Distribution of surface partial pressure of CO_2 and related parameters off the Galician coast

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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 over-saturated in CO_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 using wind speed, salinity and water temperature. The main objective of the University of Liège in the OMEX II-II project is to contribute to the understanding of inorganic carbon dynamics and identify sources / sinks for atmospheric CO_2.

Methodology: The determination of the partial pressure of CO_2 (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 be used to calculate the dissolved inorganic carbon (DIC) which can be used, together with dissolved oxygen (Winkler method and polarographic electrode) to discuss CO_2 dynamics with linked biological, physical and chemical processes.

*Inorganic carbon dynamics at daily time scale **(Task I.2)**:* Underway measurements of pCO_2 were carried out throughout the *Charles Darwin CD114A* and *B* cruise (29th July to 24th August 1998); vertical profiles of pH, Total Alkalinity and dissolved oxygen were obtained at 33 stations (229 depths). **Figure 1** shows the position of the stations during the three Lagrangian experiments carried out during the cruise. **Figure 2** shows the distribution of subsurface underway parameters along a cross-shelf transect carried out on the 2nd of August, that was used to choose the location for the deployment of the buoy for the Lagrangian experiment of Leg A. The comparison of atmospheric pCO_2 (open circles) and dissolved pCO_2 (full circles) shows throughout the transect under-saturation with respect to atmosphere, related to important primary production as shown by the O_2 distribution. However, close to the coast equilibrium with the atmosphere was observed. This can be related to upwelling (as shown by the distribution of temperature) that brings water with a high content of inorganic carbon. The salinity distribution suggests that the coastal water (between -9.1°E and -9.3°E) where these important gradients of pCO_2 were observed could be related to outwelling from the Ría of Muros. The vertical line in the plots of **Figure 2** shows the site of deployment of the drifting buoy that was used as a water mass marker during the Lagrangian experiment of Leg A. The Lagrangian experiment of Leg A (03.08.98 - 07.08.98) begun on the shelf and the buoy drifted into an upwelling filament. During Leg B, the Lagrangian experiment (14.08.98 - 19.08.98) was carried out in the upwelling filament and the buoy drifted along the northern boundary of the filament except in the last day when the residual current turned inshore and the buoy shifted into the southern boundary of the filament. The third Lagrangian experiment consisted in a daily cycle (09.08.98 - 10.08.98) carried out over the continental shelf. **Figure 3** shows the evolution of subsurface underway parameters during the Lagrangian experiments carried out during leg A, leg B and the daily cycle. During the three experiments, temperature variations were very important. Temperature affects pCO_2 by altering the equilibrium constants of the inorganic carbon system among which the solubility coefficient of CO_2. To filter this factor and concentrate on the effect of biological effects, the pCO_2 values were normalised to an average temperature of 17°C. During Leg A, the overall evolution is the decrease of pCO_2 (17°C) values and the increase of oxygen saturation values, showing that primary production affected these parameters in a significant way. During the first two days of Leg A, it is clear that pCO_2 and dissolved O_2 evolve in periodical way. This can be related to the diel cycle of primary production and respiration. Indeed, the periodical signal of pCO_2 and

O_2 is well correlated to the daily signal of light (data not shown). The fact that this periodical signal disappears after two days can be explained by the fact that during the experiment the maximum of phytoplanktonic biomass shifted from the subsurface to around 30 m (data from IIM and PML; not shown). In parallel, the mixed layer became shallower, shifting from 15 to 5 m (data not shown). Thus, during the last two days of the experiment, the diel cycle of primary production and respiration was not affecting the surface values of pCO_2 (17°C) and O_2 in a periodical way and these parameters tended to stabilise. During Leg B, pCO_2 (17°C) and O_2 were quite stable in comparison to Leg A. This is coherent with other partners' data that show that the mixed layer was nutrient depleted and primary production low. The most noticeable variation was observed in the last day of the experiment when the shift from the northern to southern boundary of the upwelling filament occurred. At this occasion, the oxygen saturation decreased and temperature increased, as water with more offshore characteristics was sampled. During the daily cycle experiment, pCO_2 (17°C) and the dissolved O_2 show a distinct periodical signal with an amplitude of the same order of magnitude as the signal observed during the first two days of the Lagrangian experiment of Leg A. The presence or the absence of a daily periodical signal of subsurface pCO_2 (17°C) and oxygen saturation seems to be related to the amount of phytoplankton close to the sea surface. Indeed, during first two days of the Leg A and during the daily cycle Lagrangian experiments, a daily periodical signal is apparent and the chlorophyll *a* concentration within the first 10 m is respectively of 1.0-1.3 and 0.8 $\mu g\ l^{-1}$ as opposed to 0.2 $\mu g\ l^{-1}$ during the Leg B Lagrangian experiment when a daily periodical signal was absent (chlorophyll *a* data from PML).

Inorganic carbon dynamics at seasonal time scale ***(Task II.7)****:* In 1998 and 1999, underway data was obtained throughout the *Belgica BG9815* (27th June to 7th July 1998) and *Meteor M43/2* (28th December 1998 to 14th January 1999) cruises; vertical profiles of pH, Total Alkalinity and dissolved oxygen were obtained at 51 stations (236 depths) and 12 stations (169 depths) respectively. **Figure 4** shows the distribution of subsurface pCO_2 during the *Belgica BG9815* cruise. The same pattern was observed as during *Belgica BG9714* cruise (Frankignoulle *et al.*, 1998): over-saturation at Cape Finisterre, under-saturation off the Rías Baixas area and values close to saturation offshore. However the amplitude of the gradients of pCO_2 was higher and the spatial extent of the coastal features was larger during *Belgica BG9815* than *Belgica BG9714*. This can be related to upwelling intensity as confirmed by the ship's wind measurements (data not shown). **Figure 5** shows the theoretical evolution with a temperature increase of a water parcel with an original pCO_2 value of 400 µatm at 13.5°C. The in-situ data is below the theoretical curve showing that as newly upwelled water warms (i.e. ages) it is strongly affected by net primary production. At around 15 - 16°C, this trend is reversed and pCO_2 values increase with temperature. Nutrient data obtained by IIM during the cruise show that above 15 - 16°C the mixed layer is nitrate depleted. In absence of significant primary production in the mixed layer, the observed increase of pCO_2 can be explained by the warming of water because temperature affects pCO_2 by altering the equilibrium constants of the inorganic carbon system among which the solubility coefficient of CO_2. This is shown by the parallelism between in-situ data and the theoretical evolution with a temperature increase of a water parcel with an original pCO_2 value of 300 µatm at 16°C. However, this increase of pCO_2 related to temperature only concerns the mixed layer and this does not exclude the fact that if one looks at the entire water column the influence of heterotrophic processes on inorganic carbon could become preponderant as shown in offshore waters by Fernández *et al.* (1999). **Figure 4** shows that the strong under-saturation off the Rías Baixas is related to upwelling however associated to slightly warmer and slightly lower salinity water than off Cape Finisterre. The plot of salinity versus temperature in **Figure 5** shows that a significant number of data points have a salinity lower than the mixing line of ENAW and correspond to strong pCO_2 under-saturation. These observations can be explained by the fact that during an upwelling event, upwelled water enters the Rías where important primary production, mixing with fresh water and warming occurs. This water is then pushed to the shelf by on-going upwelling. In conclusion, the water outwelled onto the shelf from the Rías, is under-saturated in pCO_2, slightly fresher and slightly warmer than surrounding shelf water. This process does not of course occur off Cape Finisterre so that over-saturation is observed in this area. **Figure 6** summarizes the TS diagrams for shelf and shelf break casts that show a clear signal of fresh water input in surface waters (*i.e.*, outwelling from the Rías). To further investigate the role of the Rías in the studied area, **Figure 7** shows a compilation of data obtained in the Ría of Vigo. The Ría of Vigo was sampled in various hydrographic conditions as shown by the temperature plot: strong stratification (20 June 97), strong upwelling (20 August 98) and intermediate conditions - relaxation of upwelling or moderate upwelling - (27 June 98 and 11 August 98). In strong stratified conditions (20 June 97), it is apparent that the influence of fresh water is important in the Ría and on the adjacent shelf as opposed to the other observed hydrographic conditions. During strong upwelling (20 August 98), pCO_2 is higher in the Ría than on the shelf in spite of the fact that water is warmer. This is related to the enrichment of upwelled water in pCO_2 by input from the sediment as described for nutrients in literature (Álvarez-Salgado *et al.*, 1993). In other hydrographic conditions pCO_2 is lower in the Ría than on the adjacent shelf in relation to primary production as shown by the distribution of oxygen saturation and pCO_2 (17°C). **Figure 8** shows that during *Charles Darwin CD114* cruise, the distribution of pCO_2 follows the same pattern as the one described for *Belgica BG9815* cruise. There are however two differences: *i*) outwelling from the Rías of over-saturated water that can be related to strong upwelling as discussed from **Figure 7**; *ii*) the presence of an important upwelling filament extending from 42.3°N -9.4°E to 41.9°N -10.2°E. The upwelling filament is cooler and under-saturated in comparison to surrounding offshore water. **Figure 9** shows the distribution of pCO_2 during the *Meteor M43/2* cruise. During winter, surface water is under-saturated in pCO_2 in relation to cooling of surface seawater because temperature affects pCO_2 by altering the equilibrium constants of the inorganic carbon system among which the solubility coefficient of CO_2. The distribution of pCO_2 also depends on the different water masses present. The saltier and warmer water (ENAW tropical end member) of southern origin that is brought into the area by the poleward slope current has lower pCO_2 values than the ENAW polar end member. The SST satellite data shows that upwelling conditions prevailed during fall and winter 1998 (Miller *et al.*, 1999). This implies that during the *Meteor M43/2* cruise, a mixed situation between upwelling and downwelling was observed. This explains the fact that the effect of the poleward slope current on the distribution and extent of different water masses is not as clear as during the *Charles Darwin CD110B* cruise described by Frankignoulle *et al.* (1998) when 'typical' downwelling conditions were encountered.

*Conclusions and future work **(Task IV.2)**:* During the three first years of the OMEX II-II project, the University of Liège has carried out three summer cruises and two winter cruises (*Belgica BG9714*, *Belgica BG9815*, *Charles Darwin CD114A* and *B*, *Charles Darwin CD110B* and *Meteor M43/2*) during which underway measurements of pCO_2 (78265 data points) and vertical profiles of pH, Total alkalinity and dissolved oxygen (147 stations and 1002 depths) were carried out. These data have been processed and banked at BODC.
The order of magnitude of the variation of pCO_2 at daily scale (~10 µatm) is smaller than at seasonal scale (~200 µatm). The dynamics of subsurface pCO_2 are related to the daily cycle of biological activity (photosynthesis and respiration) when the phytoplanktonic biomass is located close to the sea surface. This depends on nutrient availability in the mixed layer so directly depends on upwelling. The temperature variation in surface water, related to heat exchange, has also a strong effect on the variation of subsurface pCO_2.
The pattern of the distribution of subsurface pCO_2 in the OMEX box during summer is complex but reproducible from one cruise to another: over-saturation at Cape Finisterre, under-saturation off the Rías Baixas area and values close to saturation offshore. This pattern is imposed by the input of over-saturated water by upwelling, primary production, outwelling from the Rías and seawater temperature variation. The variability from one cruise to another is imposed by the intensity of upwelling. The variability consists in the intensity of the pCO_2 gradients, the extent of spatial features, the presence of upwelling filaments and the outwelling from the Rías either of over-saturated or under-saturated water.
During winter in the OMEX box, under-saturation of pCO_2 is observed in relation to cooling of surface seawater. The presence of different water masses related to the poleward slope current also induces variability, the saltier and warmer ENAW tropical end member being characterised by lower pCO_2 values than the polar end member of ENAW. The variability from one cruise to another depends on the intensity of the poleward slope current related to general meteorological conditions.
Future work by the University of Liège:

- Cruise aboard the *Belgica* in late August 1999.
- Computation and integration of exchange of CO_2 across the air-sea interface.
- Modelling of inorganic carbon dynamics at seasonal and daily time scales in collaboration with

SINTEF, IST and NIOO. Conceptual aspects of modelling were discussed during the Trondheim (18.02.99 - 21.02.99) and Plymouth (25.03.99 - 27.03.99) meetings. Lagrangian experiments and macroscale distribution of subsurface pCO_2 are in relation to the work of University of Liège the two main objects of modelling. The interannual variation observed during the two winter cruises should make a challenging test case for task I.7.

- The intercalibration with GEOMAR of equilibrators was carried out during the *Meteor M43/2* cruise. The data from the University of Liège has been processed and made available to GEOMAR.

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Figure 1: Position of the three Lagragian experiments during *Charles Darwin* CD114 cuise

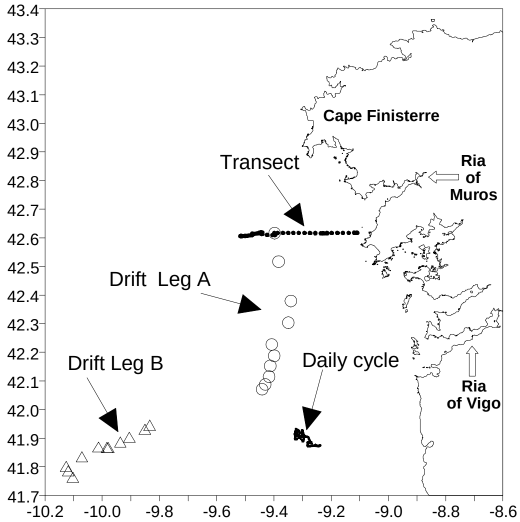


Figure 2: Distribution of underway parameters along cross-shelf transect of Figure 1

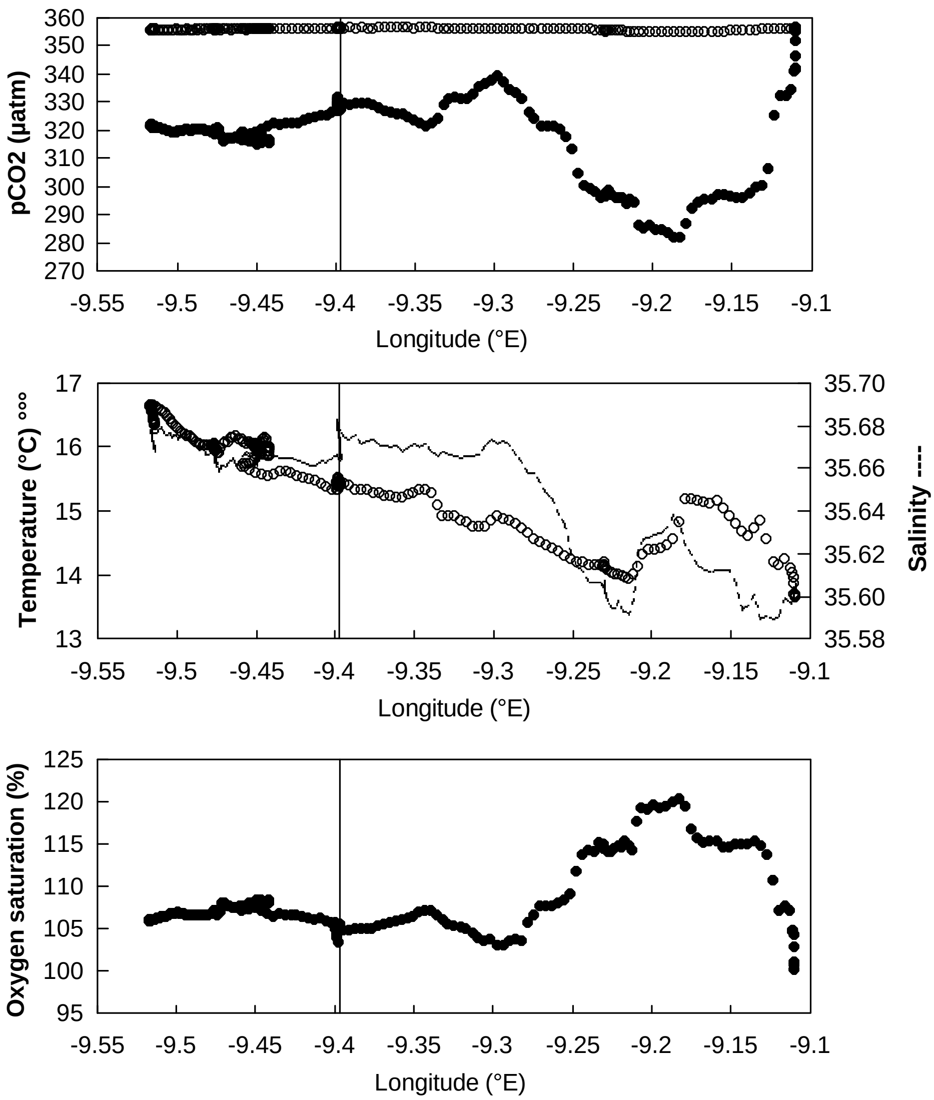


Figure 3: Evolution of underway parameters during the three Lagrangian experiments during *Charles Darwin* CD114 cruise

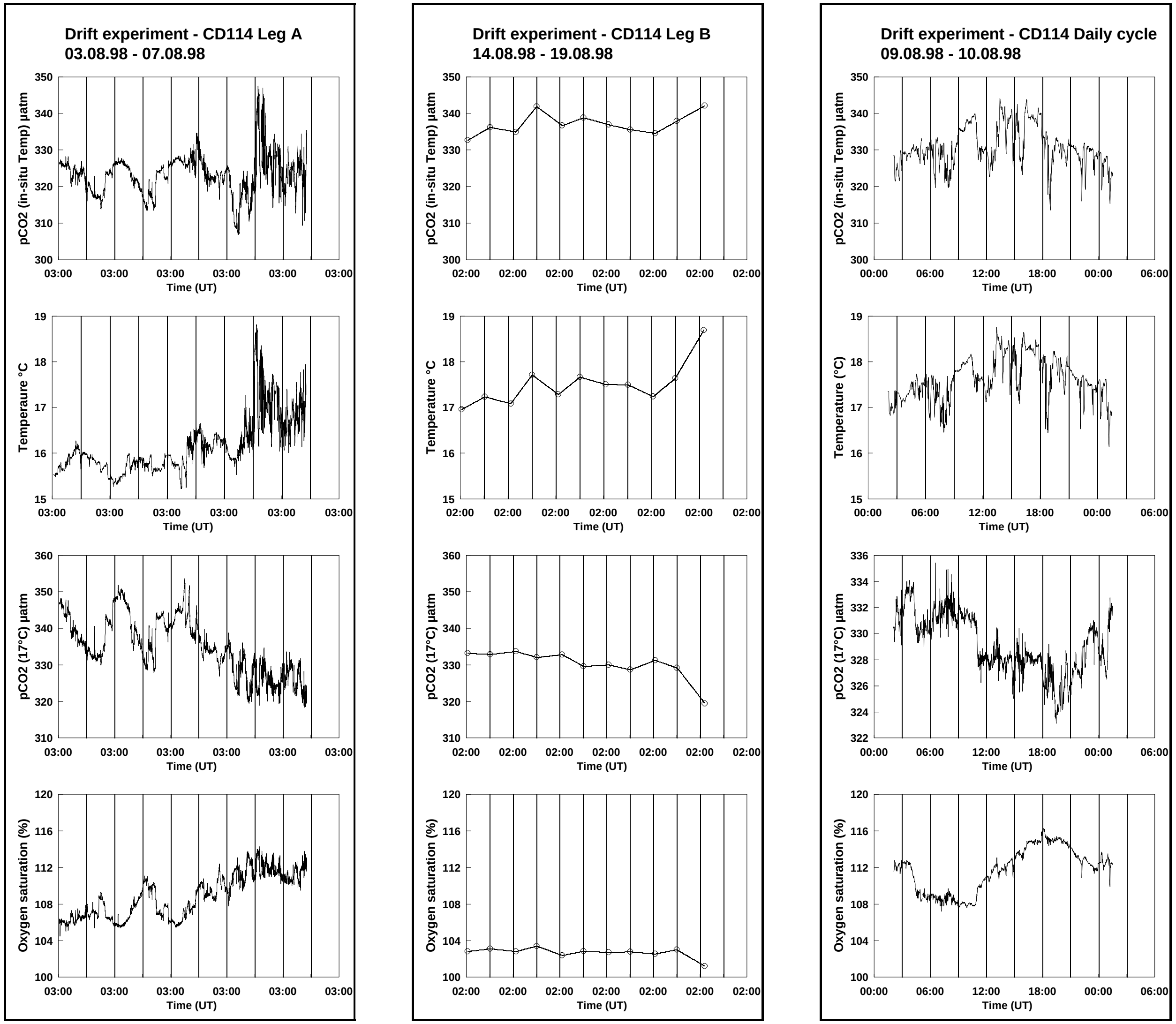


Figure 4: Distribution of underway parameters during *Belgica* BG9815 cruise

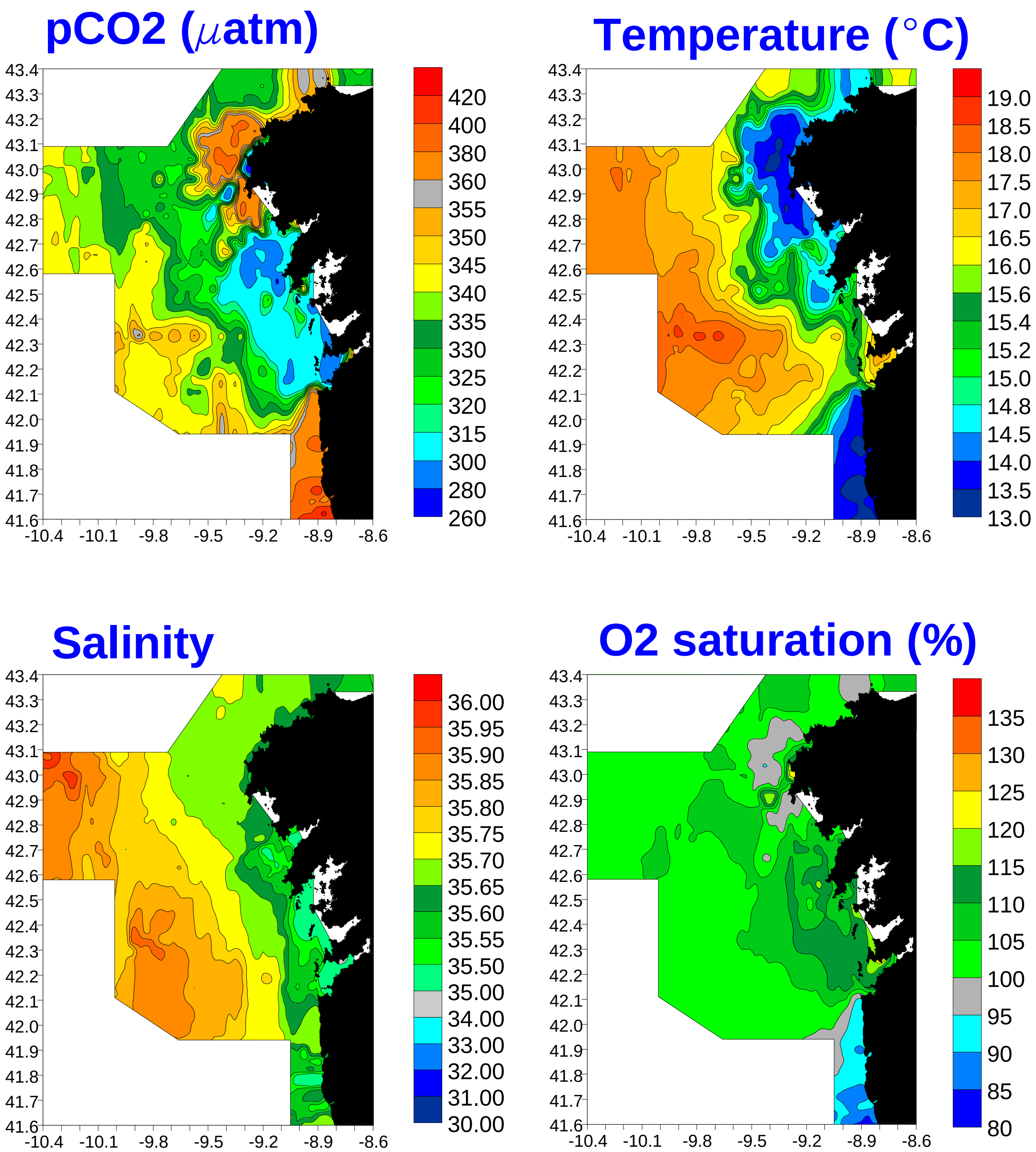
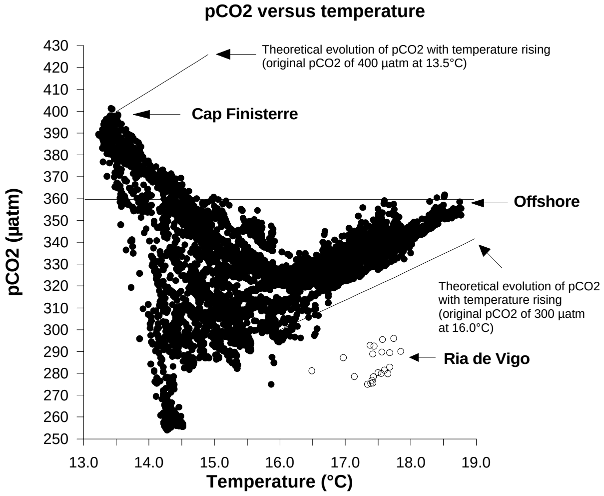


Figure 5: Distribution of underway parameters *versus* temperature during *Belgica* BG9815 cruise



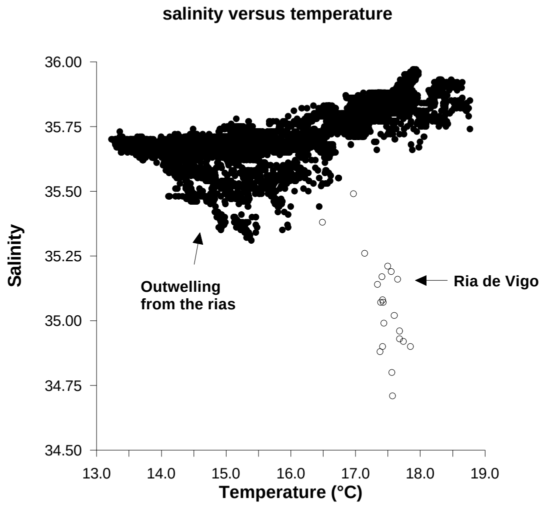


Figure 6: TS diagrams for shelf and shelf break stations during *Belgica* BG9815 cruise

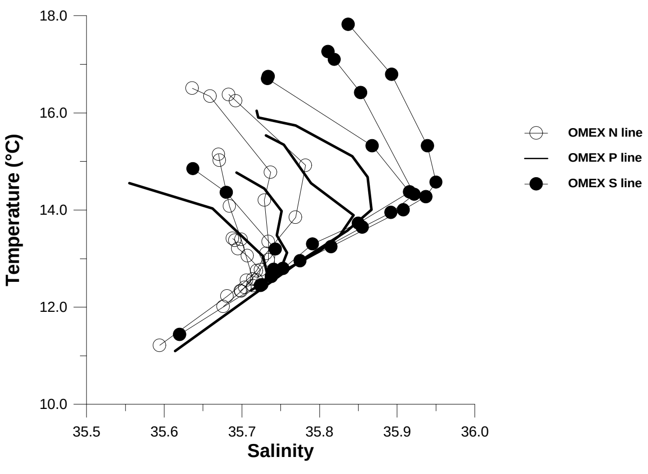


Figure 7: Distribution of underway parameters in the ria of Vigo and adjacent shelf
(the vertical dotted line corresponds to the mouth of the ria of Vigo)

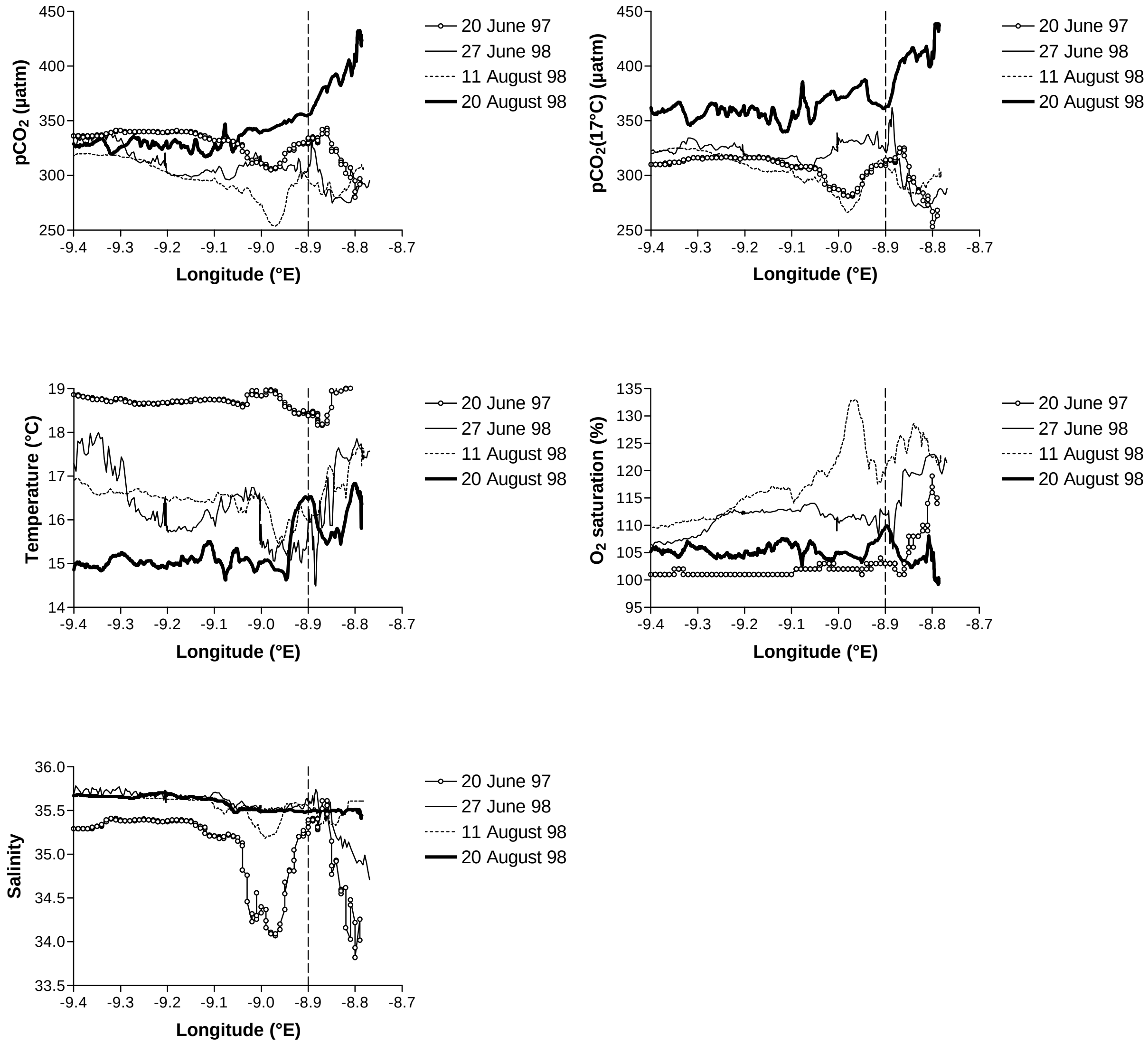


Figure 8: Distribution of underway parameters during *Charles Darwin* CD114 cruise

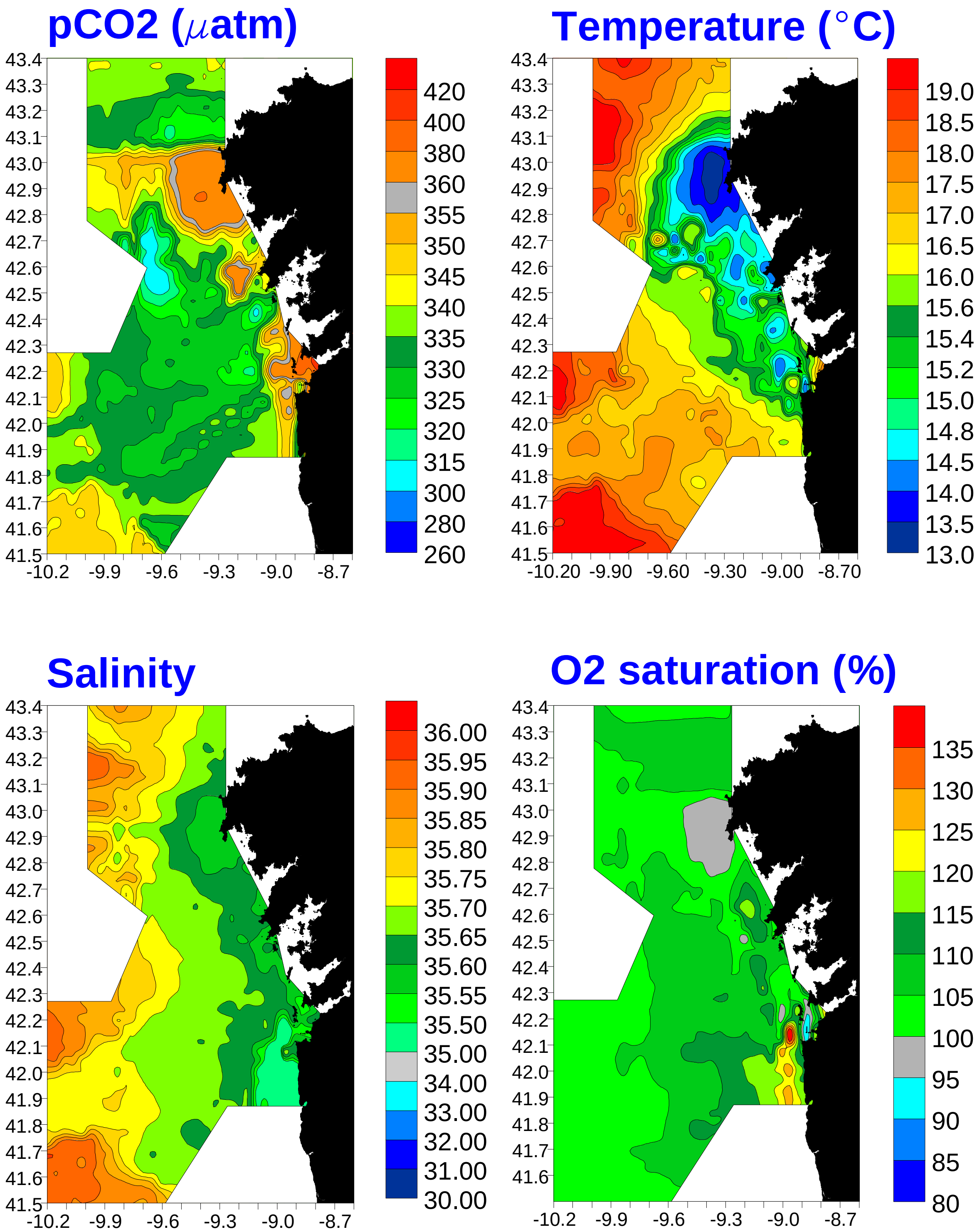


Figure 9: Distribution of underway parameters during *Meteor* M43/2 cruise