

## ESTIMATING PCO<sub>2</sub> FROM REMOTE SENSING IN THE BELGIAN COASTAL ZONE

A.V. Borges<sup>(1)</sup>, K. Ruddick<sup>(2)</sup>, G. Lacroix<sup>(2)</sup>, B. Nechad<sup>(2)</sup>, R. Asteroica<sup>(3)</sup>, V. Rousseau<sup>(3)</sup>, J. Harlay<sup>(1)</sup>

<sup>(1)</sup> University of Liège, Chemical Oceanography Unit, Institut de Physique (B5), B-4000 Liège, Belgium, Email: [alberto.borges@ulg.ac.be](mailto:alberto.borges@ulg.ac.be), [jerome.harlay@ulg.ac.be](mailto:jerome.harlay@ulg.ac.be)

<sup>(2)</sup> Royal Belgian Institute of Natural Sciences (RBINS), Management Unit of the North Sea Mathematical Models (MUMM/UGMM/BMM), 100 Gulledele, B-1200 Brussels, Belgium, Email: [k.ruddick@mumm.ac.be](mailto:k.ruddick@mumm.ac.be), [g.lacroix@mumm.ac.be](mailto:g.lacroix@mumm.ac.be), [b.nechad@mumm.ac.be](mailto:b.nechad@mumm.ac.be)

<sup>(3)</sup> Université Libre de Bruxelles, Ecologie des Systèmes Aquatiques, Campus Plaine CP 221 B-1050 Ixelles, Belgium, Email: [rastorec@ulb.ac.be](mailto:rastorec@ulb.ac.be), [vrousso@ulb.ac.be](mailto:vrousso@ulb.ac.be)

### ABSTRACT

In coastal waters, a purely field observation based approach will probably be insufficient to better constrain estimates of air-sea CO<sub>2</sub> fluxes, to study their inter-annual variability and their long-term changes. One approach to achieve these goals is to use remotely sensed fields of relevant biogeochemical variables to extrapolate available data, and produce maps of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and air-sea CO<sub>2</sub> fluxes. In the open ocean this approach has to some extent been successfully used based on fields of chlorophyll-a (Chl-a) and sea surface temperature (SST). This approach remains challenging in coastal waters that have complex optical properties (Case-II waters) and that exhibit highly dynamic pCO<sub>2</sub> temporal and spatial variations. In the frame of the Belgian funded BELCOLOUR-II project (Optical remote sensing of marine, coastal and inland waters; <http://www.mumm.ac.be/BELCOLOUR/>), three field cruises per year (April, July and September) for optical measurements were carried in 2007, 2008, 2009 in the Southern Bight of the North Sea (SBNS). Based on these data-sets, we derived algorithms to compute pCO<sub>2</sub> from Chl-a and sea surface salinity (SSS) using multi-polynomial regressions (MPR). Here we report the first application of the MPR algorithms to derive pCO<sub>2</sub> fields in the Belgian coastal zone based on data gathered in 2007, using remote sensed Chl-a (MERIS) and SSS computed with a 3-D hydrodynamical model of SBNS (COHERENS).

### 1. INTRODUCTION

The exchange of carbon dioxide (CO<sub>2</sub>) between coastal environments and the atmosphere is significant for the global carbon budget (Thomas et al. 2004; Borges 2005; Borges et al. 2005; Cai et al. 2006; Chen and Borges 2009; Laruelle et al. 2010). The most recent estimate of the overall sink of CO<sub>2</sub> in continental shelf seas is ~0.22 PgC yr<sup>-1</sup> (Laruelle et al. 2010), corresponding to 16% of the open oceanic sink (Takahashi et al. 2009), while continental shelves only represent 7% of the oceanic surface area. Yet, these estimates are prone to a large

uncertainty related to sparse data coverage in time and space. This can be to some extent overcome with long-term observations. However, the improvement of the description of CO<sub>2</sub> dynamics in coastal environments and quantification of air-sea CO<sub>2</sub> fluxes will require a combination of field observations, remote sensing and numerical modelling.

The air-sea CO<sub>2</sub> flux is evaluated according to:

$$F = k \alpha (p\text{CO}_{2\text{sea}} - p\text{CO}_{2\text{air}})$$

where F is the air-sea CO<sub>2</sub> flux, k is the gas transfer velocity, α is the CO<sub>2</sub> solubility coefficient, pCO<sub>2sea</sub> is the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in surface waters and pCO<sub>2air</sub> is the pCO<sub>2</sub> in the atmosphere.

k is derived from parameterisations as a function of wind speed that can be derived from a variety of sources (meteorological stations, synthetic products (e.g. NCEP, ECMWF), scatterometers (e.g. Quikscat)). In regions of relatively constant salinity, α is mainly a function of sea surface temperature (SST) that can be remotely sensed. pCO<sub>2air</sub> follows relatively regular seasonal cycles and latitudinal changes, and data can be obtained from numerous monitoring stations (e.g. NOAA Climate Monitoring and Diagnostics Laboratory air sampling network). Hence, the most crucial variable in the computation of F is pCO<sub>2sea</sub>.

The use of remote sensing to extend in space and time sparse data-sets of seawater pCO<sub>2</sub> has to some extent been achieved in open oceanic regions (e.g., Lefèvre et al. 2002; 2004; Rangama et al. 2005; Jamet et al. 2007; Friedrich and Oschlies 2009; Telszewski et al. 2009) and also in coastal environments (e.g., Olsen et al. 2004; Lohrenz and Cai 2006; Salisbury et al. 2008; Gledhill et al. 2008). Yet, such an approach has seldom been applied in near-shore estuarine environments. These areas are challenging in terms of the dynamic range of pCO<sub>2</sub> (strong horizontal gradients and very rapid seasonal variations) but also in terms of optical remote sensing of chlorophyll-a (Chl-a). Coastal waters which are turbid and rich in yellow substances usually require specific atmospheric corrections (e.g., Ruddick et al. 2000) as well as Chl-a retrieval algorithms which take account of non-algal particulate and dissolved matter (Doerffer and Schiller, 2007).

Here, we report the first trials to retrieve  $p\text{CO}_2$  fields from a combination of remote sensed Chl-a and modelled sea surface salinity (SSS) fields, based on data acquired in April 2007, July 2007 and September 2007 in the Belgian coastal zone, in the frame of the BELCOLOUR-2 project (Optical remote sensing of marine, coastal and inland waters, <http://www.mumm.ac.be/BELCOLOUR/>).

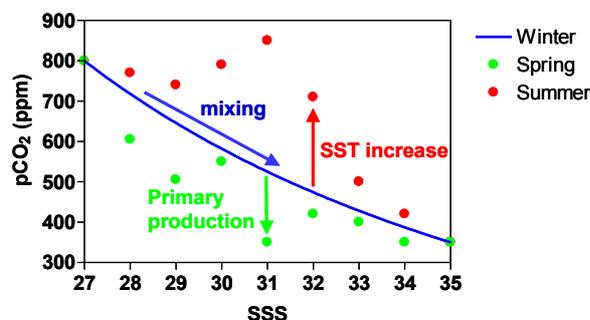


Figure 1 – Conceptual seasonal variation of  $p\text{CO}_2$  as a function of SSS in the Belgian coastal zone

## 2. MATERIAL AND METHODS

### 2.1. Site description

The Belgian coastal zone is strongly influenced by river inputs from the Scheldt, and indirectly from the Rhine and the Seine (Lacroix et al. 2004), resulting in strong horizontal gradients of SSS and high nutrient levels leading to high biological activity. The combination of river inputs with a high  $\text{CO}_2$  content and strong biological activity results in marked seasonal cycles and spatial gradients of  $p\text{CO}_2$  and air-sea  $\text{CO}_2$  fluxes (Borges and Frankignoulle 1999; 2002; Gypens et al. 2004; Schiettecatte et al. 2006; 2007). The area is permanently well mixed due to strong tidal currents.

### 2.2. Algorithm development

Figure 1 shows the conceptual seasonal variability of  $p\text{CO}_2$  in the Belgian coastal zone along the SSS gradient. In winter,  $p\text{CO}_2$  follows closely the mixing line from low SSS high  $p\text{CO}_2$  waters to high SSS low  $p\text{CO}_2$  waters. In spring, primary production related patchy phytoplankton blooms leads to negative deviations of  $p\text{CO}_2$  from the winter-time mixing line. In summer, warming of surface waters and reduced biological activity (following the collapse of the spring bloom) lead to an increase of  $p\text{CO}_2$  due to the thermodynamic decrease of  $\text{CO}_2$  solubility.

Based on this conceptual understanding of  $p\text{CO}_2$  dynamics in the study area, we developed algorithms to compute  $p\text{CO}_2$  from Chl-a and SSS. The  $p\text{CO}_2$  data were normalised to a temperature of  $10^\circ\text{C}$  ( $p\text{CO}_2@10^\circ\text{C}$ ) to remove the thermodynamic effect of temperature change on the solubility coefficient of  $\text{CO}_2$ . We used multiple polynomial regressions to derive the algorithms due to the non-linear relationship between

$p\text{CO}_2$ , SSS and Chl-a. Initial tests using SST as a variable in the algorithms showed that inclusion of SST degraded algorithm performance. Based on past data-sets and the present data-sets, no clear relationship could be found between coloured dissolved organic matter (CDOM) and SSS. This is related to autochthonous (phytoplankton) and allochthonous (riverine) sources of CDOM in the Belgian coastal zone that are variable seasonally and spatially (Astoreca et al. 2009). Hence, the approach adopted by Lohrenz and Cai (2006) for the Mississippi plume of deriving SSS from remote sensed CDOM was not used here. Instead SSS was derived from a 3-D hydrodynamical model.

### 2.3. Methods

Three cruises were carried out in 2007 on board the research vessel *Belgica*, to cover spring (23-26/04/2007), summer (02/07-06/07/2007) and fall periods (17/09-19/09/2007), on a regular grid (Fig. 2).

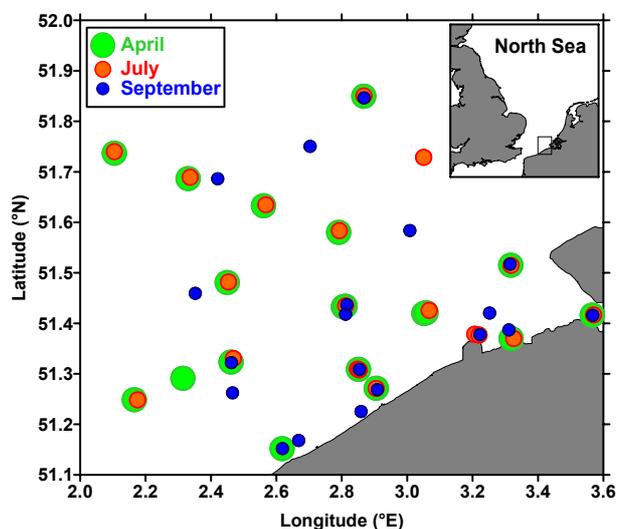


Figure 2 – Map and sampling stations in Belgian coastal zone during the April, July and September 2007 Belcolour-II cruises

Underway measurements of  $p\text{CO}_2$  were carried out in surface waters (2 m depth) using an equilibrator (Frankignoulle et al. 2001), and a non-dispersive infrared  $\text{CO}_2$  analyzer (Li-Cor 6262) calibrated with pure nitrogen (Air Liquide Belgium) and two gas mixtures with a  $\text{CO}_2$  molar fraction of 366 and 810 ppm (Air Liquide Belgium), that were calibrated against standards with a  $\text{CO}_2$  molar fraction of 361 and 774 ppm acquired from the National Oceanic and Atmospheric Administration (NOAA, Global Monitoring Division, Carbon Cycle Greenhouse Gases Group).

Chl-a was analysed according to Wright et al. (1991), using a Waters high performance liquid chromatography system (Waters 600 Controller, Waters 717 Autosampler and Waters 996 Photodiode Array Detector).

Chl-*a* input data for the pCO<sub>2</sub> algorithm was obtained from the Medium Resolution Imaging Spectrometer Instrument (MERIS) algal2 pigment index product. MERIS images are from 22<sup>nd</sup> April (10:19 UTC), 8<sup>th</sup> July (09:59 UTC), 15<sup>th</sup> September (10:30 UTC) 2007. The standard MEGS7.1-processed reduced resolution data was extracted and remapped using a nearest neighbour technique onto a uniform 1 km grid of the Southern North Sea. Cloud and land flags were used to mask data. The algal2 Product Confidence (PCD) flag was used to mask chlorophyll *a* data presented in maps, but was not used to mask input data for the pCO<sub>2</sub> algorithm. Procedures for quality control of the input and output of this algorithm are not yet mature but preliminary tests suggested that masking of PCD-flagged Chl-*a* data removed too much useful data. Validation of the MERIS Chl-*a* data for Belgian coastal zone is reported by Park et al. (2006).

SSS data used as input for the pCO<sub>2</sub> algorithm was obtained from the COHERENS 3D hydrodynamical model as implemented for the Southern North Sea and English Channel by Lacroix et al. (2004) on a 5.8 km x 4.6 km (1/12°x1/24°) horizontal grid. A standard hindcast simulation was made without any special adaptation for the current study, using river input data from Administratie Waterwegen en Zeewezen (AWZ-BE), Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling, Ministerie van Verkeer en Waterstaat (RIZA-NL), Cellule anti-pollution DDE-Service de Navigation de la Seine de Rouen SNS (FR), Agence de l'eau Artois Picardie (FR), National River Flow Archive-UK Environment Agency (NRFA-UK). The field of surface SSS simulated for the central day of each cruise week (24<sup>th</sup> April, 4<sup>th</sup> July, and 18<sup>th</sup> September 2007) was input to the pCO<sub>2</sub> algorithm. This model could be used to analyse also temporal variability of SSS during the cruise and hence transfer this variability of SSS into corresponding variability for pCO<sub>2</sub>.

### 3. RESULTS AND DISCUSSION

Modelled SSS and field data compared well with observations in terms of spatial patterns and seasonality (Fig. 3). The most prominent seasonal feature of SSS was the decrease of the extension of the river plume in July compared to April and September. Point by point comparison shows that modelled SSS was within about ± 1 of observations (Fig. 4A). Remote sensed Chl-*a* compared well with observations in terms of spatial patterns and seasonality (Fig. 5). The most prominent seasonal feature of Chl-*a* was the marked phytoplanktonic bloom in spring. Point by point comparison suggest that remote sensed Chl-*a* could have been under-estimated compared to observations (Fig. 4B).

We calculated pCO<sub>2</sub>@10°C in seawater using a multiple polynomial regression of the second degree as a

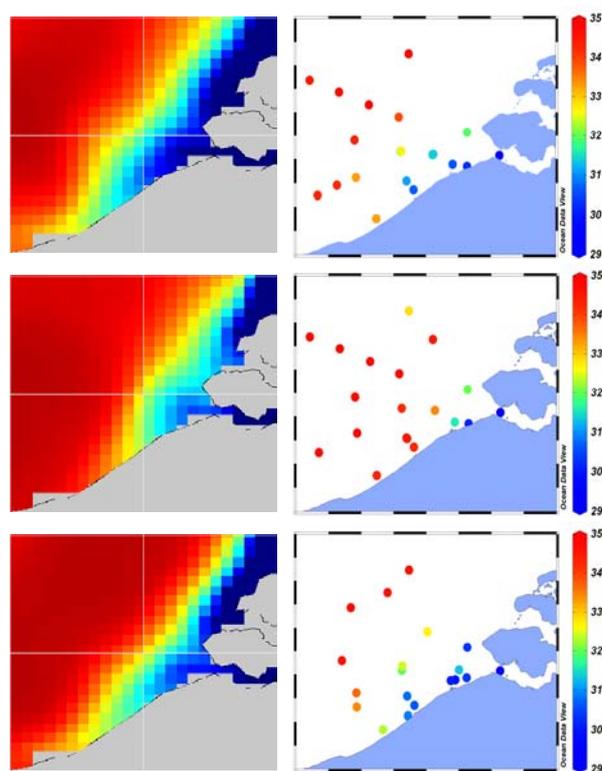


Figure 3 – Comparison of modelled (left panels) and measured (right panels) SSS in the Belgian coastal zone in April (top), July (middle) and September (bottom) 2007.

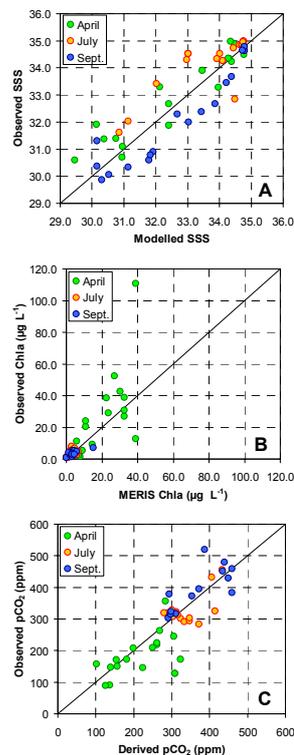


Figure 4 – Point by point comparison of SSS, Chla ( $\mu\text{g L}^{-1}$ ) and pCO<sub>2</sub>@10°C (ppm) in the Belgian coastal zone in April, July and September 2007.

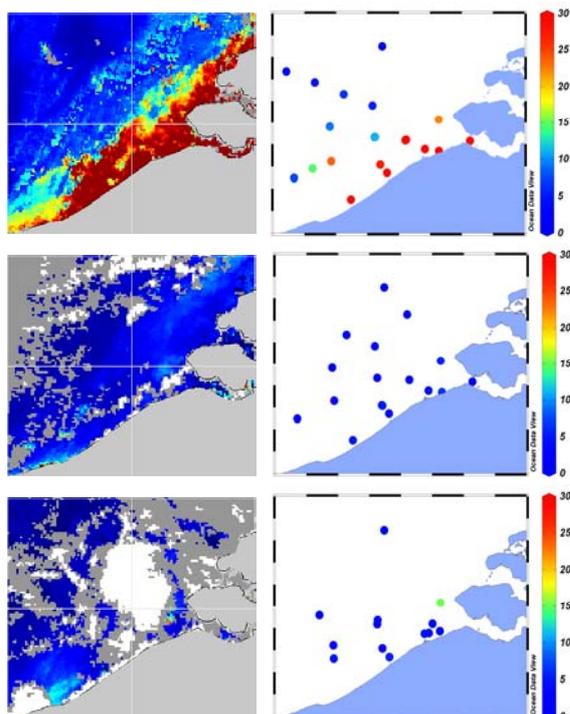


Figure 5 – Comparison of remote sensed (left panels) and measured (right panels) Chl-a ( $\mu\text{g L}^{-1}$ ) in the Belgian coastal zone in April (top), July (middle) and September (bottom) 2007. White areas are clouds; grey areas were flagged as land or suspect quality for the algal2 product (PCD flag).

function of SSS and Chl-a derived from the data-set merging the three cruises together:

$$p\text{CO}_2@10^\circ\text{C} = 0.108815 x_1^2 + 0.96603 x_1 x_2 - 4.57619 x_2^2 - 44.13737 x_1 + 254.67758 x_2 - 3011$$

where  $x_1 = \text{Chl-a}$ ,  $x_2 = \text{SSS}$ , derived from data in the domain  $[2.105^\circ\text{E}; 3.570^\circ\text{E}; 51.152^\circ\text{N}; 51.850^\circ\text{N}]$ , for SSS values ranging between 27.0 and 35.0 and Chl-a values ranging between 0.5 and  $110.0 \mu\text{g L}^{-1}$ .

Derived  $p\text{CO}_2@10^\circ\text{C}$  compared well with observations in terms of spatial patterns and seasonality (Fig. 6). The most prominent seasonal feature of  $p\text{CO}_2@10^\circ\text{C}$  was the marked decrease of  $p\text{CO}_2@10^\circ\text{C}$  during the spring phytoplankton bloom. Point by point comparison suggest that derived  $p\text{CO}_2@10^\circ\text{C}$  could have been over-estimated compared to observations (Fig. 4C), due to the possible under-estimation of Chl-a.

It should be noted that the modelled SSS fields correspond to the climatologies for the whole week corresponding to the cruises, while the remote sensed images of Chl-a are the “best” (i.e. less cloudy) available image for the duration of the week corresponding to the cruise. Hence, the point by point comparison of modelled SSS data and remote sensed Chl-a with field data (obtained throughout a cruise of 5 days) can be degraded by unresolved temporal variability. Besides short-term variability related to

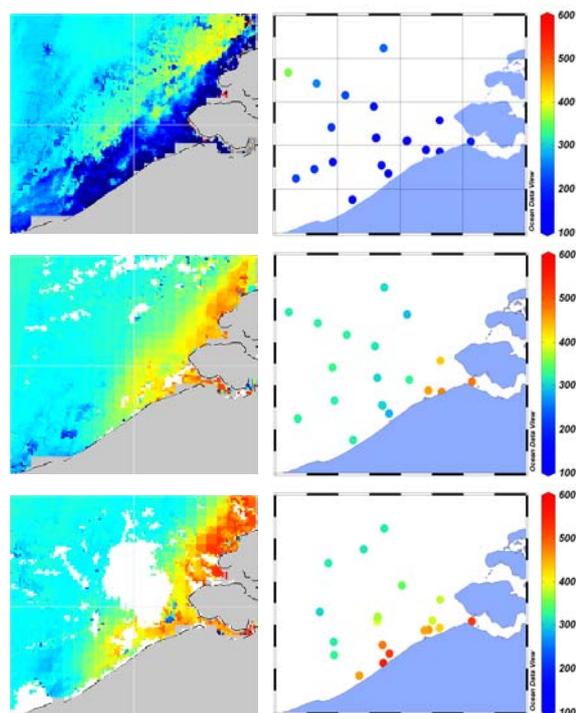


Figure 6 - Comparison of derived (left panels) and measured (right panels)  $p\text{CO}_2@10^\circ\text{C}$  (ppm) in the Belgian coastal zone in April (top), July (middle) and September (bottom) 2007. White areas correspond to lack of CHL input because of clouds.

advection of water masses and/or biological processes (e.g. massive aggregation and sedimentation) during the time interval (max. 2.5 days) between sampling and the modelled and remote sensed products, there is a marked sub-daily variability in surface waters related to tidal advection of water masses. For instance, Borges and Frankignoulle (1999) reported at a fixed station in the Belgian coastal zone during spring-time a daily variability (between high and low tide) in SSS of  $\sim 1$ , in Chl-a of  $\sim 10 \mu\text{g L}^{-1}$ , and in  $p\text{CO}_2$  of  $\sim 25$  ppm. Such strong variability due to tidal displacement of water masses with different chemical and biological signatures alone could explain some of the scatter in the comparisons between modelled SSS and observations, and between remote sensed Chl-a and observations (Figs. 4A and 4B).

#### 4. CONCLUSIONS

The use of multiple polynomial regression algorithms to retrieve  $p\text{CO}_2$  fields in the Belgian coastal zone from modelled SSS and remote sensed Chl-a based on a set of 3 cruises carried out in 2007 gave very encouraging results. Future work will:

- allow to better verify the modelled SSS and remote sensed fields, since the present comparison with field data was rough although overall very encouraging.

- use remote sensed products that were processed with cloud filling procedures carried out in the frame of a parallel project (RECOLOUR, <http://modb.oce.ulg.ac.be/projects/2>).
- include the analysis of data obtained during cruises in 2008 and 2009 also covering the three seasons (spring, summer and fall).
- allow to compute the air-sea CO<sub>2</sub> fluxes by the use of SST (to compute pCO<sub>2</sub> at in-situ temperature from pCO<sub>2@10°C</sub> and  $\alpha$ ) either derived from remote sensing products or the 3-D COHERENS model, and wind speed (to compute  $k$ ).
- allow to verify whether the algorithm we developed for the Belgian coastal zone could be applied to other regions of the North Sea where data were acquired in the frame of the Belcolour-II project such as the Thames river plume.

We are confident that the approach we used can be applied in general in near-shore coastal environments if the quality of remotely sensed Chl-a has been checked and if a regional hydrodynamical 3-D model can provide robust SSS fields. However, based on our understanding of CO<sub>2</sub> dynamics in coastal environments, we suspect that regional algorithms have to be developed and that a single algorithm cannot be universally applied.

## 5. ACKNOWLEDGEMENTS

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