {}^{15}\varepsilon_{wc} \times \%WC + {}^{15}\varepsilon_{sed} \times \%Sed$$

Using a value of 25 ‰ for the water column fractionation factor and 1.5 ‰ for the sedimentary fractionation factor we calculated the percent of N loss that had occurred in each environment [1]. Based on this approach, more water column denitrification is accompanied by a larger $^{15}\varepsilon_{app}$.

Date	Depth (m)	$[NO_3]$ (µM)	$[NO_2]$ (µM)	$\delta^{15}N_{NO3}$ (‰)	$\delta^{18}O_{NO3}$ (‰)	$\delta^{15}N_{NO2}$ (‰)	$\Delta\delta^{15}N$ (‰)
7/2013	570	19.10	2.08	16.97	13.58	-16.34	33.31
11/2013	515	9.10	8.19	31.02	23.97	4.44	26.58
11/2015	570	10.70	3.24	24.32	18.45	-1.87	26.19
1/2016	540	11.40	1.68	20.79	14.63	-7.91	28.70
1/2016	570	7.60	2.80	26.11	16.44	1.68	24.43

Table S1. Nitrogen isotopes of nitrite from the Santa Barbara Basin

Initial date	Final date	Depth (m)	$[NO_3]_{initial}$ (µM)	$[NO_3]_{final}$ (µM)	$[NO_2]_{initial}$ (µM)	$[NO_2]_{final}$ (µM)	$\delta^{15}N_{NO3, initial}$ (‰)	$\delta^{15}N_{NO3, final}$ (‰)	$^{15}\varepsilon$ (‰)	$denitr_{WC}$ %
1/2011	4/2011	540	29.70	25.00	0	0	9.89	11.29	8.13	28
1/2011	4/2011	570	27.30	24.40	0	0	10.18	11.68	8.06	28
4/2011	7/2011	515	28.60	26.20	0	0.14	10.15	10.98	9.32	33
4/2011	7/2011	570	24.40	13.90	0	2.82	11.08	17.91	12.14	45
7/2011	10/2011	515	26.20	10.00	0.40	6.19	10.98	29.81	19.55	77
10/2011	2/2012	570	8.50	3.70	7.27	6.82	24.68	44.32	24.31	97
3/2012	7/2012	515	26.20	23.90	0.04	0.32	10.77	12.26	16.18	63
4/2013	7/2013	570	32.50	19.10	0.09	2.08	10.18	16.97	12.78	48
7/2013	11/2013	515	27.80	9.10	0.02	8.19	10.61	31.02	18.28	71
11/2015	1/2016	515	23.43	18.08	0.01	0.07	10.99	14.33	15.50	60
11/2015	1/2016	540	18.19	11.37	0.78	1.68	14.82	20.79	12.70	48

Table S2. Estimated nitrogen isotope fractionation factors for nitrate reduction between subsequent periods when no flushing has occurred. Fractionation factors were calculated by finding the slope of a linear fit to a closed system Rayleigh model.

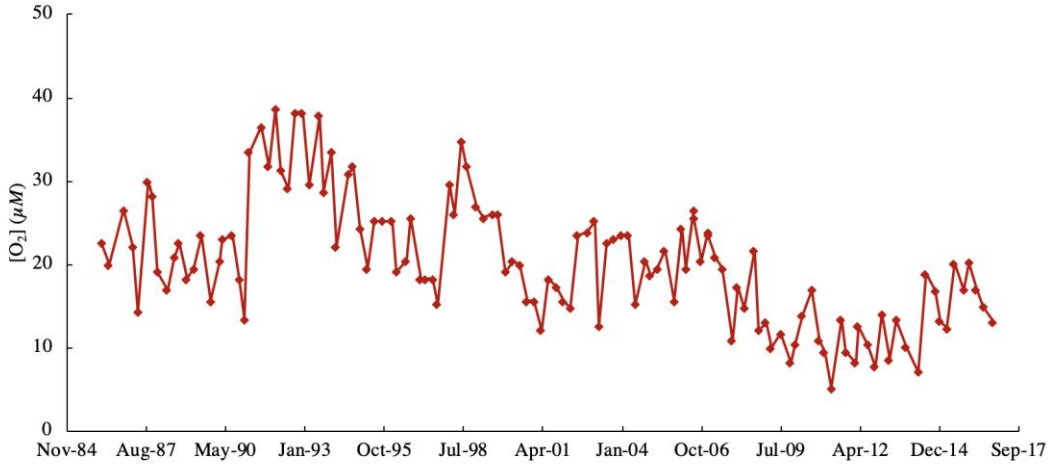

Figure S1. Time series of oxygen concentration at 450m in the Santa Barbara Basin

References

Sigman DM, Robinson R, Knapp AN, et al. Distinguishing between water column and sedimentary denitrification in the Santa Barbara Basin using the stable isotopes of nitrate. *Geochemistry, Geophys Geosystems*. 2003;4(5):n/a-n/a. doi:10.1029/2002GC000384.