SO_DYFAMED Time Series - 1991-> ...

JC. MARTY : head of mission and project leader

Diss. Org. Carbon : **DOC** : G. COPIN, B. AVRIL

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METHOD

DOC Analysis (1991-1994 samples)

We mostly followed the sampling and analytical procedures presented earlier by Copin-Montégut and Avril (1993). DOC concentrations were obtained on discrete water samples (24 to 36 depths) after GF/F filtration using an HTCO method that is now widely accepted (Sharp *et al.*, 1995). Samples were stored in 100-ml glass flasks, at 4°C and in darkness, after addition of 0.1 ml of a saturated $HgCl_2$ solution. The storage procedure prevents thermal and photochemical degradations and the poisoning stage prevents any further biological evolution of the DOM pool. The day following the cruise, samples were filtered gently (P<150 mm Hg) on precombusted (450°C, usually for 12 h.), prewashed (200-ml Milli-Q water) Whatman GF/F (0.7-µm porosity) filters. The poisoning and filtration procedures were consistent with JGOFS protocol for DOC analysis (JGOFS, 1996). However, it is noteworthy that DOC (as practically determined) incorporates some limited amounts of small particles and colloids which could include some living biomass such as bacteria or viruses, and to a smaller extent, small phytoplankters (*e.g.*, prochlorophytes, and possibly cyanobacteria). Just before their analysis, the samples were acidified to pH 2 using 0.25-ml HCl 2N solution and purged for 10 minutes using purified (quality 45, [CO + CO_2]<2 vpm) synthetic air (20% O_2) bubbling (150-200 $ml.min^{-1}$). The purging stage is required to remove the inorganic carbon initially present in the sample. It also largely removed the volatile organic carbon that might represent about 5% of the initial so-called DOC. The acronym DOC thus represents the non-purgeable 0.7–µm-filtered HTCO-analysable organic carbon.

The analyses were performed using from 3 to 5 repetitive injections on an automatic analyzer of Shimadzu Corp., model TOC-5000. After catalyst conditioning and intensive washing of the catalyst with multiple Milli-Q water injections, and when needed, regular removal of the salty accumulation on the top of the catalyst column, the analytical blank was typically better than 8 µM-C, mainly due to carbon residue in Milli-Q water and to instrumental blank (catalyst). It could be kept consistent over one-day, *i.e.*, throughout the analysis of a complete set of samples, by systematical injections of Milli-Q water before each marine sample. The daily calibration curve was based on 2-3 standard solutions of potassium acid phthalate (0-167 µM-C), with satisfactory regression coefficient (usually r^2>0.998). The accuracy for a single sample was about 2 µM-C.

Copin-Montégut, G., Avril, B., 1993. Vertical distribution and temporal variations of dissolved organic carbon in the North-Western Mediterranean Sea. Deep-Sea Research 40(10), 1963-1972.

Sharp, J.H., Benner R., Bennett L., Carlson C.A., Fitzwater S.E., Peltzer E.T., Tupas L.M., 1995. Analyses of dissolved organic carbon in seawater: the JGOFS EqPac methods comparison. Marine Chemistry 48(2), 91-108.

Determination of dissolved organic carbon concentrations (1999 samples)

Samples for DOC analysis were collected in combusted (450°C for 4-5 h) glass ampoules, flame-sealed immediately after collection and stored frozen (-18°C) until analysis. The samples were not filtered as the POC content of the samples is low at this site (< 3.6 µmol l^{-1} C, Copin-Montégut & Copin-Montégut 1983) and should not, therefore, contribute significantly to the DOC values. The DOC analysis was performed using high temperature combustion on a Shimadzu TOC-5000 total organic carbon analyser. A four-point calibration curve (range: 0 to 200 µmol l^{-1} C) was constructed for each measurement day using potassium phthalate standards prepared fresh in UV-treated Milli-Q water. The instrument blank was assessed using two external standards (Certified Reference Materials, Hansell Laboratory, Bermuda Biological Station). It was between 10 and 12 µmol l^{-1} C for all samples and was subtracted from the measurements. All DOC concentrations reported are the average of three injections from each sample.