



Direct and Indirect pCO₂ Measurements in a Wide Range of pCO₂ and Salinity Values (The Scheldt Estuary)

MICHEL FRANKIGNOULLE and ALBERTO VIEIRA BORGES

Université de Liège, Unité d'Océanographie Chimique, Institut de Physique B5, B4000 Sart Tilman, Belgium

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Abstract. Recent improvements in both Infra-red spectroscopy and equilibrator techniques have allowed to determine, for the first time, pCO₂ using simultaneously and continuously both the direct and indirect methods in an estuary where pCO₂ values range from 500 to 8500 μ atm and salinity from 0 to 30. Our results show that both methods are in excellent agreement in the whole estuary ($r^2 = 0.999$, $n = 1075$, $p < 0.0001$). Thus, the NBS (US National Bureau of Standards) scale, although inadequate for seawater samples, is appropriate for estuarine waters and can be applied with confidence to calculate pCO₂.

Key words: pH, estuaries, NBS Scale, pCO₂, equilibrator, Infra-red Gas Analyser

1. Introduction

Estuaries are known to display high pCO₂ values in the upper part, due to heterotrophic respiration of organic carbon (Heip et al., 1995; Frankignoulle et al., 1998; Gattuso et al., 1998; Cai et al., 1999). In the highly polluted Scheldt estuary (Belgium/Netherlands), pCO₂ can be as high as 9000 μ atm, that is about 25 times the value of atmospheric equilibrium (presently around 370 μ atm). These high pCO₂ values induce high CO₂ efflux and the entire Scheldt can emit up to 790 tC per day to the atmosphere (Frankignoulle et al., 1998).

pCO₂ can be determined using either a direct or an indirect method. The direct method is based on the equilibrator technique and further measurement of pCO₂ in equilibrated air using Infra-red spectrometry or gas chromatography (see DOE, 1994; Körtzinger et al., 1996, for reviews). The most commonly used IR analysers are the Li-Cor[®] 6252 and 6262. While this method is recognized to be the most accurate one to determine pCO₂ in subsurface seawater (DOE, 1994), it suffered from two major problems in coastal and estuarine environments: 1) most equilibrators were not designed to work properly in turbid waters (blockage by suspended material); 2) The Li-Cor range of measurements was limited to 0–3000 μ atm and

this technique was then not appropriate for the measurement of $p\text{CO}_2$ in some estuaries (see Frankignoulle et al., 1998).

The indirect method consists to calculate $p\text{CO}_2$ from measurements from at least two of the following parameters: pH, total alkalinity (TAlk) and total dissolved inorganic carbon (DIC). The most commonly used parameters are pH and TAlk. The pH in natural waters is however well known to be difficult to measure with sufficient accuracy, because it is not possible to quantify the effect of salinity on the activity coefficient of H_3O^+ . If pH is determined with combined electrodes, an additional incertitude arises from the so-called junction potential developed at the reference electrode (e.g., Whitfield et al., 1986; Butler et al., 1986). For seawater samples, three pH scales have been proposed (seawater scale, total proton scale, free proton scale, see Dickson, 1993 for a review) and pH is nowadays determined by a spectrophotometric technique which offers quite accurate results (Clayton and Byrne, 1993). However, the validity of this technique in highly turbid water is doubtful and this method can not be applied for high frequency (1 min) underway measurement. Finally, these pH scales are not appropriate for estuarine research because related equilibrium constants and buffer values have not been determined so far at low salinity. The most commonly used set is therefore the NBS scale, where pH is defined as the negative decimal logarithm of the proton activity, and for which constants have been determined in the salinity range from 0 to 40 (Mehrbach et al., 1973, Millero, 1979) but also refitted for estuarine environment (Cai and Wang, 1998). However, the consistency of the inorganic carbon computations based on the NBS scale has not been so far cross-checked in estuarine waters with direct $p\text{CO}_2$ measurements.

In this paper, we present recent results obtained using both the direct and the indirect methods in the whole Scheldt estuary, in a salinity range from 0 to 30 and a $p\text{CO}_2$ range from 500 to 8500 μatm . The use of the direct method in the whole estuary has been made possible by two recent technical developments: 1) Li-Cor has developed a procedure that allows to use the IR Li-6262 in a $p\text{CO}_2$ range from 0 to 10000 μatm (Li-Cor Application Note 122), 2) a new design of equilibrator has recently been proposed to measure $p\text{CO}_2$ with a short response time (equilibration interval with a half live constant of 30 s) and in highly turbid water (Suspended Particulate Matter, SPM, up to 1 g l^{-1}) (Frankignoulle et al., 2001).

2. Material and Methods

Data presented in this paper were obtained from the 4th to the 6th of July 2000, on board the R. V. Belgica (cruise 2000/18). Underway parameters (pH, $p\text{CO}_2$, salinity and *in situ* temperature) were sampled with a frequency of 1 minute from the non-toxic seawater supply of the ship (pump inlet at a depth of -2.5 m). Discrete parameters (pH, TAlk and O_2) were sampled in subsurface water from a Niskin bottle. Salinity and temperature were determined underway using a Seabird[®] SBE 21 thermosalinograph and discretely using a SBE 19 CTD. Dissolved oxygen

was measured using the classic Winkler method with a potentiometric end-point determination. pH was measured using a combination electrode (ORION[®] for discrete samples and METROHM[®] for underway measurements) calibrated on the NBS scale, using home-made phthalate (C₈H₅KO₄ 0.05 mol kg⁻¹, pH = 4.002 (mol kg⁻¹) at 25 °C) and phosphate (KH₂PO₄ 0.025 mol kg⁻¹ and Na₂HPO₄ 0.025 mol kg⁻¹, pH = 6.881 (mol kg⁻¹) at 25 °C) buffers (Bates, 1973). The calibration temperature correction was made according to Fuhrmann and Zirino (1988) and the correction to *in situ* temperature according to Pérez and Fraga (1987).

A non-dispersive infrared gas analyser (Li-cor[®], LI-6262) was used to measure pCO₂ in wet air equilibrated with sample water. The Li-cor[®] was calibrated daily, using pure nitrogen (0 ppm, *Air Liquide Belgium*) and three gas mixtures with a CO₂ molar fraction of 360.5 (*National Oceanic and Atmospheric Administration*), 4000 and 8000 ppm (*Air Liquide Belgium*). The equilibrator consists of a Plexiglas cylinder (height: 80 cm, diameter: 10 cm) 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), see Frankignoulle et al. (2001) for more details. The temperature at the outlet of the equilibrator was monitored using a platinum resistance thermometer (PT100, METROHM[®]). The pCO₂ values are corrected for the temperature difference between *in situ* seawater and water in the equilibrator, using the algorithm proposed by Copin-Montégut (1988). The offset in temperature varied between 0.1 and 0.5 °C. Discrete sampling was carried out for the determination of total alkalinity (TAlk), using the classical Gran (1952) electro-titration method, on 100 ml GF/F filtered samples, taking into account the corrections for sulfate and fluoride interaction, according to Hansson and Jagner (1973). The reproducibility of TAlk and pH measurements performed on board were, respectively, 4 µeq kg⁻¹ and 0.005. pCO₂ was also computed from measurements of pH and TAlk using the carbonic acid constants sets proposed by Cai and Wang (1998) or by Mehrbach et al. (1973), the borate acidity constant from Lyman (1957) (the latter two are refitted by Millero, 1979) and the CO₂ solubility coefficient of Weiss (1974). Constants and pH were converted to the molality scale (moles per kilogram of solution, mol kgW⁻¹).

3. Results and Discussion

Figure 1 shows pH and TAlk profiles obtained through the whole Scheldt estuary in July 2000. As already reported by Frankignoulle et al. (1996), the total alkalinity is not conservative in the upper estuary (salinity 0 to 5) due to intense nitrification which produces H₃O⁺ and leads to a decrease of total alkalinity and a minimum of both pH and oxygen saturation level at the turbidity maximum. For salinities higher than 5, the total alkalinity has a conservative behaviour (dilution profile).

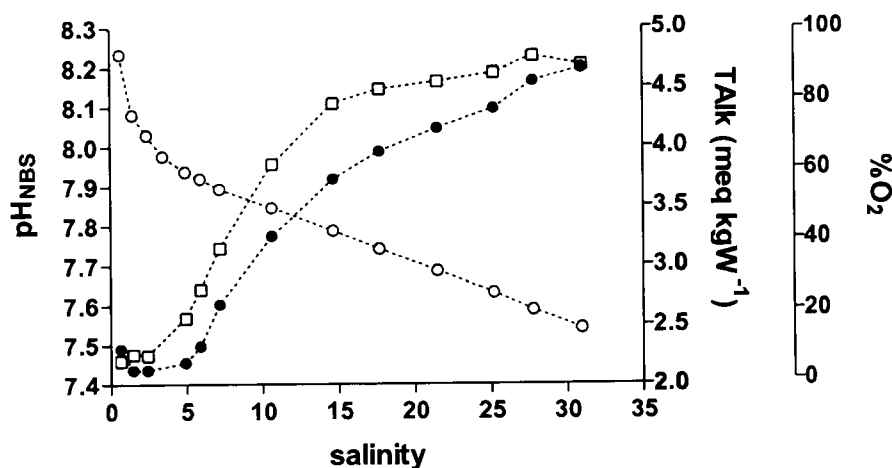


Figure 1. Evolution of pH (full circles), TAlk (open circles) and oxygen saturation level (open squares) as a function of salinity.

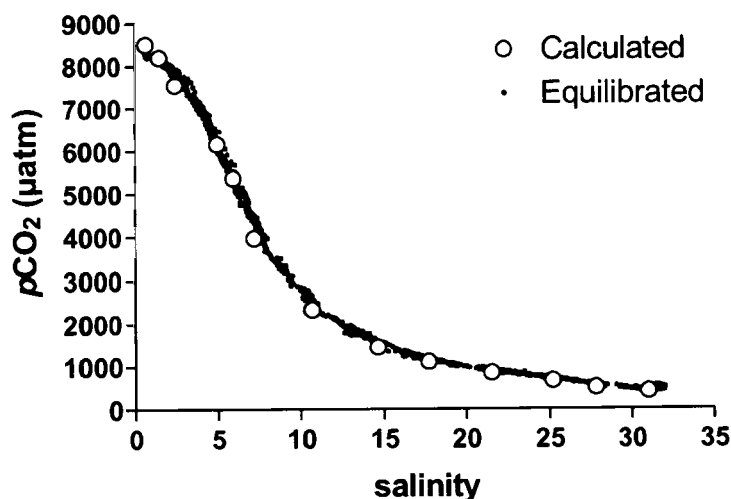


Figure 2. Calculated and equilibrated (direct measurement) of pCO₂.

Figure 2 shows the pCO₂ profiles versus salinity obtained by both direct and indirect methods, the latter calculated using the constants from Mehrbach et al. (1973). The agreement is excellent in the whole range of salinity and of pCO₂.

Indirect pCO₂ has also been computed using continuous underway pH measurement and total alkalinity values interpolated between discrete experimental values using a five degree polynomial relationship ($\text{TAlk} = 17.91265 - 46.2026.S + 68.5288.S - 57.46276.S^{1.5} + 29.6165.S^2 - 9.7315.S^{2.5} + 2.0447.S^3 - 0.2659.S^{3.5} + 0.0195.S^4 - 0.000617.S^{4.5}$, Table curve[®], Jandel Scientific, $r^2 = 1$). Calculations were made using the carbonic acid constants proposed by both Mehrbach et

al. (1973) and Cai and Wang (1998) and the linear correlation between direct and indirect values yields the following ($n = 1075$):

$$\text{pCO}_2 (\text{indirect}) = -30 (\pm 91) + 1.020 * \text{pCO}_2 (\text{direct}) (r^2 = 0.9991)$$

with constants from Mehrbach et al. (1973), and

$$\text{pCO}_2 (\text{indirect}) = -48 (\pm 76) + 0.994 * \text{pCO}_2 (\text{direct}) (r^2 = 0.9994)$$

with constants from Cai and Wang (1998).

Figure 3 shows the difference between direct and indirect pCO₂, expressed in percent, as a function of both pCO₂ and salinity. For pCO₂ > 2500 μatm (i.e., for salinity <20, see Figure 2), the constants set from Mehrbach et al. (1973) yields indirect pCO₂ values which are systematically higher, while values from the set of Cai and Wang (1998) are lower. However, both sets gives values that are ≤2%, which is in the expected range of error if one combine reproducibility of both pH and TALK measurements. For pCO₂ > 2500 μatm (i.e., salinity >20, see Figure 2), the difference increases exponentially, underlining the problems arising from the use of the NBS scale in salty water (increase with salinity of the difference of the liquid junction potential between buffer and sample), although the set of constants from Mehrbach et al. (1973) appears to be more consistent. One solution to this problem is the calibration of the electrode on the Total Hydrogen Ion Scale (Dickson, 1993) using the TRIS buffers made at different salinities as described by Millero (1986). However, Whitfield et al. (1986) show that in practice the error on pH measurements is only marginally reduced by the use of various saline buffers to cover the estuarine salinity range. Thus, a single buffer of salinity 15 or 20 should be sufficient for calibration purposes in the high salinity range (Millero, 1986; Whitfield et al., 1986).

4. Conclusions

From the results presented in this paper, we can conclude:

- Both the direct and indirect methods yield coherent results whatever the constants used, on the NBS scale, to calculate pCO₂ from measurements in estuarine water of pH using a combination electrode and the value of TALK.
- The new design of equilibrator proposed by Frankignoulle et al. (2001) works correctly even in highly turbid and CO₂ over-saturated water.
- The procedure proposed by Li-Cor[®] to extend the range of pCO₂ measurement up to 10000 μatm is adequate.

It is also worth to note that the indirect method is by far less expensive and more easy to set up than the direct one. The indirect method can be easily used in any field sampling condition, e.g., sampling from a bridge or using a small boat.

Finally, we would also like to underline that the use of the indirect method requires extreme care in analytical procedures and notably:

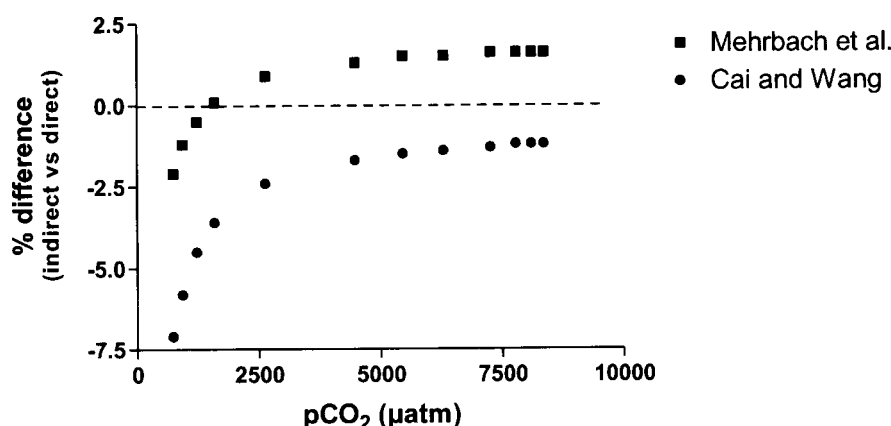


Figure 3. Evolution of the difference (% left axis) between calculated and measured pCO₂ using two different set of constants for carbonic acid.

- The electrode used to measure pH should be calibrated with fresh (<2 weeks) home-made buffers as described by Bates (1973) and using dried analytical quality reagents.
- The measurement of pH should be carried out within minutes after sampling, to prevent CO₂ evasion and biological modifications of the sample.
- Total alkalinity has to be measured within hours after sampling and GF/F filtration has to be made immediately after sampling to avoid the alteration of the sample related to biological activity and chemical carbonate precipitation (Frankignoulle, unpublished data).
- Calculations have to be on the molality scale (mol kgW⁻¹) rather than on the molarity scale (mol l⁻¹).

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