Discussion


Gwenael Abril

Laboratoire Environnements et Paléoenvironnements Océaniques (EPOC), UMR CNRS 5805, Université Bordeaux1, Talence, France

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A B S T R A C T

Silva et al. propose a new method for quantifying benthic net community production (NCP) of tidal flats under submerged condition, based on the monitoring of water pCO2 in a transparent benthic chamber around high tide. I demonstrate here with theoretical considerations that this method is inappropriate for coastal environments, because it allows only the quantification of the change in the dissolved CO2 which, at classical seawater pH, is only ~ 10% of the change of the dissolved inorganic carbon (DIC). Total Alkalinity and/or DIC must be measured at the beginning and end of incubations in order to compute NCP in coastal environments. However, I also demonstrate that when pH is below 7, more than 95% of the DIC change occurs in the CO2 pool. The method proposed by Silva et al. is thus valuable for freshwater environments with acidic, low alkalinity waters, where monitoring the water pCO2 in a vial or chamber provides alone a very close approximation of the planktonic or benthic net community production.

When dissolved CO2 in the ocean exchanges with the atmosphere, is used by photosynthesis or is released by respiration, all the chemical species that form the dissolved inorganic carbon (DIC, the sum of free dissolved CO2, carbonic acid H2CO3, bicarbonate and carbonate ions, HCO3 and CO32−), are affected. Photosynthesis and respiration do not affect the seawater Total Alkalinity (TA, dominated at classical seawater conditions by the term [HCO3−]+[CO32−]) (Frankignouille, 1994), except when they are associated with intense nitrogen transformations (ammonification, nitrification, denitrification), when respiration occurs in anoxic conditions, and when calcification and carbonate dissolution occur (Gattuso et al., 1999; Abril and Frankignouille, 2001; Barron et al., 2006). In seawater, CO2* (the sum of dissolved free CO2 and carbonic acid), HCO3 and CO32− are in a dynamic equilibrium and the input or uptake of any chemical specie immediately generates a change in pH and in the proportions of all the others species (Fig. 1A). This property of the carbonate acid/base system, called “buffer capacity”, always tends to “absorb” the specie that has been gained or to “replace” the specie that has been lost. In other terms, when dissolved CO2 diffuses from the atmosphere or is released by aquatic respiration, water pCO2 indeed increases and the pH decreases, but a large fraction of the additional CO2 joins the HCO3− and CO32− pools because of the buffering capacity of the seawater.

This property gives to the ocean its great potential to store anthropogenic CO2, until the seawater pH drops too much (Sundquist and Plummer, 1981). On the contrary, when primary production occurs, pCO2 decreases and the pH increases, but dissolved CO2 is continuously fueled from the HCO3− pool, which, in turn, also contributes to the DIC uptake and the biomass finally produced. As a consequence, in order to quantify primary production and respiration in seawater the changes in the whole DIC pool must be quantified, and the change in the CO2* pool is always much lower. This is the main reason why the method of Silva et al. (2008), which consists in monitoring continuously water pCO2 in a transparent benthic chamber, does not provide (in the way it is used), a measurement of net community production (NCP) in coastal waters as the authors state, but something that is much lower and that, in addition, strongly depends on experimental conditions, as I will discuss later.

Benthic primary production of seagrasses is indeed a potential significant component of the global oceanic cycle (Duarte et al., 2004) and there is a need for developments of innovative techniques to measure benthic NCP, in particular techniques based on sensors that allow a monitoring at different temporal and spatial scales. With the development of accurate and relatively cheap CO2 gas analyzers, the measurement of pCO2 changes in the air enclosed in a static chamber provides an accurate estimation of NCP in intertidal areas at low tide during the emersion (Migné et al., 2002). This method has been used with great success and provided...
error, it would be easily corrected, but in reality the change of the DIC induced by net community production. In contrast, in acid waters the ratio is close to one (0.953 at pH 7).

Fig. 1. A: The Bjerrum diagram of a typical coastal water (Temperature 15 °C, Salinity 30, TA 2.2 mmol kg⁻¹; Cases 1, 3–5 in Table 1); Molar contribution of each chemical species to the total DIC as a function of pH. B: Ratio between the change in CO₂* concentration (delta CO₂*) and the change in DIC concentration (delta DIC) induced by an input/output of dissolved CO₂ during primary production, respiration and/or air–sea exchange. Changes in concentrations were calculated for 0.1 pH increments and refer to the maximal pH value of the interval. At classical seawater pH of ~8.2, the ratio is ~0.1, which means that, in a benthic chamber, the change of CO₂* is only ~10% the change of the DIC induced by net community production. In contrast, in acid waters the ratio is close to one (0.953 at pH 7).

fundamental information on the factors controlling autotrophic and heterotrophic activities in emerged conditions (Migné et al., 2004; Davout et al., 2004; Spilmont et al., 2005, 2007; Hubas et al., 2007). It would indeed be very useful to benefit from a similar technique at high tide during the submersion, as propose Silva et al. in their paper. However, in Migné’s chamber, the pCO₂ evolution is measured in a given volume of air (not of water), where CO₂ is largely the dominant carbon form. NCP in mol of C per surface area is simply calculated from the geometry of the chamber, the slope of pCO₂ versus time and the molar volume of CO₂, assuming it behaves as an ideal gas. The system of Silva et al. is based on the same principle when used at low tide. In contrast, at high tide, their system measures the evolution of pCO₂ in a volume of water enclosed in the chamber. The authors do not clearly specify in their paper, how they calculate NCP in this latter case. If their objective is to quantify the change in CO₂* in the chamber during the incubation, why don’t they refer to the solubility of CO₂ in water (Weiss, 1974), the parameter that allows a conversion from CO₂ partial pressures to moles? The molar volume of an ideal gas cannot be applied to the case of CO₂ dissolved in water. In case of such an error, it would be easily corrected, but in reality the change of the CO₂* pool is still inappropriate for NCP quantification.

To illustrate how the change in CO₂* in a chamber is a great underestimation of benthic NCP, I have taken 6 theoretical cases. 5 cases with classical chemical and biological conditions found in the coastal zone and the 6th case classical for freshwaters (Table 1). I first take classical initial conditions in the chamber (temperature, salinity, TA, pH and pCO₂) and I calculate the initial DIC and CO₂*. concentrations solving the equations of carbonate system in Fig. 1A. I used for these calculations the carbonic acid constants sets proposed 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). Then, postulating a given NCP, and with the geometry of the chamber of Silva et al., I calculate the theoretical change in DIC it must induce after one hour of incubation. Then I solve the equations of the carbonate system at the end of the incubation, but this time, introducing the temperature, salinity, TA and DIC values, the later being the initial DIC minus the DIC consumed by NCP in the chamber during one hour, pH, pCO₂ and the CO₂* concentration are then calculated.

As result of the buffering effect discussed previously, the change in CO₂* is only ~10% of the change in DIC (Table 1), and thus the method of Silva et al. under submerged conditions, greatly underestimates NCP. The ratio of the changes in CO₂* and DIC concentrations (delta CO₂*/delta DIC) strongly depends on pH and is about 0.1 at typical seawater pH values of 8.2 (Fig. 1B). If the Silva et al. chamber gives very contrasted results under emerged and submerged conditions (their Fig. 4), it might be because their method is inappropriate in submerged condition. This might be part of the reason for the rapid drop in NCP under submerged conditions in their Fig. 4B. The comparison of cases 1 and 2 in Table 1 illustrates the effect of the buffer capacity of the water, the underestimation being higher when the TA is higher (Case 1). In cases 3, 4 and 5, the initial pCO₂ in the chamber is set at different values, all other initial parameters being unchanged. For the same NCP and water TA, the loss in CO₂* in the chamber decreases when the initial pCO₂ decreases, as result of the acid/base CO₂ system properties. When the initial concentration of CO₂* is high, there is less need to compensate its loss during photosynthesis by a displacement of the CO₂*/HCO₃⁻ equilibrium toward the CO₂* form. This explains why the evolution of water pCO₂ with time in the chamber is not linear (Fig. 3 in Silva et al.). At these pH values, the change in CO₂* is not proportional to the change in DIC. Another interesting fact is that at classical low pH freshwaters conditions (case 6), the method of Silva et al. would work very well. Indeed, as shown in Fig. 1B, at lower pH and higher pCO₂, the delta CO₂*/delta DIC ratio induced by CO₂ input/output is close to 1 and most of the DIC change occurs in the CO₂* pool. In addition, the pCO₂ change measured in the chamber is the largest for the same NCP (Table 1) and thus easy to detect with Silva et al.’s chamber design. Also, time course of pCO₂ in such freshwaters conditions should be close to linear for a constant NCP. As a result, deployments of Silva et al.’s chamber in acid freshwaters would allow the computation of precise NCP values, even after short deployment times.

Several statements in the manuscript of Silva et al. reveal that they do not fully understand how the CO₂ system works. The sentence “in the case of underwater incubation there is also a need to avoid significant alteration in the carbonate balance, related to pH changes”, suggests that there could be cases where primary production and respiration could occur without affecting the whole carbonate system and without changing the pH. In seawater at 15 °C and at atmospheric pCO₂, the buffer factor pH/DIC for a CO₂ input or uptake is ~2214 mol⁻¹, (Frankignoulle, 1994), which means that an uptake of 10 μmol kg⁻¹ of CO₂ by photosynthesis generates alone an increase of the pH of 0.02 units. It seems also that in the author’s mind, there might be cases when CO₂ and HCO₃⁻ behave independently in seawater, as they write “… in communities dominated by plants that use bicarbonate (…) pH and alkalinity must be checked at
the beginning and at the end of the incubations, as a way of determining the relative amounts of bicarbonate and carbon dioxide being taken by the plants*. The truth is that, even in an ideal case where only CO₂ is used by the whole benthic community, measuring the evolution of water pCO₂ in a benthic chamber cannot provide alone a quantification of benthic NCP in coastal waters (see Table 1). The other parameters of the carbonate system must be followed in parallel to pCO₂ in order to allow a quantification of the DIC change. For TA and/or DIC determination, water must be sampled at the beginning and at the end of incubations. Significant pCO₂ changes can indeed be observed after very short (~30 min) deployment times of the chamber (Fig. 3 in Silva et al.), but the TA and DIC changes during such short periods might be too small to be quantified accurately with classical methods. Monitoring pH together with pCO₂ in the chamber should allow in theory the computation of DIC and TA changes. However pH and pCO₂ strongly influence each other in the carbonate system and in such a computation, the DIC change would be very sensitive to the absolute accuracy of pCO₂ and pH measurements and would rely on several technical aspects: pH calibration and electrode drift, effects of pressure changes with the tide ... An alternative would be to calculate the initial and final DICs from the pCO₂ and CO₂* change, assuming that TA remains constant. Such hypothesis is however very strong and not valid for many coastal sediments, not only because some plants use bicarbonates, as argue Silva et al., but also because calcification by benthic macrofauna and carbonate dissolution in sediments can be major CO₂ and TA sources and sinks (Barrón et al., 2006).

Monitoring continuously pCO₂ in benthic chamber thus constitutes a minor technical advance for benthic NCP quantification in coastal waters, in comparison with classical chambers where pH and dissolved oxygen are monitored continuously and water is sampled, at the beginning and end of the incubation for chemical analysis (e.g. Invers et al., 1997; Barrón et al., 2006; Thouzeau et al., 2007). pH and TA measurements allow the computation of DIC fluxes that can be compared with the measured oxygen fluxes, but a minimum of 3 h of contact is necessary (Thouzeau et al., 2007). Sampling for TA, Ca²⁺ and Mg²⁺ can also provide important additional information on the contribution of carbonate precipitation and dissolution in benthic communities (Barrón et al., 2006). In intertidal area, although benthic chambers are very powerful tools during the emersion, under submerged conditions technical and theoretical constraints remain very strong and submersion time might be too short to deploy chambers during enough time. The eddy correlation technique recently developed by P. Berg and collaborators (Berg et al., 2003) is in my opinion much more promising for future underwater measurement of marine benthic NCP, because it integrates surface areas representative of seagrass meadows, it does not affect the hydrodynamics and it can generate autonomously long data time series.

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References


