KNOX22RR BOTTLE DATA

4December2008 to 2January2009
Montevideo, Uruguay to Punta Arenas, Chile
R/V Roger Revelle
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NUTRIENTS

The cruise started with new pump tubes and then they were changed once during the expedition.

Sampling and Data Processing

Nutrient samples were drawn into 45 mL polypropylene, screw-capped "oak-ridge type" centrifuge tubes. The tubes were rinsed with 10% HCl and then with sample three times before filling. After each group of samples was analyzed, the raw data file was processed to produce another file of response factors, baseline values, and absorbances.

Nutrients, when reported in micromoles per kilogram, were converted from micromoles per liter by dividing by sample density calculated at 1 atm pressure (0 db), *in situ* salinity, and the sample temperature measured at the time of analysis.

Equipment and Techniques

Nutrient analyses (nitrate+nitrite, nitrite, phosphate, silicate, ammonium) were performed on an ODF-modified 5-channel Technicon AutoAnalyzer II, generally within one to twelve hours after sample collection. The samples were kept in the dark by covering with tin foil or refrigerated at 4℃, if necessary, but brought to within 5℃ of lab temperature before analysis. The analog outputs from each of the six channels were digitized and logged automatically by computer (PC) at 2-second intervals.

A modification of the Armstrong *et al*. (Armstrong 1967) procedure was used for the analysis of nitrate and nitrite. For the nitrate plus nitrite analysis, the seawater sample was passed through a cadmium reduction column where nitrate was quantitatively reduced to nitrite. The stream was then passed through a 15mm flowcell and the absorbance measured at 540nm. The same technique was employed for nitrite analysis, except the cadmium column was bypassed, and a 50mm flowcell was used for measurement. Periodic checks of the column efficiency were made by running alternate equal concentrations of NO_2 and NO_3 through the NO_3 channel to ensure that column efficiencies were high (> 97%). Nitrite concentrations were subtracted from the nitrate+nitrite values to obtain nitrate concentrations.

Phosphate was analyzed using a modification of the Bernhardt and Wilhelms [Bernhardt 1967.] technique. The reaction product was heated to ~55ºC to enhance color development then passed through a 50mm flowcell and the absorbance measured at 820m.

Silicate was analyzed using the technique of Armstrong *et al*., (Armstrong, 1967). The sample was passed through a 15mm flowcell and the absorbance measured at 660nm.

Ammonium was determined by the Berthelot reaction (Patton and Crouch 1977) in which sodium hypochlorite and phenol react with ammonium ion to produce indophenol blue, a blue compound. The solution was heated to 55°C and passed through a 50mm flowcell at 640nm.

Nutrient Standards

Na_2SiF_6, the silicate primary standard, was obtained from Johnson Matthey Company and Fisher Scientific and was reported by the suppliers to be >98% pure. Primary standards for nitrate (KNO_3), nitrite ($NaNO_2$), and phosphate (KH_2PO_4) were obtained from Johnson Matthey Chemical Company, and the supplier reported purities of 99.999%, 97%, and 99.999%, respectively. Ammonia, ($NH_4(SO_4)_2$) primary standard was obtained from Fisher Scientific and reported to be >99% pure.

Standardizations were performed at the beginning and end of each group of analyses (12-38 samples) with an intermediate concentration mixed nutrient standard prepared prior to each run from a secondary standard in a low-nutrient seawater matrix. The secondary standards were prepared aboard ship by dilution from the pre-weighed primary standards. Three sets of primary/secondary standards made up over the course of the cruise.

A set of seven different standard concentrations (table 1) were analyzed periodically to determine the deviation from linearity, if any, as a function of concentration for each nutrient. Residuals were determined and fit to a 3rd order polynomial, which was then used to calculate the non-linear corrections and applied to the nutrient concentrations.

Table 1: Concentration of standards (µmol/L)

std	N+N	PO4	SiO3	NO2	NH4
1)	0.0	0.0	0.0	0.0	0.0
2)	7.75	0.6	30	0.25	1.00
3)	15.50	1.2	60	0.50	2.00
4)	23.25	1.8	90	0.75	3.00
5)	31.00	2.4	120	1.00	4.00
6)	38.75	3.0	150	1.25	5.00
7)	46.50	3.6	180	1.50	6.00

All glass volumetric flasks and pipettes were gravimetrically calibrated prior to the cruise. The primary standards were dried and weighed prior to the cruise. The exact weight was noted for future reference. When primary standards were made, the flask volume at 20ºC, the weight of the powder, and the temperature of the solution were used to buoyancy correct the weight, calculate the

exact concentration of the solution, and determine how much of the primary was needed for the desired concentrations of secondary standard.

All the reagent solutions, primary and secondary standards were made with fresh distilled deionized water (DIW).

Working standards were made up in low nutrient seawater (LNSW). The water is collected off shore of coastal California and treated in the lab. The water was first filtered through a 0.45 micron filter then re-circulated for ~8 hours through a 0.2 micron filter and UV lamp. The actual concentration of nutrients in this water was empirically determined during the calculation of the non-linear corrections that were applied to the nutrient concentrations.

Quality Control

As is standard ODF practice, a deep calibration "check" sample was run with each set of samples. The tabulated data below is the average and standard deviation of the check sample concentration over the course of the expedition.

Parameter	Concentration (µmol/L)
NO3	30.51 uM +/- 0.13
PO4	2.11 uM +/- 0.01
SIL	97.3 uM +/- 0.5