Dissolved Trace Metals

Sampling

Samples for trace metal analysis were collected, using clean techniques, in 10 litre Teflon-lined Go-Flo bottles, modified to reduce the contamination potential for trace metals, fitted to the CTD rosette sampler. Initial sample handling for trace metals was carried out on board using the facilities of the RVS clean chemistry container (Morley et al., 1988).

Each sea water sample was pressure-filtered (ca. 0.7 bar) in-line through a 0.4 µm Nuclepore membrane filter. The filtrate (samples for dissolved metal analysis) were acidified to ca. pH 2 by the addition of sub-boiled nitric acid (1 ml per litre of sea water) in order to stabilise the total-dissolved concentrations of metals. For a substantial proportion of the samples large volume filtration systems were used to obtain sufficient suspended particulate material for trace metal analysis.

The filters were stored and processed for particulate trace metals. Consequently, the particulate and dissolved trace metal data form an integrated data set from a single set of samples using compatible analytical procedures which greatly enhances their value.

Analysis of Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn

This was undertaken using the specialised clean facilities in the Department of Oceanography, University of Southampton. Dissolved metals were extracted and preconcentrated following the dithiocarbamate complexation-freon extraction method of Danielsson et al. (1978), as modified by Statham (1985) and Tappin (1988), and were determined by graphite furnace atomic absorption spectrophotometry (GFAAS). Within batch analytical precision of the method is generally less than 10% (coefficient of variation) for each metal. More details of the method are given in Tappin et al. (1992).

Quality control (i.e.. accuracy and between batch analytical precision) of the data was assessed by regularly analysing aliquots of the CASS-1 coastal sea water reference sample for dissolved trace metals and a bulk filtered acidified sea water sample which was used for batch-to-batch quality control.

Results of these analyses were satisfactory, with very few exceptions, and ensure that the data are of high quality.

Additionally, the data set was examined to identify any values which appeared to have been affected by contamination on the basis of supporting data. Only an insignificant fraction of the total data were shown to have been contaminated and rejected.

Analysis of aluminium

An aliquot of the water sample was separately vacuum filtered through a 0.4 µm Nucleopore membrane and analysed for aluminium using the method of Hydes and Liss (1972). The complete analytical procedure was undertaken at sea, usually in the general laboratory.

It should be noted that whilst most samples were collected using the ultra-clean trace metal bottles described above, a few were collected using standard 10 litre Go-Flo bottles. As a general rule if there is aluminium data for a sample but no other trace metals then it should be assumed that a standard bottle was used to collect the sample.

Analysis of arsenic

A separate aliquot of water was filtered, in the clean laboratory, through a 0.45 µm Millipore filter for arsenic analysis. The samples were stored at 4°C to reduce biological activity and keep losses of monomethyl arsenic (MMA) and dimethyl arsenic (DMA) to a minimum. Nevertheless, some losses were inevitable as the samples had to be stored on board ship for the cruise duration (up to 2 weeks) and subjected to a 2-3 week analytical procedure. These losses have been quantified for samples from the Tamar Estuary in Kitts (1991).

The technique used for inorganic arsenic was to add 6M Analar HCl and 2 per cent Spectrosol $NaBH_4$ solution to the water sample to generate arsines. These were purged from the apparatus by a stream of nitrogen for analysis by flame atomic absorption spectroscopy.

MMA and DMA were analysed using a similar technique using a lower acid concentration (1M) to favour the formation of organic arsines. The lower concentrations required the incorporation of an arsine trapping procedure. The nitrogen purgative, dried by NaOH traps, was passed through a glass U tube packed with glass beads cooled to -196°C by liquid nitrogen. The trap was allowed to gradually warm to room temperature giving up the trapped arsines as a series of pulses, thus achieving separation of the arsenic species. Each species was analysed by flame atomic absorption spectroscopy.

A full description and discussion of the analytical techniques is given in Kitts, 1991.

Analysis of mercury

Reactive mercury, i.e. mercury which can be determined without prior oxidation, was determined by the reduction of the mercury in the acidified sample to elemental form by the addition of tin (II) chloride. This was then removed from solution by purging with oxygen-free nitrogen and the mercury vapour trapped as an amalgam on gold chips. Once purging was complete, the gold chips were inductively heated to vaporize the mercury as a pulse which was quantified by atomic absorption spectroscopy.

Total mercury was measured by the above method on samples which had been oxidised by addition of hydrochloric acid, potassium bromide and potassium bromate. Samples were left to oxidise for at least an hour before the bromine was reduced by the addition of excess hydroxylammonium chloride solution.

Total mercury was determined on both unfiltered sea water and on sea water which had been filtered through an ashed (450°C for 24 hours) GFF filter paper. Reactive mercury was determined on filtered samples only. Full details of the methodology are given in Harper et al (1989).

References

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