



Discussion

Comments on: “Underwater measurements of carbon dioxide evolution in marine plant communities: A new method” by J. Silva and R. Santos [Estuarine, Coastal and Shelf Science 78(2008) 827–830]

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ABSTRACT

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 $p\text{CO}_2$ 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 CO_2 which, at classical seawater pH, is only $\sim 10\%$ 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 CO_2 pool. The method proposed by Silva et al. is thus valuable for freshwater environments with acidic, low alkalinity waters, where monitoring the water $p\text{CO}_2$ in a vial or chamber provides alone a very close approximation of the planktonic or benthic net community production.

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When dissolved CO_2 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 CO_2 , carbonic acid H_2CO_3 , bicarbonate and carbonate ions, HCO_3^- and CO_3^{2-}), are affected. Photosynthesis and respiration do not affect the seawater Total Alkalinity (TA, dominated at classical seawater conditions by the term $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) (Frankignoulle, 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 Frankignoulle, 2001; Barrón et al., 2006). In seawater, CO_2^* (the sum of dissolved free CO_2 and carbonic acid), HCO_3^- and CO_3^{2-} 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 CO_2 diffuses from the atmosphere or is released by aquatic respiration, water $p\text{CO}_2$ indeed increases and the pH decreases, but a large fraction of the additional CO_2 joins the HCO_3^- and CO_3^{2-} pools because of the buffering capacity of the seawater.

This property gives to the ocean its great potential to store anthropogenic CO_2 , until the seawater pH drops too much (Sundquist and Plummer, 1981). On the contrary, when primary production occurs, $p\text{CO}_2$ decreases and the pH increases, but dissolved CO_2 is continuously fueled from the HCO_3^- 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 CO_2^* pool is always much lower. This is the main reason why the method of Silva et al. (2008), which consists in monitoring continuously water $p\text{CO}_2$ 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 CO_2 gas analyzers, the measurement of $p\text{CO}_2$ 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

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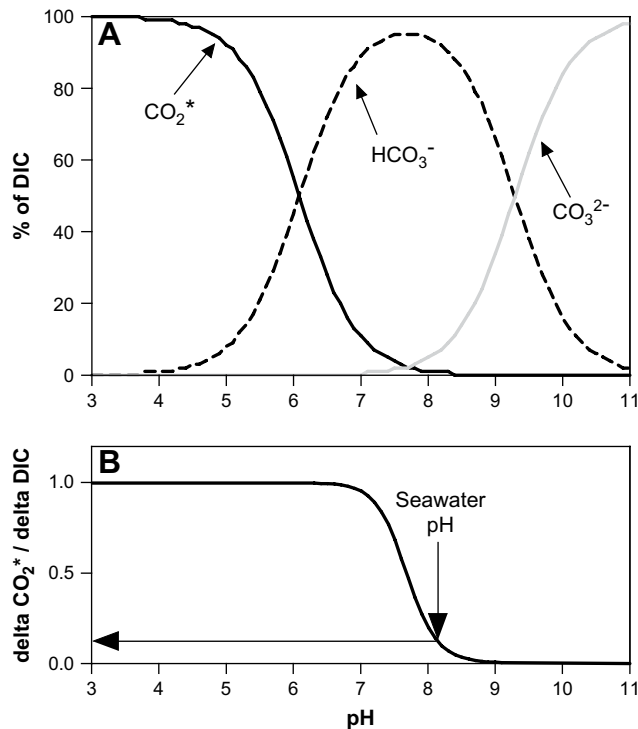


Fig. 1. A: The Bjerrum diagram of a typical coastal water (Temperature 15 °C, Salinity 30, TA 2.2 mmol kg⁻¹; Cases 1, 3–5 in Table 1); Molar contribution of each chemical species to the total DIC as a function of pH. B: Ratio between the change in CO_2^* concentration (ΔCO_2^*) and the change in DIC concentration (ΔDIC) induced by an input/output of dissolved CO_2 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 CO_2^* 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; Davoult 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 pCO_2 evolution is measured in a given volume of air (not of water), where CO_2 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 pCO_2 versus time and the molar volume of CO_2 , 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 pCO_2 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 CO_2^* in the chamber during the incubation, why don't they refer to the solubility of CO_2 in water (Weiss, 1974), the parameter that allows a conversion from CO_2 partial pressures to moles? The molar volume of an ideal gas cannot be applied to the case of CO_2 dissolved in water. In case of such an error, it would be easily corrected, but in reality the change of the CO_2^* pool is still inappropriate for NCP quantification.

To illustrate how the change in CO_2^* 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 pCO_2) and I calculate the initial DIC and CO_2^*

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 CO_2 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, pCO_2 and the CO_2^* concentration are then calculated. In Table 1, NCP deduced from the pCO_2 monitoring is finally calculated as in Silva et al. In Method 1, the gas molar volume is applied to CO_2 dissolved in the water of the chamber volume, as in emerged conditions. In method 2, NCP is calculated as the change in CO_2^* based on the CO_2 solubility coefficient given by Weiss (1974).

As result of the buffering effect discussed previously, the change in CO_2^* 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 CO_2^* and DIC concentrations ($\Delta \text{CO}_2^* / \Delta \text{DIC}$) strongly depends on pH and is about 0.1 at typical seawater pH 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 pCO_2 in the chamber is set at different values, all other initial parameters being unchanged. For the same NCP and water TA, the loss in CO_2^* in the chamber decreases when the initial pCO_2 decreases, as result of the acid/base CO_2 system properties. When the initial concentration of CO_2^* is high, there is less need to compensate its loss during photosynthesis by a displacement of the $\text{CO}_2^* / \text{HCO}_3^-$ equilibrium toward the CO_2^* form. This explains why the evolution of water pCO_2 with time in the chamber is not linear (Fig. 3 in Silva et al.). At these pH values, the change in CO_2^* 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 pCO_2 , the $\Delta \text{CO}_2^* / \Delta \text{DIC}$ ratio induced by CO_2 input/output is close to 1 and most of the DIC change occurs in the CO_2^* pool. In addition, the pCO_2 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 pCO_2 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 CO_2 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 pCO_2 , the buffer factor $\partial \text{pH} / \partial \text{DIC}$ for a CO_2 input or uptake is -2214 mol^{-1} , (Frankignoulle, 1994), which means that an uptake of $10 \mu\text{mol kg}^{-1}$ of CO_2 by photosynthesis generates alone an increase of the pH of 0.022 units. It seems also that in the author's mind, there might be cases when CO_2 and HCO_3^- behave independently in seawater, as they write “... in communities dominated by plants that use bicarbonate (...) pH and alkalinity must be checked at

Table 1

Six theoretical case studies of changes in the concentration of dissolved inorganic carbon species in a benthic chamber. Comparison of true theoretical NCP with the ones derived from the method of Silva et al. Cases 1–5 are typical of coastal waters, whereas Case 6 is a freshwater case.

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Net Community Production (NCP) ($\text{mmol m}^{-2} \text{h}^{-1}$)	5	5	10	10	10	10
Theoretical DIC change in the chamber ^a ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	–16.1	–16.1	–32.2	–32.2	–32.2	–32.2
Constant conditions in the chamber						
Temperature ($^{\circ}\text{C}$)	15	15	15	15	15	15
Salinity	30	28	30	30	30	0
Total Alkalinity ($\mu\text{mol kg}^{-1}$)	2200	1900	2200	2200	2200	500
Initial conditions in the chamber						
pCO ₂ (ppmv)	380	380	500	380	316	9 125
pH	8.185	8.138	8.082	8.185	8.253	6.500
DIC ($\mu\text{mol kg}^{-1}$)	1999	1748	2 043	1999	1967	916
CO ₂ * ($\mu\text{mol kg}^{-1}$)	14.7	14.8	19.2	14.7	12.2	415.6
Final conditions in the chamber after one hour						
pCO ₂ (ppmv)	346	339	408	316	266	8 420
pH	8.220	8.181	8.159	8.253	8.317	6.535
DIC ($\mu\text{mol kg}^{-1}$)	1983	1732	2011	1967	1935	884
CO ₂ * ($\mu\text{mol kg}^{-1}$)	13.3	13.2	15.7	12.2	10.2	383.5
Changes during one hour incubation						
ΔpCO_2 (ppmv)	–34	–41	–92	–64	–50	–705
pH	0.035	0.043	0.077	0.068	0.064	0.035
ΔDIC ($\mu\text{mol kg}^{-1}$)	–16.1	–16.1	–32.2	–32.2	–32.2	–32.2
ΔCO_2^* ($\mu\text{mol kg}^{-1}$)	–1.4	–1.6	–3.5	–2.5	–2.0	–32.1
NCP Silva et al method 1 ^b ($\text{mmol m}^{-2} \text{h}^{-1}$)	0.23	0.28	0.63	0.44	0.35	4.9
Underestimation	95%	94%	93%	96%	97%	51%
NCP Silva et al. method 2 ^c ($\text{mmol m}^{-2} \text{h}^{-1}$)	0.4	0.5	1.1	0.8	0.6	9.9
Underestimation	92%	90%	89%	92%	94%	1%

^a Using the chamber design of Silva et al. (2008): diameter 30 cm and volume 22 L.

^b Silva et al. method 1 consists in applying the same calculation as in air, as in emerged conditions. The CO₂ molar volume (assuming it behaves as an ideal gas) is applied to the volume of water and the slope of the pCO₂ versus time.

^c Silva et al. method 2 considers the theoretical change in CO₂* concentration in the chamber during the incubation, as derived from the water pCO₂ evolution in the chamber (their Fig. 3) and a solubility coefficient of CO₂ K_0 of $0.0385 \text{ mol kg}^{-1} \text{ atm}^{-1}$ (Weiss, 1974).

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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