

DIC dynamics in the upper Scheldt estuary

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Fig. 2: Station Sainte-Anna, located on the left bank of the Scheldt estuary, seaward of Antwerp.

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INTRODUCTION

The Scheldt estuary has a total length of 160km extending from Gent to Vlissingen where it opens to the North Sea (see **Fig.1**). Its catchment area is highly polluted in terms of organic matter and nutrients originating from industrial, domestic and agricultural waste products. From a hydrological point of view, the Scheldt estuary can be divided in 3 sections: the lower estuary, or marine zone (**zone 1**, from the mouth of the estuary to Hansweert), a brackish zone (**zone 2**) and a freshwater zone (**zone 3**). Zone 2 can also be distinguished in a mesohaline zone (from Hansweert to the Dutch-Belgian border) and an oligohaline zone also called the High Turbidity Zone (HTZ), which is the last part of the maximum turbidity zone located upward. Because of hydrodynamics, 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 nutrient during estuarine transit and subsequent atmospheric CO₂ emissions.

In order to better understand the cycle of the **dissolved inorganic carbon cycle (DIC)** in the HTZ, the partial pressure of CO₂ (pCO₂) of surface brackish water is measured continuously (every minutes) since november 2002 until 2004, at the Sainte-Anna station near the city of Antwerp (see **Fig. 1** and **Fig. 2**). Results presented here show in a first part the **pCO₂ seasonal cycle in 2003**, and in a second part **relations between DIC and oxygen**.

RESULTS AND DISCUSSION

Figure 5A shows the annual salinity cycle and the Scheldt discharge during year 2003. Salinity amplitude signal is inversely correlated to the Scheldt discharge. Highest run-off is observed in winter leading to a decrease of salinity amplitude signal. On the contrary, from spring to fall, run-off decreases, intrusion of seawater along the estuary becomes important as shown by the wide salinity amplitude signal.

Figure 5 B and C shows the seasonal cycle of pCO₂ in the HTZ for surface brackish water of salinities 1, 2 and 4. The observed decrease of pCO₂ along the salinity range is due to a dilution and ventilation effect. The Scheldt estuary is through the year strongly oversaturated with respect to the atmospheric pCO₂ (**up to 2200%**). Highest pCO₂ values are observed from spring to early summer, principally due to a temperature effect as the temperature normalized pCO₂ is stable during that period. Nevertheless, some part of this increase during spring, shown by red arrows, could also be explained by bacterial activity as a consequence of temperature increase (see **Fig. 6**). In summer, the pCO₂ decrease down to 2000ppm related to primary production. Gazeau *et al.* 2004 (this session) reported high gross primary production rates in the upper Scheldt during this period (see green lines). During late summer and early fall, increase of both pCO₂ and normalized pCO₂ could be due to a decrease of gross primary production and maintained strong heterotrophic activities. In winter, the decrease of temperature and bacterial activity lead to the decrease of pCO₂ and normalised pCO₂.

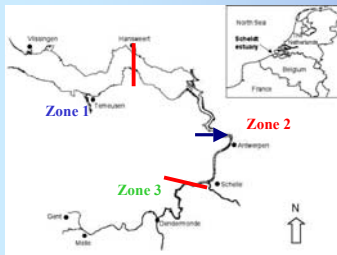


Fig. 1: The Scheldt estuary can be divided in 3 zones: **marine, brackish** and **freshwater zone**. The blue arrow shows the position of the station of pCO₂ measurements.

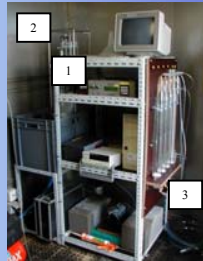


Fig. 3: system for the measurement of surface brackish water pCO₂, salinity and temperature.

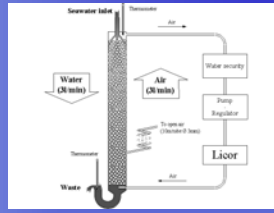
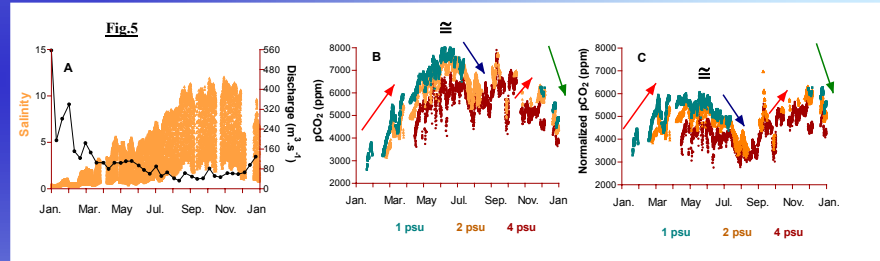


Fig. 4: The equilibrator from Frankignoulle *et al.* 2001, *Wat. Res.*, 35 (5), 1344-1347.



Figures 6 show the annual cycle of temperature, salinity, oxygen and pCO₂ for the weekly samples. **Physical processes** (tides and run-off, see Fig. 5) strongly affects the variables from spring to summer, the mixing between seawater (more oxygenated and poor in DIC) and freshwater (less oxygenated and rich in DIC) occurring along the estuary can be observed on the pCO₂, oxygen and salinity profiles. **Bacterial activity** is responsible from late February to April to a decrease of oxygen (10% to 50% saturation in winter), and pCO₂ increases from 4000 to 8000ppm. In summer, increase of oxygen and decrease of pCO₂ are both explained by the seawater intrusion in the estuary (marine waters are more oxygenated) but also by the **primary production**. Finally during fall through winter, **thermodynamic processes** (temperature drop) lead to a decrease of pCO₂ and bacterial activities.

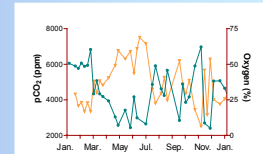
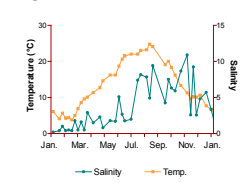


Fig. 6



MATERIALS AND METHODS

Underway parameters (pCO₂, salinity and temperature) are measured with a frequency of 1 minute in surface water pumped from a depth of 1m, see **Fig. 3**. A non dispersive gas analyser (LI-cor, LI-6252, *case 1* in **Fig.3**) is used to measure pCO₂ in dry air equilibrated with sampled water. The Licor is calibrated weekly using 3 dry gas standards (pure nitrogen (0ppm), and 2 gas mixtures with a CO₂ mole fraction of 4000 and 8000ppm). The equilibrator (see *case 2* in **fig.3** and **Fig. 4** for details) consists of a plexiglas cylinder filled with marbles to increase the exchange surface area. Seawater runs (3 L.min⁻¹) from the top to the bottom of the equilibrator, and air is pumped upwards (3 L.min⁻¹). Equilibrated air is dried with a Permatube dessicant (*case 3* in **Fig.3**). Salinity and temperature are measured at the outlet of the equilibrator, and *in situ* temperature is measured once a week. We then assumed that the temperature difference between *in situ* brackish water and water in the equilibrator is constant during the week (offset in temperature varies between -0.5 to +0.5°C). The pCO₂ values are finally corrected for this temperature difference using the algorithm proposed by Copin-Montégut (1988).

Oxygen is sampled every week and measured using the Winkler method.

Acknowledgments

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CONCLUSION

This work showed that the DIC cycle in the HTZ of the strongly heterotrophic Scheldt estuary, is governed on an annual scale by a complex combination of physical (tides, run-off), thermodynamical and biological factors at different time scales. Among them, the most important are temperature and its effect on heterotrophic activities and the thermodynamic of the DIC system.