Control of air-sea CO_2 disequilibria in the subtropical NE Atlantic by planktonic metabolism under the ocean skin

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[1] The air-sea CO_2 gradient at the subtropical NE Atlantic was strongly dependent on the metabolism of the planktonic community within the top cms, but independent of that of the communities deeper in the water column. Gross primary production (GPP) and community respiration (R) of the planktonic community within the top cms exceeded those of the communities deeper in the water column by >10-fold and >7 fold, respectively. Net autotrophic metabolism (GPP > R) at the top cms of the water column in some stations drove CO_2 uptake by creating a CO_2 deficit at the ocean surface, while net heterotrophic metabolism (GPP < R) at the top cms of the water column in other stations resulted in strong CO_2 supersaturation, driving CO_2 emissions. These results suggest a strong control of the air-sea pCO_2 anomaly by intense biological processes. **Citation:** Calleja, M. Ll., C. M. Duarte, N. Navarro, and S. Agustí (2005), Control of air-sea CO_2 disequilibria in the subtropical NE Atlantic by planktonic metabolism under the ocean skin, *Geophys. Res. Lett.*, *32*, L08606, doi:10.1029/2004GL022120.

[2] Physical and biological processes render the ocean a major sink for anthropogenic CO_2 [*Watson and Orr*, 2003; *Sabine et al.*, 2004]. Biological processes affect the partial pressure of CO_2 at the ocean surface (pCO_2w) relative to that in the atmosphere (pCO_2a), hence generating disequilibria ($\Delta pCO_2 = pCO_2w - pCO_2a$) leading to gradient-driven CO_2 flux. Whereas evidence for physical controls of air-sea CO_2 fluxes abounds [cf. *Watson and Orr*, 2003], the relationship between planktonic metabolism and ΔpCO_2 is only apparent where large phytoplankton blooms draw pCO_2 down [*Watson and Orr*, 2003], a situation rarely encountered in tropical and subtropical seas. The key biological process affecting pCO_2w is planktonic metabolism [*Ducklow and McCallister*, 2005], specifically the balance between the gross primary production (GPP) and community respiration (R), represented by the net community production (NCP, NCP = GPP − R). Net autotrophic (GPP > R) and net heterotrophic (GPP < R) metabolism should drive pCO_2w towards a CO_2 deficit (i.e. $\Delta pCO_2 < 0$) and a CO_2 excess (i.e. $\Delta pCO_2 > 0$) at the ocean surface, respectively. However, the effect of planktonic metabolism on pCO_2w is compounded with that of hydrodynamic inputs of DIC, $CaCO_3$ precipitation and dissolution [e.g., *Robertson et al.*, 1994], thermodynamic effects related to temperature changes, and the history of the water mass, among others [*Watson and Orr*, 2003; *Ducklow and McCallister*, 2005], which may mask the relationship between ΔpCO_2 and planktonic metabolism. In addition to planktonic metabolism, planktonic calcification can also affect pCO_2w by producing CO_2 and, therefore, raising pCO_2w [*Robertson et al.*, 1994].

[3] Here we demonstrate a strong relationship between ΔpCO_2 and planktonic metabolism within the top 2 cm layer in the subtropical NE Atlantic, suggesting a strong control of air-sea CO_2 exchange by the metabolism of the planktonic community located just below the ocean skin. We do so on the basis of examination of NCP for the communities located within the top 2 cm, just below the ocean skin, those at 5 m depth - conventionally sampled to represent the ocean surface in research cruises - and that integrated across the photic layer, along with estimates of ΔpCO_2 across the air-sea interface.

[4] Sampling just below the ocean skin (top 2 cm of the ocean) and measurements of pCO_2w and pCO_2a were conducted at 7 stations away from coastal influences along the NE subtropical Atlantic between 23 May and 6 June, 2003 (Table 1), from a boat sailing, at about 09:00 GMT (10:00 local time), away from any possible contamination from the research vessel. The number of stations where measurements were conducted was limited by the oceanic conditions when a boat could be safely deployed to conduct these measurements. Sampling was possible at wind velocities <12.5 m s^{-1} with the wind velocity at the time of sampling averaging 8.1 m s^{-1}, above the mean wind velocity for the region of 6.5 m s^{-1} (data by *Takahashi et al.* [2002]). The cruise ranged from highly oligotrophic waters near the subtropical gyre (0.05 μg Chl a L^{-1}) to highly productive waters off the NW African coast (3.5 μg Chl a L^{-1}), and ranged from surface waters undersaturated in CO_2 (333 μatm) to supersaturated (379 μatm) relative to atmospheric equilibrium. Water samples within the top cms of the ocean were collected using a peristaltic pump. The inlet was held within the top cm of the water column by a floating device, so that we estimate that water samples represent a layer of few cms thick, centered at about 2 cm depth. We, therefore, hereafter refer to these samples as 2 cm depth, although the exact thickness of the water layer sampled is undetermined. pCO_2a and pCO_2w were determined using a high-precision (±1 ppm) non-dispersive infrared gas analyzer (EGM-4, PP-systems). Before entering the gas analyzer, the gas stream was circulated through a calcium sulfate column to avoid interferences from water vapor. A peristaltic pump and a gas exchange column (Mini-Module 1.25 × 9 Membrane Contactor, Celgard) with an effective surface area of 0.5 m^2, a total volume of 52 ml and a

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Table 1. Planktonic Metabolism at Different Depths, Wind Velocity, and the pCO_2 Anomaly Between the Top Cms of the Water Column and Air and 5 m Depth in the Stations Sampled Along the NE Atlantic[a]

| | | Top 2 cm | | 5 m | | Integrated Photic Layer | | | ΔpCO_2 2 cm-Air, | ΔpCO_2 2 cm-5 m, |
Lat °N	Long °W	GPP	R	GPP	R	GPP	R	Wind Vel., m s^{-1}	μatm	μatm
26.53	16.02	3.07	5.65	0.09	1.92	0.35	0.73	5.2	−8	9
25.98	18.00	1.36	15.34	0.48	0.87	0.18	0.40	6.5	14	37
25.98	26.06	3.37	5.54	0.29	0.02	0.18	0.38	7.4	12	9
21.08	25.99	4.34	0.28	0.73	2.47	0.67	1.31	8.5	−16	9
20.99	23.02	7.15	1.60	1.91	1.56	1.21	0.57	7.9	−22	−17
21.02	21.00	5.54	7.16	2.63	0.75	4.97	1.28	10.3	−11	15
20.98	19.03	23.90	11.41	24.84	7.75	8.05	4.80	12.3	−33	9

[a]GPP = Gross primary production. R = Community respiration. All rates in mmol O_2 m^{-3} d^{-1}.
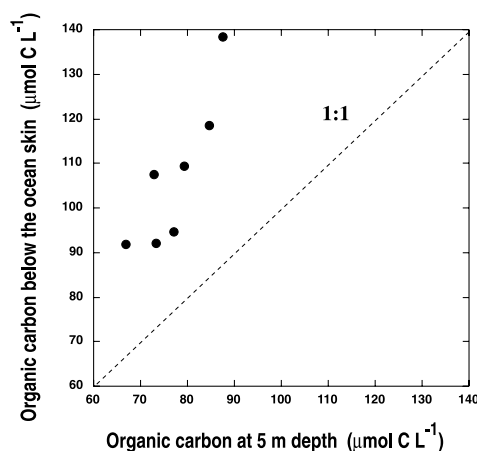
water flow of about 300 ml min^{-1} were utilized for air-surface sea-water equilibration, resulting in a residence time of only 10 s. The gas phase was continuously circulated through the equilibrator and the infrared gas analyzer. pCO_2 measurements correspond, therefore, to that in dry air, as measured, and no efforts were made to correct this for the atmospheric moisture. pCO_2 measurements were also conducted, using the same equipment described above, from 5 m depth, to compare these values with those measured at the top 2 cm layer, with the 5 m samples collected from a pump placed in the haul of the ship except at two stations, where 5 m samples were also collected from the boat using the peristaltic pump described above. Parallel measurements of atmospheric pCO_2 were registered at 1 min intervals using a similar equipment set up on board the research vessel, away from any sources of contamination. The water temperature within the top 2 cm was measured to the nearest ±0.1°C using a digital thermometer. The analyzer was calibrated with a commercial air mix composed by 541 ppm of CO_2 and N_2 gas, which revealed an accuracy of ±1 ppm in the determinations of pCO_2.

[5] Additional water samples for planktonic metabolism estimates and organic carbon determinations were collected using a Rosette sampler system at 5 m depth and 3 additional depths extending along the photic layer (i.e. at depths receiving >1% of the light incident just below the surface), selected following examination of underwater photosynthetically active radiation (PAR) penetration derived from vertical profiles with a PAR sensor. Wind velocity at the time of sampling was recorded at 1 min intervals from the ship's meteorological station, and used to estimate the gas exchange coefficient using the parametrisation of *Nightingale et al.* [2000].

[6] Water samples for community metabolism determinations were carefully siphoned into 5 (for the top 2 cm layer samples) to 7 replicated 125 ml clear and dark glass Winkler bottles, and incubated just below the water surface in a tank held on deck flushed with surface seawater to maintain surface temperature (top 2 cm water samples), and, for deeper samples, suspended at the depth of sampling from a free-drifting buoy. The use of glass Winkler bottles removed UV radiation relative to the light environment in situ. The Winkler bottles were retrieved after 24 h of incubation and immediately fixed. NCP and R were determined from the rate of dissolved oxygen change, measured using high-precision Winkler titration with potentiometric end-point detection [*Oudot et al.*,

1988], over 24 h in the clear and dark bottles, respectively. The coefficient of variation of replicated oxygen determinations averaged 0.2%. GPP was calculated as the sum of NCP and R. The average metabolic rates across the photic layer were calculated as the ratio of the rates derived by vertically integrating the measurements obtained and the depth of the photic layer. Water samples for TOC analysis were transferred to precombusted glass ampoules (450°C for 4.5 h) and kept acidified (pH: 1−2) until analysis on a Shimadzu TOC-5000A. Standards of 44−45 μmol C and 2 μmol C provided by D. A. Hansell and Wenhao Chen (Univ. of Miami) were used to assess the accuracy of the estimates. Chlorophyll *a* concentrations were analyzed spectrofluorimetrically.

[7] Although organic carbon concentrations in the upper 2 cm of the water column were correlated with those at 5 m depth (R^2 = 0.69, p = 0.01, Figure 1), the upper 2 cm of the water column was greatly enriched in TOC relative to 5 m depth at all stations investigated (Figure 1), with TOC within the top 2 cm of the water column exceeding that at 5 m depth by, on average, 30.0 ± 4.3 μmol C L^{-1} (Figure 1). Chlorophyll *a* concentrations within the top cms of the water column exceeded those at 5 m depth in all stations sampled by, on average, 24.3 ± 3.3%. The organic carbon enrichment at the top 2 cm layer relative to 5 m depth did not decline with increasing wind speed, within the range observed in this study, and the highest enrichment

Figure 1. The relationship between organic carbon concentration at 5 m depth and just below the ocean skin (i.e., within the top 2 cm of the water column).
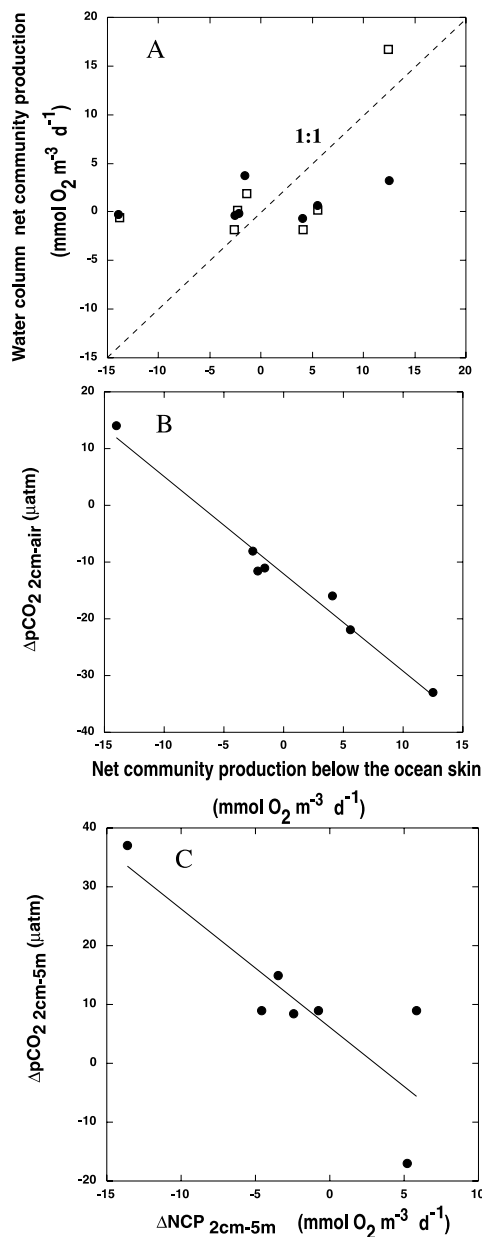
>10-fold and >7 fold higher, respectively, Table 1), and the corresponding NCP independent (P > 0.05; Figure 2a) of those of the communities at 5 m depth and that integrated across the photic layer. The difference between water column NCP and that at the upper 2 cm of the water column was highest when NCP therein was most negative (Figure 2a), suggesting a particularly important role of microheterotrophs in generating the observed difference in planktonic metabolism between the top layer and deeper waters. The pCO$_2$ within the top cms of the water column was not in equilibrium with either the air or the underlying waters at 5 m depth (Table 1). Indeed, our measurements indicated that pCO$_2$ values differed systematically, but not consistently, between the top 2 cm and 5 m depth, the depth conventionally sampled in along-way pCO$_2$surveys [*Fung and Takahashi*, 2000], with the mean absolute difference being 13.4 ± 4.3 μatm, despite no significant temperature difference between these two depths (mean difference = 0.05°C). The pCO$_2$ within the top cms of the ocean tended to be higher than that at 5 m depth in all but one of the stations sampled (Table 1).

[8] There was a remarkably strong relationship (R^2 = 0.99, P < 0.001) between the ΔpCO$_2$ and the NCP of the planktonic community in the top 2-cm layer of the ocean (Figure 2b), with high NCP at the upper 2 cm in some stations resulting in strongly negative ΔpCO$_2$, driving a CO$_2$ uptake by the ocean, while net heterotrophic metabolism at the upper 2 cm in some other stations, reflected in negative NCP, resulted in strongly positive ΔpCO$_2$ (Figure 2b), consistent with the postulated direction of the biological effects on ΔpCO$_2$. There was, however, no statistically significant relationship between ΔpCO$_2$ and NCP for the communities at 5 m and that integrated across the photic layer (P > 0.09). The pCO$_2$ anomaly between the top cms of the ocean and 5 m depth water was closely dependent (R^2 = 0.64, p = 0.02, Figure 2c) on the difference in NCP between the corresponding communities, with a higher pCO$_2$ within the top cms of the ocean at some stations resulting from a greater dominance of heterotrophic processes there compared to the community at 5 m depth, and lower pCO$_2$ within the top cms of the ocean at other stations resulting from a greater dominance of autotrophic processes there compared to the community at 5 m depth (Figure 2c).

[9] The control of the metabolism at the top layer of the ocean in controlling pCO$_2$ and, therefore, air-sea CO$_2$ fluxes was maintained despite wind velocities in excess of the regional average values. However, this control is likely to disappear at stronger wind intensities, sufficient to effectively homogenize the top 2 cm layer with the underlying water column.

[10] However, NCP at the top 2 cm layer could not possibly be the sole control on ΔpCO$_2$, as CO$_2$ undersaturation occurred at balanced NCP (Figure 2b), suggesting other processes, such as hydrodynamic inputs of DIC, CaCO$_3$ dissolution, thermodynamic effects related to temperature changes, and the history of the water mass, to also affect pCO$_2$w [e.g., *Robertson et al.*, 1994; *Watson and Orr*, 2003; *Ducklow and McCallister*, 2005]. As the temperature of the 2 cm layer differed, albeit modestly, across the stations surveyed (standard deviation = 0.45°C), we standardized the pCO$_2$ to the mean temperature across stations

Figure 2. The relationship between (a) net community production (NCP) at 5 m depth (open squares) and integrated across the water column (full circles) and that just below the ocean skin (i.e., within the top 2 cm of the water column); (b) the gradient in the partial pressure of CO$_2$ between the sea surface and the atmosphere (ΔpCO$_2$) and NCP just below the ocean skin and (c) the gradient in the partial pressure of CO$_2$ between the sea surface and 5 m depth and the difference in NCP between communities at these two layers. The dotted line in (a) represents the 1 to 1 line, whereas the solid line in (b) and (c) represents the fitted regression equation ΔpCO$_2$ 2 cm-air = −12.0 − 1.7 (±0.1) NCP; R^2 = 0.99, P < 0.001, and ΔpCO$_2$ 2cm-m = 6.0 − 2.0 (±0.6) ΔNCP$_{2cm-5m}$, where the standard error of the slope is provided.

(50.2 μmol C L^{-1}) was observed at the station sampled under the highest wind speed of 12.3 m s^{-1}. The metabolism of the community at the upper 2 cm of the water column was more intense (R and GPP, on average,

and re-assessed the relationship of the ΔpCO$_2$, corrected for temperature differences, and NCP. This correction did not alter the relationship obtained (t-test comparison of regression slopes and intercepts, p > 0.05), indicating that this was not affected by the modest temperature differences across stations.

[11] The results presented suggest that the metabolism at the top centimeters of the ocean play a disproportionate role in controlling air-sea CO$_2$ exchange and requires, therefore, specific attention. The presence of a thin upper layer, enriched in organic carbon and microrganisms, in the ocean, able to affect air-sea exchange [e.g., *Liss and Duce*, 1997], has been known for over three decades [*McIntyre*, 1974]. Multiple, complex mechanisms are involved in the formation and maintenance of this surface layer [*Liss and Duce*, 1997], which seem to be able to maintain a distinct surface layer even under significant wind speeds. Our results show that the microbial community within the upper surface layer supports an intense, on a volumetric basis, metabolism below the ocean skin, although accounting for these high rates at this rather thin layer would not alter estimates of mixed layer metabolism. However, our measurements indicated that pCO$_2$ values differed systematically, but not consistently, between the top 2 cm and 5 m depth, the depth conventionally sampled in along-way pCO$_2$ surveys [*Fung and Takahashi*, 2000], with the mean absolute difference being 13.4 ± 4.3 µatm, despite no significant temperature difference between these two depths (mean difference = 0.05°C). This observation suggests that the use of pCO$_2$ measured at 3–5 m depth to represent that of the ocean surface may be a potentially important source of error in the estimation of air-sea CO$_2$ exchange. Indeed, the absolute difference in flux estimates computed using pCO$_2$ values measured at 5 m and 2 cm depth averaged 1.5 ± 0.4 mmol C m^{-2} d^{-1}, representing a deviation equivalent to about 90% of the fluxes calculated using the pCO$_2$ values measured at 5 m. The suggestion that air-sea CO$_2$ flux estimates may be greatly affected by differences in pCO$_2$ values measured at 5 m and 2 cm depth, a possibility already anticipated in the past [*Fung and Takahashi*, 2000], must be, however, re-assessed once a larger data set becomes available, as the present data set is limited in size.

[12] These results confirm the expected role of planktonic metabolism in driving ΔpCO$_2$ at the air-sea interface [*Ducklow and McCallister*, 2005], but point to the community extending over the top centimeters of the water column, just below the ocean skin, and not those deeper in the water column, as being that controlling ΔpCO$_2$ and, therefore, the dominant source of biological effects on air-sea CO$_2$

exchange. Because the surface films often found within the ocean skin, the top mm of the ocean, are known to greatly affect CO$_2$ fluxes, through their effect on gas transfer [cf. *Liss and Duce*, 1997], the finding that the planktonic community just below the ocean skin affects the ΔpCO$_2$ suggests a dominant role of the top 2 cm of the ocean in controlling air-sea CO$_2$ fluxes. These results suggest that understanding the controls of the metabolism of the communities just below the ocean skin will improve our understanding of the role of biological processes in controlling air-sea CO$_2$ exchange.

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