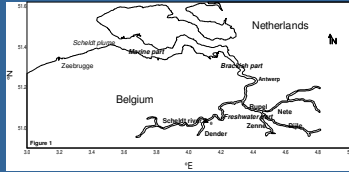


# Variations of the partial pressure of carbon dioxide in the Scheldt estuary from 1993 to 2006; preliminary results

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The Scheldt estuary, of a total length of 160km, extends from Gent to Vlissingen where it opens to the North Sea (Figure 1). From a hydrological point of view, it can be divided in 3 sections: a marine zone, a brackish zone where occurred a high turbidity zone (HTZ, in the vicinity of Antwerp) and a freshwater zone. Its catchment's area from the freshwater to the brackish parts are highly polluted in terms of organic matter and nutrients originating from industrial, agricultural and domestic waste products. Latter ones are essentially brought by the Rupel that drains Brussels city where there is a lack of waste water treatment. As a macrotidal estuary, the residence time of the water masses in the HTZ is long (from 1 to 3 months) which leads to important biogeochemical transformation of carbon and nutrients during estuarine transit. It leads to high CO<sub>2</sub> build up (up to 11000 ppm, Frankignoulle et al Science, 282, and Schiettecatte, unpublished data) and subsequent atmospheric CO<sub>2</sub> emissions (up to 0.66 molC m<sup>-2</sup> day<sup>-1</sup>, Frankignoulle et al 1998, Science, 282). Over the last 50 years, major changes have occurred in the Scheldt estuary, e.g. whereas by the end of the 1970ies the Scheldt estuary was severely impacted by hypoxia, it turned owing to waste water treatment policies toward improvement of the oxygen concentration during early 1980ies. These O<sub>2</sub> changes but also significant reduction of ammonium inputs are concomitant with the Scheldt paradox; i.e. the estuary shifted from denitrification in the 1970ies to nitrification conditions since the 1980ies (Billen et al, 2005, Hydrobiologia, 540; Soetaert et al, 2006, Limnology and Oceanography, 51(1)).

This study shows preliminary results of a long term monitoring of the surface partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) within the Scheldt estuary (1993-2006) in relation with other parameters (here Scheldt discharge and O<sub>2</sub>).

## Database and data analysis

pCO<sub>2</sub> data were collected from the BIOGEST and EUROTROPH projects and from the automated pCO<sub>2</sub> measurement system deployed since September 2000 on the *R. V. Belgica*. Oxygen (%O<sub>2</sub>) data were gathered for the studied period from the EUROTROPH and OMES database. Overall data covered a period from 1993 to 2006 but with high sampling variability in time and space. Thus pCO<sub>2</sub> data were more abundant since 2000 owing to the automated system whereas before that, pCO<sub>2</sub> was punctually measured during 2 up to 5 annual cruises. Before 1995, pCO<sub>2</sub> was calculated from total alkalinity and pH measurements, the latter being calibrated using buffers proposed by the U.S. National Bureau of Standards. After 1995, a non-dispersive infrared gas analyzer (IRGA, Li-Cor®; Li-6262) and an equilibrator were used to measure the pCO<sub>2</sub>. For the automated system the IRGA was calibrated weekly using pure nitrogen (Air Liquide Belgium) and two gas mixtures with a CO<sub>2</sub> molar fraction of 366 and 810 ppm (Air Liquide Belgium) that were calibrated against National Oceanic and Atmospheric Administration standards of a CO<sub>2</sub> molar fraction of 361 and 774 ppm. The temperature at the outlet of the equilibrator was monitored with a platinum resistance thermometer (PT100, METROHM®). The pCO<sub>2</sub> values were corrected for the temperature difference between *in-situ* seawater and water in the equilibrator using the algorithm proposed by Copin-Montégut (1988, 1989). Salinity, temperature and pCO<sub>2</sub> were sampled with a 1 min frequency from the surface seawater supply of the ship (pump inlet at a depth of 2.5 m). Salinity and temperature were measured using a SeaBird® SBE21 thermosalinograph. Indeed, another difficulty of this work relies on the fact that other parameters than pCO<sub>2</sub> were not sampled at the same time and/or same position. Then it was chosen to study the seasonal and interannual variability of the different parameters and their relation according to salinity within the conservative part of the estuary (e.g. at salinity 10). Scheldt discharge were provided by the Ministerie van de Vlaamse Gemeenschap.

## Results and Discussion

Figure 2 shows results from pCO<sub>2</sub> surveys (total data 25700) within surface waters from 1993 to 2006. Highest pCO<sub>2</sub> are observed at the lowest salinities, e.g. in the high turbidity zone of the estuary (Figure 1) where degradation processes are the most intense. Above salinity 10, the pCO<sub>2</sub> profiles are rather conservative owing to a dilution and ventilation effect. Beside biological and chemical processes that affect the pCO<sub>2</sub> dynamics at a seasonal and/or annual scale, Scheldt discharge (full dataset not shown) is also a potential factor. During the studied period Scheldt discharge range from 31 to 622 m<sup>3</sup> s<sup>-1</sup> in respectively 1996 and 1993, with highest values generally observed during winter and related to rainfalls and the North Atlantic Oscillation as demonstrated by Breton et al (2006, Limnology and Oceanography, 51(3)). Here a negative correlation is found between Scheldt discharge and the pCO<sub>2</sub> normalized to an annual mean temperature of 13°C (pCO<sub>2</sub>@13°C, Figure 3) which suggests that during strong Scheldt runoff events time CO<sub>2</sub> build up in the surface waters and prevent its ventilation through a decrease water masses time residence. Figure 4 shows surface waters pCO<sub>2</sub>@13°C along the estuary from salinity 10 up to 35 for period of November 1994 to 2006. This month was chosen as it is representative of the most sampling period during which biological activities are rather low and where interannual variability could be due changes of discharge and/or water quality at the upstream boundaries. Thus a strong pCO<sub>2</sub>@13°C interannual variability is apparent: maximum values along the estuary (~5000 µatm at salinity 10) are observed in the late 1990ies, the pCO<sub>2</sub>@13°C decreases during the new century with lowest values were recorded in November 2000 before fluctuating between 2000 and 3000 µatm at salinity 10 without ever reaching back the maximum values observed in 1994. These results are consistent with the annual means of the pCO<sub>2</sub>@13°C and %O<sub>2</sub> from 1993 to 2006 shown in Figure 5. pCO<sub>2</sub>@13°C and %O<sub>2</sub> profiles are well correlated (pCO<sub>2</sub>@13°C = -48.1%O<sub>2</sub> + 5672, r<sup>2</sup> = 0.61, p = 0.0028), and shows an improvement of the %O<sub>2</sub> (from ~50% prior to 1998 to ~70% at the beginning of the new century) parallel to a decrease of the surface waters pCO<sub>2</sub>@13°C (from 3000 µatm prior to 1998 to 2000 µatm in 2000). These trends in pCO<sub>2</sub> and %O<sub>2</sub> are also consistent with the results from Soetaert et al (2006, Limnology and Oceanography, 51(1)), who observed a significant decrease of ammonium, increase of nitrification and a reduction of organic matter (via a decrease of the chemical oxygen demand). Although this work needs further investigations, these preliminary results apart reflecting improvement of oxygen in the surface waters consecutive to waste water treatment policies as also observed by Soetaert et al (2006), suggest that water quality has also improved with regards to pCO<sub>2</sub>. As mentioned above, the Scheldt estuary received considerable amounts of domestic waste through the Rupel that drains untreated waste water from Brussels. It seems then reasonable to expect that the implementation and functioning of the waste water treatment plant of Brussels (for April 2007) should improve water quality in terms of %O<sub>2</sub> and pCO<sub>2</sub> within the Scheldt estuary, as studied by Vanderborght et al (2006, Marine Chemistry, in press). The surface waters pCO<sub>2</sub> monitoring (every minutes) in the HTZ of the Scheldt estuary (closed to Antwerp) started since 2002 should be a key master to highlight these expected changes (Schiettecatte and Borges unpublished data).

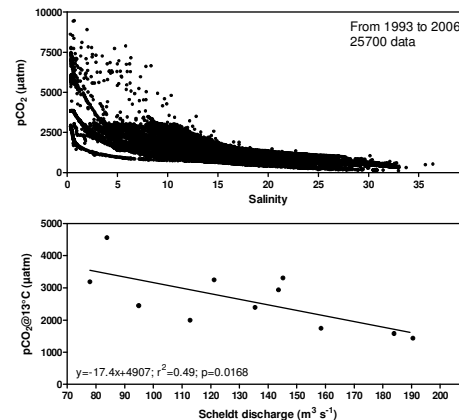


Figure 2 (top): pCO<sub>2</sub> data gathered from 1993 to 2006 in the entire Scheldt estuary. Figure 3 (bottom): Relationship between pCO<sub>2</sub>@13°C and Scheldt discharge.

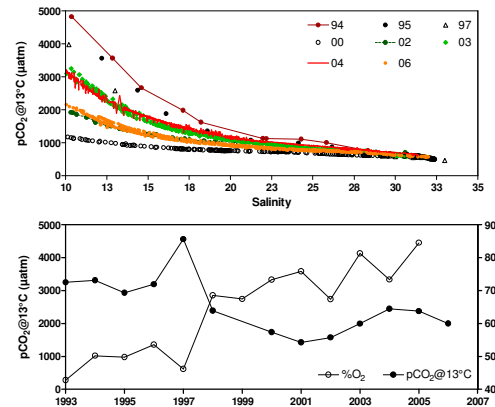


Figure 4 (top): Interannual variability of pCO<sub>2</sub>@13°C for November's 1994 to 2006. Figure 5 (bottom): Annual means of the pCO<sub>2</sub> and %O<sub>2</sub> at salinity 10 from 1993 to 2006.



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