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Approaches to Assessing Nutrient Coupling in Open Ocean Datasets

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Approaches to Assessing Nutrient Coupling in Open Ocean Datasets

James M. Moore* & Claire P. Till, Cal Poly Humboldt

Abstract

Nutrient coupling describes a process where the biogeochemical cycles of two elements are linked by being incorporated similarly into biomass. This paper uses data from the GEOTRACES GP16 cruise (Eastern Pacific Zonal Transect) to investigate the relationship between certain macronutrients generally coupled to trace elements in terms of their oceanic distributions with the notable exception of in an oxygen minimum zone: cadmium-phosphate and zinc-silicate. There are many methods applied to oceanographic data to correlate analyte concentrations; while they are often presented independently in literature, here we attempt to use them in conjunction for a more thorough interpretation. By compiling 1) depth profiles, 2) differences between the concentrations after applying a scale factor, and 3) direct comparisons of the analytes, greater insight into the correlations between coupled nutrients is achievable. Because the goal of studying this phenomenon is to learn about the underlying causes of these biogeochemical cycles, being able to characterize the decoupling in a way that is easy to visualize is extremely important to the efficacy of this area of research. Variation between results is elaborated on as a caution towards carefully considered and consistent data manipulation. Calculating a difference between the coupled analytes after applying a scaling factor provided the most useful information about decoupling. current lives are symbolic.

Keywords: Nutrient Coupling, Coupled Datasets, Biogeochemical Cycling, GEOTRACES, GP16, Trace Elements.

Introduction

The study of Earth's systems chemistry is critical to gaining a deeper understanding of the dynamics underlying air, water, and land masses. Earth maintains a complex network of concentration gradients spanning the entire globe, and our level of understanding of those biogeochemical cycles limits the capabilities of global mathematical models.

The GEOTRACES program is an international collaboration of scientists working to expand understanding of marine biogeochemical cycles by analyzing ocean samples for trace chemical constituents. GEOTRACES uses scientific research vessels to sample the ocean at a wide range of depths, longitudes,

latitudes, and times to quantify the ocean's trace constituents. Along with trace element concentrations, isotope ratios can be used to identify and track water masses as well as physical and chemical processes.¹ The immediate result of a research cruise is a better understanding of the water chemistry along that specific transect of the ocean, but over a longer period, these kinds of datasets help elucidate the mechanisms controlling biogeochemical cycles as well and allow for substantial improvements to mathematical models of the ocean as a whole.²⁻⁴ Ultimately, large-scale efforts like this benefit mankind because our ability to predict and control our environment on a large scale becomes increasingly feasible with more data and better Earth systems modeling.

Oceanographic data has been used to observe that some macronutrients are coupled to trace elements in terms of their oceanic distribution.^{2,5} This work addresses a few relationships between a macronutrient and a trace metal that have nutrient-type distributions evident in their depth profiles: cadmium-phosphate, zinc-silicate, and copper-silicate.² Nutrient coupling can occur when two dynamic analyte concentration cycles are incorporated similarly into biomass.⁶ Bruland⁷ describes three main factors that influence whether a trace element will have a distribution correlated with a nutrient element: similar internal cycles, a long oceanic residence time relative to the time scale of ocean mixing, and that deep water scavenging is insignificant compared to the time scale of ocean mixing.

A deviation between coupled analytes from their expected values has been correlated to oxygen minimum zones (OMZs). OMZs are regions in the water column that have the relative least oxygen concentration, and severe OMZs often correspond to oxygen level below 5% saturation or $< 20 \mu\text{mol/L}$.⁸ There are rapid changes in the rates of uptake and remineralization between coupled analytes at depths correlated to OMZs, occurring before their difference in rates settle and the two analytes couple again at greater depths.^{5,9} The vertical depth profile of the OMZs show variation throughout the world, making the relationship between OMZs and nutrient coupling harder to isolate.¹⁰ Often OMZs lie below the euphotic zone in the range of approximately 100-1000 m, but Peru has an OMZ that partially reaches in the euphotic zones. The euphotic zone is described as a region receiving at least 1% the photosynthetically active radiation as the surface. Oxygen levels for OMZs in the Northeastern Pacific do not show a recovery in oxygen levels until 1000-1500 m deep though this Peru transect has its OMZ reported as stretching as low depths of > 3000 m.¹¹ Resolution on the spatial distribution of the OMZ is limited by the constant fluctuations that come with time. For instance, periodic El Niño events have shown increased oxygenation and decreased nutrient availability due to downwelling, with more extreme fluctuations during equatorial Pacific El Niño events compared to central Pacific El Niño events, while the OMZ is also subject to non-periodic long-term changes such as the decrease in oxygen concentrations over the previous five decades.¹²

Reports for the GP16 transect show decoupling of their concentration profiles in the phototrophic zone by a loss of cadmium relative to phosphate² and a loss of zinc relative to silicate¹³. There are several proposed explanations for this decoupling. One idea is that the decoupling is due to sulfide precipitation in low oxygen zones¹⁴; if cadmium precipitates out as CdS in a sulfidic environment, then it stands to reason that the decoupling would be observed in this sulfur rich and oxygen

starved region. Middag et al. postulates that it is not the oxygen levels that cause the decoupling but a difference in biological remineralization rates which happens to be indirectly related to oxygen levels (due to the aerobic biota consuming oxygen).⁹ They supported this with data that showed the decoupling phenomenon occurring in higher oxygen waters ($>75 \mu\text{M}$), and they demonstrated a kink in the relationship between cadmium and phosphate could be observed by modeling the mixing of water masses only.⁹ Determining the exact cause of the decoupling is outside the scope of this paper; instead, herein, we focus on tools that can be used to assess coupling.

One difficulty faced when addressing this topic is the lack of standardization in the method of comparing coupled elements. Currently, common methods to compare relationships between two elements are to plot the difference between the values scaled appropriately,^{2,15,16} to plot the concentration of one element against another,^{7-9,15,17-23} or to use a spot test that tabulates average ratios of the analytes for different water masses.^{9,15} Each comparison has its own benefits and drawbacks, and all are valuable; the key aspect is to select the comparison method intentionally and with full understanding of its significance. Ideally, the same comparison method would be the go-to approach across different regions and transects, to allow for broader conclusions to be more easily made.

This paper is a review of approaches, with commentary, and a suggestion of a new approach using the data from the GEOTRACES Eastern Pacific Zonal Transect (EPZT) GP16 cruise to provide real world insight on how the different comparison methods extract information from the cruise sample data. Stations 1-17 were used in this study which stretch from Peru to Tahiti, 80 W to 150 W roughly along the latitude 12 S. The transect passes right through one of the world's most extreme OMZs, the OMZ off Peru, reported to be between 80 to 90 W and 0 to 18 S.¹¹ These data are used to justify the methods researchers have used to report the extent of decoupling and distinguishes between the different methods.

Methods

Sample and Instrumentation Procedure

Samples from GP16 were collected following GEOTRACES protocols²⁴ from the carousel of Teflon-coated 12 L Go-Flo bottles, filtered through 0.2-micron supor acropak capsule filters, and acidified at sea with 4 mL of 6 M quartz-distilled HCl per liter of seawater. Samples were analyzed in the Bruland lab at UC Santa Cruz after sitting for several months acidified. The analytical method is described in Biller and

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Bruland²⁵ with adaptations as in Parker et al.²⁶ Briefly, this method involves offline pre-concentration on Nobias chelate PA1 resin at pH 6.0 +/- 0.2, followed by analysis on the high resolution, extended range, Thermo Element inductively coupled plasma mass spectrometer (HR ICP-MS). All concentration data used here underwent intercalibration and are available at the GEOTRACES Intermediate Data Product.³

Plots Used for Investigating Decoupling in the GP16 Dataset

Three main methods were compiled to analyze analyte coupling phenomenon in the EPZT GP16 transect: depth profiles, differences between the concentrations after applying a scale factor (section plots), and direct comparisons of the analytes (concentration ratios as well as spot tests). Depth profiles of cadmium, phosphate, zinc, silicate, and copper were made to begin assessing the analytes for stations 1-17 of the GEOTRACES GP16 cruise (see Supplemental).

Concentrations of elements in the ocean range 15 orders of magnitude (from ~0.5 mol/kg for sodium and chloride to less than 1 fmol/kg for iridium).² The first consideration for comparing the depth profiles was how to compare the molality of one analyte to another when they have orders of magnitude differences in concentration. A ratio was required to convert

units of $\mu\text{mol/kg}$ phosphate to pmol/kg cadmium and nmol/kg zinc to $\mu\text{mol/kg}$ silicate. The new values are of arbitrary units, but they allow for an easier comparison while still representing the way the analyte concentrations change with depth. Options for choosing a ratio to scale by include to set a single global ratio for different water columns¹⁶ or to scale by a ratio representing regions such as water masses or oceans.^{5,9,15,20} For instance, a Cd/Pdeep ratio of 250 ($\text{pM}/\mu\text{M}$) has been reported in literature for the North Atlantic assuming the ratio is relatively constant throughout the deep oceans.¹⁶ Janssen et al. opted for two ratios, 0.25 for Atlantic samples and 0.35 for Pacific and Southern Ocean–subantarctic samples.⁵ Middag et al. reports using Cd:PO₄ remineralization ratio of $0.21 \pm 0.01 \text{ nmol}/\mu\text{mol}$ for the Atlantic deep water values⁹ but acknowledges that Baars et al. has found ratios with higher Cd content in Antarctic waters, between 0.48-0.65 $\text{nmol}/\mu\text{mol}$.¹⁵

In this work, we added an additional approach to determining the scaling factor: the bottom depth concentration ratio between the two analytes for each separate station. This was done in an effort to account for some regional variability while staying well away from the biological activity in the surface ocean. That being said, it should be acknowledged that the bottom depth ratio reflects the source of the bottom water more closely than the water column above it⁹ and that with

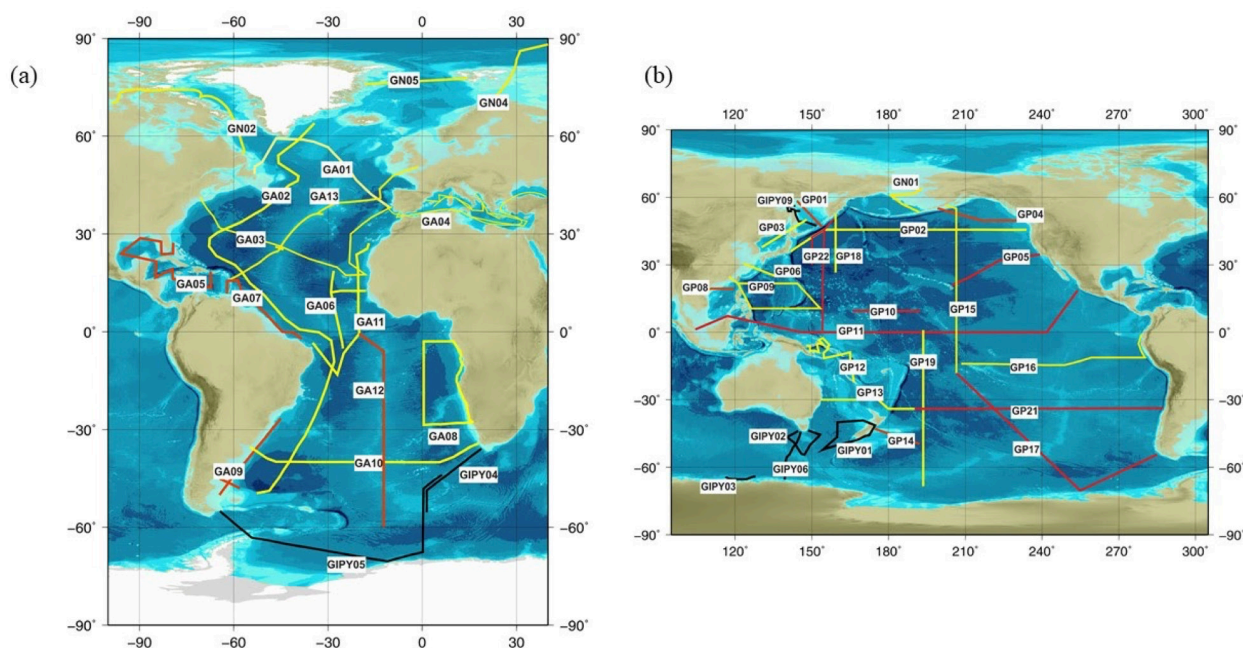


Figure 1. Data from GEOTRACES Pacific cruises GP10 and GP16 (a) were used to investigate methods of assessing coupled analytes²⁷ and (b) Atlantic cruises GA02, GA03, and GA10.²⁸

this approach the deep-water ratio and thus the normalization is extremely sensitive to the depth of deep-water sampling. We use the concentration ratio at the bottom depth as a scale factor to normalize one of the concentration profiles before taking a difference. These difference plots will be compared against plots simply taking the ratio.

The bottom depth ratios from the Atlantic and Pacific cruises GA02, GA03, GA10, GP10 (Figure 1a and b), obtained from data in the Intermediate Data Product³, were each compared to the ratios found at the bottom depths of GP16 stations and found to be reasonably close (Figure 2a and b), enough to justify using the bottom depths as scaling factors. The GP16 cruise fell within the values from the other cruises, so a bottom depth ratio may be a way to find a scaling factor while dealing with some of the inconsistencies from one water column to the next.

The data for phosphate and zinc were scaled with their deep-water ratio from that station, noted as Cd/P_{deep} and Si/Zn_{deep} respectively, before being compared to cadmium and silicate. The scaling and differences between analytes were taken as follows: 2

The coupled analytes can be plotted as depth vs analyte concentration on the same graph to see a superimposed comparison of shape between the plots (Figure 3a and b). Using the bottom depth concentration va

$$Si^* = Si - \left(\frac{Si}{Zn_{deep}} \right) Zn \quad \text{Equation 1.}$$

$$Cd^* = \left(\frac{Cd}{P_{deep}} \right) P - Cd \quad \text{Equation 2.}$$

difference at zero. Any deviation away from zero represents greater decoupling, so the analytes are the most decoupled at the depth of the maximum deviation from zero. To investigate how decoupling maxima relate to oxygen minima, plots of the oxygen concentrations vs depths were created and superimposed onto the difference vs depth plots (Figure 3c and d).

Plotting the slope of the Cd^* and Si^* plots vs depth is also shown (Figure 3e and f). This is in essence a discrete optimization problem, looking for optima by locating where the derivate plot crosses the domain axis. A moving two-point window average of the slope was one attempt to identify the maximum peak (represented by a slope of zero) by reducing noise. Two points were chosen as more points trades off a decrease in noise for a decrease in sensitivity. Because it graphs the slope at each point, the first and last point are not accurate, but the points of interest are well represented in the upper region of the water

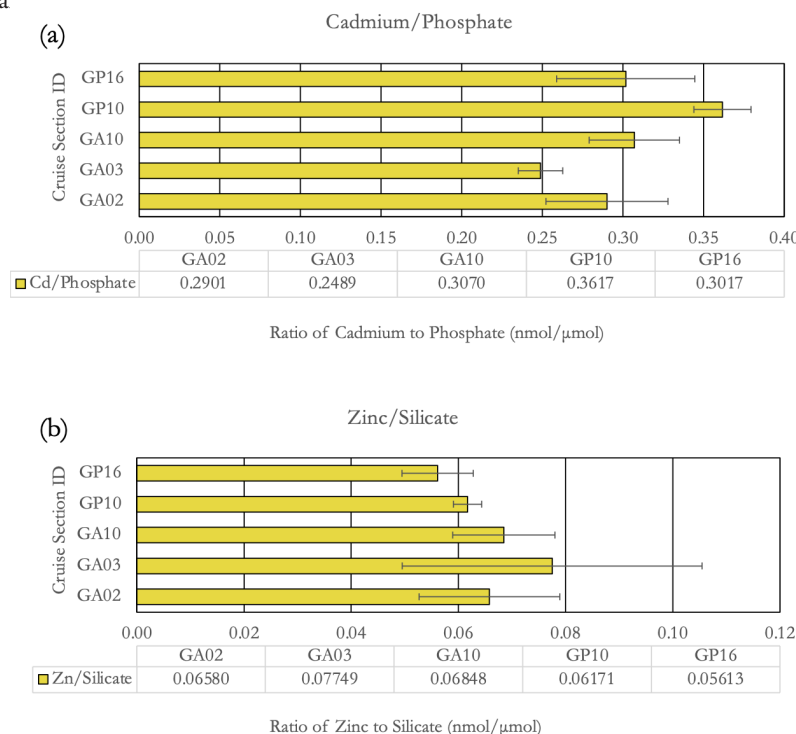


Figure 2. Comparisons between bottom depth concentration ratios found throughout separate GEOTRACES cruise sections for cadmium to phosphate (a) and zinc and silicate (b). Errors Bars represent $\pm 1\sigma$.

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column. Because the upper water column is the main focus, only the upper 1500 m of the water column is shown. Each decoupling maximum was compared to regions of oxygen minima in **Table 1**.

Section Plots

Ocean Data View (ODV) was used to create weighted average gridding section plots of the depth profiles for 17 stations of the GP16 transect (**Figure 4**).

Spot Test

The spot test simply takes a ratio of concentrations at a single point. It does not require that the transect be broken

up into water masses beforehand as was done for here (**Table 2**) and can provide useful information from a single sample. If the spot test is needed to represent a wider region, multiple spot tests can be averaged and reported along with their standard deviation. Alternatively, many spot tests could be conducted for a single point over time and averaged to get a sense of how the ratio changes over time.¹⁵ To assign spot test ratios to a given water mass, the optimum multiparameter analysis (OMPA) performed by Peters *et al.* for the GP16 cruise was used to help select the locations for sample ratios.¹ An OMPA uses computer modeling to determine the source origin for different water masses within a region.

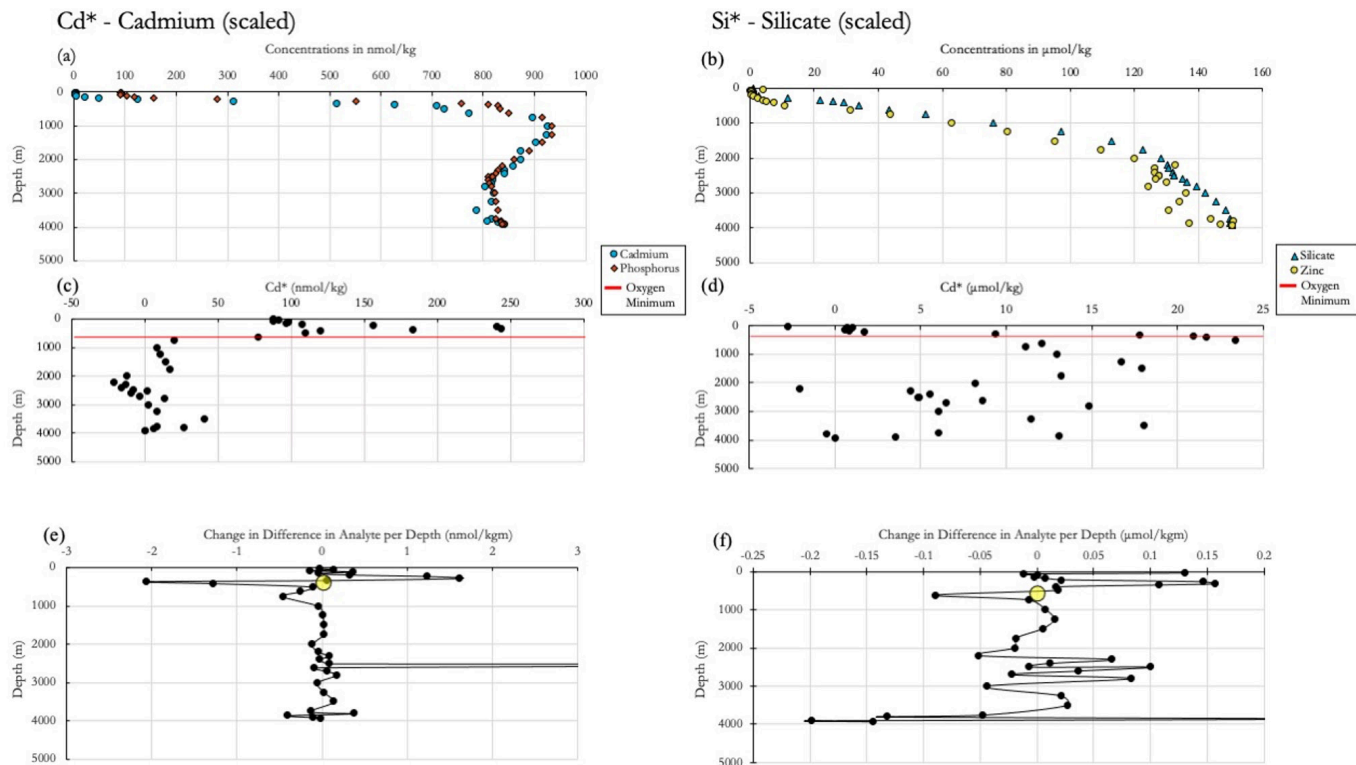


Figure 3. GP16 Station 15 data was used to plot coupled analytes to compare their shapes by superimposing their depth profiles after scaling with the deep-water ratio (a) and (b). Differences between these two curves allow for the greatest deviation between coupled analytes to be found as the greatest difference in (c) and (d). The rate of change in difference is approximated by plotting slope vs depth between points from the difference vs depth plot (e) and (f). Lower depths provide less useful information when looking at the change in differences, but in the upper 1500 m (our region of interest) the point where the change in differences reaches 0 after a local maximum in change correlates closely to the maximum difference: the maxima of decoupling of the two analytes (circles in (e) and (f)). The point of maximum decoupling is circled in plots (e) and (f). The region of maximum decoupling is where the change reaches 0 after reaching the maximum rate of change. This can be interpreted as the entire interval of depths between the last positive of a maximum and the first negative rate of change.

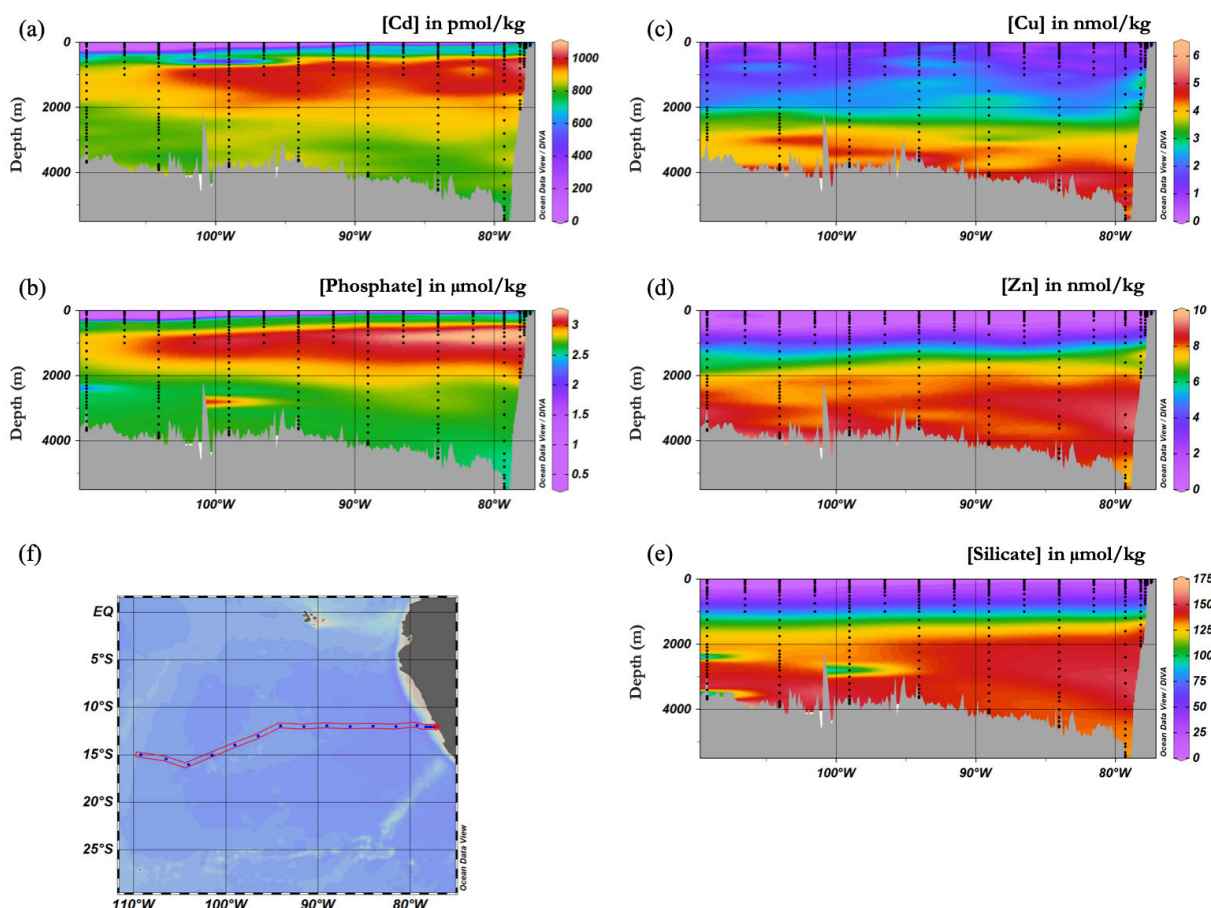


Figure 4. Stations 1-17 along the GP16 transect, and corresponding section plots of the micro and macronutrients investigated in this study. Station 1 is the most inshore while 17 was the furthest offshore station of the transect.

Guidelines for Oxygen Minimum Zone (OMZ)

The OMZ was defined using the limits set by the IOC and UNESCO in a summary to policy makers regarding declining oxygen levels in the ocean: oxygen poor regions were defined as anoxic with sublethal biological effects at $< 63 \mu\text{mol/L}$ of O_2 and as an OMZ at $< 20 \mu\text{mol/L}$.⁸ Ranges were tabulated along with the maxima of the analyte differences for comparison (Table 1). The table only contains maxima in the region of interest within the upper water column since there were occasional deviations much further down the water column.

Initial Analysis

Determining the impact of using differences or using a ratio to compare analytes was done with the help of plots of the real data as well as mock data. These initial plots were very useful in

seeing how coupling presented itself in different plots and how to best represent it. Basing the comparison off of differences gives better detail and a slightly different maximum than basing the comparison off of ratios (Figure 5). For this reason, the final analysis (Figure 9) was conducted as the difference between scaled values.

Mock Data

It is important to note the difference between the two because, for a concentration ratio to remain constant along a water column, the differences between the analyte's concentrations would have to change accordingly to keep up. Mock data was generated in order to further investigate. For instance, Figure 6a shows analytes that are coupled with a constant ratio, while Figure 6b shows analytes coupled that differ by a constant

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amount. With a constant ratio, the analyte represented in orange has to assume more drastic net changes than the blue, and so it is not as close to the blue's curve as it is when coupled by a constant difference (Figure 6b). Again, this mock data supports the use of differences instead of a simple ratio.

To help test the integrity of the scaled differences vs depth plots, the data on the first 1000 m for stations 14 and 15 was taken and had the values for cadmium altered around the oxygen minimum zone. Figure 7a and b shows the unaltered version, and then how a loss of cadmium, arbitrarily reduced the cadmium concentrations by 1.5x (66% original value) in the

region of interest, to show it increases the difference (Figure 7c and d) while a gain, or arbitrary increase of cadmium concentration by 1.1x in the region of interest, can decrease the difference drastically (Figure 7e and f). This helped show that the plots did visualize a greater decoupling.

Excluding Copper and Silicate

The concentrations for copper and silicate were also investigated for coupling, as they have been shown to follow a similar distribution as each other.² Copper and silicate both increased with depth, but not in a similar pattern. Figure 8 shows the con-

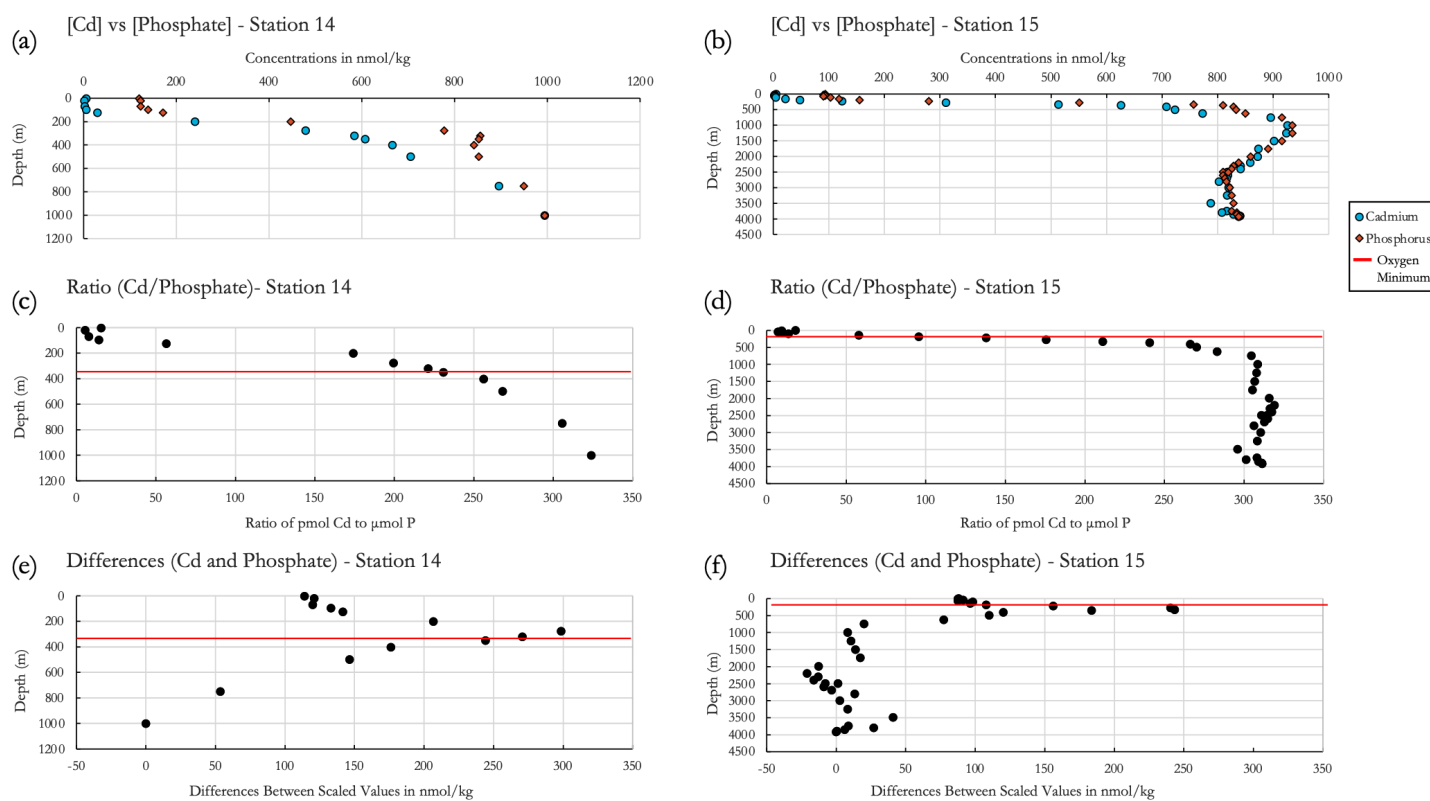


Figure 5. The greater difference in the superimposed values is shown well in (e and f) which compares using differences, but not as well when comparing by ratios (c and d).

centrations of silicate and copper for several different stations. The two values are not able to be neatly superimposed on each other after scaling for the upper depths. The two analytes do not follow the same pattern, at least not in the upper water column. The relationship between copper and silicate could not be interpreted the same way as the relationship between zinc and silicate, and so it was omitted from further analysis.

Results

The goal of using the different types of graphs is to tell if the two analytes are coupled. The fluctuations of cadmium

and phosphate,15,21,23,27,28 zinc and silicate,13,22,23 and copper and silicate18 have been well documented as coupled in their oceanographic distribution. The ability for the various methods to evaluate coupled trends was gauged using data from the GEOTRACES EPZT GP16 cruise. We were able to detect the decoupling for cadmium-phosphate and zinc-silicate along the Peru transect using the section plots of Cd^* and Si^* against depth and longitude as well as with the ratio plot.

Depth of Max Based on Scaled Differences

A bottom depth scaling value allowed for an initial analysis of the differences in analyte concentrations. To help

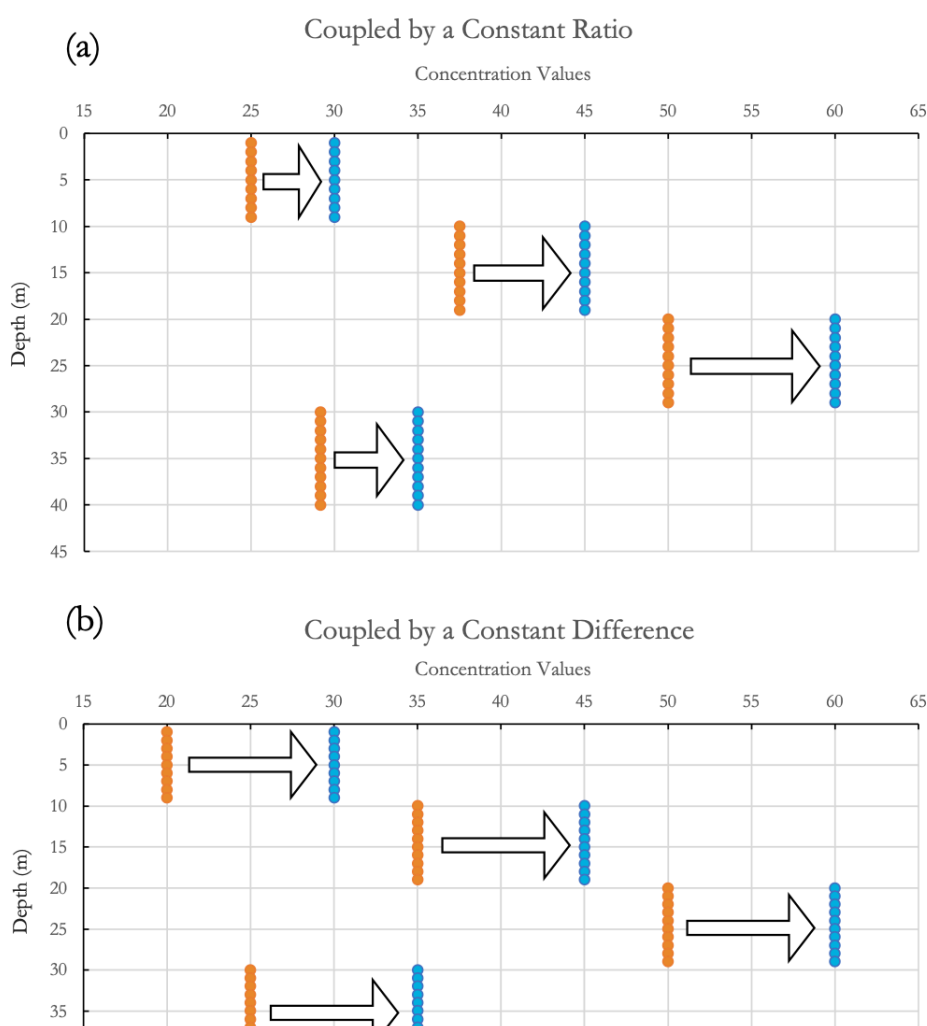


Figure 6. The orange and blue represent theoretical concentrations of different analytes changing with depth, where the analytes are coupled either by a constant ratio (a) or a constant difference (b). Coupling by a constant difference (b) produces more similar rates of change to those observed. Note that the 25m depth arrows are the same distance in both panels.

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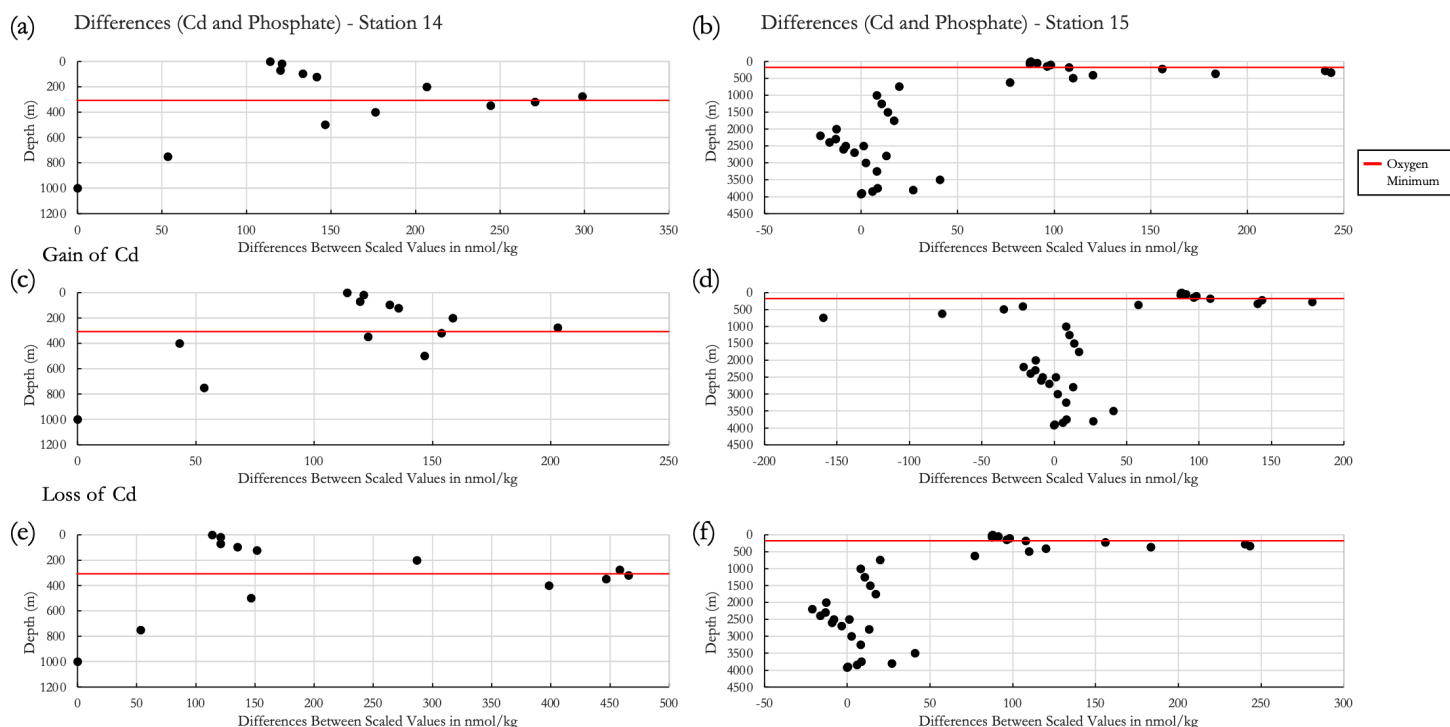


Figure 7. As a precautionary check, mock data was used to depict how the graph of differences vs depth can be altered by an increase and decrease of cadmium within the range of interest. Differences between cadmium and phosphorus are shown and give profiles for station 14 and 15. Unaltered data (a and b) is shown for the two stations, as well as the change when there is a gain of Cd (c and d), and the change due to losing Cd (e and f) within the region of interest. This helped show how using scaled differences can visualize the depth of the decoupling, which correlates as expected with the oxygen minimum (red line). Gain of Cd corresponds to an increase to 110% cadmium concentration. Loss corresponds to cadmium concentration of 66% the original (arbitrary).

determine if the decoupling correlates with oxygen deficiency, the IOC-UNESCO definitions for hypoxia ($< 63 \mu\text{mol/L}$ of O_2) and OMZ ranges ($< 20 \mu\text{mol/L}$ of O_2) acted as guidelines to quantify oxygen deficient waters within our stations.⁸ Table 1 lists the results for stations 1-17 of GP16. The maximum differences are recorded as the single depth where the sample with the maximum difference in concentration was collected. Dissolved oxygen (DO) for that point is also included. The oxygen minima are recorded as the range of depths that were either hypoxic or within an OMZ range.

Cd and Si* vs Depth*

To better understand and visualize where the decoupling is occurring, the graphs relating Si^* and Cd^* to depth for each station (as in Figure 2b and f) were translated into ODV plots

(Figure 9). Plotting against longitudes (Figure 9a and b) helps preserve information about what regions exhibit analyte deviations from coupling. The decoupling pattern becomes more easily identified as the bright red regions. While the OMZ seen in Figure 9c dwindles with increasing oxygen concentrations to the west, the plots of Si^* and Cd^* to depth do not exhibit the same decrease. This suggests that the decoupling event is not directly related to an oxygen minimum as previously literature has suggested.

Concentration Ratios

Unlike comparing Cd^* and Si^* to depths and longitudes, plotting two concentrations against each other does not preserve information about the regions of decoupling. However, this approach is valuable in investigating how the

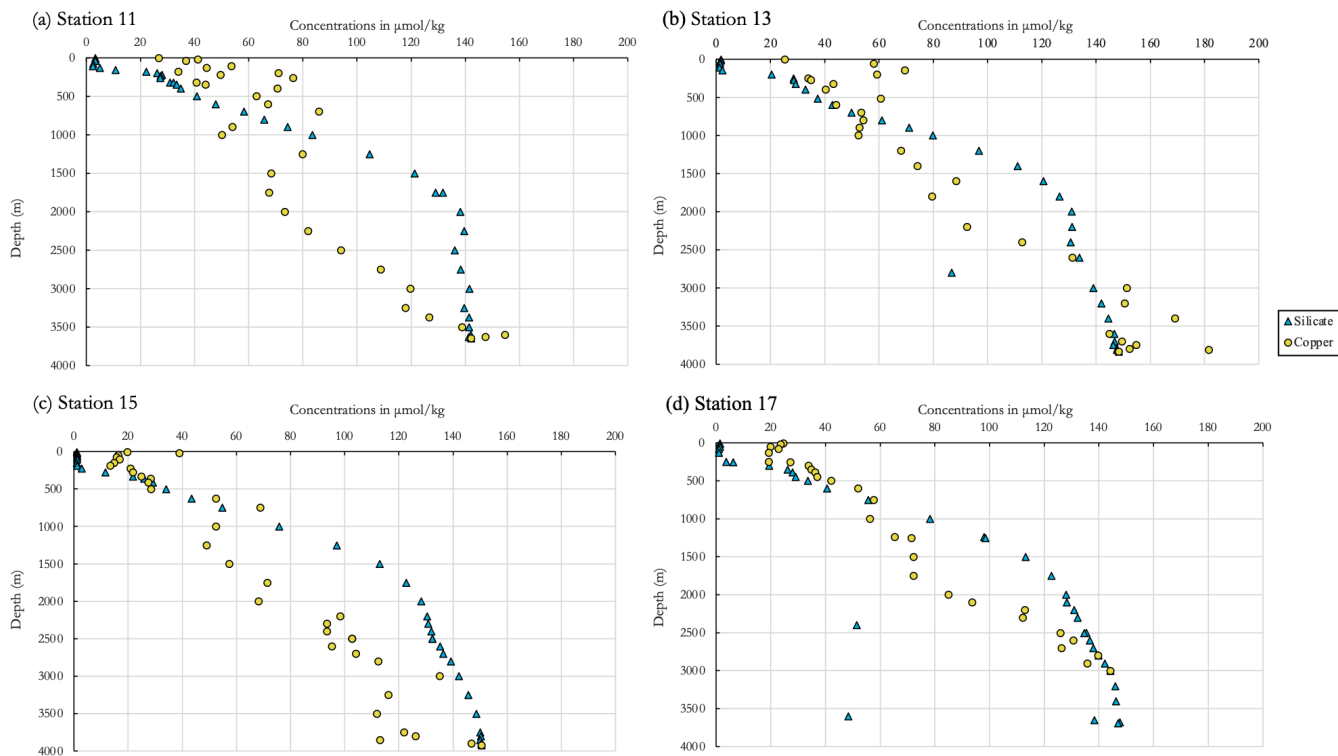


Figure 8. Copper and silicate are compared where the lowest point is set as the scaling factor. The two analytes do not follow a similar curve, especially not in the upper waters where the oxygen minimum occurs (a-d).

concentrations relate over an entire transect, and the loss of locations can be partly amended by overlaying a third axis representing the positions of samples (e.g., Figure 9d and e). Using this plot, coupled analytes display a linear relationship between their concentrations along a water column. A bilinear plot, such as those shown and highlighted in Figure 9d and e, represent a decoupling event⁹ where the analytes were coupled, underwent some event that decoupled them, and then once the external influence was no longer applied, they returned to a linear coupled state.

For phosphate and cadmium, the greater differences were in the upper water column where the oxygen concentration was minimal (Figure 9a and c). Zinc and silicate exhibit a similar correlation, but much looser. Notably, oxygen levels in the upper water column change over the transect due to Peru having one of the largest OMZs right offshore.¹¹ This is corroborated by the purple oxygen minimum region in Figure 9c that shows the OMZ range of depths narrowing significantly once further offshore than approximately 100 degrees West.

Spot Ratios

Similar to the concentration ratios but at a point in space, a spot ratio can represent the concentration ratio for a given water mass. It does not necessarily show decoupling of analytes alone, but it is useful in conjunction with the aforementioned graphs for a clearer picture. The GP16 cruise data product had to be split up so that a sample from each water mass could be used. Peters et al.¹ used an OMPA to determine the percentage contributions of different water masses. The Equatorial Subsurface Water (ESSW) and Pacific Deep Water (PDW) showed relatively less mixing making them more representative of a single water mass and were used to find a sample that would adequately represent just that water mass. The other regions had water masses that were more mixed, and they were reported as their constituent water masses (Table 2). A single ratio helps to quickly compare spatially disjunct regions and allows researchers to quickly compare whether two regions are similar. This can be used to tell whether a dynamically interesting region like the phototrophic zone's concentration ratios match that of what we expect from a more stable zone such as further down the water column.

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Station	Oxygen Levels			< 63 μM		< 20 μM	
	Depth of Max Cd* (m)	Depth of Max Si* (m)	Depth of DO Min (m)	Upper Depth Limit (m)	Lower Depth Limit (m)	Upper Depth Limit (m)	Lower Depth Limit (m)
1	300	235	80	66	1000	80	676
2	111	111	90	20	111	30	111
3	171	50	171	20	171	30	171
4	201	111	111	50	755	50	755
5	500	331	380	56	999	56	600
6	301	400	95	81	1000	95	601
7	251	126	150	110	1000	110	750
8	280	227	161	126	999	126	451
9	300	300	136	120	1000	120	625
10	166	166	201	166	802	166	399
11	236	320	201	180	901	180	401
12	230	230	230	211	1000	211	401
13	250	250	250	201	1000	250	400
14	275	401	320	275	1001	320	350
15	278	500	361	332	750	361	-
16	295	351	351	351	601	351	-
17	245	351	351	301	500	351	386

Table 1. Comparing Dissolved Oxygen (DO) Minima to the Maxima of Decoupling.

Discussion

Standardizing a Scale Factor

The goal of this study was to compare the patterns of change between two analytes at very different concentrations. To compare a trend, plots of concentration vs. depth were made for each analyte, and a scaling factor was used to compare their depth profiles. A difference between the concentration of one analyte and the scaled concentration of another (e.g. Figure 5e and f) provides a means to assess where the analytes maintain a coupled relationship. In this work, bottom depth ratio between analytes was set as the scaling factor, which in turn tethers the zero value to the bottom depth the ratio was measured. Any deviation from zero can be considered a location with decoupling. If a global average is used instead to scale the concentration value of one analyte, then the values will be centered around some non-zero value determined by that global ratio. Deviations from this value

are analogous to deviations from zero in the bottom depth scale factor plot. These plots provide an abundance of specific data on locations where the paired analytes diverge.

The biggest fault of these graphs is the difficulty in selecting a scaling factor that is appropriate. It would be beneficial to find a globally applicable method to determine a scale factor to allow researchers to compare concentration profiles between locations, however it might not be possible to find a globally relevant value: Quay et al. has reported that interbasin variation of particulate Cd/P exported from the surface and subsequently degraded indicate that a consistent bottom Cd/P slope is not expected and that a ubiquitous ratio is unwarranted²¹. Figure 2a shows broadscale agreement in deep-water Cd/P and Si/Zn across ocean basins, and perhaps one average value could be selected not because it is perfect, but because having an agreed upon scaling factor could be a useful tool.²¹

There are also some issues presented by using a bottom depth value as a scaling factor that were found and must be ac-

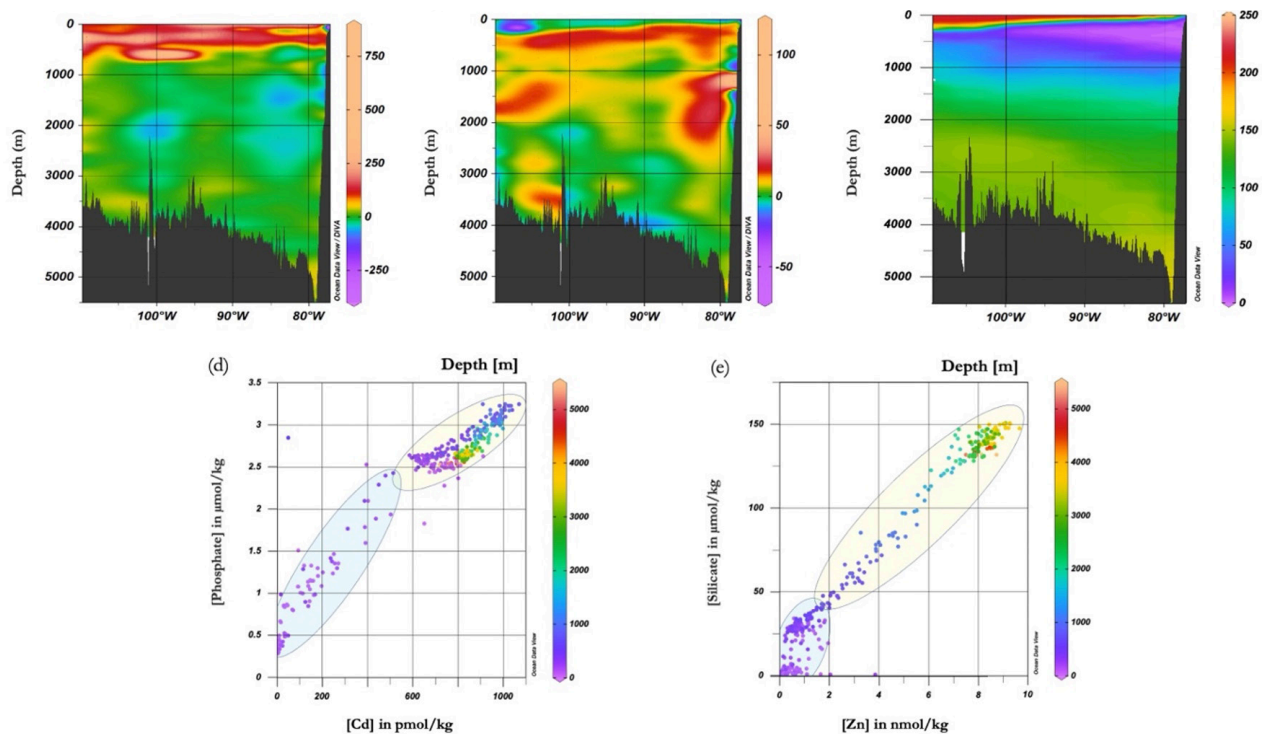


Figure 9. The extent of decoupling is shown over the transect with greater decoupling represented by a larger difference between pairs phosphate and cadmium (a) as well as silicate and zinc (b). This shows as a red band in the upper waters. Note the OMZ distinguished as a purple band of low oxygen (c). Both the decoupling event (shown in a and b), and the OMZ (shown in c) occupy similar depths, but the decoupling event extends further west than the OMZ region without reduction in intensity. The decoupling is shown again for phosphate and cadmium (d) as well as silicate and zinc (e), with the bilinear nature of the plots - indicating the decoupling - highlighted with colored ellipses. Each ellipse represents the nutrient profile under two different stable regimes.

knowledge: the sensitivity to sampling of that bottom depth sample the ratio is determined from the variation in bottom depths along the transect, and that the bottom depth represents a ratio from the region that water mass comes from and not the water column above it.⁹ There is also the issue that copper analysis showed, likely from being more heavily impacted by processes such as co-scavenging⁴ and remineralization from the sea floor⁷ which skew the bottom depth ratio. Though using a bottom depth ratio had its faults and difficulties, it was able to consider specific station variation without instilling bias by using another author's global average ratio of coupled analytes (Table 1). One possible alternative to this method is to include a normalization ratio developed from pre-formed signatures for each water mass instead of the bottom depth water mass. Averaging concentration ratios over entire water masses would have to be approached with careful consideration but may provide a better scaling factor. It would aim to give the improved reproducibility between datasets that a global average gave while also rep-

resenting some local variation that was captured by the bottom depth value. Pre-formed concentration ratio signatures are used in literature in the analysis of isotopes of iron,^{2,18} isotopes of lead,²⁹ isotopes of cadmium,^{5,16,30} isotopes of zinc,^{16,22} and isotopes of helium.¹ Some pre-formed concentration ratios are also reported between two unrelated chemical species including ratios between cadmium and phosphate,^{9,15,23,31} zinc and silicate,¹³ and for zinc/silicate/cadmium,²³ but there is little consistency between reported methods that incorporate preformed signature for specific water masses. Also, though preformed signatures may address several limitations associated with using the bottom depth ratio, issues arise in the complexity of having to annotate each point with its water mass in order to consider a different nutrient coupling ratio for each water mass. Accuracy and simplicity of analysis must be balanced to find methods to scale the concentration profiles by so that deviations in coupled analytes can be measured more precisely and be compared between researchers.

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Water Mass	ESSW	ESSW/ SPCW/ ESPIW	AAIW/ EqPIW	PDW	PDW/ UCDW	PDW/ LCDW	AABW/ LCDW
Longitude	-81.50	-115.00	-99.00	-84.00	-99.00	-84.00	-152.00
Latitude	-12.00	-14.77	-14.00	-12.00	-14.00	-12.00	-10.50
Station Number	6	21	13	7	13	7	36
Depth (m)	300.9	2200.3	900.2	2751.3	1800.3	3625.2	4000.1
Cadmium <u>pmol/kg</u>	608.3	805.1	983.5	872.1	934.3	789.5	735.9
Phosphate <u>μmol/kg</u>	2.620	2.530	3.110	2.760	2.830	2.640	2.420
Zinc <u>nmol/kg</u>	0.7315	8.138	3.492	8.701	7.259	8.065	7.353
Copper <u>nmol/kg</u>	0.6059	2.983	1.476	3.593	2.227	4.471	3.480
Silica <u>μmol/kg</u>	31.23	123.7	71.16	147.0	126.5	138.4	133.1
<u>Cd:P</u>	232	318	316	316	330	299	304
<u>Zn:Si</u>	0.0234	0.0658	0.0491	0.0592	0.0574	0.0583	0.0552
<u>Cu:Si</u>	0.0194	0.0241	0.0207	0.0244	0.0176	0.0323	0.0261

Table 2. Analyte Ratios at Given Points; ESSW = Equatorial Subsurface Water; ESPIW = Eastern South Pacific Intermediate Water; SPCW = South Pacific Central Water; AAIW = Antarctic Intermediate Water; EqPIW = Equatorial Pacific Intermediate Water; PDW = Pacific Deep Water; AABW = Antarctic Bottom Water; LCDW = Lower Circumpolar Deep Water; UCDW = Upper Circumpolar Deep Water

Direct Concentration Ratios

Coupling can be determined by plotting concentration of one analyte to another. A plot directly comparing two concentrations is less time intensive than scaling and taking a difference, and it can be created from a GEOTRACES data product with significantly less effort. A constant ratio between analyte concentrations conveys that they remain proportional with a linear trend, and, inversely, a linear regression can be used to determine an expected concentration of one analyte using known concentrations of another element coupled to it. A bilinear trend means that the coupled analytes underwent a decoupling event, and then once that event passed, they had returned to being coupled. An R2 value can be used to quantify how linear the relationship is, or such plots can be used to see how the profile adheres to a conceptual conservative mixing line.¹⁹

Figure 6 highlights that coupling is sensitive to how it is defined. A completely linear concentration ratio implies the difference between values should grow or shrink proportionally. A linear concentration ratio will lead to varying scaled differences; and therefore, consideration should be given that the linearity of concentration ratio plots may not represent the strongest correlation index. A constant scaled difference provides a more accurate definition to show when two analytes are not aligned or superimposable in their depth profiles.

The Spot Test

The spot test is very similar to comparing the ratio of concentrations of analytes. The spot test takes a concentration ratio or an average concentration ratio within a water mass to compare it to different water masses. The spot test simplifies

portions of the data into a single reportable value or an easy-to-read table. A spot ratio is simpler to make and interpret than a graph comparing the concentration ratios. While Table 1 characterizes a huge area of ocean with just a handful of ratios, it does not convey as much detail on specific regions like a depth profile or transect plot would. The spot test can represent a water mass with less requirements, but it can be elaborated on further such as graphing spot test values over time for a given region.³²

A plot over a region considers the range of possible concentrations while the spot test represents the actual values of the analytes at a spot, and for that reason, the spot test's interpretation is not as biased by other points.⁹

Using Depth Profiles

Depth profiles are time consuming to make because a new plot must be created and interpreted for each station and for each analyte. It was useful to have depth profiles for our transect when a specific region needed to be analyzed further, but so many can distract from the key region and become a needlessly exhaustive effort.

Plotting the concentration vs. depth for each station makes it easier to extract values for a given station and highlight the depths decoupling occurs when two plots are superimposed on each other. It falls behind the other methods in that it displays such a small portion of any cruise's data product that more graphs are needed to represent data from the transect. A less time-consuming method would be to start with an ODV plot of the entire transect before investigating specific stations to further investigate a specific water column. An ODV plot of the entire transect contains essentially all the information several depth profiles would, with the caveat that certain values may be harder to discern directly off an ODV plot.

Limitations to Consider for Nutrient Coupling Ohnemus et al. used factor analysis to assess relationships between analytes without the need for any ratios or normalization.⁴ They also chose to omit spatial information (such as station number, latitude/longitude, and depth) or other chemical variables (dissolved oxygen/macronutrient concentrations) in the analyses, because they suggest these variables are likely to affect particulate phase concentrations in nonadditive or nonlinear fashions. Their analysis resulted in many elements being categorized into 6 types based on their depth profiles. They focus explicitly on particulate data and well-defined basins that have strong particle locality due to the persistent downward settling of particles. They suggest this allows 3d dissolution (which more greatly affects dissolved concentrations as they

settle) to be ignored partly in the way data are taken. Factor analysis can quantify variables latent or difficult to directly measure variables that are still thought to drive the variability of measured variables and elucidate potential shared transport mechanisms that affect multiple elements. In this case, particulate trace element concentrations (the measured variables) are presumed to be the result of additive particulate phase abundances (the unmeasured or latent variables), even if the individual particulate phases themselves are difficult to separate analytically. Ohnemus et al. reported that they were able to perform the statistical analysis independent of spatial information such as station number, latitude/longitude, and depth or other chemical variables like dissolved oxygen or macronutrient concentrations in the analyses, ideal features to an improved analysis as these variables likely affect particulate phase concentrations in nonadditive or nonlinear fashions. This method has only had success with certain analytes so far, but statistical methods such as these that avoid bias by not requiring as much initial input are ideal to standardizing analysis.

The limitations seen with comparing copper concentrations highlight that analytes coupled in distribution are the exception, and that comparisons of different analyte pairs must be on a careful case-by-case basis. Though copper is incorporated into biomass, copper concentrations produce different depth profiles that could not be superimposed regardless of the scale factor used (Figure 8). Copper's concentration profile increased relatively linearly with depth, in contrast to the other analyte profiles which had a sharply diminishing increase in concentration with depth. Copper is influenced heavily by rapid surface water scavenging as well as in-situ deep water scavenging and bottom water injections that recycle copper back into the overlying water column, and it does not appear to show a nutrient like distribution in the deep ocean waters.⁷ Both silicate and copper concentrations have increasing concentrations with depths, but they do not show a similar curve when superimposed.⁵ Jacquot & Moffett corroborated reports that copper and silicate do not share a strong correlation in their distribution in the water column above 2000m.¹⁸ The lack of correlation may be due to the exceptionally deep maximum for silicate and a slowly increasing but stable rate for copper concentrations below 1000m. Interestingly, Zn is also known to have significant hydrothermal inputs from the sea floor within the GP16 transect,²⁰ but did not exhibit a similar distribution pattern to copper. Roshan suggests that Si has a heavy input from river systems and Zn from hydrothermal vents, but the biological control imposed on both of them in the upper biological active region by the uptake of nutrients and subsequent sink has such profound effects that it couples them over vast areas

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of the ocean. The factor analysis by Ohnemus et al. shows that copper is more similar to elements scavenged throughout the water column (similar to iron and manganese hydroxides that settle), and that zinc belongs grouped as a nutrient type.⁴ The stark contrast between the two may be largely attributed to persistent iron oxide scavenging of copper as it settles in the water column. Factor analysis helps justify the lack of similar profiles between copper and silicate in the upper water column, but it does not give enough information in terms of where or if the analytes decouple (only an index of similarity between the two factors' transport mechanisms).

Peru results (Oxygen and Sulfur's Role) The plots made (Figure 9) suggest a correlation between depths of oxygen minima and the decoupling of cadmium-phosphate along with the zinc-silicate. The correlation between the oxygen minimum and decoupling of nutrients may be due to the depth of the water column which relates them indirectly through biological uptake in the euphotic zone. Figure 9a, b, and c highlight that while oxygen minima and the greatest decoupling are found in approximately the same depths, the decoupling is still observed further offshore outside the oxygen minimum zone. This is likely due to other factors than solely CdS precipitation, as CdS was not found in extraordinary amounts along this transect.¹⁶ Bourne et al. already has elaborated on six specific factors driving the variation observed in particle concentrations in regards to cadmium cycling: (1) passive uptake by marine organisms, (2) deliberate uptake (in the case of Cd and diatoms as a substitute in low Zn culture), (3) bio-dilution (biological ratios can change if constant uptake of a trace mineral is met with changing growth rates), (4) species composition (especially cyanobacteria vs microscopic eukaryotes), (5) cadmium sulfide (CdS) precipitation in euxinic microenvironments of sinking aggregate particles, and (6) the uptake is proportional to dissolved concentrations (and the dissolved concentrations change a lot - the author specifically points to variation due to latitude).³¹ Their results support 1-3: iron limited conditions yield higher Cd:P ratios (3) and that low concentrations of dissolved Fe, Zn and Mn can lead to increased uptake of Cd (1 and 2). Bourne also found the variation noticed in the Pacific to be unlikely caused by the oxygen minimum or sulfur leading to cadmium precipitation. Other authors have suggested that the loss of dissolved cadmium is due to preferential uptake by microbes,¹⁴ but more attention to the different ways a microbe can interact with biogeochemical cycles is needed. Biogeochemical cycling is very sensitive to species composition, and special attention is required to the forms of life found so that the key interactions previously mentioned can be better characterized for an area. The differences between organisms such as

prokaryotic cyanobacteria and eukaryotic diatoms are so great, that their roles in biogeochemistry cannot be oversimplified if an accurate representation is trying to be achieved.⁴ Biochemical flux should be considered from the perspective of multiple biological pools, and deeper investigation of all the complex biological interactions is required before the necessary biological factors are delimited.

The reason for decoupling most likely begins with biota. Some specific ways that microbes may interact with settling elements in this transect are presented herein for the sake of drawing analogy with other analytes. Microbes have been posited to be present in higher amounts within the euphotic zone and subtending OMZ which causes a biogenic sink of both Cd^{5,18,21,23,31} and Zn.^{13,16,20,22} Some authors suggest that these microbes increase the sulfur levels as part of a cryptic sulfur cycle leading to CdS formation (though it is unclear whether this is the major driving force).¹⁰ Another cause of biogenic sink may be due to the uptake of Cd due to organic ligands and a subsequent sink in the concentration of cadmium.²⁷ Similarly, organic ligands cause a sink for many elements such as Cu.¹⁸ Bourne et al. mentions that P lability changes depending on what biochemical it constitutes.³¹ They considered phosphorus bound in ATP or DNA to be more labile than some other pools such as phospholipids, and they found Cd to have a lability between those two. This highlights the significance of determining what molecules the element gets biochemically sequestered into has on remineralization. Ohnemus et al. suggests that the initial aggregation and export of surface particles and especially the subsequent biological accumulation that occurs right below the surface drives concentration decreases as they settle and scavenge.⁴ As the particles sink, the influence of biological drains becomes less intense and particle disaggregation begins to dominate. Finer refractory particles tend to accumulate. Phosphorus and cadmium have similar depth profiles due to a lack of external input and the influence of the above dynamics. It seems that each analyte has an independent depth profile, and that the major groupings (such as a nutrient-type curve) are only able to suggest what the major driving force is.

Conclusion

This paper sought to review approaches for investigating nutrient coupling and to suggest a new approach using the data from the GEOTRACES GP16 cruise to be able to characterize the extent of decoupling between solutes with similar distribution types along a transect of the eastern South Pacific. Nutrient type distributions are coupled when solutes in the ocean are

taken up and re-mineralized at similar biological rates. Investigating where perturbations from that coupled state occur in the water column provides insight into obscure phenomena that contribute to concentration fluxes which may allow for more realistic modeling of biogeochemical cycles. Here we consider the potential benefits of standardization across methods of assessing nutrient coupling by specifically comparing and contrasting current methods reported in literature.

A more insightful analysis to the correlations between coupled nutrients was achievable by compiling three standard approaches 1) depth profiles, 2) differences between the concentrations after applying a scale factor, and 3) direct comparisons of the analytes. Differences between concentrations after applying a scale factor offered the most insight, though it required a considerable amount more manipulation of the data compared to other methods. The inconsistent usage of scaling factors throughout literature is a challenge for this method; selecting some form of standardization would make this method more readily applicable for comparisons between expeditions and datasets. Basing the comparison off of differences gives better detail and a slightly different maximum than basing the comparison off of ratios (Figure 6).

Plotting the differences between concentrations after applying a scale factor allowed a comparison between cadmium and phosphate to oxygen minima to show that the decoupling extends past the oxygen minimum zone that resides off the coastline of Peru. Because the goal of studying this phenomenon is to learn about the underlying causes of these biogeochemical cycles, being able to characterize the decoupling in a way that is easy to visualize is extremely important to the efficacy of research. Other methods that are quicker occasionally miss the nuance that is required to identify biogeochemical processes from data products.

More work is needed to resolve our understanding of nutrient coupling throughout Earth's systems. The success of these large-scale data collection programs such as GEOTRACES goes hand-in-hand with our increasing ability to interpret data in a standardized way and report the results in a detailed yet clear manner. As the community continues to get more adroit with large datasets, the amount of information we can glean from them will expand as well.

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References

- Peters, B.D., Jenkins, W.J., Swift, J.H., German, C.R., Moffett, J.W., Cutter, G.A., et al. (2018) Water mass analysis of the 2013 US GEOTRACES eastern Pacific zonal transect (GP16), *Marine Chemistry* 201, 6–19. <https://doi.org/10.1016/j.marchem.2017.09.007>
- Bruland K.W., Middag R. and Lohan M.C. (2014) Controls of Trace Metals in Seawater, *Treatise on Geochemistry*, 2nd ed., 8, 19–51. <https://doi.org/10.1016/B978-0-08-095975-7.00602-1>
- Schlitzer, R., *Chemical Geology* (2018a) <https://doi.org/10.1016/j.chemgeo.2018.05.040>
- Ohnemus, D. C., Torrie, R., & Twining, B. S. (2019) Exposing the distributions and elemental associations of scavenged particulate phases in the ocean using basin-scale multi-element data sets, *Global Biogeochemical Cycles*, 33, 725–748. <https://doi.org/10.1029/2018GB006145>
- Janssen, D.J., Conway, T.M., John, S.G., Christian, J.R., Kramer, D.I., Pedersen, T.F., Cullen, J.T. (2014) Undocumented water column sink for cadmium in open ocean oxygen-deficient zones, *Proceedings of the National Academy of Sciences of the United States of America*, 111(19), 6888–6893. <https://doi.org/10.1073/pnas.1402388111>
- Williams, G.R. (1987) The coupling of biogeochemical cycles of nutrients, *Biogeochemistry*, 4(1), 61–75. <https://doi.org/10.1007/BF02187362>
- Bruland, K.W. (1980) Oceanographic Distributions of Cadmium, Zinc, Nickel, and Copper in the North Pacific, *Earth and Planetary Science Letters*, 47, 176–198. [https://doi.org/10.1016/0016-7037\(81\)90099-5](https://doi.org/10.1016/0016-7037(81)90099-5)
- Breitburg, D., Grégoire, M., Isensee, K., Chavez, F., Conley, D., Garçon, V., et al. (2018). The Ocean is Losing its Breath: Declining Oxygen in the World's Ocean and Coastal Waters, *Intergovernmental Oceanographic Commission of UNESCO (IOC-UNESCO)*, 10.
- Middag, R., van Hueven, S.M.A.C., Bruland, K. W., and de Baar, H.J.W. (2018) The relationship between cadmium and phosphate in the Atlantic Ocean unraveled, *Earth and Planetary Science Letters*, 492, 79–88. <https://doi.org/10.1016/j.epsl.2018.03.046>
- Gilly, W.F., Bernan J.M., Litvin, S.Y., Robsion, B.H. (2013) Oceanographic and Biological Effects of Shoaling of

Approaches to Assessing Nutrient Coupling

- the Oxygen Minimum Zone, *Annual Review of Marine Science*, 5, 393–420. <https://doi.org/10.1146/annurev-marine-120710-100849>
- Paulmier, A., Ruiz-Pino, D. (2009) Oxygen minimum zones (OMZs) in the modern ocean, *Progress in Oceanography*, 80, 113–128. <https://doi.org/10.1016/j.pocean.2008.08.001>
- Graco, M.L., Purca, S., Dewitte, B., Castro, C.G., Morón, O., Ledesma, J., *et al.* (2016) The OMZ and nutrient features as a signature of interannual and low-frequency variability in the Peruvian upwelling system, *Biogeosciences*, 14(20), 4601–4617. <https://doi.org/10.5194/bg-14-4601-2017>
- de Souza, G.F., Khatiwala, S.P., Hain, M.P., Little, S.H. (2018) On the origin of the marine zinc-silicon correlation, *Earth and Planetary Science Letters*, 492, 15–34. <https://doi.org/10.1016/j.epsl.2018.03.050>
- Guoinseau, D., Abouchami, W., and Galer, S.J.G. (2018a) Effect of CdS precipitation of Cd isotopes: implications for Cd oceanic cycle, *Geophysical Research Abstracts*, 20, 10835. <https://ui.adsabs.harvard.edu/abs/2018EGUGA..2010835G> (Accessed Nov2020)
- Baars, O., Abouchami, W., Galer, S.J.G., Boye, M., and Croot, P.L. (2014) Dissolved cadmium in the Southern Ocean: Distribution, speciation, and relation to phosphate, *Association for the Sciences of Limnology and Oceanography*, 59(2), 385–399. <https://doi.org/10.4319/lo.2014.59.2.0385>
- John, S.G., Helgoe, J., and Townsend, E. (2018) Biogeochemical cycling of Zn and Cd and their stable isotopes in Eastern Tropical South Pacific. *Marine Chemistry*, 201, 256–262. <http://doi.org/10.1016/j.marchem.2017.06.001>
- Butler, E.C.V., Butt, J.A., Lindstrom, E.J., Teldesley, P.C., Pickmere, S., Vincent, W.F. (1992) Oceanography of the Subtropical Convergence Zone around southern New Zealand, *New Zealand Journal of Marine and Freshwater Research*, 26(2), 131–154. <https://doi.org/10.1080/00288330.1992.9516509>
- Jacquot, J.E. and Moffett, J.W. (2014) Copper distribution and speciation across the International GEOTRACES Section GA03, *Deep-Sea Research II*, 116, 187–207. <https://doi.org/10.1016/j.dsr2.2014.11.013>
- Pelizardi, F., Bea, S.A., Carrera, J., Vives, L. (2017) Identifying geochemical processes using End Member Mixing Analysis to decouple chemical components for mixing ratio calculations, *Journal of Hydrology*, 550, 144–156. <https://doi.org/10.1016/j.jhydrol.2017.04.010>
- Roshan, S., Devires, T., Wu, J., Chen, G. (2018) The Internal Cycling of Zinc in the Ocean, *Global Biogeochemical Cycle*, 32(12). <https://doi.org/10.1029/2018GB006045>
- Quay, P., Cullen, J. Landing, W., and Morton, P. (2015) Processes controlling the distributions of Cd and PO₄ in the ocean, *Global Biogeochem. Cycles*, 29, 830 – 841. <https://doi.org/10.1002/2014GB004998>
- Weber T, John S, Tagliabue A, DeVries T. (2018) Biological uptake and reversible scavenging of zinc in the global ocean, *Science*, 361(6397), 72 – 76. <https://doi.org/10.1126/science.aap8532>
- Roshan, S., and Wu, J. (2015) Cadmium regeneration within the North Atlantic, *Global Biogeochem. Cycles*, 29, 2082–2094. <https://doi.org/10.1002/2015GB005215>
- Cutter, G. A., and Bruland, K. W. (2012) Rapid and non-contaminating sampling system for trace elements in global ocean surveys. *Limnol Oceanogr Methods* 10, 425–436. <https://doi.org/10.4319/lom.2012.10.425>
- Billier, D.V., and Bruland, K.W. (2011) Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias–chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS), *Marine Chemistry*, 130–131, 12–20. <https://doi.org/10.1016/j.marchem.2011.12.001>
- Parker, C.E., Brown, M.T., Bruland, K.W. (2016) Scandium in the open ocean: A comparison with other group 3 trivalent metals, *Geographical Research Letters*, 43(6), 2758–2764. <https://doi.org/10.1002/2016GL067827>
- GEOTRACES, International Data Assembly Center, Pacific Ocean (2007) https://www.bodc.ac.uk/geotraces/cruises/section_maps/pacific_ocean/ (accessed Nov 2020)
- GEOTRACES, International Data Assembly Center, Atlantic Ocean (2007) https://www.bodc.ac.uk/geotraces/cruises/section_maps/atlantic_ocean/ (accessed Nov2020)
- Noble, A.E., Echegoyen-Sanz, Y., Boyle, E.A., Ohnemus, D.C., Lam, P.J., Kayser, R., *et al.* (2015) Dynamic variability of dissolved Pb and Pb isotope composition from the U.S. North Atlantic GEOTRACES transect, *Deep Sea Research Part II: Topical Studies in Oceanography*, 116, 208–225. <http://doi.org/10.1016/j.dsr2.2014.11.011>
- Guoinseau, D., Galer, S.J.G., and Abouchami, W. (2018b) Effect of cadmium sulphide precipitation on the partitioning of Cd isotopes: Implications for the oceanic Cd cycle, *Earth and Planetary Science Letters*, 498, 300–308. <https://doi.org/10.1016/j.epsl.2018.06.039>
- Bourne, H. L., Bishop, J. K. B., Lam, P. J., & Ohnemus, D. C. (2018) Global spatial and temporal varia-

tion of Cd:P in euphotic zone particulates. *Global Biogeochemical Cycles*, 32, 1123 – 1141. <https://doi.org/10.1029/2017GB005842>

Karl, D.M. (2002). Nutrient dynamics in the deep blue sea, *Trends in Microbiology*, 10(9), 410–418. [https://doi.org/10.1016/S0966-842X\(02\)02430-7](https://doi.org/10.1016/S0966-842X(02)02430-7)

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Press Summary

The GEOTRACES program aims to better the understanding of Earth's oceans by extensively studying their composition. The chemical analysis of water samples from around the world generates large data products that detail the makeup of water masses throughout the ocean. This paper aims to explore some of the different methods used to investigate coupling between pairs of analytes. Coupling suggests a possible underlying mechanism, and the extent of coupling between two nutrients needs to be quantified to further consider the root of the cause. Using a data product generated by the GEOTRACES GP16 cruise (Eastern Pacific Zonal Transect), the relationship between pairs of macronutrients and trace elements are compared to an oxygen minimum to relate oxygen concentrations to the extent of nutrient coupling. In order to analyze the extent of decoupling, three types of plots were created: 1) depth profiles, 2) differences between the concentrations after applying a scale factor, and 3) direct comparisons of the analytes. Compiling these methods provides a better visualization of transect data, and it is pertinent to research that investigators can identify the location and extent of decoupling events out of massive data sets. Calculating a difference between the coupled analytes after applying a scaling factor provided the most useful information about decoupling.