Plume Cruise Box Core Studies

Sampling

The cores were obtained using an SMBA (now DML) box corer deployed over the 'A' frame at the stern of the ship. This provides a square core approximately 0.25 m^2 in area and 30 cm deep.

Subcores were carefully extracted from the box cores using hand corers for sedimentological analysis, redox profile determination and microcosm incubation.

Determination of whole core properties

Particle size distributions were determined by wet sieving 1cm sections of a subcore. Classification was made according to the Wentworth scale. Median particle size, degree of sorting and the proportion of silt (<63 µm) were determined from the grain size distribution.

Redox potential profiles were determined at 0.5 or 1.0 cm intervals using a platinum electrode with a combination Ag/AgCl electrode mounted in a rack and pinion profiler.

To minimise errors due to electrode poisoning and variability in liquid junction potentials the electrode was cleaned before determining each profile and checked against two redox standards (pH4 and pH7 buffers saturated with quinhydrone). Profiles were only taken if the combination electrode potential was within 10 mV of the theoretical standard values. Errors due to lack of redox equilibria in the sediment were reduced by allowing 1 minute for stabilisation at each step in the profile. Redox potentials were reproducible to +/- 20 mV.

Porosity was determined by freeze drying core sections of known volume taken using a piston corer. Determinations were reproducible to +/- 5 per cent.

Depth profiles of total carbon and total nitrogen were determined on freeze dried vertical core sections. Samples were ground and homogenised in an agate ball mill and analysed in a Carlo Erba 1106 combustion analyser to a precision better than 1 per cent.

Core incubations and pore water extraction

The subcores, approximately 5.4 litres volume and 0.2 m deep, were incubated in Perspex cylinders. The samples were overlain by 2.8 litres of sea water, obtained using the CTD rosette sampler and stored in a nonmetallic tank, supplied at a flow rate of approximately 0.75 litres per hour by perisaltic metering pumps.

Pore water samplers (Watson and Frickers, 1990) were located in the top 10 cm of the sediment capable of providing samples at 1 cm depth intervals. Samples were obtained without atmospheric contact.

Pore water analysis

Pore water samples were filtered through 0.45 µm Millipore filters and analysed using the following techniques.

pH was measured using a Corning 109 meter in conjunction with a glass electrode and a double junction reference electrode. Before measurements were taken, the pH meter was calibrated using buffer solutions of pH 7 and pH 9.

Alkalinity, defined as the amount of hydrogen ion needed to convert all the anions of the weak acids to their unionised acids, was determined by pH potentiometric titration using an E 636 Titroprocessor. Hydrochloric acid (0.01N) was titrated against 5 ml of the sample until the final end-point was reached. Alkalinity was computed from the required titre.

Ammonia was analysed by a flow injection technique. This is a rapid and sensitive technique based on the conversion of the ammonium ion in sea water into gaseous ammonia across a hydrophobic membrane. The method has a sensitivity of 0.05 μM and is linear up to about 50 μM.

Further details of the method, including a schematic diagram of the system, are given in Howland et al. A description of the development of the method and the gas diffusion cell is given in Willason and Johnson (1986).

Other nutrients were determined using a Technicon AA2 autoanalyser. The method used for phosphate was based on the reduction of a phosphomolybdate complex in acid solution to 'molybdenum blue' by ascorbic acid with sensitivity enhanced by the catalytic action of antimony potassium tartrate.

The method used for silicate was based on the reduction of a silicomolybdate in acidic solution to 'moybdenum blue' by ascorbic acid. Oxalic acid is introduced into the sample stream before the addition of ascorbic acid to eliminate interference from phosphates.

Nitrate was reduced to nitrite by a Cu/Cd reduction coil. The nitrite was then reacted with sulphanilamide in acidic conditions to form a diazo compound which then couples with N-1-napthylethylenediamide dihydrochloride to form a reddish purple azo dye. With this method nitrite interference cannot be eliminated and consequently the parameter measured is nitrate plus nitrite.

Nitrite was analysed by the same method as nitrate with no reduction prior to complexing.

In all cases the colorimeter output was to a chart recorder. Data processing, essentially a peak height comparison between samples and standards, was undertaken manually.

The trace metals Fe, Mn, Zn, Ni, Cu, Cd, Pb were analysed using a method based on that of Danielsson et al (1978). The metal species were converted into their dithiocarbamate complexes, extracted into Freon and back extracted into a small volume of dilute acid. Metal concentrations in the resulting solutions were determined by atomic absorption. Precautions taken against contamination included the use of acid cleaned plastic and glassware, a clean environment for sample handling and the use of high purity reagents.

Arsenic species were determined using the following protocol. 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).

Trace metal data were supplied to BODC in units of µg/l. These were converted to nanomolarities by multiplying by 1000 and dividing by 74.922 (As), 139.97 (MMA), 137.998 (DMA), 112.4 (Cd), 63.54 (Cu), 55.847 (Fe), 54.938 (Mn), 58.69 (Ni), 207.19 (Pb) or 65.37 (Zn).

Diffusional flux determinations

The diffusional fluxes were determined by analysing two samples of the overlying water from the microcosm. Initial samples were taken from the microcosm outflow. The input flow was then stopped and the samples allowed to incubate with continuous gentle stirring for 5-6 hours. A second sample was then extracted by siphoning.

The samples were filtered though 0.45 µm Millipore filters and analysed as described above for pore water samples. Fluxes were calculated from the concentration difference, length of incubation and core sample area.

Resuspension flux determinations

Resuspension fluxes were determined by taking a sample from the overlying water and then increasing the stirring rate to a level sufficient to disturb the surface sediment. A second water sample was taken after vigorous stirring for about five minutes. Both samples were filtered through 0.45 µm Millipore filters. The filter for the second sample was pre-weighed to allow the suspended matter concentration induced by the simulated resuspension event to be determined.

Once filtered, the samples were analysed using the techniques described above for pore water chemistry. The resuspension flux was calculated from the resulting concentration difference and the area of the incubated core sample.

References

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