

Direct and indirect pCO₂ measurements in oceanic and coastal waters

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Estuaries are known to display high pCO₂ values in the upper part, due to heterotrophic respiration of organic carbon. In the highly polluted Scheldt estuary (Belgium/Netherlands), The partial pressure of CO₂ (pCO₂) can be as high as 9000 µatm, that is about 25 times the value of atmospheric equilibrium (presently around 370 µatm).

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). 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 µatm and this technique was then not appropriate for the measurement of pCO₂ in some estuaries.

The indirect method consists to calculate pCO₂ 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 H₃O⁺. If pH is determined with combined electrodes, an additional uncertainty arises from the so-called junction potential developed at the reference electrode. For seawater samples, three pH scales have been proposed (seawater scale, total proton scale, free proton scale) and pH is nowadays determined by a spectrophotometric technique which offers quite accurate results. 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. We present here some very satisfactory data obtained in oceanic water, using both the direct and indirect techniques, the latter based on measurement of pH using a glass electrode calibrated on the total proton scale (TRIS and AMP buffers, Dickson, 1993).

However, 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 but also refitted for estuarine environment. But the consistency of the inorganic carbon computations based on the NBS scale has not been so far cross-checked in estuarine waters with direct pCO₂ measurements.

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 pCO₂ range from 500 to 8500 ppm. 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 pCO₂ range from 0 to 10000 µatm (Li-Cor Application Note 122), 2) a new design of equilibrator has recently been proposed to measure pCO₂ 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).