## Transfer and Fluxes of Elements in Relation with the Carbon Cycle in the Iberian Upwelling Margin

Roland WOLLAST, Lei CHOU, Kinh Trang DOTANSI, Michèle LOIJENS, Nathalie ROEVROS and Olivier DUFOUR

> Laboratoire d'Océanographie Chimique Université Libre de Bruxelles Campus de la Plaine - C.P. 208 Boulevard du Triomphe B-1050 Brussels, Belgium

## **INTRODUCTION**

Within the framework of the OMEX II-II project, ULB-b has the following specific objectives, contributing to Work Packages II and IV:

- (I) To gain a better understanding of the physical and chemical factors controlling the primary production in order to develop predictive models which can be incorporated in the biogeochemical cycle of carbon in an upwelling system, at the ocean margins;
- (ii) To characterize the suspended matter by its composition in order to evaluate the sources, biogeochemical behaviour in the water column and fate of particulate material in the system studied.

During the first year, ULB-b participated in two cruises: Belgica BG9714 (20 June - 2 July 1997) and Charles Darwin CD110B (5-19 January 1998). In the present report, only the preliminary results obtained for the BG9714 cruise are presented.

The ship track and the stations visited along the Galician coast during the BG9714 cruise are shown in Figure 1. During this cruise, there was a strong thermal stratification at all stations with however a decrease of the temperature gradient at the shallow stations (Figures 2 and 3). Cold water at the surface could only be detected at station 37 along the transect O2N. There was thus no upwelling in the Vigo area except very locally at Cape Finisterre. This distribution of salinity in the surface water indicates on the other hand the input of fresh water from the rias all along the coast with a salinity minimum in front of Vigo. The layer of low salinity water is restricted to the upper 20 meters and is still visible at the 2000m depth stations, as demonstrated by the surface distribution of salinity reported by Frankignoulle *et al.* (Partner 22, this volume).

During the BG9714 cruise, ULB-b performed the following tasks:

- determination of the vertical distribution of orthophosphate, silicate and chlorophyll *a*;
- incorporation experiments of <sup>14</sup>C and <sup>32</sup>P under variable and constant light conditions, including size fractionation experiments and in the case of phosphorus utilisation of biological inhibitors;
- collection of suspended matter by *in-situ* pumping of large volumes of water at various depths;
- collection of suspended matter in surface water by continuous centrifugation.

Samples of suspended matter are analysed for major and trace elements in the laboratory and this task is still in progress. ULB-b also collected nutrient samples for an intercomparison exercise between PML-c, IIM, ULB-b and VUB.

#### **RESULTS AND DISCUSSION**

#### Task II.4.1 Nutrient Oceanography

Nutrient samples were collected and stored at  $4^{\circ}$ C. They were analysed on board manually for orthophosphate and silicate using the molybdate blue methods described in Grasshoff *et al.* (1983). A separate set of samples was collected and kept frozen for the determination of nitrate/nitrite, the analysis of which is still in progress.

Figures 2 and 3 show as an example the vertical distribution of phosphate along two transects (O2N and O2S). The depth over which this nutrient is depleted increases with the bottom depth of the water column. Phosphate is significantly present near the surface only at station 37. Similar profiles have been observed for dissolved silicate with however a relatively larger residual concentration in the euphotic zone near the surface.

## Task II.5.4 Pigment Biomarker

Chlorophyll *a* samples in the upper 200m were collected by filtering water onto GF/F filters. The filters placed in centrifuge tubes were first quickly frozen in liquid nitrogen and then kept frozen in a deep freezer until analysis. The measurements of chlorophyll *a* content were performed using the fluorometric method (Yentsch and Menzel, 1963).

The vertical profiles of the concentration of orthophosphate shown in Figures 2 and 3, indicate clearly that the depth of the maximum phytoplankton biomass increases from the shallow coastal stations to the deep ocean station. The abundance of phytoplankton is nicely correlated with the nutricline. The maximum of chlorophyll *a* is within the upper 20 meters at the shallowest stations and may reach 80 meters at the deepest stations. Similar vertical distributions of chlorophyll *a* were also observed by Gibb *et al*. (Partner 4a, this volume). It is also interesting to note that the concentration of chlorophyll *a* at coastal stations 6 and 37 are very similar although upwelling of cold water with higher concentrations of nutrients has been observed at station 37. This probably indicates that this upwelling event is very young, which confirmed by the remote sensing observations provided by Miller *et al*. (Partner 4d, this volume).

#### Task II.8.3 Parameterisation of primary production

Photosynthesis as a function of irradiance have been determined during the BG9714 cruise by performing <sup>14</sup>C uptake experiments on water samples collected at two depths and incubated under an artificial light gradient ranging from 0 to 600  $\mu$ E m<sup>-2</sup>s<sup>-1</sup>. The incubation time was limited to ~6 hours in order to avoid the effect of rapidly recycled organic compounds. This approach will allow us to evaluate the photosynthetic parameters in the classical Platt *et al.* (1980) equation, describing the relation between the phytoplankton growth rate and irradiance.

$$\boldsymbol{m}^{\text{chl}} = \boldsymbol{m}^{\text{chl}}_{\text{max}} [1 - \exp(-\boldsymbol{a} I / \boldsymbol{m}^{\text{chl}}_{\text{max}}] \exp(-\boldsymbol{b} I / \boldsymbol{m}^{\text{chl}}_{\text{max}})$$

where  $\boldsymbol{m}_{\text{max}}^{\text{chl}}$  is the maximum photosynthetic capacity

 $\alpha$  the photosynthetic efficiency

 $\beta$  the index of photoinhibition

I the incident photosynthetically available radiation (PAR).

Figure 4 shows as an example the rate of uptake of carbon as a function of light intensity observed on water samples collected at 10m depth at the coastal station 8 and at the open ocean station 12 situated on the transect O2S. There is a very good agreement between the experimental data and the theoretical curve which allows one to define the fundamental parameters controlling the influence of light on the primary production. It is interesting to note that for surface samples (10m) there is no photoinhibition ( $\beta$ =0) acting on two phytoplankton communities considered here. Table I gives the parameters  $\mathbf{m}_{max}^{chl}$ ,  $\alpha$  and the light adaptation parameter  $I_k = \mathbf{m}_{max}^{chl} / \alpha$  for the nine stations where the influence of light intensity on carbon uptake was investigated. From the light penetration curve and the vertical distribution of the chlorophyll *a* concentration, it will be possible to calculate the production as a function of depth, which can be integrated on a daily basis from the incident light intensity recorded on the deck of the ship. It should be pointed out that we encountered technical difficulties in the light measurement in the water column and not all light profiles can be exploited at the time being.

The potential production was also investigated at various stations by measuring the <sup>14</sup>C incorporation during incubation experiments under constant light conditions (80, 188 and 530  $\mu$ E m<sup>-2</sup>s<sup>-1</sup>). Size fractionation was performed on the incubated samples by filtering the water through 0.2, 2 and 20  $\mu$ m porosity filters. Typical results are shown in Figure 5 where only results for the less and greater than 2  $\mu$ m size are indicated. The distributions of potential primary production mimics very well the distribution of chlorophyll *a*. In other words the maximum photosynthetic capacity is very similar for all the stations. Also, the picoplankton (< 2 $\mu$ m) is dominant everywhere.

## Task II.8.5 Assimilation and regeneration of phosphorus

The rate of assimilation of <sup>32</sup>P by phytoplankton was determined during the BG9714 cruise also at two depths (surface and chlorophyll maximum) at 9 stations under well controlled conditions similar to those for <sup>14</sup>C. Samples were additionally incubated with the addition of sodium azide in order to evaluate the fraction of <sup>32</sup>P uptake due to abiotic processes such as passive adsorption. The contribution of the heterotrophic bacteria to the assimilation of phosphorus was investigated by performing incubation experiments using antibiotics (a mixture of Streptomycin Sulfate and Polymyxin B Sulfate) on the same water sample, and by size-fractionated uptake (0.2µm and 2µm). Figure 6 shows as an example size fractionated assimilation of phosphorus at three stations situated across the slope along the transect O2N off Cape Finisterre. It indicates that similar to the results obtained during OMEX-I, in all cases the phosphorus uptake is dominated by the fraction less than 0.2µm. Incubations in the dark shows the importance of non-photosynthetic uptake with respect to that due to photosynthesis. The role of bacterial activity is clearly demonstrated by comparing uptake rates under constant light conditions with and without the addition of antibiotics. The contribution of the heterotrophic activity can be as high as 80% of the overall assimilation, which is further confirmed by the dominance of the smaller size fraction. The incorporation of this element due to inorganic processes represents less than 10%.

A limited number of incubations were performed during a short period of time (6 hours) under variable light conditions in order to evaluate the dependence of the uptake rate of phosphorus as a function of light intensity. Figure 7 gives one example for Station 37. Using the same approach as described in the previous section for <sup>14</sup>C, one can derive the photosynthetic parameters for the phosphorus assimilation. The curve in Figure 7 corresponds to a  $\mathbf{m}_{max}^{chl}$  of 1.76 nmol PO<sub>4</sub> ( $\mu$ g Chl)<sup>-1</sup>h<sup>-1</sup>,  $\alpha$  of 0.0158 nmol PO<sub>4</sub> ( $\mu$ g Chl)<sup>-1</sup>h<sup>-1</sup>( $\mu$ E m<sup>-2</sup>s<sup>-1</sup>)<sup>-1</sup> and I<sub>k</sub> of 111  $\mu$ E m<sup>-2</sup>s<sup>-1</sup>.

#### Task II.5.1 Biomineral and Lithogenic Composition

Suspended matter collected by centrifugation and *in-situ* pumping are analysed for major, minor and trace elements to distinguish the biogenic from lithogenic fraction. The biogenic elements include particulate organic carbon (POC), particulate nitrogen (PN) and calcium carbonate (CaCO<sub>3</sub>). POC/PN will be determined, if there is sufficient material collected, by high temperature catalytic combustion using a CHN analyser (Fisons). Calcium carbonate is measured using the same method, by analysing the particulate inorganic carbon content (PIC) and by determining the total Ca content. The major particulate elements (Al, Si, Fe, Na, K, Mg, Ca ) and trace elements (Mn, Cr, Co, Ni, Cu, Zn, Cd and Pb) are determined with Inductively Coupled Plasma emission spectroscopy after complete digestion of the samples with a HNO<sub>3</sub>-HCl-HF mixture.

Figure 8 shows as an example the vertical profiles of particulate major and trace elements at two

contrasting stations along the transect O2N. The surface suspended matter at the shelf station 37 is dominated by particles of continental origin as reflected by its high Al content. On the other hand, at the oceanic station 42 the surface particulate material is significantly diluted by the organic matter and contain less particulate Al and other major elements representative of terrestrial source. These results will be compared later with the distribution of particulate trace metals observed during upwelling events in order to evaluate the influence of phytoplankton on the biogeochemical behaviour of trace elements.

## Task IV.3 Nutrients, Trophodynamics and Fertility

During the BG9714 cruise, ULB-b collected filtered samples for a nutrient intercalibration exercise among PML-c, IIM, ULB-b and VUB. The results of intercomparison are presented in the report of Joint *et al.* (Partner 4c, this volume).

#### REFERENCES

- Frankignoulle M., A. Borges and K.T. Dotansi (1998) Preliminary results of the distribution of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and related parameters off the Galician coast, in summer 1997 and winter 1998. OMEX II-II First Annual Report.
- Gibb S.W., D.G. Cummings and R.F.C. Mantoura (1998) Pigment biomarkers and dissolved organic matter fluxes, Part A. Phytoplankton pigment biogeochemistry across the Iberian shelf. OMEX II-II First Annual Report.
- Grasshoff K., M. Ehrhardt and K. Kremling, editors (1983) *Methods of Seawater Analysis*. Verlag Chemie, 317 pp, 2nd edition.
- Joint I., A. Pomroy and A. Rees (1998) Primary, new and size fractionated primary production. OMEX II-II First Annual Report.
- Miller P., S. Groom, T. Smyth and S. Lavender (1998) Remote sensing in OMEX II-II. OMEX II-II First Annual Reprot.
- Platt T., C. L. Gallegos and W. G. Harrison (1980) Photoinhibition of photosynthesis in natural assemblages of marine phytoplankton. *J. Mar. Res.*, **38**, 687-701.
- Yentsch C.S. and D.W. Menzel (1963) A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. *Deep-Sea Res.*, **10**, 221-231.

# **BELGICA 9714**



Figure 1. Ship track and sampling stations of the Belgica BG9714 cruise.



Figure 2. Vertical profiles of temperature, salinity, chlorophyll and phosphate in the upper 200m along the transect O2N.

σ



Figure 3. Vertical profiles of temperature, salinity, chlorophyll and phosphate in the upper 200m along the transect O2S.

7



Figure 4. P-I curves obtained at a shelf station (St. 8) and an open ocean station (St. 12).

Station	$m_{ m max}^{ m chl}$	α	I <sub>k</sub>	chloro		$m_{ m max}^{ m chl}$	α	I <sub>k</sub>	β	chloro	
Shelf -200m line											
	-10m					-60m					
2	0.82	0.0041	200	0.28							
8	0.93	0.0052	180	0.33		1.57	0.0075	210	50	0.36	
19	0.65	0.0035	185	0.31		0.82	0.0042	195	5	0.07	
25	0.41	0.0023	180	0.29		0.048	0.0006	76	1.2	0.77	
37	0.77	0.0045	170	0.68		0.15	0.0012	165	9.3	0.03	
Open ocean											
	-10m					-60m					
12	0.72	0.0044	163	0.11		0.62	0.0036	170	49	0.65	
29	0.50	0.0024	205	0.12		0.42	0.0047	90	15	0.47	
40	0.94	0.0052	180	0.12		0.67	0.0038	175	38	0.75	
42	0.79	0.0041	190	0.09		1.58	0.0102	155	27	0.22	

Table 1.	Photosynthetic parameters determined from experiments conducted under variable light
condition	18.

$$\begin{split} \boldsymbol{m}_{max}^{chl} & \text{ in } \mu g \ C \ (\mu g \ Chl)^{-1} h^{-1} \\ \alpha \ \text{ and } \beta \ \text{ in } \mu g C \ (\mu g \ chl)^{-1} (\mu E \ m^{-2} s^{-1})^{-1} h^{-1} \\ I_k \ \text{ in } \mu E \ m^{-2} s^{-1} \\ Chlorophyll \ a \ \text{ in } \mu g/l \end{split}$$



**Station 40** 

Station 37



**Station 29** 

0,1

0

0

(m) 40 DEPTH (m)

80

µMC/hr

0,2

0,3

0,4





**Station 25** 













3000m

~2000m



Figure 6. Size-fractionated assimilation of phosphorus measured at 188  $\mu$ E m<sup>-2</sup>s<sup>-1</sup> at stations along the O2N transect. CL denotes constant light, ANCL constant light with antibiotics added, D dark, AND dark with antibiotics added, AZ inhibition with azide.



Figure 7. Assimilation of phosphorus as a function of light intensity.



Figure 8. Vertical profiles of particulate major and trace elements at station 37 (shelf) and station 42 (oceanic) along the transect O2N.