Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt and Thames)

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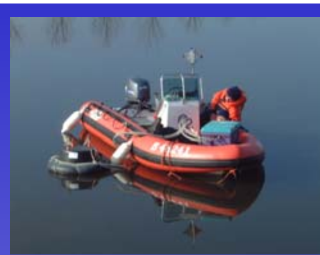

Fig. 1: The floating dome

The dome is a plastic right circular cone (top radius = 49 cm; bottom radius = 57 cm; height = 28 cm) mounted on a float, and, connected to a closed air circuit with an air pump (30 L min^{-1}) and an Infra Red Gas Analyzer, both powered with a 12 Volts battery.

Abstract:

The flux of CO_2 across the air-water interface was measured with the floating dome method in three European estuaries with contrasting physical characteristics (Randers Fjord, Scheldt and Thames). The gas transfer velocity of CO_2 was computed from concomitant measurements of the air-water gradient of the partial pressure of CO_2 (pCO_2). The contribution of tidal currents to the gas transfer velocity of CO_2 is significant in macrotidal estuaries (Scheldt) and negligible in microtidal estuaries (Randers Fjord). Our results strongly suggest that, in estuaries, a simple parameterization of the gas transfer velocity of CO_2 as a function of wind speed is site specific.

Introduction:

The flux of CO_2 across the air-water interface can be computed according to:

$F = \varepsilon.k.\alpha.\Delta pCO_2$

where α is the solubility coefficient of CO_2, ΔpCO_2 is the air-water gradient of pCO_2, k is the gas transfer velocity of CO_2 (also referred to as piston velocity) and ε is the chemical enhancement factor of gas exchange. In both open oceanic and coastal environments, highly precise and accurate methods to measure ΔpCO_2 can nowadays be easily achieved, thus, the largest incertitude in the computation of F comes from the k term (α is straightforwardly computed from salinity and water temperature, and, the contribution from ε is usually negligible, except under very low turbulent conditions, see *e.g.* Wanninkhof, 1992, J. Geophys. Res. 97: 7373-7382). Based on numerous theoretical, laboratory and field studies, it is well established that k depends on a variety of variables but the most important one is turbulence at the air-water interface (in the case of sparingly soluble gases such as CO_2 the critical variable is turbulence in the liquid phase). In a recent review that compiles available measurements of k in various estuaries, and, based on different methodologies, Raymond & Cole (2001, Estuaries 24: 312-317) suggested that the parameterization of k as a function of wind speed could be significantly different in estuarine environments than those developed in open oceanic waters (higher values of k in estuaries for the same wind speed). To contribute to the debate we analysed a reasonably large data-set of k values (totalling 360 measurements), based on the floating dome method, in three European estuaries with contrasting physical characteristics.

Methods:

The air-water CO_2 fluxes were measured with the floating dome method (Fig. 1) described by Frankignoulle (1988, Limnol. Oceanogr. 33: 313-322) from a drifting rubber boat, in order to avoid the interference of water turbulence within the dome created by the passing water current, observed in earlier measurements carried out from a fixed point. The flux was computed from the slope of the linear regression of pCO_2 against time (r^2 usually $\geq$ 0.99) according to Frankignoulle (1988, Limnol. Oceanogr. 33: 313-322). The gas transfer velocity of CO_2 was computed from the CO_2 flux and ΔpCO_2 measurements: atmospheric pCO_2 was measured and recorded at the start of each flux measurement; water pCO_2 was either computed from pH and Total Alkalinity measurements (Frankignoulle and Borges, 2001, Aquat. Geochem. 7: 267-273) or measured by equilibration (Frankignoulle, Borges and Biondo, 2001, Water Res. 35: 1344-1347).

Results:

• A simple parametrization of k_{600} as a function of wind speed is estuary specific

Figure 2 shows the averaged k_{600} over wind speed bins of 2 m s^{-1} *versus* wind speed in the Randers Fjord, the Scheldt and the Thames. In the three estuaries, **k_{600} steadily increases with wind speed, but the k_{600} values are highly variable from one estuary to another**. Indeed, at low wind speeds, k_{600} is about 8 times higher in the Thames than in the Randers Fjord (at high wind speeds about 2 times higher). For winds above 9 m s^{-1}, the k_{600} values from the three estuaries fall within the range of values from published parameterizations of k_{600} as a function of wind speed. However, for wind speeds below 9 m s^{-1}, the k_{600} values in both the Scheldt and the Thames are above any of the published parameterizations of k_{600} as a function of wind speed. The k_{600} values in the Randers Fjord follow relatively closely the parameterization of k_{600} as a function of wind speed given by Carini et al. (1996, Biol. Bull. 191: 333-334).

• Water currents significantly contribute to k_{600} in macrotidal estuaries

Water currents measurements concomitant to flux measurements were obtained during the Randers Fjord cruises and a Scheldt cruise in November 2002. Although water currents are expected to contribute to water turbulence whatever the wind speed, their effect is best identified if the contribution to turbulence from wind stress is low. Thus, the k_{600} data-set of the Randers Fjord was filtered by rejecting data for wind speeds above 4 m s^{-1} and for nil water currents (Fig. 3). A power-law function that accounts for current speed and depth in the same fashion as the conceptual relationship of O'Connor & Dobbins (1958, Trans. Am. Soc. Civ. Eng. 123: 641-684) developed for streams, was established from the observed k_{600} and water current, and both relationships are very similar (Fig. 3). This strongly suggests that for the observed range of water currents, **the O'Connor & Dobbins (1958, Trans. Am. Soc. Civ. Eng. 123: 641-684) relationship gives a fairly adequate estimation of the contribution of water currents to the gas transfer velocity in estuaries.**

From the water current measurements concomitant to those of the CO_2 flux, the contribution of water current to the gas transfer velocity of CO_2 was computed according to the O'Connor and Dobbins (1958, Trans. Am. Soc. Civ. Eng. 123: 641-684) relationship and was removed from the observed k_{600}. This gives in theory the contribution of wind speed alone to k_{600} ($k_{600wind}$). At low wind speeds, $k_{600wind}$ is about 3 times lower than the observed k_{600}, suggesting that the contribution of water currents to water turbulence is substantial when wind stress is low (Fig. 4). At high wind speeds, $k_{600wind}$ is about 1.1 times lower than the observed k_{600}, showing that the relative contribution of water currents to the gas transfer velocity decreases with increasing wind. Note that, for wind speeds below 8 m s^{-1}, $k_{600wind}$ values are in fairly good agreement with the relationship proposed by Raymond & Cole (2001, Estuaries 24: 312-317). The same computations as those outlined above were carried out for the Randers Fjord (not shown) and the $k_{600wind}$ and observed k_{600} are very similar. This suggests that the overall contribution of water currents to k_{600} is negligible in this particular estuary. Indeed, 78 % of the observed water currents are below 10 cm s^{-1} (Fig. 5) and, thus, the high water currents in Figure 3 are exceptional values. Furthermore, the k_{600} data of the Randers Fjord follow closely the relationship of Carini et al. (1996, Biol. Bull. 191: 333-334) for the Parker River estuary (Fig. 2) that according to Raymond & Cole (2001, Estuaries 24: 312-317) is also characterised by low tidal currents. In contrast, only 33 % of the observed water currents in the Scheldt estuary are below 10 cm s^{-1} and the range of variation of the observed water currents is one order of magnitude higher than in the Randers Fjord (Fig. 5). **We suggest that the difference of k_{600} between the Randers Fjord and the Scheldt is related to the contribution of water currents to k_{600} that is substantial in the Scheldt (and probably also in the Thames) and negligible in the Randers Fjord.**

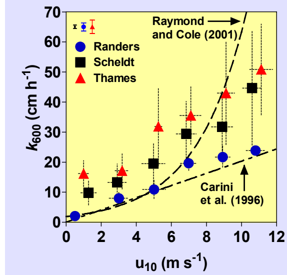

Fig. 2: Gas transfer velocity of CO_2 versus wind speed

The data were averaged over wind speed bins of 2 m s^{-1}. Standard deviations are shown by the horizontal and vertical dotted lines for the bin averages of u_{10} and k_{600}, respectively. The error bars on top left corner of the plot correspond, for each of the three estuaries, to the average uncertainty on the k_{600}, estimated using the individual standard error on the slope of the regression of pCO_2 in the floating dome against time and assuming an error on ΔpCO_2 of ±3%. The Raymond & Cole (2001) relationship is based on a compilation of published k_{600} values. The Carini et al. (1996) relationship is based on a SF_6 release experiment.

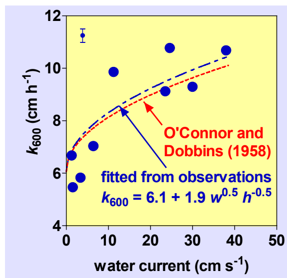

Fig. 3: The gas transfer velocity of CO_2 in the Randers Fjord as a function of water current

Are shown the k_{600} data for u_{10} < 4 m s^{-1} and for non nil water currents. The dashed line corresponds the k_{600} predicted from the conceptual relationship of O'Connor & Dobbins (1958). The dashed-dotted line corresponds to a power-law function ($k_{600} = 6.1 + 1.9\ w^{0.5}\ h^{-0.5}$, r^2 = 0.725) that accounts for water current (w in cm s^{-1}) and depth (h in m) in the same fashion as the O'Connor & Dobbins (1958) relationship. The value 6.1 cm h^{-1} is the average of the k_{600} observed at low water currents (< 10 cm s^{-1})

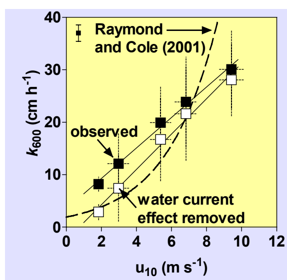

Fig. 4: Gas transfer velocity of CO_2 versus wind speed in the Scheldt (November 2002)

The open symbols correspond to k_{600} from which the contribution of water currents was removed. The contribution of water currents to k_{600} was estimated from the conceptual relationship of O'Connor & Dobbins (1958), using water current measurements concomitant to the CO_2 flux measurements and it was removed from individual k_{600} estimates before the data were bin averaged. Solid lines correspond to linear regressions.

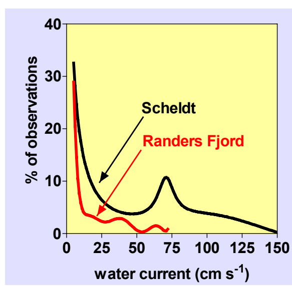

Fig. 5: Frequency distribution of water current measurements

During the Randers Fjord cruises, data were recorded every min at three stations (56.46°N 10.04°E, 56.62°N 10.23°E, 56.61°N 10.30°E) that were occupied during 24 h. During the November 2002 Scheldt cruise, data were recorded every min at four stations (51.13°N 4.31°E, 51.23°N 4.40°E, 51.41°N 4.04°E, 51.39°N 4.21°E) that were occupied during 24 h. Mean current speeds are 8 (±12 sd) and 44 (±40 sd) cm s^{-1} in the Randers Fjord and the Scheldt, respectively.

EGS-AGU-EUG Joint Assembly
Nice, France, 06 - 11 April 2003

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Acknowledgements:
Renzo Biondo, Emile Libert and Jean-Marie Théate, BIOGEST (ENV4-CT96-0213) and EUROTROPH (EVK3-CT-2000-00040)

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