

5. Inorganic nutrients

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Preamble



Analysis for nitrate + nitrite (hereinafter nitrate), phosphate and silicate was undertaken on a skalar sanplus autoanalyser following methods described by Kirkwood (1994) with the exception that the pump rates through the phosphate line are increased by a factor of 1.5 which improves reproducibility and peak shape. Samples were drawn from niskin bottles into 25ml sterilin coulter counter vials and kept refrigerated at 4 C until analysis which commenced within 24 hours. Stations were run in batches of 1-3 with most runs containing 1 or 2 stations. Overall 40 runs were undertaken. An artificial seawater matrix (ASW) of 40 g/l sodium chloride was used as the intersample wash and standard matrix. The nutrient free status of this solution was checked by running Ocean Scientific International (OSI) nutrient free seawater on every run. A single set of mixed standards were made up at the start of the cruise and used throughout the cruise. These were made by diluting 5 mM solutions made from weighed dried salts in 1 l of ASW into plastic 1l volumetric flasks that had been cleaned. Three low silicate standards were also used after several initial run without them. It proved difficult to detect the peak heights for the surface silicate values using the deep water standards. This was in an effort to minimise the run to run variability in concentrations observed on previous cruises. OSI nutrient standard solutions were used sporadically during the cruise to monitor the degradation of these standards. Data was transferred to another computer initially using a floppy disk and then by means of a memory stick. The floppy disk transfer route was unreliable and resulted in a delay between sample analysis and data work up of 8-10 stations. Data processing was undertaken using Skalar proprietary software. Generally this was straightforward. The wash time and sample time were 75 seconds, the lines were washed daily with 0.25M NaOH (P) and 10% Decon (N, Si). Time series of baseline, bulk standard concentration, instrument sensitivity, calibration curve correlation coefficient, nitrate reduction efficiency and duplicate difference were compiled and updated on a daily basis.

Performance of the analyser:

- 1) During one run the water bath failed. The problem was discovered and the waterbath was sent to the technicians to be fixed. They were able to fix it and the waterbath was back up and running before the end of the run. This resulted in one station that had to be re-run, but overall no samples were lost because of its malfunction.
- 2) The first nitrite standard that was made up seemed to produce reduction efficiencies from the cadmium column of only 60%. This was more than likely an error in the dilution of the nitrite standard than with the column itself as all standards made up after the first one show column efficiencies approaching 100%. On the 30th of November, at the end of a run, the column was broken. This required the column to be replaced. The new column was fitted and the auto-analyser was left to run with reagents to flush through the nitrate

line. The nitrate baseline took a long time to settle down again, almost 12 hours. When it eventually did settle down samples could be analysed as normal and no samples were lost because of this process. There was no change in the column efficiency either between the two columns.

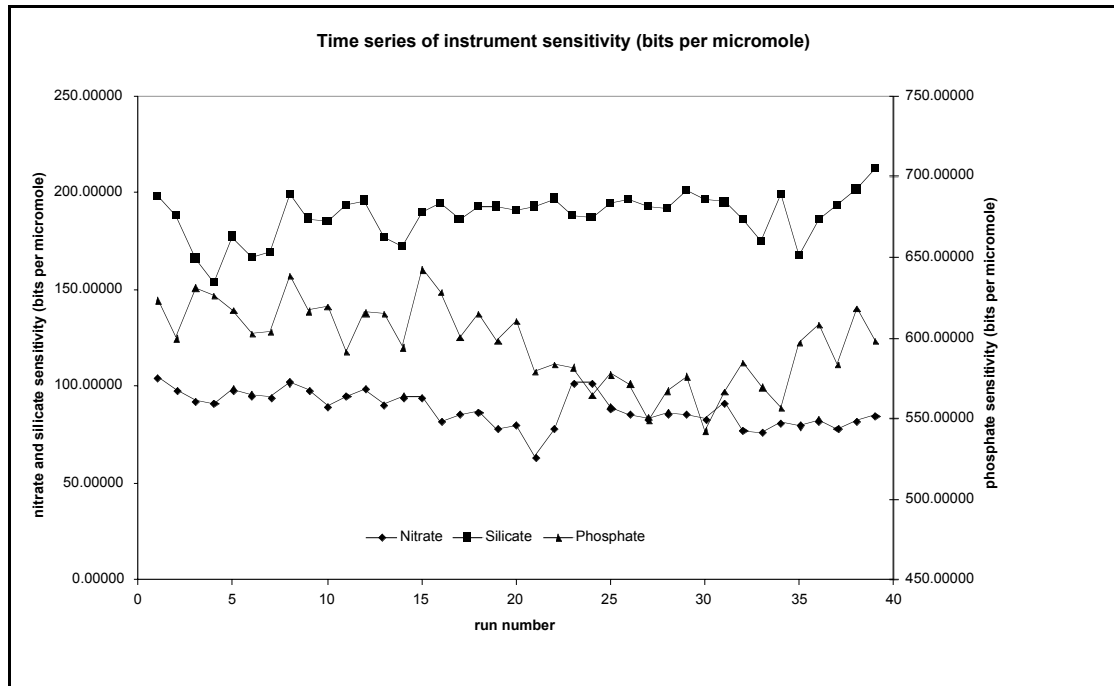


Fig. 5.1 Time series of instrument sensitivity (bits per micromole)

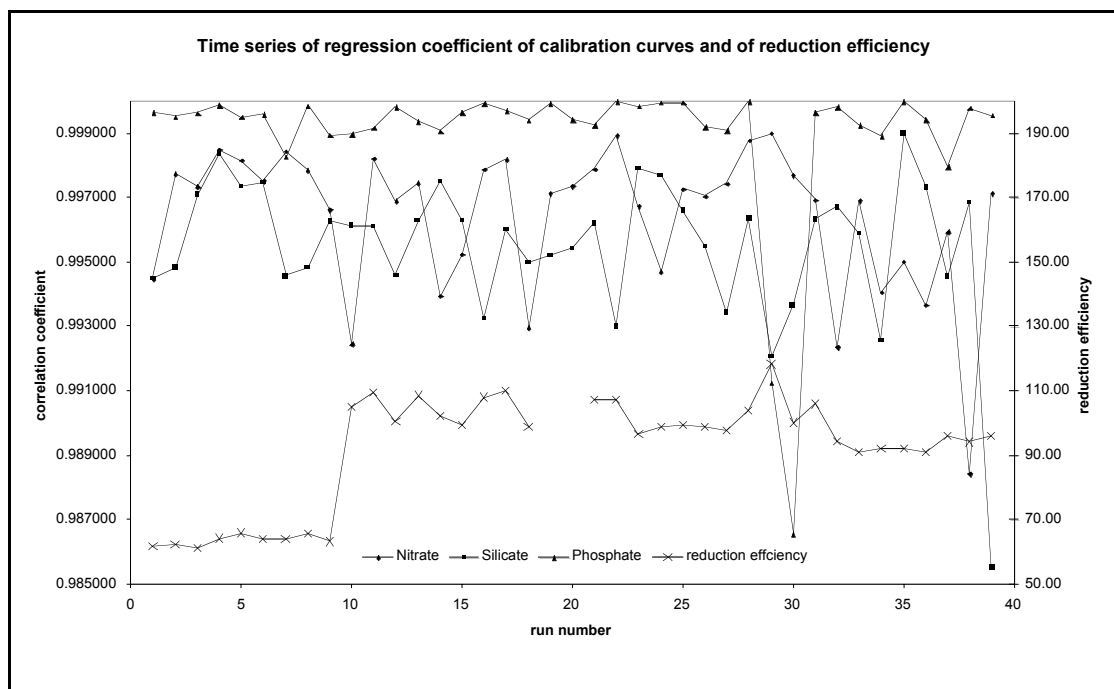


Fig. 5.2 Time series of regression coefficient of calibration curves and of reduction efficiency

Analyser performance

The performance of the autoanalyser is monitored via the following parameters: baseline value, calibration curve slope, regression coefficient of the calibration curve, nitrate reduction efficiency. Time series of these parameters are shown in Figures 5.1-5.5.

The instrument sensitivity for nitrate and silicate varied by only 10%, though a few runs did vary by up to 40%. Phosphate sensitivity behaved much more reproducibly with these parameters varying by about 10% over the 5 week period of observations.

For nitrate and silicate, a 2nd order bent calibration curve was fitted to the standards. A linear regression was fitted to the phosphate standards. The quality of the calibration curves was generally good with 95% having regression coefficients of better than 0.993 for silicate and nitrate, and 95% having regression coefficients of better than 0.999 for phosphate. The reduction efficiency of the cadmium column was 60% during the early part of the cruise due to an error in diluting the nitrite standard. This increased to approximately 100% after run 9 at which point we changed the nitrite standard. Then the efficiency increased to approximately 100%. The change of the column on the 30th November had no discernable effect on the reduction efficiency.

The baseline value of the instrument barely changed through the cruise.

Data quality

Precision of measurements: The short term precision of the measurements was evaluated by running one duplicate sample per station. Figure shows time series of the ratio between the duplicates for silicate, nitrate and phosphate. The mean ratios for Si, N and P were 1.00, 1.00 and 1.00.

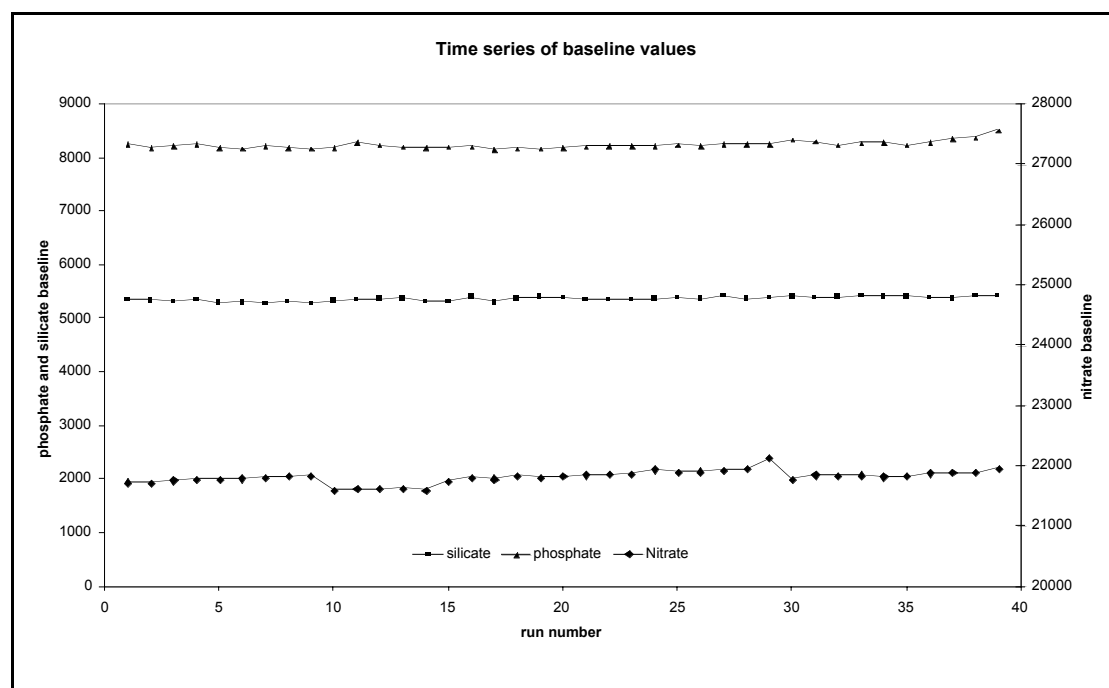


Fig. 5.3 Time series of baseline values

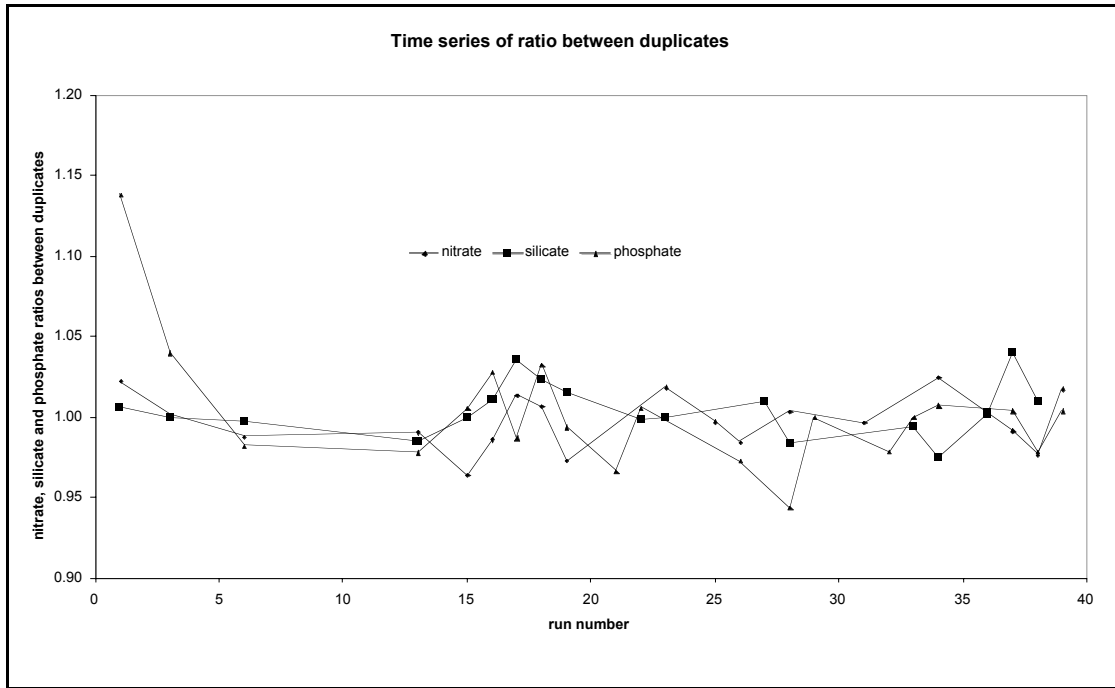


Fig. 5.4 Time series of ratio between duplicates

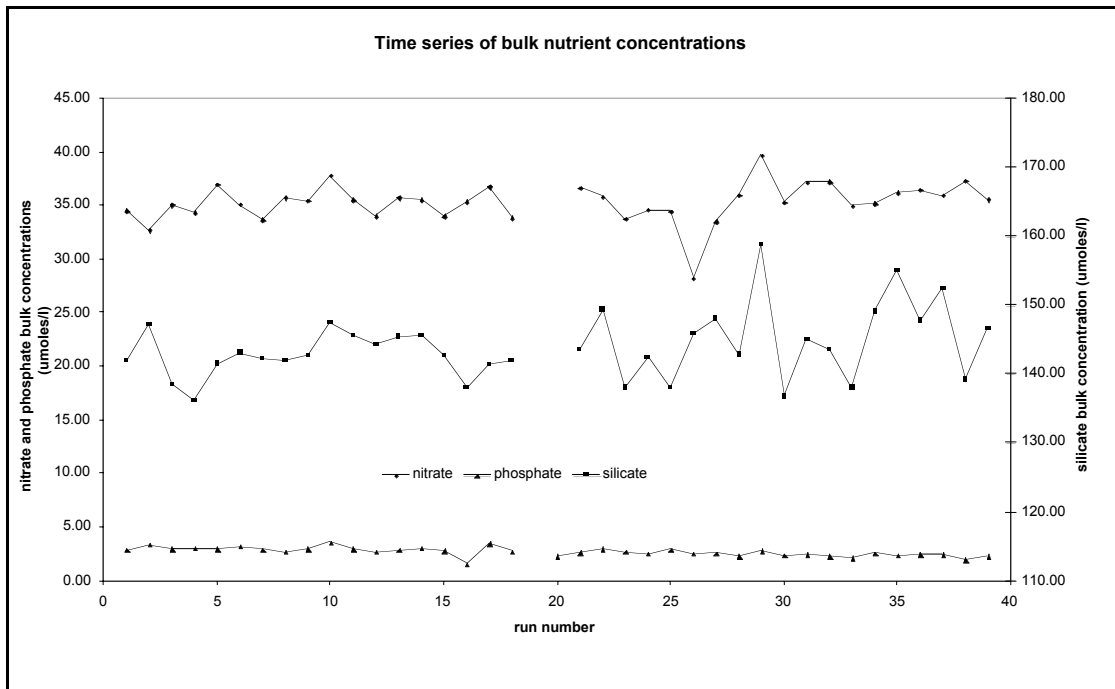


Fig. 5.5 Time series of bulk nutrient concentrations

Internal consistency of measurements: This was evaluated by using a deep water sample taken on station 1. This was run on every station. The concentrations of nitrate, phosphate and silicate in this sample over time are shown in Figure. Despite some variability, especially in the silicate lines, there was no overall degradation of the bulk

samples and the data points are normalised about the mean values which are for N, 35.29 umoles, Si, 144.00 umoles and for P, 2.70 umoles.

Samples taken

Samples were taken for analysis from the three types of CTD cast undertaken and the non-toxic water supply. All samples were run within 24 hour of being collected and were kept at 4oC in a fridge. There were approximately 400 samples taken from the non-toxic supply with a sample being taken at least once an hour, though sometimes more regularly if we were passing by an interesting feature or water mass.

All three different CTD casts (standard, thorium and iron casts) were samples from. From the 24 standard casts, approximately 550 samples were taken. They were taken from each bottle, even if several bottles were fired at the same depth. From the 10 thorium casts, there were approximately 90-100 samples were taken. 9 or 10 samples were taken from each of the thorium casts and these represented the 9 or 10 depths at which the bottles were fired. Depths weren't repeated from this cast although the final cast did have three replicas from 125m. There were also 12 iron casts using the titanium CTD. From these 12 casts there were approximately 200 samples. One sample was taken from each bottle depth and the depths were not repeated if more than one bottle was fired at the same depth. The only times samples weren't taken from any CTD bottle was when the bottle had been leaking as it hadn't shut properly. The only exceptions to this were thorium casts 15512 and 15523 when no nutrients were taken. The reason for this is unclear, but maybe a lack of communication.