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TECHNICAL NOTE

A NEW DESIGN OF EQUILIBRATOR TO MONITOR CARBON DIOXIDE IN HIGHLY DYNAMIC AND TURBID ENVIRONMENTS

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Abstract—A new design of equilibrator for carbon dioxide monitoring in natural waters is described. It consists in a vertical tube filled with marbles through which water is flowing while equilibrating with a closed air circuit. It offers several advantages compared with classical equilibrators, among which is a fast response time (half-life constant ≈ 30 s) and the potential to work in very turbid water. The proposed equilibrator is of particular interest to monitor carbon dioxide in coastal ecosystems, such as estuaries, which are known to be turbid and highly dynamic. Two performance tests and some field results are presented to illustrate the efficiency of the proposed system. © 2001 Elsevier Science Ltd. All rights reserved

Key words—equilibrator, CO_2 monitoring, turbid environments, coastal systems

INTRODUCTION

For many years, the monitoring of the surface seawater partial pressure of CO_2 (pCO_2) is recognized as a priority in order to identify source and sink areas for atmospheric carbon dioxide. While available data are so far sparse, the coastal ocean is known to display a wide range of pCO_2 values due to specific processes such as upwelling, tidal fronts, river inputs, exchange with sediments and intense biological processes (Kempe, 1982; Walsh, 1988; Mackenzie, 1991; Wollast, 1991; Bakker *et al.*, 1996; Frankignoulle *et al.*, 1996a, b; Borges and Frankignoulle, 1999). Inventory of sinks and sources for atmospheric CO_2 in the coastal ocean is now recognized as essential to get a better understanding of the global carbon cycle. As an example, Frankignoulle *et al.* (1998) have recently estimated that European estuaries emit to the atmosphere 5–10% of the total anthropogenic input caused by combustion from Western Europe. However, monitoring of CO_2 in coastal areas has to address two major problems which are liable to limit the use of classical equilibrators: first, coastal waters are usually turbid and, second, coastal ecosystems are highly dynamic and CO_2 changes are often rapid.

Among the various methods to assess pCO_2, the direct one using an air-flushing equilibrator coupled to an IR gas analyser is presently recognized as the best experimental approach (DOE, 1994). Until now, 3 designs of equilibrators, or combination of them, are commonly used: the "bubble Weiss type" equilibrator, the "laminary flow type" equilibrator and the "shower type" equilibrator (Takahashi, 1961; Keeling *et al.*, 1965; Kelley, 1970; Weiss, 1981; Copin-Montegut, 1985; Goyet *et al.*, 1991; Schneider *et al.*, 1992; Poisson *et al.*, 1993; Roberston *et al.*, 1993; Wanninkhof and Thoning, 1993; Goyet and Peltzer, 1994). Körtzinger *et al.* (1996) have recently proposed a review of these equilibrators and have compared results obtained at sea using two different designs of "bubble type" equilibrators. They found an excellent agreement but mainly when pCO_2 variations were not too abrupt. Indeed, most equilibrators suffer from different and often slow response time, which may range from 5 to 20 min (personal communication from several equilibrator users/designers). While such response time is adequate to study large-scale processes occurring in the open ocean, it may become limiting to study small scale processes as often observed in coastal environments. Moreover, turbidity may cause severe limitation for "classical" equilibrators. As an example, Bakker *et al.* (1996) have recently reported frequent blockage of their shower-type equilibrator during an

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algal bloom, i.e. when pCO_2 monitoring is of particular interest. In order to avoid these problems inherent to classical equilibrators, some new designs have recently been proposed. To solve blockage problems, Cooper *et al.* (1998) have developed an equilibrator with short lengths of glass tubing to proceed equilibration on a large surface, but this system was produced for long time series measurements in the open ocean and to avoid any need for maintenance. Sabine and Key (1996) have developed a system using 60 rotating disks within a cylinder to increase response time and got a half-life time constant for equilibration of about 1 min but nothing is mentioned concerning its behaviour in turbid environments.

In this paper, we present a new design of equilibrator which offers a fast response time and works in highly turbid environments, as shown by some selected laboratory and field experiments in estuarine waters.

DESCRIPTION OF THE SYSTEM

The equilibrator consists in a vertical Plexiglas tube (height: 80 cm, diameter: 10 cm, Fig. 1) which is filled up with marbles in order to increase the surface exchange and reduce the air volume. The seawater ($3\,l\,min^{-1}$) reaches the equilibrator from the top of the tube and a closed air circuit ($3\,l\,min^{-1}$) ensures circulation through the equilibrator (from the bottom to the top), a membrane air pump (GAST®), a regulator and an IR analyser (Licor® 6262). The barometric pressure inside the equilibrator is kept equal to atmospheric using a 10 m fine plastic tube (Ø3 mm) open to the atmosphere outside the ship. Both the barometric pressure and temperature are monitored in the air circuit, while seawater temperature is measured before and after equilibration. The IR analyser is calibrated daily using available pure nitrogen (CO_2 free) and commercial standards

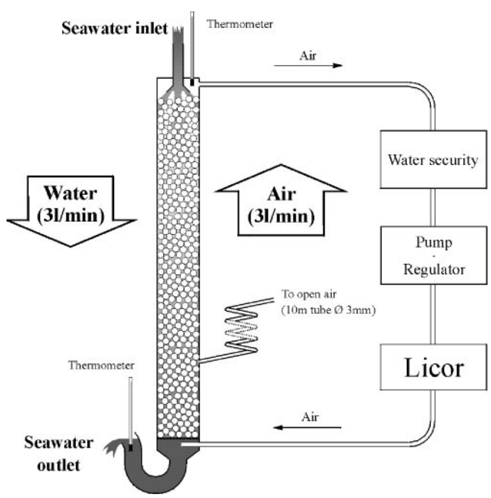

Fig. 1. The equilibrator (see text for detailed description).

(*Air Liquide Belgium*) within 1 µatm. The total surface exchange for equilibration, including the vertical tube and ~600 marbles, is estimated to be $1.3\,m^2$. To complete equilibration within 2 min, the exchange coefficient should then be at least $1.5 \times 10^{-5}\,m\,s^{-1}$ ($5\,cm\,h^{-1}$), which is quite a low value for such a turbulent flowing system. The Licor® is connected to a computer interface which enables acquisition of pCO_2, pH (potentiometric), temperature and atmospheric pressure data every minute.

The relatively high water flow through the system has two consequences: (1) there is no stagnant water within the equilibrator which would lead to a slower equilibration time, as confirmed from visual observation, (2) the thermal equilibration of the system is fast. Field data (not shown) have evidenced that, even when temperature change amounts to several degrees in a few minutes (estuarine fronts), the difference of temperature between water inlet and outlet is below 0.2°C and that the time shift, if any, is less than 1 min.

Finally, it should be pointed out that the proposed design is quite simple to build and set up, and that it does not need any specific technical expertise for operating or for maintenance.

PERFORMANCE TESTS AND RESULTS

Two performance tests have been carried out in the laboratory to determine the response time of the proposed equilibrator. The first test consisted in running the equilibrator with two batches of water, one which presents CO_2 under saturation with respect to the atmosphere ($pCO_2 = 328$ µatm) and the other which is over saturated ($pCO_2 = 397$ µatm). We started the experiment using the first batch, then we submitted the second batch until stability, and then the first batch again. Results are presented in Fig. 2. The data have been fitted into an exponential relationship which reads: *Fraction of achieved equilibrium* $= 1 - \exp(-2.15t)$, where t is the time in minute. The half-life time constant of equilibration is then 27.6 s and one may use this equation to compute that 66, 96 and 99% of equilibrium are achieved in 30, 97 and 118 s, respectively.

The second performance test was carried out by adding HCl to seawater which was running within the equilibrator in a closed water circuit (5 l). Using buffer factor formulations proposed by Frankignoulle (1994), one may calculate that 1 ml of 0.1N HCl should be added to the water to increase its pCO_2 to about 30 µatm. Figure 2 shows an example of the results which can be interpreted as follows:

(1) at the time of HCl injection, the pCO_2 suddenly increases by more than 100 µatm.
(2) The system then goes back to new equilibrium conditions and the kinetics of this process, which

includes both equilibration and water mixing, is described by the following equation: *Fraction of achieved equilibration* $= 1 - \exp(-2.05t)$, where t is the time in minutes. The half-lifetime constant obtained from this experiment is 29.3 s, which is slightly higher than in the first test due to the time required for water mixing process.

To illustrate the efficiency of the proposed system in extreme conditions of turbidity and rate of concentration change, we selected results obtained in two European estuaries that display singular characteristics.

Figure 3 shows results obtained in the Gironde estuary (France, June 1997), which is known to be extremely turbid (Allen *et al.*, 1977). The pCO_2 were determined using both the direct method (equilibrator) and the indirect one. The later, less accurate than the direct method, is based on experimental determination of pH (NBS scale) and total alkalinity (Gran electrotitration on GFC filtered samples), with appropriate constants for carbonic acid (Mehrbach *et al.*, 1973). Results were obtained while sailing across the whole salinity gradient, from the river mouth to the city of Bordeaux. The suspended matter in surface water ranges from 30 mg l^{-1} at the mouth, up to 750 mg l^{-1} at salinity 0. Due to heterotrophy (Frankignoulle *et al.*, 1998) CO_2 over saturation is quite high in the whole estuary and pCO_2 regularly rises from 500 to 1500 µatm when salinity decreases from 30 to 3, and then displays an abrupt increase to 3000 µatm at salinity 0. Results yielded from the equilibrator are in excellent agreement with discrete indirect determinations of pCO_2 within the whole data range, even at salinity 0 where turbidity is the highest and close to 1 g l^{-1}.

Figure 4 shows results obtained in the Douro estuary (Portugal, Sep 1997), which is characterized by the fact that mixing between freshwater and sea water occurs in a very short distance in the river mouth area. As a consequence, horizontal gradients are very important and salinity may change from 5 to 35 in less than 2 min, while sailing within the river mouth. Such substantial salinity changes induce large pH and pCO_2 variations and, as shown in Fig. 4, the asymmetry between salinity and pCO_2 is nearly perfect. The pCO_2 can display changes from 500 to 2000 µatm in less than one minute (time 55), corresponding to a salinity decrease of about 30. For the purpose of this figure, the pH signal was left in mV (i.e. electrode signal) because the drastic

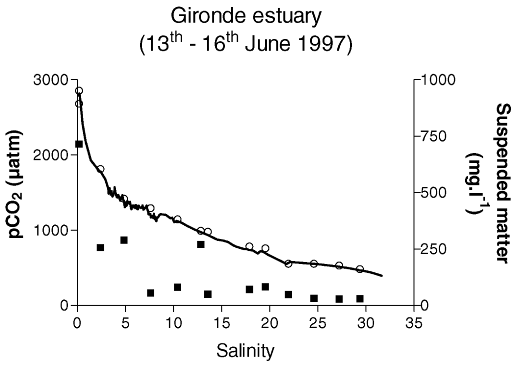

Fig. 3. Measured pCO_2 (full line) from a cruise in the Gironde estuary (France). Open circles indicate pCO_2 as calculated from pH and total alkalinity, and full squares refer to suspended matter.

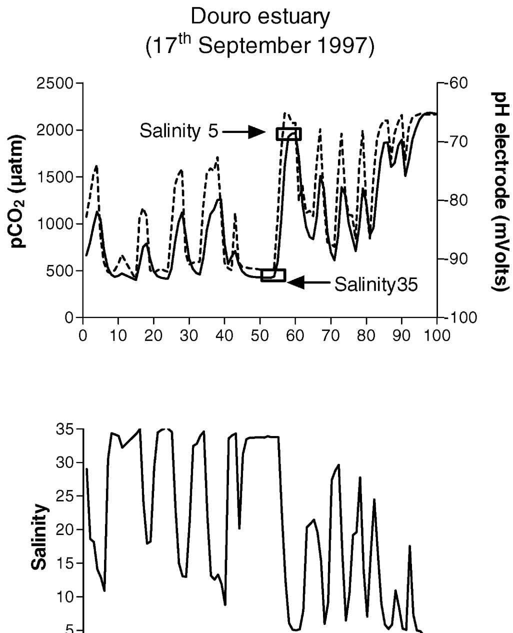

Fig. 4. Measured pCO_2 (full line), pH (dotted line) and salinity data from a cruise in the Douro estuary (Portugal). Arrows indicate the pCO_2 values obtained by the indirect method from discrete samples.

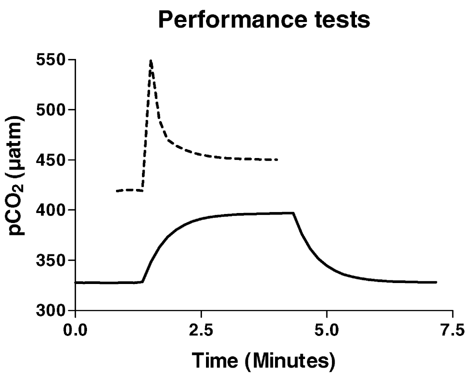

Fig. 2. Performance tests carried out to determine the response time of the equilibrator. Dotted line corresponds to HCl experiment (see text). For the purpose of these experiments, data were acquired each 10 s.

changes in both salinity and temperature did not allow the pH to be calculated. The agreement between the electrode signal and pCO_2 is excellent. Moreover, pCO_2 values provided by the equilibrator are again in good agreement with the ones calculated by the indirect method from discrete Niskin sampling at salinities 5 and 35 (see arrows on Fig. 4).

Results presented in this paper show that the proposed equilibrator design is appropriate to monitor pCO_2 in highly dynamic, and turbid systems encountered in the estuarine and coastal environments.

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REFERENCES

Allen G. P., Sauzay G., Castaing P. and Jouanneau J. M. (1977) Transport and deposition of suspended sediment in the Gironde estuary, France. In *Estuarine Processes*, Vol. 2, ed M. Wiley. Academic, New York.

Bakker D. C. E., De Baar H. J. W. and de Wilde H. P. J. (1996) Dissolved carbon dioxide in Dutch coastal waters. *Mar. Chem.* **55**, 247–263.

Borges A. and Frankignoulle M. (1999) Daily and seasonal variations of the partial pressure of CO_2 in surface seawater along Belgian and southern Dutch coastal areas. *J. Mar. Syst.* **19**, 251–266.

Cooper D. J., Watson A. J. and Ling R. D. (1998) Variation of P_{CO_2} along a North Atlantic shipping route (U.K. to the Caribbean): a year of automated observations. *Mar. Chem.* **60**, 147–164.

Copin-Montegut C. (1985) A method for the continuous determination of the partial pressure of carbon dioxide in the upper ocean. *Mar. Chem.* **17**, 13–21.

DOE (1994) In *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water; Version 2*, eds A. G. Dickson and C. Goyet. Unpublished manuscript.

Frankignoulle M. (1994) A complete set of buffer factors for acid/base CO_2 system in seawater. *J. Mar. Syst.* **5**, 111–118.

Frankignoulle M., Abril G., Borges A., Bourge I., Canon C., Delille B., Libert E. and Théate J.-M. (1998) Carbon dioxide emission from European estuaries. *Science* **282**, 434–436.

Frankignoulle M., Bourge I., Canon C. and Dauby P. (1996a) Distribution of partial CO_2 pressure in the surface water of English Channel and the Southern Bight of the North Sea. *Cont. Shelf Res.* **16**(3), 381–395.

Frankignoulle M., Elskens M., Biondo R., Bourge I., Canon C., Desgain S. and Dauby P. (1996b) Distribution of inorganic carbon and related parameters in surface seawater of the English Channel. *J. Mar. Sys.* **7**(2–4), 427–434.

Goyet C., Beauverger C., Brunet C. and Poisson A. (1991) Distribution of carbon dioxide partial pressure in surface waters of the Southwest Indian Ocean. *Tellus* **43B**, 1–11.

Goyet C. and Peltzer E. (1994) Comparison of the August–September 1991 and 1979 surface partial pressure of CO_2 distribution in the equatorial Pacific Ocean near 150°W. *Mar. Chem.* **45**, 257–266.

Keeling C. D., Rakestraw N. W. and Waterman L. S. (1965) Carbon dioxide in surface waters of the Pacific Ocean. 1. Measurement of the distribution. *J. Geophys. Res.* **70**, 6087–6097.

Kelley J. J. (1970) Carbon dioxide in the surface waters of the North Atlantic Ocean and the Barents and Kara Seas. *Limnol. Oceanogr.* **15**, 80–97.

Kempe S. (1982) Valdivia Cruise, October (1981): carbonate equilibria in the Estuaries of Elbe, Weser, Ems and in the Southern German Bight. *Mitt. Geol.-Paläont. Inst. Univ. Hamburg* **52**, 719–742.

Körtzinger A., Thomas H., Schneider B., Gronau N., Mintrop L. and Duinker J. C. (1996) At-sea intercomparison of two newly designed underway pCO_2 system-encouraging results. *Mar. Chem.* **52**, 133–145.

Mackenzie F. T. (1991) What is the importance of ocean margin processes in Global Change? In *Ocean Margin Processes in Global Change*, eds R. F. C. Mantoura, J. M. Martin and R. Wollast. Wiley, New York.

Mehrbach C., Culberson C. H., Hawley J. E. and Pytkowicz R. M. (1973) Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* **18**, 897–907.

Poisson A., Metzl N., Brunet C., Schauer B., Bres B., Ruiz-Pino D. and Louanchi F. (1993) Variability of sources and sinks of CO_2 in the Western Indian and Southern Oceans during the year 1991. *J. Geophys. Res.* **98**, 22,759–22,778.

Robertson J. E., Watson A. J., Langdon C., Ling R. D. and Wood J. W. (1993) Diurnal variations in surface pCO_2 and O_2 at 60°N, 20°W in the North Atlantic. *Deep Sea Res.* **40**, 409–422.

Sabine C. L. and Key R. M. (1996) *A New Instrument Design for Continuous Determination of Oceanic pCO_2*. Tech. Rep. #96-12, Ocean Tracer Laboratory, Dept. of Geosciences, Princeton University, Princeton, 20pp.

Schneider B., Kremling K. and Duinker J. C. (1992) CO_2 partial pressure in Northeast Atlantic and adjacent shelf waters: processes and seasonal variability. *J. Mar. Syst.* **3**, 453–463.

Takahashi T. (1961) Carbon dioxide in the atmosphere and in Atlantic Ocean water. *J. Geophys. Res.* **66**, 477–494.

Walsh J. J. (1988) *On the Nature of Continental Shelves*, Academic Press, New York, 520 pp.

Wanninkhof R. and Thoning K. (1993) Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods. *Mar. Chem.* **44**, 189–204.

Weiss R. F. (1981) Determinations of CO_2 and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. *J. Chromatogr. Sci.* **19**, 611–616.

Wollast R. (1991) The coastal organic carbon cycle: fluxes, sources and sinks. In *Ocean Margin Processes in Global Change*, eds R. F. C. Mantoura, J. M. Martin and R. Wollast. Wiley, New York.