Preliminary results of the distribution of the partial pressure of CO$_2$ (pCO$_2$) and related parameters off the Galician coast, in summer 1997 and winter 1998

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**Introduction:** The role in the global inorganic carbon cycle of continental shelf seas influenced by seasonal upwelling remains controversial because they are sites of processes that have antagonist effects on the flux of CO$_2$ across the air-sea interface. Upwelling brings to the shelf water oversaturated in pCO$_2$ with respect to the atmosphere. This water also has an important nutrient content which enhances primary production that in turn reverses the air-sea gradient of pCO$_2$. To improve our understanding of these regions more field data is needed with an adequate resolution at both daily and seasonal time scales. The net annual air-sea flux of CO$_2$ can then be estimated from calculations. The main objective of the ULg in the OMEX project is to contribute to the understanding of inorganic carbon dynamics and identify sources/sinks for atmospheric CO$_2$. To meet this objective two approaches are used: the mapping of surface of pCO$_2$ and the description of the vertical distribution of inorganic carbon both with a Lagrangian (OMEX WPI) and Eulerian (OMEX WPII) approaches.

**Methodology:** The determination of pCO$_2$ is carried out using both direct and indirect methods. The direct one consists to equilibrate seawater with air and then measure CO$_2$ using an IR analyser. The indirect method relies on the calculation of pCO$_2$ from experimental determination of pH and Total Alkalinity. These measurements can also been used to calculate the dissolved inorganic carbon (DIC) which will be used, together with dissolved oxygen (Winkler method and polarographic electrode) to discuss CO$_2$ dynamics with linked biological, physical and chemical processes.

**Status of research (Table 1):** Task I.2 and I.7: Work will start with the first WPI cruise in August 1998 (Charles Darwin CD114). Task II.4.2: AOU data was obtained during the Belgica 97/14 (June 1997) and the CD 110B (January 1998) cruises; data processing is complete. Task II.7.1: Surface mapping of pCO$_2$, pH, O$_2$ was accomplished during Belgica 97/14 and CD 110B cruises covering upwelling and downwelling situations; data processing is complete. Two more cruises are planned for the near future on board the Belgica (July 1998) and the Meteor (January 1999). Task II.7.2: Preliminary calculations of air-sea exchange, in collaboration with RISØ, started in May using the Belgica 97/14 data set. Task II.7.3: Intercalibration with GEOMAR of underway pCO$_2$ systems will be carried out during the Meteor cruise in January 1999. Task II.9: AOU data was obtained during Belgica 97/14 and CD 110B cruises and preliminary calculations of air-sea exchange, in collaboration with RISØ, started in May using the Belgica 97/14 data set. Task II.12.2: Surface mapping of pCO$_2$ was accomplished during Belgica 97/14 and CD 110B cruises and preliminary correlations between pCO$_2$ with in situ SST were attempted and discussed with NSS. Task IV.2: work in this task will start when a more complete data set will be available.

**Results:** Figure 1, shows the sampling grids of the Belgica 97/14 cruise (June 1997) carried out at the beginning of the upwelling season and the Charles Darwin CD110B cruise (January 1998) carried out during the downwelling season. Figure 2 shows, that during the Belgica 97/14 cruise the distribution of pCO$_2$ is very heterogenous. The surface water is relatively warm due to thermal stratification except for a narrow band of cool upwelled water close to the coast. The distribution of temperature also shows that upwelling was stronger off cap Finnisterre where oversaturation of pCO$_2$ with respect to the atmosphere was observed (atmospheric equilibrium at 363 µatm). On another hand, in the upwelled waters south of cap Finnisterre, strong undersaturation was observed related to phytoplanktonic activity has shown by the distributions of O$_2$ saturation, pH and fluorescence in Figure 3. To dissipate this apparent contradiction we must take into account the fact that when the strongly undersaturated upwelled water was sampled, 5 days had elapsed since the observation of the
oversaturated upwelled water. We can conclude that during this time laps an important phytoplanktonic bloom developed and reversed the air-sea gradient of pCO$_2$. Finally, moderate undersaturation of pCO$_2$ was observed in the offshore areas and strong undersaturation of pCO$_2$ was also observed at the mouth of the Vigo Ria. Figure 4, shows clearly the different surface water masses sampled. The stratified offshore water shows a relatively constant pCO$_2$ (338 µatm) as opposed to recently upwelled water that shows pCO$_2$ values between 260 and 390 µatm in relation to the occurrence of antagonistic processes discussed above.

Figure 5 shows the distribution of surface parameters during the CD110B cruise. The distribution of salinity shows that the fresh water from the rias are trapped by the convergence front related to downwelling in a narrow band along the coast. The very distinct temperature gradient in the offshore region, suggests the transport from south to north of a warm water mass in relation to the polarward current. The undersaturation of pCO$_2$ was observed through out the sampled area (pCO$_2$ values ranged from 305 to 355 µatm). As expected, primary production measured by IIM was very low so that this process can not explain the observed undersaturation. The other process that may induce undersaturation is the cooling of surface water: the drop of temperature modifies the solubility coefficient of CO$_2$ and induces the decrease of pCO$_2$. This is in agreement with the fact that in the cooler coastal waters, pCO$_2$ values are lower than in the offshore areas. However, the pCO$_2$ distribution does not follow the distribution of temperature in a strict way because vertical mixing is also affecting the distribution of pCO$_2$. This process pushes the pCO$_2$ values towards atmospheric equilibrium and so has an antagonist effect on the distribution of pCO$_2$ in comparison to water cooling.

The vertical distributions of inorganic carbon and dissolved oxygen will be discussed in this report for the Belgica 97/14 cruise along two transects (lines S and N) that illustrate the two hydrological conditions (stratification and upwelling) encountered. Figure 6, shows the vertical distribution of parameters along line S: temperature shows that the thermocline was situated between -20 m and -70 m trough out the transect. The chlorophyll data from ULB shows that the highest phytoplankton biomass was associated to the thermocline but phytoplankton was also present in the mixed layer. The distribution of O$_2$ and pCO$_2$ clearly follow that of phytoplankton confirming that in this situation primary production is the main forcing factor of the surface distribution of pCO$_2$. As expected, below the thermocline water is oversaturated in pCO$_2$. Figure 7, shows the vertical distribution of parameters along line N: temperature shows that upwelling was occurring in the coastal station but that the offshore region remained stratified. The distribution of pCO$_2$ in the offshore area is similar to that described for line S but in the coastal station it is clear that the upwelled water has a high CO$_2$ content and a low O$_2$ content. In both these transects, the lowest values of O$_2$ were observed above the sediments of the shelf. To investigate if this is related to the input from the sediments or just due to different water masses, we plotted the parameters versus temperature for the station closest to the shelf and the station furthest from the coast. In figure 8, the plot of salinity versus temperature shows that the same water mass is present below the thermocline (at low temperature) at the offshore and coastal stations, despite the fact that the coastal station has a lower oxygen content. This is confirmed by the DIC and pCO$_2$ plots. We conclude that the sediments of the shelf enrich in inorganic carbon the bottom water in relation to remineralisation of organic matter. This is related to the fact that the sedimentation of organic matter is stopped by the shelf as opposed to the offshore region. It is interesting to note that this process is present in both transects which means that upwelled water is also enriched by the sediments in inorganic carbon and most probably also in nutrients.

**Conclusion:** Preliminary results of the distribution of the partial pressure of CO$_2$ (pCO$_2$) and related parameters during the first year of activity show that the distribution of pCO$_2$ in surface seawater off the Galician coast during summer is controlled by two antagonistic processes: upwelling and primary production. Our data also shows that the transition from oversaturation to undersaturation of pCO$_2$ in recently upwelled water is accomplished within a few days. Future work during Work Package I cruises, should allow to describe this evolution. The vertical distribution of parameters in summer, are controlled by upwelling, stratification, primary production and remineralisation in the sediments. During winter, two antagonistic processes control the distribution of pCO$_2$: water cooling and vertical mixing. As expected, the influence of the fresh water input from the rias is more marked in winter than in summer.
Table 1: Status of research

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Figure 1: Distribution of stations during the Belgica 97/14 and CD110B cruises. The black crosses correspond to samples from the non-toxic supply. Other symbols correspond to Rosette samples. The red circles correspond to the transects in figures 6 and 7.
Figure 2: Distribution in surface water of $p$CO$_2$ (µatm), temperature (°C) and salinity, during the Belgica 97/14 cruise (June 1997), off the Galician coast.
Figure 3: Distribution in surface water of O₂ saturation levels (%), pH and fluorescence (µg.l⁻¹), during the Belgica 97/14 cruise (June 1997), off the Galician coast.
Figure 4: Plots of salinity and pCO$_2$ (µatm) versus temperature (°C) in subsurface water during the Belgica 97/14 cruise.
Figure 5: Distribution in surface water of pCO$_2$ (µatm), temperature (°C) and salinity, during the CD110B cruise (January 1998), off the Galician coast.
Figure 6: Distribution in the upper layer waters of temperature (°C), pCO₂ (µatm), O₂ saturation level (%) and chlorophyll a (µg.l⁻¹), during the Belgica cruise (June 1997), along the OMEX S line.
Figure 7: Distribution in the upper layer waters of temperature (°C), pCO$_2$ (µatm), O$_2$ saturation level (%) and chlorophyll a (µg/l$^{-1}$), during the Belgica cruise (June 1997), along the OMEX N line.
Figure 8: Plots of salinity, pCO$_2$ (µ atm), DIC (mmol kg$^{-1}$), O$_2$ saturation (%) versus temperature (°C) for both coastal (in red) and offshore stations (in blue), along transects S and N of the Belgica 97/14 cruise (June 1997).