http://dx.doi.org/10.7773/cm.v5i1.317

MULTIPLE LINEAR REGRESSION MODELING AS A TEST FOR THE REDFIELD RATIO IN THE SOUTH ATLANTIC AND DRAKE PASSAGE.

by

CLIFFORD N. DAHM
School of Oceanography, Oregon State University
Corvallis, Oregon 97331
U.S.A.

and

P. KILHO PARK
NOAA/NOS/C3x4 6001 Executive Blvd.
Rockville, Md. 20852
U.S.A

ABSTRACT.

A Test of the Redfield ratio for the proportional increase of phosphate and nitrate concurrent with a decrease of oxygen was performed on GEOSECS data in the South Atlantic and Drake Passage. An apparent breakdown in the predicted ratios was seen in the bottom waters of both regions. In both cases, the multiple linear regression model expressing oxygen as a function of a nutrient yielded a $\Delta O_2 : \Delta PO_4$ and $\Delta O_2 : \Delta NO_3$ ratio much lower than the predicted Redfield values of -138 and -138/16. Further analysis of the data showed that the apparent error is a function not of biochemical oxidation of material deviating from Redfield's proposed average elemental composition, but a statistical problem resulting from the oxygen concentration being almost completely a function of the conservative variable in the model. In the bottom waters of both the South Atlantic and the Drake Passage, nitrate and phosphate concentrations operate as pseudo-conservative parameters with mixing and advection effectively controlling the oxygen, nitrate, and phosphate distributions and overwhelming any measurable in situ changes resulting from biochemical oxidation in these waters.

RESUMEN.

Se realizó una prueba de la razón propuesta por Redfield (1934) para el aumento de fosfato y nitrato en correlación con la disminución de oxígeno, utilizando datos de GEOSECS del Atlántico Sur y del Passage Drake. Aparentemente las aguas del fondo de ambas regiones no presentan los valores predichos. En ambos casos se utilizó un modelo de regresión lineal múltiple expresando oxígeno como función de un nutriente y temperatura potencial. Esto dió como resultado razones ΔO_2: ΔPO_4 y ΔO_2: ΔNO_3 mucho menores que -138 y -138/16 respectivamente. Un análisis más profundo de los datos mostró que el error aparente no es una función de la oxidación boiquímica de material que se desvía en su composición elemental de las proporciones propuestas por Redfield, sino que es un problema estadístico que se debe a que el oxígeno es casi completamente una función de la variable conservadora en el modelo. En las aguas del fondo del Atlántico Sur y del Pasage Drake, el fosfato y el nitrato son variables seudoconservadoras. Los procesos de mezcla y de advección controlan los valores de oxígeno, fosfato y nitrato, y obscurecen cualquier cambio "in situ" que resulte de la oxidación bioquímica en estas aguas.

INTRODUCTION.

Multiple linear regression has been adopted in recent years as a tool for viewing various chemical and physical processes in the ocean (Dahm et al., 1977; Ben Yaakov, 1971; and Alvarez Borrego et al., 1975). One application of this technique has been used to separate conservative and nonconservative fractions from the nitrate and phosphate distributions in the ocean and thereby provide a means for testing the Redfield ratio (Alvarez-Borrego, Guthrie, Culberson, and Park, 1975).

Redfield (1934) proposed a biochemical oxidation ratio for the oceans of the world which related the observed oxygen (O_2) content to the extent of O_2 consumption through oxidation. Redfield, Ketchum and Richards (1963) altered this ratio slightly by considering a more extensive suite of planktonic elemental composition data. This ratio of 276 atoms of oxygen consumed for each atom of phosphorus, 16 atoms of nitrogen, and 106 atoms of carbon regenerated is now generally accepted. By utilizing this ratio, the PO_4 and NO_3

concentrations at any point can be further divided into an oxidative and preformed proportion. The preformed portion is conservative (Pythowicz ε Kester, 1966) in that it represents the amount of nutrient present at the time of formation for the water parcel and altered henceforth only by physical processes such as mixing and advection. The oxidative component results from the addition of the nutrient species to the water parcel during its history by biochemical oxidation.

The development of a multiple linear regression model for describing oxygen as a function of a nutrient parameter and a conservative variable has been adequately described elsewhere (Alvarez-Borrego et. al., 1975; and Dahm et al., 1977). The use of these models as means for water mass identification and elucidating circulation patterns has also been published (Alvarez-Borrego et. al., 1975). The utility of this form of modeling is not limited to purely physical oceanographic questions.

An additional benefit of the derived model is present in the significance of the constant a_1 in the equation

$$O_2 = a_0 + a_1 \; (PO_4 \text{ or } NO_3) + a_2 \; (\theta \text{ or } S) \qquad (1)$$

where a_1 corresponds to the $\Delta O_2 : \Delta PO_4$ or $\Delta O_2 : \Delta NO_3$ ratio respectively, θ is the potential temperature and S is the salinity. Redfield's ratio predicts that 276 oxygen atoms are consumed to produce 16 atoms of nitrogen and 1 atom of phosphorus. Redfield (1934) noted the variability of this ratio from species to species, but the averaged ratio appears to hold in the Northern Atlantic and Pacific oceans where a statistical uniformity in composition is approximated (Alvarez-Borrego, 1973).

The plot of the O_2 residuals versus either θ or S gives an indication of the water types present, where the O_2 residual is defined as the observed O_2 data minus the predicted O_2 value of the model (Dahm et al., 1977). Taking a linear portion from the O_2 residual versus θ or S diagram and reapplying the model should yield a random O_2 residual distribution attributable only to random errors in the O_2, PO_4 or NO_3, and θ°C or S measurements. The random distribution indicates the model is statistically correct, and 95% confidence intervals may be calculated for the constants in it. The 95% confidence intervals on the constant a_1 should include -138 for PO_4 and 130/16 (-8.63) for NO_3 if the Redfield ratio holds.

MULTIPLE LINEAR REGRESSION MODELING

This technique of examining the constant a_1 in the model and comparing it to the predicted Redfield values for PO_4 and NO_3 requires stations where a large enough number of samples were taken to retain an adequate number of degrees of freedom for the model in each segment. The Geochemical Ocean Section Program (GEOSECS) in the Atlantic Ocean meets the necessary criteria both in terms of sampling density and data quality for this method to be attempted. Selected stations in the South Atlantic and Drake Passage will be fitted to the model to assess the general applicability of the Redfield's ratio.

OBSERVATIONS AND METHODS.

From July 18, 1972 to April 1, 1973, as part of GEOSECS, the R/VKnorr of the Woods Hole Oceanographic Institution carried out a detailed survey of the Atlantic Ocean for more than 40 physical and chemical parameters. The goal of the GEOSECS program is to obtain coordinated chemical and radiochemical data in each major ocean at a level of sophistication higher than any previous work.

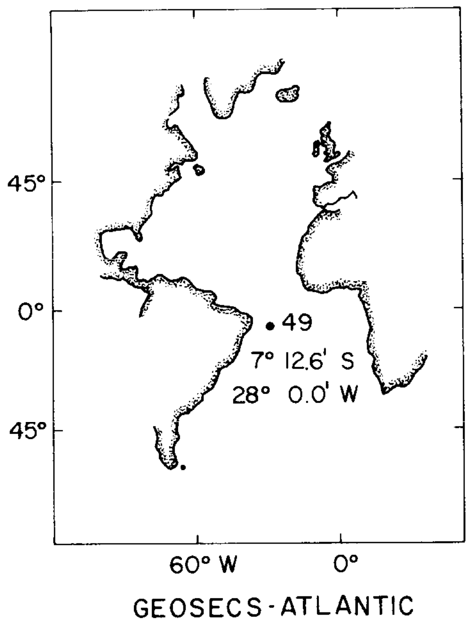
The nutrient data for the Atlantic GEOSECS program used in this work was collected with a modified Autoanalyzer-II system. Description of the methods, chemistries, and intercalibration tests have been presented by Atlas et al. (1971) and Hages et al. (1972). Analyses are run inmediately after sampling with precisions of better than ±1% attained for the Atlantic data.

Oxygen was measured by the Carpenter modification of the Winkler titration (Carpenter, 1965). Precision for this data has been shown to be better than ±.5 percent. All nutrient and oxygen data are expressed in μM/Kg.

The stations selected for this study were station 49, off the coast of central Brazil, at 7° 12.6'S and 28° 0.0'W and three stations in the Drake Passage south of the southern tip of South America (fig. 1 and 2). The Drake Passage stations, numbers 76,77 and 78, are located at 57°44.0'S, 66° 08.0'W; 59°39.5'S, 64°30.0'W, and 61°03.0'S, 62°58.0'W respectively.

RESULTS AND DISCUSSION.

The multiple linear regression model was applied to the four selected stations and, in addition, to a composite of the data from all three of the Drake Passage stations. The data was fitted using a computer routine as outlined in Draper and Smith (1966).



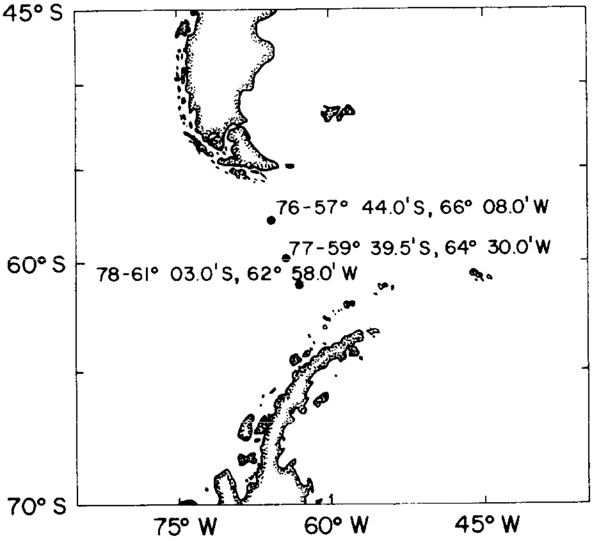


Fig. 1. Location of the GEOSECS-ATLANTIC STATION.

Fig. 2. Location of the Drake Passage stations.

The results for the model at station 49 are:

$$O_2 = 452.97 - 9.84 \cdot \theta - 120.51 \cdot PO_4$$

$$O_2 = 449.79 - 10.22 \cdot \theta - 7.56 \cdot NO_3$$

where O_2 is a predicted value from the model based on the independent variables θ and PO_4 or NO_3. Potential temperature was chosen as the conservative variable due to the large temperature variation being the major factor in determining the O_2 saturation at various dephts for this station. The resulting plots of θ versus the O_2 residual for the nutrient parameters PO_4 and NO_3 are shown in figures 3 and 4.

The results for the model at stations 76, 77, and 78 plus the composite data are:

Station 76 (57°44.0' S, 66°08.9' W)

$$O_2 = 5003.50 - 134.27 \cdot S - 71.67 \cdot PO_4$$

$$O_2 = 4039.40 - 103.06 \cdot S - 8.35 \cdot NO_3$$

Station 77 (59°39.5' S, 64°30.0' W)

$$O_2 = 4724.80 - 121.60 \cdot S - 144.53 \cdot PO_4$$

$$O_2 = 4458.60 - 112.96 \cdot S - 10.73 \cdot NO_3$$

Station 78 (61°3.0' S , 62°58.0' W)

$$O_2 = 4457.20 - 113.94 \cdot S - 140.83 \cdot PO_4$$

$$O_2 = 4278.60 - 107.84 \cdot S - 10.44 \cdot NO_3$$

All three stations together:

$$O_2 = 4940.00 - 131.35 \cdot S - 87.34 \cdot PO_4$$

$$O_2 = 4277.40 - 109.38 \cdot S - 8.86 \cdot NO_3$$

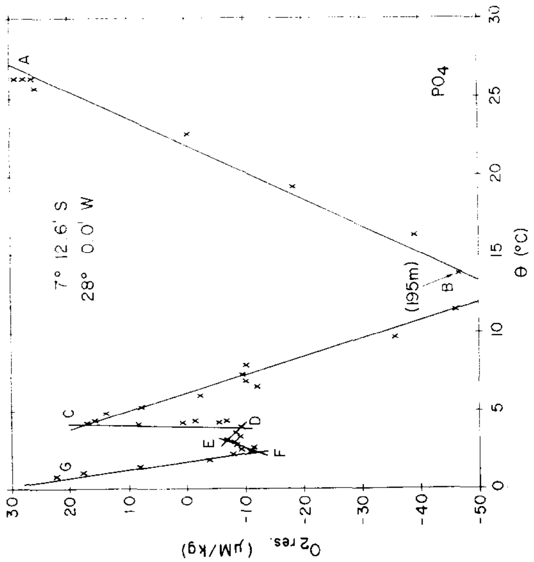
Salinity was used as the conservative variable in these Antarctic stations as the temperature range was small and complicated plot interpretation resulted from the series of temperature maxima and minima found throughout the water column. The Plots of S versus the O_2 residual for the three Drake Passage stations are presented in figures 5-10.

Further analysis was performed on the residuals from the combined stations. Best least square fits were calculated for the linear segments of each station from the combined regression residual values. These lines were then plotted on a O_2 residual - S plot (figure 11) with PO_4 as the nutrient parameter. Using NO_3 in the model results in a similar diagram. The influence of the various water types are clearly shown by the plot. For the near surface data, station 76, the northern most station, shows high negative O_2 residual values with progressively less negative estimates proceeding southward. Since

$$O_{2_{res.}} = \hat{O}_2 - O_2$$

where $\hat{O}_2$ is the value predicted by the model and O_2 is the observed field data, the actual O_2 value is lower than predicted by the model. The increased biological depletion of PO_4 (and NO_3) moving northward causes the increasingly negative character of the residuals from South to North.

A second observation on the combined model occurs for the deep water with salinities near 34.7°/₀₀ . Increasingly more positive O_2 residuals are obtained by the model proceeding southward. The bottom water to the south in the Drake Passage is showing the influence of a richer oxygen source, as the PO_4, NO_3, and S levels at the three stations vary only slightly. Reid and Nowlin (1971) describe this cold oxygen rich intrussion into the southeastern Drake Passage and conclude from current measurements that a weakening of eastward flow may cause an exchange by mixing due to the strong gradients of temperature, salinity, and oxygen between the bottom water of the Drake Passage and bottom water from the Scotia Sea.



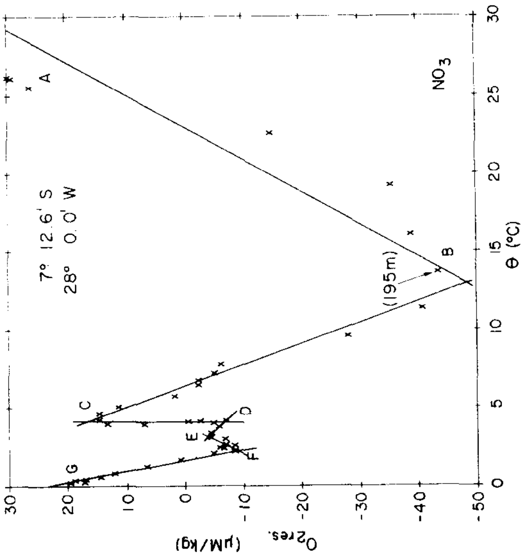
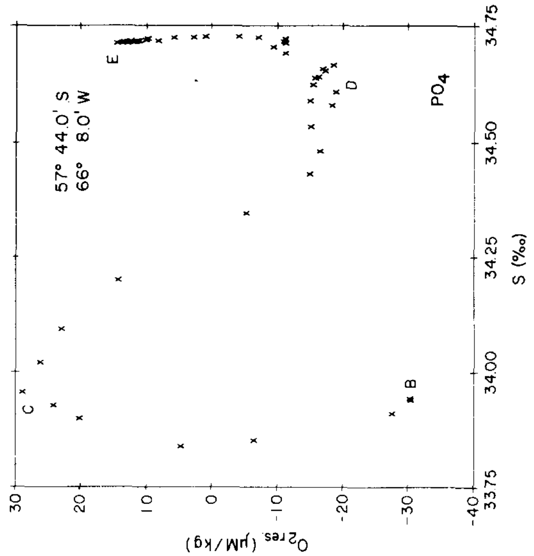


Fig. 3. Oxygen residuals versus potential temperature diagram for station 49, when phosphate is used in the regression equation.

Fig. 4. Oxygen residuals versus potential temperature diagram for station 49, when nitrate is used in the regression equation.



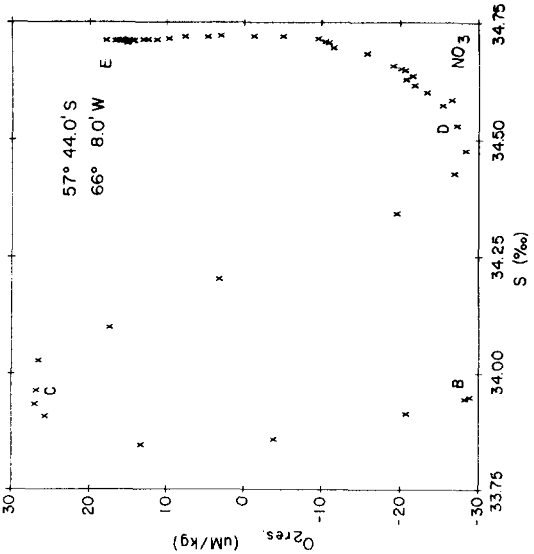
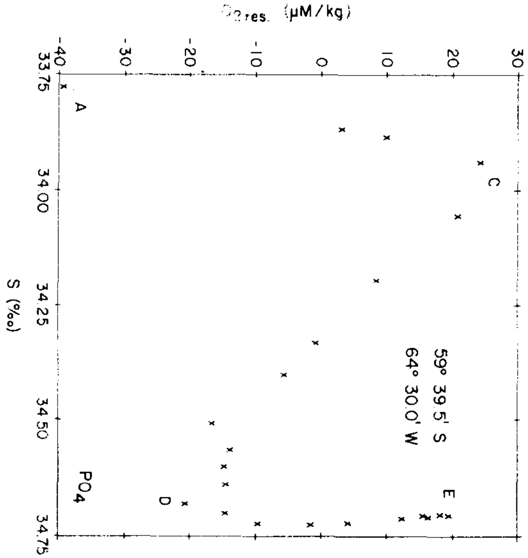


Fig. 5. Oxygen residuals versus salinity diagram for station 76, when phosphate is used in the regression equation.

Fig. 6. Oxygen residuals versus salinity diagram for station 76, when nitrate is used in the regression equation.



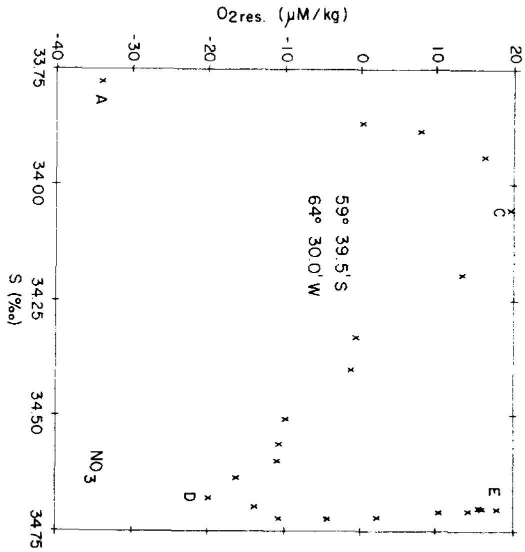
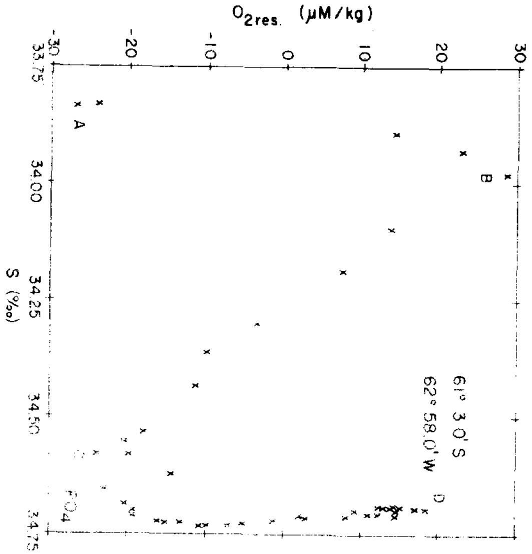


Fig. 7. Oxygen residuals versus salinity diagram for station 77, when phosphate is used in the regression equation.

Fig. 8. Oxygen residuals versus salinity diagram for station 77, when nitrate is used in the regression equation.



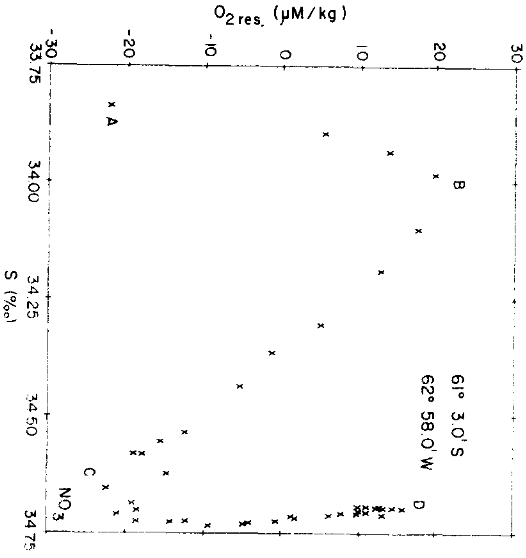


Fig. 9. Oxygen residuals versus salinity diagram for station 78, when phosphate is used in the regression equation.

Fig. 10. Oxygen residuals versus salinity diagram for station 78, when nitrate is used in the regression equation.

C. R. Mann (personal communication) obtained data in the Drake Passage during the Hudson 70 expedition from twelve current meters which indicates an actual westwardly component in the bottom water flow. This is in contrast to the measurements of Reid and Nowlin (1971). The westwardly flow in the south of the Drake Passage supports the conclusion of Gordon (1966) of a bottom water flow from the Scotia Sea into this region. The combined residual plot also supports this occurence of a westward flow in the southern portion of the Drake Passage during the period of GEOSECS sampling. The effects of this current are observed on the combined multiple linear regression analysis as increasingly high positive residuals southward. From the conflicting data available, variable and intermittent currents in the deep and bottom waters of the Drake Passage are not inconsistent with the distribution of properties in and around the Drake Passage.

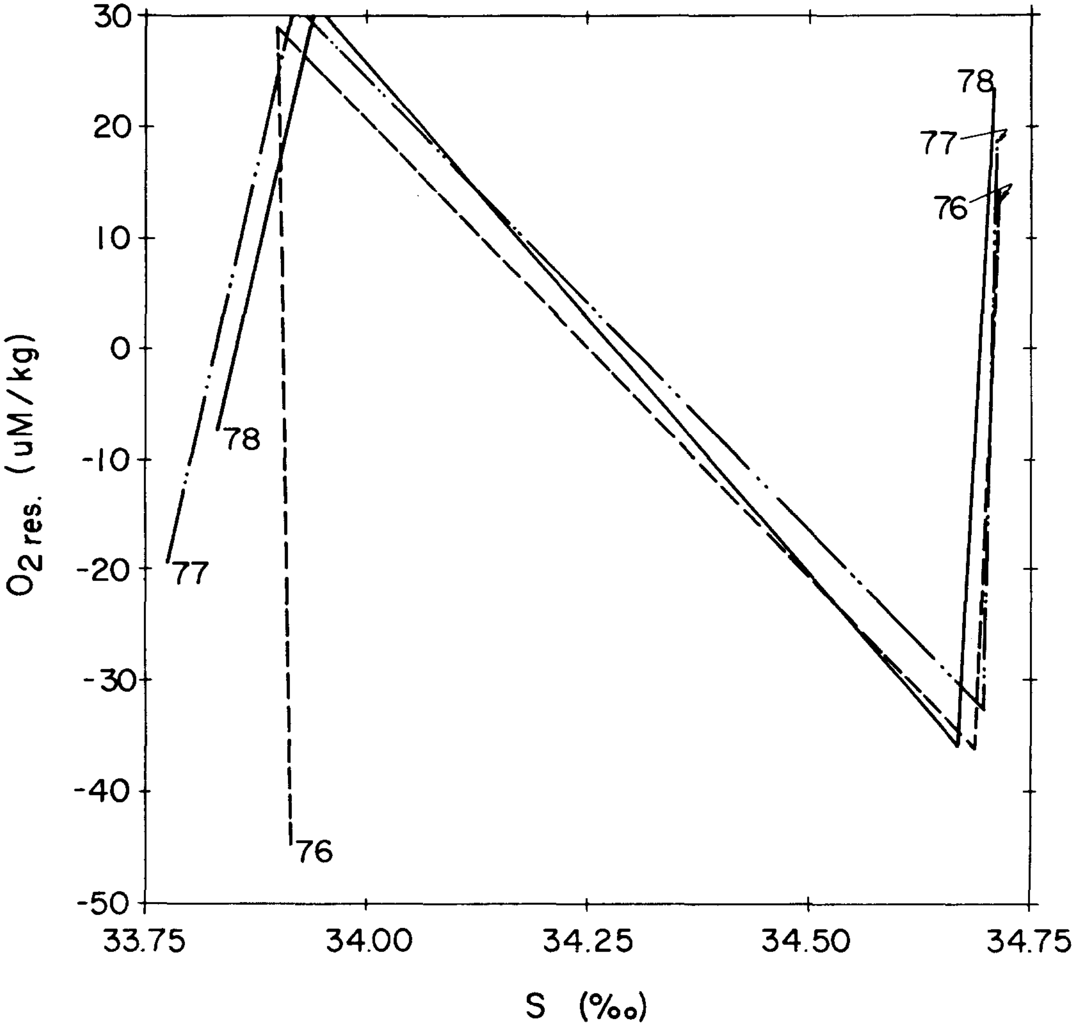


Fig. 11. Oxygen residuals versus salinity diagram, using phosphate in the regression equation, with data from stations 76, 77 and 78 treated together in a single regression equation.

Returning to the question of the agreement between the predicted and observed Redfield ratio on the South Atlantic and Drake Passage, The southernmost Drake site, station 78 with the apparent influence of more recently renewed and more oxygen rich bottom waters, and station 49 will be analyzed. To test Redfield's ratio for ΔO_2: ΔPO_4 and ΔO_2 : ΔNO_3, station 49 was broken into four linear portions as indicated by the O_2 residual - θ diagrams (figures 3 and 4). The water types present, and identified as A-G, are listed in table 1. The three portions of North Atlantic Deep Water were included as one segment since insufficient data points existed for the analysis of each portion. The water column at station 78 was divided into three linear portions as indicated by the O_2 residual - S diagrams (figures 9 and 10). The water types at stations 76-78 are labeled A-E and characterized in table 2.

The model was then refitted to the linear segments for stations 49 and 78. The residual plots which were obtained all showed a random distribution indicating the model was statistically describing the data and resulted only due to analytical variability in the measurements of O_2, θ , S, PO_4, and NO_3. All the linear segments were run with θ as the conservative variable except for the middle portion of station 78 where a relatively unchanging temperature passing through a slight maximum around 500 meters produces slopes approaching infinity when θ is used as the conservative variable in the model. The results of the regressions with 95% confidence levels for stations 49 and 78 are tabulated along with the depth range, the coefficient of determination R^2, and the residual degrees of freedom (n-p-1) (tables 3 and 4).

At station 49, in the depth range 0-195 m and 256-909 m, the Redfield ratio holds at a 95% confidence interval or is extremely close with the exception of the NO_3 coefficient for 0-195 m. The apparent lack of inorganic nitrate oxidation can be satisfactorily explained by the limiting nature of NO_3 in this depth interval. No NO_3 or NO_2 is measureable in the upper 100 meters and unoxidized nitrogen compunds such as ammonia and urea decrease the coefficient of oxygen change due to nitrate regeneration near the surface. The inconsistency of the Redfield proportion below one kilometer is much harder to justify. The segment from 1009-3478 m did include grouping the different North Atlantic Deep Water types which might bias the model sufficiently to yield the slightly lower ratios of -94:1 for ΔO_2 : ΔPO_4 and -6.22:1 for ΔO_2 : ΔNO_3. No such justifications exist for the bottom segment which would explain the very low ratios found by the regression equation.

TABLE 1.- Characterization of water masses at station 49 by θ , S, $PO_{4(p)}$ and $NO_{3\ (p)}$.

Water Mass	Name	θ	S	$PO_4(p)$	$NO_3(p)$
A	Surface Water	26.1	36.20	0.1	0.0
B	Subsurface Water	13.6	35.41	0.3	3.9
C	Antarctic Intermediate Water	4.5	34.47	1.09	16.5
D	Upper North Atlantic Deep Water	3.7	34.95	0.81	12.7
E	Middle North Atlantic Deep Water	2.7	34.92	0.84	13.0
F	Lower North Atlantic Deep Water	2.3	34.91	0.82	12.8
G	Antarctic Bottom Water	0.2	34.70	1.21	17.7

TABLE 2.- Characteristic S, θ, $PO_{4(p)}$ and $NO_{3(p)}$ for the water types present in the Drake Passage.

	Cumulative Water Type	S (°/₀₀)	θ (°C)	$PO_4(p)$ (μM/kg)	$NO_3(p)$ (μM/kg)
A	Antarctic Surface Water	33.75-33.85	1.0-2.0	1.6-1.7	25-26
B	Warmed Antarctic Surface Water	33.90-34.00	4.0-5.0	1.35	23.5
C	Intermediate Antarctic Water	33.90-34.05	-1.0-0.0	1.8	26-27
D	Transition Water	34.64-34.69	2.0	1.0	15
E	Bottom Water	34.69-34.71	0.0-1.0	1.15-1.20	16-17

TABLE 3.- Regression equations of O_2 on PO_4 and θ°C and on NO_3 and θ°C for linear segments of the $O_{2_{res}}$ –θ plot for station 49.

Depth Range (m)	Regression Equations (with 95% confidence intervals)	R^2	n-p-1
0-195	$O_2 = (254.04 \pm 114.74) - (1.23 \pm 4.32)\theta - (96.09 \pm 45.02)PO_4$	.995	5
	$O_2 = (120.76 \pm 78.45) + (3.57 \pm 3.12)\theta - (2.83 \pm 1.96)NO_3$	.979	5
256-909	$O_2 = (634.33 \pm 74.80) - (23.17 \pm 2.75)\theta - (169.92 \pm 28.15)PO_4$	.989	7
	$O_2 = (533.45 \pm 64.79) - (19.34 \pm 2.40)\theta - (8.36 \pm 1.54)NO_3$	.986	7
1009-3478	$O_2 = (410.74 \pm 7.78) - (10.89 \pm 2.78)\theta - (93.53 \pm 6.98)PO_4$	.995	13
	$O_2 = (417.91 \pm 8.75) - (11.24 \pm 2.99)\theta - (6.22 \pm .50)NO_3$	.994	13
3690-5513	$O_2 = (297.43 \pm 61.05) + (5.14 \pm 11.63)\theta - (32.64 \pm 28.50)PO_4$	.999	7
	$O_2 = (315.59 \pm 74.63) + (3.37 \pm 12.78)\theta - (2.72 \pm 2.31)NO_3$	.999	7

TABLE 4.- Regression equations of O_2 on PO_4 and θ°C, NO_3 and θ°C, PO_4 and S, and NO_3 and S for station 78 in the Drake Passage.

Depth Range (m)	Regression equations (showing 95% confidence intervals)	R^2	n-p-1
0-96	$O_2 = (624.42 \pm 194.53) - (18.37 \pm 13.60)\theta - (154.54 \pm 108.10)PO_4$	.950	2
	$O_2 = (624.29 \pm 31.25) - (11.47 \pm 1.46)\theta - (10.47 \pm 1.81)NO_3$	.999	2
96-998	$O_2 = (6274.10 \pm 314.70) - (164.32 \pm 9.38)S - (182.44 \pm 23.35)PO_4$	.995	11
	$O_2 = (6532.60 \pm 254.44) - (172.42 \pm 7.45)S - (11.50 \pm 1.19)NO_3$	.997	11
1346-3811	$O_2 = (264.35 \pm 55.25) - (17.88 \pm 1.70)\theta - (21.05 \pm 25.44)PO_4$	.990	20
	$O_2 = (301.93 \pm 75.88) - (17.96 \pm 1.43)\theta - (2.59 \pm 2.36)NO_3$	.990	20

At station 78, the region from the surface to 96 meters approximates the predicted Redfield ratio. From 96-998 m the confidence intervals for both PO_4 and NO_3 are slightly higher than predicted. As the O_2 saturation is more dependent on θ than S, the use of S is somewhat less dependable in removing the conservative portion of the oxygen concentration and may be the cause of the slightly higher ratios. Such an explanation cannot be considered for the region from 1346-3811 meters. As for station 49, the bottom water predicts a $\Delta O_2 : \Delta PO_4$ and $\Delta O_2 : \Delta NO_3$ far below those commonly hypothesized.

An initial reaction to explain this deviation is that the material being oxidized deviates from the assumed ratio. Examination of diatom chemical compositions given in Strickland (1965) and Platt and Irwin (1973) shows approximately the predicted ratios of Redfield. As the deviating region is the lower portion of the water column including the bottom, the possible oxidation or dissolution of heavier detrital material is suggested. Vinogradov (1953) examines such materials as skeletal matter which are high in phosphate, but the oxidation or dissolution of such material does not explain the reduced $\Delta O_2 : \Delta NO_3$ ratio, In addition, the volume of water which significant bottom oxidation or dissolution must affect to deviate the ratio so greatly would require tremendous amounts of dissolution or oxidation.

As the probability of biological or geochemical changes producing such a variation in the proposed model is slight, examination of the model for statistical breakdowns was made. Assumptions, such as approximating $O_{2_{sat}} + a_1 \cdot PO_{4(p)}$ by a linear equation for temperature and such as a completely random residual distribution resulting from the model, all proved correct.

The appropriate clue for the observed deviation was finally realized through examination of the 95% confidence intervals on the variables PO_4 and NO_3. At station 49, the lower limit of this interval is 4.14 for PO_4 and 0.41 for NO_3. For station 78, the lower limits are -4.39 and 0.23 for PO_4 and NO_3 respectively. In all cases, the variation explained by the nutrient term is approaching zero or includes zero for the model at a 95% confidence level.

A regression was then run for the two strongly deviating segments at stations 49 and 78 using the following model:

$$O_2 = a_0 + a_1 \cdot \theta \qquad (2)$$

The results were:

Station 49 (3690- 5513 m)

$$O_2 = 227.53 + 18.44 \cdot \theta \qquad (3)$$

Station 78 (1346-3811 m)

$$O_2 = 218.64 - 16.64 \cdot \theta \qquad (4)$$

The coefficients of determination were .997 for 3 and .988 for 4. The entering F value of the incoming variable, θ, was 2891 for 3 and 1727 for 4. Subsequent addition of a PO_4 or NO_3 term to the models yielded entering F values in all four cases that were insignificant in removing any added variation at a 99 percent confidence level. The oxygen for the bottom water segment at stations 49 and 78 can be modeled exclusively as a funcion of the conservative variable θ.

In terms other than statistical, there is not enough oxidation occurring in the bottom water such that a test of Redfield's ratio can be made. Purely physical processes of mixing and advection control the O_2 distribution. The O_2 and subsequently the nutrients can be viewed as conservative in the bottom waters at these two stations for the level of analytical precision attained by GEOSECS for the measurement of O_2 , PO_4, and NO_3. From the formation of the bottom water through the movement northward to station 49 off Brazil, an insignificant O_2 depletion occured at the sensitivity of analytical techniques to be statistically significant in modeling oxygen as a function of θ plus a nutrient term.

SUMMARY.

The utilization of multiple linear regression modeling can be used effectively both as a method for viewing ongoing physical processes and as a means of evaluating the Redfield ratio. An analysis of a South Atlantic GEOSECS station and three stations in the Drake Passage produces some general conclusions.

1. Statistical regression modeling for a series of stations in the Drake Passage shows the extent of biological depletion across the Passage and points out the influence of an oxygen rich bottom water in the southern reaches of the Drake Passage. This is bottom water from the Scotia Sea observed by other authors.

2. An apparent breakdown of Redfield's ratio for the ΔO_2 : ΔPO_4 and the ΔO_2 : ΔNO_3 in the bottom waters of the Atlantic and Southern Ocean is seen. Analyses indicate that the variation is due not to an inconsistency in the Redfield ratio but to the very low rates of oxidation at great depths. Nearly all the variation in the oxygen content of the deep water at an Atlantic equatorial station and a station in the Drake Passage can be explained by the use of a conservative variable such as θ or S. Significant oxidation larger than the analytical errors of the GEOSECS methods cannot be detected for the stations analyzed.

3. The deep and bottom water nutrient and oxygen distributions for the South Atlantic and Drake Passage can be explained purely from hydrodynamic considerations. Nutrient and dissolved oxygen behave like conservative parameter in these waters. The rate of oxidation in the deep waters of these regions are slow relative to the physical processes of mixing and advection.

ACKNOWLEDGMENTS.

This work was supported by the United States National Science Foundation grants GX - 28167 and GA 12113. The authors would also like to thank Dr. Saúl Alvarez-Borrego for his support and help in the preparation of this manuscript and to Marilyn Guin for her assistance on the graphics.

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Recibido: Marzo 2 de 1978.