

Temporal Trends in Deep Ocean Redfield Ratios

Calvin W. Mordy
Joint Institute for the Study
of Atmosphere and Ocean
University of Washington
Seattle, WA 98195, USA

Louis I. Gordon
Andy Ross
College of Oceanic
and Atmospheric Sciences
Oregon State University
Corvallis, OR 97331, USA

Hernan E. Garcia
Scripps Institution of Oceanography
University of California at San Diego
La Jolla, CA 92093, USA

Pahlow and Riebesell (*1*), examining data for the past several decades, reported an increase of 1.9 per mil per year in the nitrogen:phosphorus (N:P) ratio for the North Atlantic and an increase of 0.7 per mil per year for apparent oxygen utilization (AOU) in the North Pacific. Although the overall data spanned 30 to 47 years, only the relatively few stations that were reoccupied can be used to examine any temporal changes, and the average interval of reoccupation was only 14 years (*1*). Pahlow and Riebesell did not report actual changes in phosphate and oxygen concentrations at those stations, and no changes in nitrate concentrations were observed (*1*). Our back-calculation, using their rates and times, indicates a $0.01 \pm 0.01 \mu\text{M}$ decrease in phosphate in the North Atlantic, and a $2 \pm 0.3 \mu\text{M}$ decrease in oxygen (equivalent to a similar increase in AOU) in the North Pacific, over the 14-year period (*2*).

The results of Pahlow and Riebesell were obtained after systematic corrections for offsets between reoccupied-station data. The offsets were determined at same-depth intervals in deep water, and then applied uniformly over the entire water column (*1*). Spencer

large, systematic uncertainties in the data and derived corrections.

A number of studies have reported discrepancies in nutrient and oxygen data collected by different laboratories on different cruises (*4–6*). Two types of systematic errors must be taken into account in constructing calibration curves. The first is an intercept offset that is related to the background signal and is independent of sample concentration. The second is an error in slope that is related to the accuracy of standards and is proportional to sample concentration. In the absence of certified reference materials for nutrient analyses, it is customary in oceanography for individual laboratories to prepare their own calibration standards. Because of errors involved in standard preparation, the second type of systematic error, slope error, tends to dominate the total systematic error (*7*) and therefore to account for most of the discrepancies observed in modern data (Table 1).

The constant-offset correction that was determined in deep water and applied over the entire water column by Pahlow and

Table 1. Summary of absolute offsets for phosphate and oxygen in the deep ocean at crossover stations. South Pacific data were compiled from figure 5.8 of (*5*); Pacific data from (*4*).

| Location | Years | Phosphate ($\mu\text{mol kg}^{-1}$) | Oxygen ($\mu\text{mol kg}^{-1}$) |
|---------------|-----------|---------------------------------------|------------------------------------|
| South Pacific | 1961–1972 | 0.1 ± 0.2 | 3 ± 7 |
| South Pacific | 1972–1993 | 0.05 ± 0.08 | 1 ± 4 |
| Pacific | 1985–1996 | 0.03 ± 0.02 | 2 ± 1 |

and Mantyla (*3*) demonstrated that this approach is risky, at least in the North Atlantic, and instead favored evaluating nutrient or oxygen concentration relative to salinity (*3*). In any event, the systematic corrections applied by Pahlow and Riebesell, and uncertainties in those corrections, actually exceeded the signal in the case of phosphate and were comparable to the signal in the case of oxygen. For example, from figure 1 of (*1*), we estimate the systematic correction applied to phosphate to be about $0.09 \pm 0.04 \mu\text{M}$ ($n = 13$). Moreover, although Pahlow and Riebesell corrected offsets using the more reliable modern data (e.g., World Ocean Circulation Experiment) as a reference, even within modern data the offsets and offset errors at reoccupied stations are larger than the inferred phosphate signal (Table 1). We suggest that small temporal signals in phosphate and oxygen can hardly be resolved in view of the

Riebesell (*1*) would necessarily undercompensate or overcompensate for the actual systematic error in different parts of the water column. In the equatorial Atlantic, for example, applying a correction for slope errors instead of an offset correction would eliminate much of the reported temporal signal (*8*). In light of these questions regarding systematic-error correction, we conclude that, although Redfield ratios in the oceans may indeed change with time, the changes inferred by Pahlow and Riebesell are probably not valid.

Jia-Zhong Zhang
Cooperative Institute for Marine
and Atmospheric Studies
Rosenstiel School of Marine
and Atmospheric Science
University of Miami
Miami, FL 33149, USA

References and Notes

1. M. Pahlow and U. Riebesell, *Science* **287**, 831 (2000).
2. Phosphate was back-calculated using an average AOU of 120 mol m^{-2} from 500 to 2000 m, with a P:AOU ratio of 1:170 and a $\delta(\text{N:P})$ of 1.9 ± 1.2 per mil per year over 14 years. Similarly, AOU in the North Pacific was 500 mol m^{-2} from 500 to 3000 m with a $\delta(\text{AOU})$ of 0.7 ± 0.1 per mil per year over 14 years.
3. D. Spencer and A. Mantyla, in *GEOSecs Atlantic Expedition, Hydrographic Data, 1972–1973*, A. E. Bainbridge, Ed. (National Science Foundation, Washington, DC, 1981), vol. 1, chap. 1, p. 5.
4. C. W. Mordy et al., *EOS Trans. Am. Geophys. Union* **80** (suppl.), OS43 (1999); <http://geoweb.princeton.edu/bigscience/GLODAP/details.html#Redfield>.
5. V. Gouretski and K. Jancke, *World Ocean Circulation Experiment Rep. No. 143/96* (WOCCE Hydrographic Program—Special Analysis Centre, Hamburg, Germany, 1996).
6. A. Ross et al., *EOS Trans. Am. Geophys. Union* **80** (suppl.), OS4 (1999); <http://ucs.orst.edu/~rossan/webversion.htm>.
7. L. I. Gordon et al., *EOS Trans. Am. Geophys. Union* **80** (suppl.), OS45 (1999).
8. From the correction range of Pahlow and Riebesell (*1*) to the nutrient maximum (approximately 1800 m to 800 m), phosphate typically increases by about $0.8 \mu\text{M}$ in the Equatorial Atlantic. Calibration errors of about 3% [deep offsets in figure 1 of (*1*) are about 7% of deep phosphate concentrations, and errors in Table 1 are about 1 to 4% of concentrations in the deep Pacific] result in an underestimation of systematic errors in (*1*) by $0.02 \mu\text{M}$ phosphate in the nutrient maximum. Over the entire comparison range in (*1*), calibration errors are roughly half of those in the nutrient maximum, or >90% of the average phosphate trend implied by the results of Pahlow and Riebesell.
9. This work was funded by the NOAA and the NSF, and was carried out under the auspices of the Cooperative Institute for Marine and Atmospheric Studies (a joint institute of the University of Miami and NOAA) and the Joint Institute for the Study of Atmosphere and Ocean (a joint institute of the University of Washington and NOAA) under cooperative agreements NA67RJ0149 and NA67RJ0155.

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Response: Zhang et al. use the temporal trends we observed in AOU and oxidative ratios to derive corresponding trends in absolute phosphate and oxygen concentrations, and on that basis raise two main points of criticism of the work reported by Pahlow and Riebesell (*1*). First, they maintain that the methodological uncertainties exceed the derived trend in phosphate concentration. And,

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second, they suggest that a correction for slope errors, rather than the offset correction that we applied, would eliminate much of the observed temporal signal. Below, we address each of these points and show that the concerns of Zhang *et al.* are unfounded.

Zhang *et al.* estimate a change in phosphate concentration of $0.01 \pm 0.01 \mu\text{M}$ over 14 years, based on an average North Atlantic AOU of 120 mol m^{-2} . The correct value for the change in phosphate concentration over that time span in our analysis, however, is actually $0.04 \pm 0.04 \mu\text{M}$ (based on a mean phosphate concentration of $1.5 \mu\text{M}$, an observed North Atlantic AOU trend of 0.3 ± 0.8 per mil per year, and an observed North Atlantic AOU:P trend of 1.7 ± 1.2 per mil per year). In either case, confidence intervals for changes in absolute nutrient concentrations are indeed similar to or larger than the changes themselves, which precluded the use of absolute concentrations in our analysis. Much of the uncertainty, however, is due to natural variability in AOU and nutrient concentrations between stations. The strong co-variation between nutrients and AOU means that the use of nutrient and oxidative ratios avoids station-to-station variability in absolute concentrations. Hence, our study's approach was to test for temporal changes in nutrient ratios rather than in absolute concentrations. Zhang *et al.* also

suggest that nutrient and oxidative ratios should be evaluated relative to salinity rather than depth; we indeed pursued such an evaluation early in our analysis and achieved identical results.

The statement by Zhang *et al.* that our systematic corrections were greater than or similar to the reported mean signals does not apply to our data analysis. Our correction procedure was not performed on the basin-wide mean temporal trends, as implied by Zhang *et al.* Instead, we applied systematic corrections for each set of reoccupied stations individually. These individual corrections were smaller than the respective signals in almost all cases [e.g., figure 1 of (1)].

Zhang *et al.* point out that our analysis did not correct for systematic slope errors arising from calibration differences between cruises. Based on a difference in phosphate concentration of $0.8 \mu\text{M}$ between our correction range and the maximum concentration in the example profile that we published [figure 1 of (1)], Zhang *et al.* suggest that the slope error could explain 90% of the observed North Atlantic phosphate change (which, as noted, they incorrectly estimate at $0.01 \pm 0.01 \mu\text{M}$) over the 14 years.

A closer examination, however, suggests that correcting for slope error would not materially change the results of our analysis. The average difference between maximum phosphate concentrations and those in the correc-

tion range was only $0.3 \mu\text{M}$, because most locations used in our analysis did not include data as close to the nutrient maximum as shown in figure 1 of (1), which was chosen to illustrate the correction procedure but not to be representative of all profiles. As we explained [note 16 of (1)], the expected error (E_n) of the mean of n measurements is $E_n = E_1/n^{1/2}$, where E_1 is the error of a single measurement. Our analysis for the North Atlantic comprised 20 combinations of different cruises ($n = 20$). The deviation due to a slope error of 3%, the figure cited in note 8 of the comment by Zhang *et al.*, would therefore be $(0.3 \mu\text{M})(0.03)/\sqrt{20} = 0.002 \mu\text{M}$. For a change in phosphate concentration of $0.04 \mu\text{M}$, therefore, the estimated impact of the slope error would not exceed $0.002/0.04$, or 5% of the trend.

Markus Pahlow*
Ulf Riebesell

*Alfred Wegener Institute for
Polar and Marine Research
Post Office Box 120161*

D-27515 Bremerhaven, Germany

**Present address: Bedford Institute of
Oceanography
Dartmouth, N.S. B2Y 4A2, Canada*

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