

*Biogeosciences Discussions* is the access reviewed discussion forum of *Biogeosciences*

# Evidence for surface organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. L. Calleja<sup>1,2</sup>, C. M. Duarte<sup>1</sup>, Y. T. Prairie<sup>3</sup>, S. Agustí<sup>1</sup>, and G. J. Herndl<sup>4</sup>

<sup>1</sup>IMEDEA (CSIC-UIB), Grup d' Oceanografía Interdisciplinar, C/ Miquel Marquès 21, 07 190 Esporles, Mallorca, Spain

<sup>2</sup>Department of Ocean Sciences, University of California, 1156 High Street, Santa Cruz, CA 95 064, USA

<sup>3</sup>Département des Sciences Biologiques, Université du Québec à Montréal, P.O. Box 8888, succ. Centre-Ville, Montreal, QC H3C 3P8, Canada

<sup>4</sup>Department of Biological Oceanography, Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Den Burg, The Netherlands

Received: 8 August 2008 – Accepted: 8 September 2008 – Published: 3 November 2008

Correspondence to: M. L. Calleja (mcalleja@ucsc.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

## Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. L. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

Air-sea CO<sub>2</sub> exchange depends on the air-sea CO<sub>2</sub> gradient and the gas transfer velocity ( $k$ ), computed as a simple function of wind speed. Large discrepancies among relationships predicting  $k$  from wind suggest that other processes may also contribute significantly to modulate CO<sub>2</sub> exchange. Here we report, on the basis of the relationship between the measured gas transfer velocity and the ocean surface organic carbon concentration at the ocean surface, a significant role of surface organic matter in suppressing air-sea gas exchange, at low and intermediate winds, in the open ocean. The potential role of total surface organic matter concentration (TOC) on gas transfer velocity ( $k$ ) was evaluated by direct measurements of air-sea CO<sub>2</sub> fluxes at different wind speeds and locations in the open ocean. According to the results obtained, high surface organic matter contents may lead to lower air-sea CO<sub>2</sub> fluxes, for a given air-sea CO<sub>2</sub> partial pressure gradient and wind speed below 5 m s<sup>-1</sup>, compared to that observed at low organic matter contents. We found the bias in calculated gas fluxes resulting from neglecting TOC to co-vary geographically and seasonally with marine productivity. These findings suggest that consideration of the role of organic matter in modulating air-sea CO<sub>2</sub> exchange can improve flux estimates and help avoid possible bias associated to variability in surface organic concentration across the ocean.

## 1 Introduction

The role of air-sea exchange as a sink for atmospheric CO<sub>2</sub> is assessed through a major concerted international effort to examine CO<sub>2</sub> fluxes across the air-sea boundary layer. The accurate parameterization of the air-sea gas exchange process is an important pre-requisite to quantify geographically the CO<sub>2</sub> uptake and release by the ocean for a better understanding of climate change feedback mechanisms. The calculation of air-sea CO<sub>2</sub> flux ( $F_{\text{CO}_2}$ ) is typically based on an indirect bulk method where data sets of global distributions of surface water CO<sub>2</sub> partial pressure, increasingly available

**BGD**

5, 4209–4233, 2008

### Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(Takahashi et al., 1997, 2002), and wind speed ( $U$ ) are used as model input variables. Fluxes are commonly determined from the bulk formula:

$$F_{CO_2} = k \times S \times \Delta pCO_2 \quad (1)$$

where  $\Delta pCO_2$  is the difference between  $CO_2$  partial pressure in the surface ocean and that in the lower atmosphere ( $\Delta pCO_2 = pCO_{2w} - pCO_{2a}$ ) and represents the thermodynamic driving force that determines both the potential extent and direction of the flux.  $k$  is the gas transfer velocity, itself driven by near-surface turbulence in the water boundary layer (Donelan, 1990), which represents the kinetic term and affects the magnitude of  $CO_2$  exchange. And  $S$  is the  $CO_2$  solubility term, easily calculable from water temperature and salinity data (Weiss, 1974).

While  $\Delta pCO_2$  can be accurately obtained by in situ measurements,  $k$  is difficult to quantify and is, in practice, predicted from one of the multiple parameterizations deriving  $k$  from wind ( $U$ ) (Liss and Merlivat, 1986; Nightingale et al., 2000a, 2000b; Wanninkhof, 1992; Wanninkhof and McGillis, 1999), as wind speed is considered the main factor affecting turbulence in the air-sea interface and fluxes can then be easily computed from accurate routinely acquired wind speed measurements. This basic assumption considers wind as the main and unique driving kinetic parameter. However, the high scatter within datasets when  $k$  is plotted against wind speed, accounting for differences among parameterizations that can lead to  $k$  values differing by more than a factor of 2, remains a source of uncertainty in flux estimates, and indicates that other processes that are not controlled by wind speed may also play an important role in modulating gas transfer kinetics. Among these are the effects of waves traveling faster than winds (Smedman et al., 1999), hydrostatic increase of the  $CO_2$  partial pressure in bubbles (Keeling, 1993), and abundance of organic surfactants (Frew, 1997). These processes occurring in the air-sea interface have been recognized by oceanographers to affect gas transfer velocity, but are considered to be of secondary importance in view of the large uncertainties that still exist in describing  $k$  as a function of wind speed, and are not yet taken into account by the various parameterizations of  $k$ .

**Organic matter  
modulation of air-sea  
 $CO_2$  gas exchange**

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**M. Ll. Calleja et al.

---

In particular, recent efforts to study organic properties near the sea-water interface over the last decades has provided evidence of accumulation of synthetic (Goldman et al., 1988) and naturally occurring (Frew et al., 1990) surface-active organic matter at the sea surface, as well as surface layer enrichment in organic carbon content (Calleja et al., 2005), bacterial concentrations (Zemmelink et al., 2005) and amino acids (Kuznetsova et al., 2004). However, the relationship between this surface-active organic material on open-ocean waters and gas transfer velocity has not yet been assessed at in situ conditions. A possible reason for that is the fact that the organic content of seawater is often determined instantaneously over discrete stations whereas  $k$  is commonly examined using tracers that integrate across space and time, making the evaluation of their relationship difficult.

Here we test the effect of the organic matter content in the ocean surface layer on the air-sea CO<sub>2</sub> gas exchange by examining the relationship between empirically determined gas transfer velocity,  $k$ , and the total organic carbon (TOC) concentration in the upper cm of water surface, at samples across a range of contrasting locations in the North East Subtropical Atlantic and the Southern Oceans. We do so by the use of the chamber method that allows CO<sub>2</sub> exchange rate measurements from short time and spatial scales, as surface TOC content may vary widely with biological processes changing along the day and across space.

## 2 Sampling and methods

### 2.1 Location

Water samples within the top cm of the sea surface and CO<sub>2</sub> measurements were conducted at 41 stations, away from coastal influences, in two different locations; along the NE Subtropical Atlantic Ocean (between 14 and 32° W, and 19 and 28° N) during September 2002 (cruise COCA 1), May–June 2003 (cruise COCA 2), and October 2004 (cruise BADE 2); and along the Antarctic Peninsula on the Southern Ocean (be-

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

tween 55 and 70° W, and 62 and 67° S) during February 2005 (cruise ICEPOS). Sampling and measurements were performed from a boat drifting upwind from the research vessel to avoid any possible contamination. The number of stations where measurements were conducted was limited by the oceanic conditions when a small boat could be safely deployed to conduct these measurements. The boat was driven some miles away from the research vessel to avoid contamination during measurements, and was left drifting during sampling. Most of the measurements ( $n=40$ ) were performed at winds between 1 and 12  $\text{m s}^{-1}$ . And one measurement alone was possible at higher (15.9  $\text{m s}^{-1}$ ) wind speeds.

## 2.2 Instrumentation

Determination of water surface  $\text{CO}_2$  partial pressure ( $p\text{CO}_{2w}$ ) and atmospheric  $\text{CO}_2$  partial pressure ( $p\text{CO}_{2a}$ ) was performed using a high-precision ( $\pm 1$  ppm) non-dispersive infrared gas analyzer (EGM-4, PP-systems) at 1 min recording interval. Before entering the gas analyzer, the gas stream was circulated through a Calcium Sulfate column to avoid interferences from water vapor. A peristaltic pump, pumping water from the top cm by the use of a floating device, and a gas exchange column (Mini-Module 1.25 $\times$ 9 Membrane Contactor, Celgard) with an effective surface area of 0.5  $\text{m}^2$ , a total volume of 52 ml and a water flow of about 300  $\text{ml min}^{-1}$  were utilized for air-surface sea-water equilibration, resulting in a residence time of only 10 s and no temperature difference between in situ seawater and water in the equilibrator. The gas phase was continuously circulated through the equilibrator and the infrared gas analyzer. Gas analyzer was calibrated using two dry standards: pure nitrogen (0.0 ppm) and a gas mixture of  $\text{CO}_2$  and  $\text{N}_2$  containing a  $\text{CO}_2$  molar fraction of 541 ppm, which revealed an accuracy of  $\pm 1$  ppm in the determinations of  $p\text{CO}_2$ . All  $p\text{CO}_2$  measurements were corrected for water vapor pressure and temperature, and final results reflected  $p\text{CO}_2$  at 1 atmospheric pressure with 100% saturation of water vapor and in situ temperature.

Water sampling for TOC measurements: Surface layer water from the top centimeter was sampled using a peristaltic pump with the inlet held within the top cm of the water

**BGD**

5, 4209–4233, 2008

## Organic matter modulation of air-sea $\text{CO}_2$ gas exchange

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

---

M. Ll. Calleja et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

column by a floating device, so that we estimate that water samples represent a layer a few cm thick. We, therefore, hereafter refer to these samples as top cm depth. Water samples from 5 m depth were collected from Niskin bottles attached to a Rosette sampler system. TOC measurements were performed from waters sampled from both, the surface top centimeters and 5 m depths. 10 ml of each sample were transferred to pre-combusted glass ampoules (450°C for 5 h) and kept acidified (pH: 1–2) until analysis by High Temperature Catalytic Oxidation on a Shimadzu TOC-5000A. Standards of 44–45  $\mu\text{mol C L}^{-1}$  and 2  $\mu\text{mol C L}^{-1}$ , provided by D. A. Hansell and W. Chen (Univ. of Miami), were used to assess the accuracy of the estimates.

Using equipment from the research vessel barometric Pressure, Wind speed, air Temperature (Aanderaa meteorological station) and sea-surface (4 m depth) Salinity and water Temperature (Seabird SBE 21 Thermo-salinographer) were measured at 1 min intervals at the time of sampling and averaged for the time period of each flux measurement. Pitch, roll and heading of the research vessel were also recorded at 1 min intervals and used in a routine embedded in the software integrating navigation and meteorological data to correct wind speed for the ship movement and flow distortion. The corrected wind velocities were then converted to wind at 10 m ( $U_{10}$ ) using the logarithmic correction  $U_{10} = U_z [0.097 \ln(z/10) + 1]^{-1}$  where  $z$  is the height of the wind sensor position (Hartman and Hammond, 1985).

### 2.3 Flux measurements

Air-Sea CO<sub>2</sub> flux measurements were conducted by the floating chamber method (Frankignoulle, 1988). The chamber, consisting in a plastic circular cone (volume 16 L, surface 0.12 m<sup>2</sup>) connected through a close air circuit to the infrared gas analyzer (EGM-4, PP-systems), was floating and drifting freely, as proposed by Frankignoulle (1988), to avoid possible unnatural turbulence on the water surface generated by the chamber pressure, during the time of sampling. It also included a weight allowing the chamber walls extending 3–5 cm into the water column, further avoiding the creation of artificial turbulence (Guérin et al., 2007). The readings of  $p\text{CO}_2$  inside the

chamber were acquired every minute during 10–20 min, and  $\text{CO}_2$  fluxes ( $F_{\text{CO}_2}$ ) were computed from the slope of the linear regression ( $R^2$  averaged  $0.93 \pm 0.01$ ) of  $p\text{CO}_2$  against time according to Frankignoulle (1988). Figure 1 provides some examples of measurements obtained once the whole system has been cleaned with fresh surface air and the chamber laid on the sea surface. The linear increase or decrease of atmospheric  $p\text{CO}_2$  in the bell provides estimates of both the direction and magnitude of the flux (Fig. 1).

Concerns have been raised that the presence of the floating device interferes with the processes governing gas exchange (Belanger and Korzum, 1991). Two main criticisms are under discussion: the main one is the idea that the chamber device isolate water from wind influence (Liss and Merlivat, 1986), hence blocking surface wind turbulence. However, as air-sea gas exchange is mainly controlled by turbulence in the aquatic boundary layer (Kremer et al., 2003; McGillis et al., 2001), if the measurements are performed over an area that is large enough relative to that influenced by the chamber device, the method should be reliable (Jähne et al., 1987). This is the case of our flux measurements that were achieved under long fetch oceanic water mass. Moreover, Kremer et al. (2003) tested experimentally the chamber disturbance on the wind speed and showed that air turbulence inside the chamber, which was generated by an attached fan, slightly increased gas flux by only 2–12%, which represent an error below classical sampling variability. The second criticism is that chamber pressure generates unnatural turbulence on the water surface resulting in artificially high exchange rates (Marino and Howarth, 1993; Matthews et al., 2003). According to Matthews et al. (2003), this becomes more important at very low wind speeds ( $<1 \text{ m s}^{-1}$ ) and over still and smooth water bodies. None of these circumstances were present within this study were wind speeds ranged from 1.8 to  $15.7 \text{ m s}^{-1}$  and measurements were achieved under rough oceanic water masses. To prevent for that effect Frankignoulle (1988) proposed a drifting system, which we have adopted on our measurement.

Despite previously described discrepancies there are also studies verifying that re-

---

**Organic matter  
modulation of air-sea  
 $\text{CO}_2$  gas exchange**M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sults using this method are consistent with those from other methods (Borges et al., 2004b; Guérin et al., 2007).

The floating chamber method has been mainly used in coastal water bodies, where temporal and spatial resolution is required. To our knowledge, this technique has not been previously used to estimate CO<sub>2</sub> fluxes under oceanic conditions, where gas transfer velocities are mostly derived by the use of tracers. For the purpose of this work, exchange rates estimated from short time and spatial scale variations were required, as the organic carbon content at the top centimeters could vary widely with the roughness conditions and with biological processes changing along the day and across space. To analyze the effect of surface TOC content on gas transfer velocity using non-intrusive methods, i.e. that integrate the gas exchange process over large spatial and time scales, were not appropriate. Thus, we used the chamber method as a valuable tool that allows discrete multi-point measurements with high temporal (min) and spatial (below m<sup>2</sup>, i.e. the area covered by the chamber) resolution scales.

#### 2.4 Calculation of the transfer velocity (*k*)

The CO<sub>2</sub> flux is derived by:

$$F_{CO_2} = -\frac{1}{A} \frac{V}{RT} \frac{dp_{CO_2}}{dt} \quad (2)$$

where *A* is the air-sea interface area, *V* is the volume of the headspace inside the chamber, *T* is the temperature, *R* is the gas constant and *dp*CO<sub>2</sub>/*dt* is derived from the slope of the linear change of *p*CO<sub>2</sub> against time (*t*) inside the chamber headspace.

Combining Eqs. (1) and (2) empirical air-water CO<sub>2</sub> gas transfer velocity, *k*<sub>emp</sub>, was estimated by:

$$k = -\frac{1}{A} \frac{V}{RT} \frac{dp_{CO_2}}{dt} \frac{1}{S \times (p_{CO_{2w}} - p_{CO_{2a}})} \quad (3)$$

where *S* is the CO<sub>2</sub> solubility in seawater at in situ conditions calculated from water Temperature and Salinity according to Weiss (1974) and *p*CO<sub>2w</sub> and *p*CO<sub>2a</sub> are the

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





measured partial pressure of CO<sub>2</sub> in the water surface and in the atmosphere respectively. Resulting  $k$  was then normalized to a Schmidt number of 660, corresponding to CO<sub>2</sub> in seawater at 20°C, by assuming that  $k$  is proportional to  $Sc^{-n}$ :

$$k_{660} = k \times \left( \frac{Sc}{660} \right)^{-n} \quad (4)$$

5 where  $n=1/2$  for  $U_{10} \geq 5 \text{ m s}^{-1}$  and  $n=2/3$  for  $U_{10} < 5 \text{ m s}^{-1}$ .

Note that the significant potential influence of organic films would probably lead to deviations on  $n$  (Jähne and Haußecker, 1998; Liss and Merlivat, 1986). The error of the estimates of obtained  $k$  was derived from the correlation coefficient of the linear regression of  $p\text{CO}_2$  against time and averaged  $3.3 (\pm 0.7) \text{ cm h}^{-1}$ .

10 All the relationships derived from the data and described in the “Results and discussion” section where weighted by the number of observations per bin-average data.

### 3 Results and discussion

Our measurements encompassed a wide range of oceanographic conditions, extending from nutrient-rich and highly productive waters in the Southern Ocean ( $4.7 \mu\text{g Chl-}a \text{ L}^{-1}$ ) to very oligotrophic and unproductive waters in the Subtropical NE Atlantic Ocean ( $0.05 \mu\text{g Chl-}a \text{ L}^{-1}$ ), with an intermediate situation in the upwelling waters of the NW African Coast of the subtropical Atlantic Ocean ( $3.5 \mu\text{g Chl-}a \text{ L}^{-1}$ ). Sampled surface waters ranged from strongly under-saturated in CO<sub>2</sub> ( $189 \mu\text{atm}$ ) in the Southern Ocean, to waters super-saturated ( $419 \mu\text{atm}$ ) relative to atmospheric equilibrium in the upwelling system; from the coldest waters ( $-0.26^\circ\text{C}$ ) to very warm ones ( $27.07^\circ\text{C}$ ); and from low marine Salinity values close to ice-melting areas during the Austral summer ( $33.1$ ) to high Salinity waters in the Atlantic Ocean ( $37.65$ ).

25 Observed TOC values ranged between  $54$  and  $131 \mu\text{mol C L}^{-1}$  in the upper 2 cm of the surface waters. Wind speeds at the time of sampling were significantly higher in the Southern Ocean ( $7.8 \pm 1.3 \text{ m s}^{-1}$ ) than in the Atlantic Ocean ( $5.6 \pm 0.3 \text{ m s}^{-1}$ ).

**BGD**

5, 4209–4233, 2008

## Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

---

M. Ll. Calleja et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

High wind speeds over the cold nutrient-rich polar waters, with high biological activity and low  $p\text{CO}_2$  values render them a strong sink for atmospheric  $\text{CO}_2$  (Takahashi et al., 1997). Accordingly, the measurements we performed during the austral summer (February) at South of  $60^\circ\text{C}$  latitudes identified a strong net uptake of atmospheric  $\text{CO}_2$  with a water surface  $p\text{CO}_{2w}$  as low as  $189\ \mu\text{atm}$ , and measured air to sea fluxes averaging  $-21.6\pm 8.4\ \text{mmolC m}^{-2}\ \text{d}^{-1}$  (Fig. 2). On the other hand, our data from the subtropical NE Atlantic Ocean was recorded in late spring (May–June), and beginning of autumn (September–October), detecting seasonal variability within the oligotrophic waters of the subtropical temperate gyre. We found these waters to be acting as a net  $\text{CO}_2$  sink during late spring, with  $\text{CO}_2$  fluxes averaging  $-3.1\pm 1.7\ \text{mmolC m}^{-2}\ \text{d}^{-1}$ , and as a net  $\text{CO}_2$  source to the atmosphere during autumn, with  $\text{CO}_2$  fluxes averaging  $6.8\pm 1.3\ \text{mmolC m}^{-2}\ \text{d}^{-1}$  (Fig. 2). Our flux results are consistent with the direction of those reported for the same geographical zone using climatological surface ocean  $p\text{CO}_2$  and seasonal, biological and temperature effects (Takahashi et al., 2002).

$\text{CO}_2$  fluxes measured within this work were compared with fluxes calculated using different parameterizations of the gas transfer velocity,  $k$ , with the wind velocity,  $U$ , (Fig. 2); the traditional linear equation of Liss and Merlivat (1986), the quadratic and the cubic formulations proposed by Wanninkhof (1992) and Wanninkhof and McGillis (1999), respectively, and the one recently proposed by McGillis et al. (2004) derived from Gas-Ex2001 data, all of them normalized to the Schmidt number of 660 by using Eq. (4). Figure 2 shows that Liss and Merlivat (1986) equation yielded calculated  $\text{CO}_2$  fluxes that were by a factor of 2 to 5 below the measured flux, with the higher discrepancies found when, on average, a net efflux was inferred during autumn at the Subtropical NE Atlantic. The differences were less drastic when a net influx was inferred in both, the Atlantic and the Southern Ocean, although the flux magnitude differ an order of magnitude among sites. When there is a net  $\text{CO}_2$  sink by the ocean, the measured flux values are in between values calculated from the quadratic (Wanninkhof, 1992) and the cubic (Wanninkhof and McGillis, 1999) equations. Nevertheless, there are still differences of up to 30% between the gas exchange rates derived in this study

---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**


---

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and the closest calculated fluxes. Similar differences, of 30–50% between short-term CO<sub>2</sub> balance-derived fluxes and wind parameterizations-derived fluxes, have been recently reported by Kuss et al. (2004), who suggested that wind speed parameterizations could considerably underestimate the air-sea CO<sub>2</sub> gas exchange. In both, the calculated and the measured flux rates of our study, the thermodynamic and solubility terms from Eq. (1) are the same, and the only changing variable is the gas transfer velocity,  $k$ . Hence, discrepancies found within the CO<sub>2</sub> fluxes should necessarily be found on discrepancies between the empirically determined gas transfer velocity and that parameterized from wind speed.

Bin-averaged gas transfer velocities estimated within this work are plotted against wind in Fig. 3. The Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and McGillis et al. (2004) equations are plotted for comparison. The relationship between the empirically-determined gas transfer velocity,  $k_{emp}$ , and bin-averaged wind speeds was best described by the fitted regression equation

$$k(U_{10})(\text{cm h}^{-1}) = 13.33 (\pm 5.50) + 0.50 (\pm 0.09)(U_{10}(\text{m s}^{-1}))^2 (R^2 = 0.88, P < 0.01) \quad (5)$$

Note that the data value derived at  $>12 \text{ m s}^{-1}$  was not considered in the fit to avoid strong bias derived from one observation alone. The quadratic wind dependency observed suggest a similar trend to that of the Wanninkhof's long-term parameterization (Wanninkhof, 1992), although with a high intercept at zero wind speed ( $13.33 \text{ cm h}^{-1}$ ). We also observed that at low wind speeds ( $U_{10} < 5 \text{ m s}^{-1}$ )  $k$  did not vary predictably, not even significantly, with wind speed ( $R^2 = 0.05$ ;  $P > 0.5$ ), and noted an increase of gas transfer at low winds. McGillis et al. (2004), during the Gas-Ex 2001 experiment in the Equatorial Pacific, also observed a very weak dependence of the gas transfer with wind when those were below  $6 \text{ m s}^{-1}$ , and a high gas transfer value at zero wind ( $8.2 \text{ cm h}^{-1}$ ). The enhancement factor under the sampling conditions in this study is calculated to be less than 7% (Wanninkhof and Knox, 1996), indicating that environmental factors, other than winds, may be also modulating low and intermediate-wind gas exchange, as also suggested by McGillis et al. (2004).

---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

---

M. Ll. Calleja et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

At low winds, surfactants are known to particularly modulate gas exchange because of dampening of waves and turbulence (Frew, 1997; McKenna and McGillis, 2004), but this effect is far from complete understanding and data derived under ambient conditions are insufficient to adequately resolve this issue. Data of surface organic carbon concentration presented here have been collected under natural conditions and may be related to the potential modulating effect of surfactants. We observed the upper top cm of the ocean to be consistently enriched by, on average,  $20.2 \pm 2.8 \mu\text{mol C L}^{-1}$  in TOC relative to that observed at 5 m depth (Wilcoxon sign ranked test,  $p < 0.0001$ ) (Fig. 4a). This enrichment in TOC did not decline significantly with increasing wind speed ( $r = 0.16$ ;  $p > 0.05$ ) within the wind range observed in this study (from 2 to  $12 \text{ m s}^{-1}$ ). This suggests that the sea surface can be enriched in dissolved organic matter both because partially hydrophobic molecules are naturally surface active and because organic matter is scavenged by rising air bubbles and then deposited at the sea surface when they break at higher wind speeds (Tseng et al., 1992). Surface-active organic substances (SAS) represent a large fraction of total organic carbon (Hunter and Liss, 1982) composing the main part of TOC being absorbed at different phase boundaries. Accordingly microlayer surfactant concentrations have been recently documented to clearly correlate with organic carbon content (Frew et al., 2002). Thus the TOC enrichment we observe at top cm point to an implicit enrichment of SAS or surfactants at the air-sea boundary layer in the open ocean, suggesting that it could have potential effects on air-sea gas exchange. To better evaluate those effects we have examined changes of gas transfer velocity related to top cm's TOC content.

At high organic carbon content at the sea surface ( $\geq 90 \mu\text{mol C L}^{-1}$ ) estimates of apparent gas transfer velocities, are significantly lower than those found at lower TOC content ( $< 90 \mu\text{mol C L}^{-1}$ ). This pattern suggests that organic content damp sea surface turbulence leading to lower gas transfer rates at a wide range of wind speeds (up to  $12 \text{ m s}^{-1}$ ), while low organic carbon content is leading to higher gas transfer rates for the same wind speed values. This modulating effect is stronger at the range of wind speed below  $5 \text{ m s}^{-1}$ . To better evaluate the possible effect of the organic carbon

content, we removed the wind dependency by inspecting the relationship between the residuals of  $k$  [our empirically-estimated apparent gas transfer velocity,  $k_{\text{emp}}$ , and that predicted from wind alone,  $k_{\text{residual}}=k_{\text{emp}}-k(U_{10})$ ] and the organic carbon content at the top cm's. To avoid bias between different techniques and models, we use the trend of  $k$  with wind observed from our data using Eq. (5), so that any possible artificially enhancement of gas transfer rates due to the chamber device will be accounted in both,  $k_{\text{emp}}$  and  $k(U_{10})$ , and hence subtracted when calculating  $k$  residuals.

We found the residuals of  $k$  to be strongly and significantly negatively correlated with TOC in the top cm of the ocean surface ( $R^2=0.84$ ,  $p<0.01$ , Fig. 3b), indicating that low TOC in surface waters could lead to faster gas fluxes than predicted from wind alone at wind speeds below  $5\text{ m s}^{-1}$ . This pattern indicates that, at surface waters with TOC content higher than  $93\text{ }\mu\text{ mol C L}^{-1}$  (where residuals are zero, on average), the organic content in the surface can reduce the transfer velocity, both statically by directly impeding the transfer of gas molecules across the sea surface, and dynamically by reducing the near-surface turbulence.

These results suggest that the surface enrichment in TOC at the top cm's brings an implicit enrichment in surface active hydrophobic organic substances at the air-sea boundary layer influencing interfacial processes and reducing air-sea gas transfer velocity. Although we have observed this enrichment to be present across a wide range of wind speeds, and experimental evidence supporting the idea that soluble surfactants can also play a major role influencing gas exchange at high turbulent conditions (Goldman et al., 1988), our data suggest that it has stronger effects under low wind regime and low turbulent conditions, as previously documented (Frew et al., 2002). Soluble surfactants modulating near-surface turbulence hydrodynamically are believed to derive largely from phytoplankton exudates and their degradation products (Frew et al., 1990; Goldman et al., 1988; Zutic et al., 1981). Production of this material appears to be seasonal and has been linked to biological productivity cycles (Gašparović and Čosović, 2001) and autochthonous production by phytoplankton (Gašparović et al., 2005). Accordingly, high release rates of organic carbon by phytoplankton are

**BGD**

5, 4209–4233, 2008

---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



documented for the studied areas (Alonso-Laita et al., in preparation), suggesting an involvement of phytoplankton in the development of the enriched TOC layer and surfactant activity in the ocean surface affecting the dissipation rate of near-surface turbulence. Atmospheric organic carbon inputs have been also reported to be very high at the time of sampling performed at the Subtropical Atlantic Ocean (Dachs et al., 2005). Thus we believe that both, atmospheric deposition and phytoplankton exudation, constitute probable allochthonous and autochthonous sources respectively of organic matter potentially contributing to the formation of surface active substances and enrichment of TOC surface concentration.

Recent work evaluating chemical composition and physicochemical properties of organic matter in the ocean surface reveal the presence of a complex mixture of molecules covering a wide range of solubility, surface activity and molecular masses with an apparent structural organization exhibiting a spatial and temporal variability (Gašparović and Čosović, 2001; Gašparović et al., 2007). Transformation and consumption of biogenic surface-active substances and subsequent production of refractory compounds have been also documented (Gašparović and Čosović, 2003). Thus, elucidation of the chemical characteristics of surface TOC content, and identification of its sources and sinks are basic clues on the understanding of its physicochemical properties and sea surface renewal time to better evaluate its modulating effects on gas transfer rates.

According to our data, at winds below  $5 \text{ ms}^{-1}$  a TOC content higher than  $93 \mu\text{mol CL}^{-1}$  in surface layer waters will have suppressive effects on  $\text{CO}_2$  gas transfer velocity (Fig. 4b). This is consistent with Frew et al. (2002) data, where suppressive effects of surfactants on gas transfer velocity tend to be stronger at surfactant concentrations higher than  $1 \text{ mg L}^{-1}$ , corresponding to an organic carbon content of around  $90 \mu\text{mol CL}^{-1}$ , during the productive spring season (Frew et al., 2002, Fig. 1a).

The formation of surfactants could also reinforce effectively the chemical enhancement as suggested by Kuss and Schneider (2004), since both processes are specially favored under conditions of low wind regimes and high biological production, which

**Organic matter  
modulation of air-sea  
 $\text{CO}_2$  gas exchange**

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



yields low surface  $p\text{CO}_2$ /pH ratios and high TOC phytoplankton production.

Models that estimate gas transfer velocity based on wind speed alone have used empirical data originated from systems with very variable organic carbon content, ranging from low-TOC oceanic waters (McGillis et al., 2004; Wanninkhof and McGillis, 1999), to high-TOC lake waters (Wanninkhof et al., 1985), or are based on laboratory experiments in wind wave tunnels (Broecker and Siems, 1984) with a highly accurate control of wind speed measurements, but with no control over the organic carbon content of the water used. Our results indicate that the bias in calculated gas fluxes resulting from neglecting TOC may co-vary geographically and seasonally with marine productivity, as unproductive areas of the ocean tend to be more depleted in TOC than productive areas. Previous results (Frew et al., 2002) are consistent with this prediction as they documented higher microlayer SAS/DOC ratios at cruises performed during the productive spring season than those performed at late summer and fall. Thus  $\text{CO}_2$  fluxes in TOC-poor unproductive areas, which are often net sources of  $\text{CO}_2$  (Duarte and Prairie, 2005; Takahashi et al., 2002), could be larger than previously assumed, while TOC-rich productive areas of the ocean may be weaker sinks than hitherto believed. This is consistent with the differences found between the averaged measured and parameterized fluxes shown in Fig. 2. Measured fluxes during the highly productive austral summer of the Southern Ocean, where high phytoplankton exudation is expected, shows influx values ranging between fluxes inferred from two widely used wind-parameterizations (Wanninkhof, 1992 and Wanninkhof and McGillis, 1999). In contrast, fluxes measured during the autumn in the oligotrophic waters of the subtropical NE Atlantic, present an average value up to 2.7 times higher than that inferred from the same parameterizations. Thus suggesting that TOC-poor unproductive areas could be greater  $\text{CO}_2$  sources to the atmosphere than previously thought. Moreover, oligotrophic regions are characterized by a small  $p\text{CO}_2$  gradient between water and air and by low wind speeds conducive to a major contribution of organic matter on modulating air-sea  $\text{CO}_2$  fluxes.

The difference of the formulation of the k-wind dependence from different sites is

**BGD**

5, 4209–4233, 2008

---

**Organic matter  
modulation of air-sea  
 $\text{CO}_2$  gas exchange**

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





not an easy question and is still under debate. The most common hypothesis is that fetch limitation of different sites modulates the slope of the linear regression of  $k$  against wind, and the water currents contribution modulates its intercept with zero (Wanninkhof, 1992; Borges et al., 2004a). The slope of our data, when linearly correlated with wind

$$k(U_{10}) (\text{cm h}^{-1}) = 0.77 (\pm 11.33) + 5.86 (\pm 1.70) U_{10} (\text{m s}^{-1}) \quad (R^2 = 0.75, P < 0.05) \quad (6)$$

fit well with the formulation as a function of log surface area proposed by Borges et al. (2004a) using the same chamber technique. The slope we obtained under oceanic conditions ( $5.86 \text{ cm h}^{-1}/\text{m s}^{-1}$ ) is higher than any of those obtained in several estuaries (Guérin et al., 2007) and might be due to the high oceanic surface area where our measurements have been performed. This further suggest that formulation of  $k$  as a function of wind speed is site specific and has a strong correlation with fetch limitation, not only for estuarine environments but also for open ocean environments. We believe that an intercept different from zero is indicative that processes other than wind occurring over short spatial and temporal scales are governing gas transfer over low wind-regime and that the wind-range at which those processes dominate gas transfer depends on each specific system.

This imply that substantial errors in flux computations may be incurred if generic  $k$ -wind relationships are employed at different sites for the purpose of computing global air-sea  $\text{CO}_2$  flux budgets or specific ecosystem metabolic studies.

## 4 Conclusions

Our findings suggests that consideration of organic carbon at the ocean surface effects on gas transfers velocity may have important implications for our understanding of the net  $\text{CO}_2$  flux across the global ocean. The examination of the gas transfer velocities, derived from this study, allows the analysis of top cm's TOC content effect on gas transfer rates and could prove useful in elucidating the role of other properties operating over short time and space scales in controlling air-sea  $\text{CO}_2$  fluxes, which has been

### Organic matter modulation of air-sea $\text{CO}_2$ gas exchange

M. Ll. Calleja et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





identified as one of the major challenges of research in this area (McGillis et al., 2001, 2004; Nightingale et al., 2000b).

In summary, our findings, obtained under in situ open ocean conditions, provide clear evidence that the organic matter content of the water surface has suppressive effects on air-sea CO<sub>2</sub> gas fluxes at low and intermediate wind speeds (<5 m s<sup>-1</sup>), confirming previous suggestions. These results indicate that the estimation of *k*, and thus of air-sea gas exchange over this wind regime, can be greatly improved by considering the TOC concentration in the top cm of the ocean along with wind velocity, once parameterizations integrating over relevant temporal and spatial scales are developed.

Accordingly, large international programs to assess air-sea CO<sub>2</sub> exchanges should be extended to consider concentrations, nature and properties of organic matter content in the ocean surface affecting the stability of the surface layer of the ocean and hence of gas transfer kinetics. We believe that this is an essential work to be done in order to accurately re-assess the role of the ocean as a CO<sub>2</sub> sink and the impact of changes in ocean ecosystems on this process.

*Acknowledgements.* This research is a contribution to the COCA, BADE, ICEPOS and RODA projects, funded by the Spanish “Plan Nacional de I+D” and the Dutch Earth and Life Sciences (ALW-NWO). We thank the crews of the R/V Hespérides and R/V Pelagia and the technical UTM personnel for assistance, J. C. Alonso, R. Santiago and C. Barrón for help and assistance in the laboratory. M.L.I.C was supported by a fellowship from the Spanish Research council (CSIC).

## References

- Belanger, T. V. and Korzun E. A.: Critique of floating dome technique for estimating reaeration rates, *J. Environ. Eng.-ASCE*, 117, 144–150, 1991.
- Borges, A. V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril G., and Frankignoulle, M.: Gas transfer velocities of CO<sub>2</sub> in three European estuaries (Randers Fjord, Scheldt and Thames), *Limnol. Oceanogr.*, 49, 1630–1641, 2004a.

**BGD**

5, 4209–4233, 2008

---

## Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Borges, A. V., Vanderborght, J. P., Schiettecatte, L.-S., Gazeau, F., Ferron-Smith, S., Delille, B., and Frankignoulle, M.: Variability of the gas transfer velocity of CO<sub>2</sub> in a Macrotidal Estuary (the Scheldt), *Estuaries*, 27, 593–603, 2004b.

Broecker, H. C. and Siems, W.: The role of bubbles for gas transfer from water to air at higher wind speeds. Experiments in the wind-wave facility in Hamburg, in: *Gas Transfer at Water Surfaces*, edited by: Brutsaert, W. and Jirka, G. H., Dordrecht, Reidel, 229–236, 1984.

Calleja, M. Ll., Duarte, C. M., Navarro, N., and Agust, S.: Control of air-sea CO<sub>2</sub> disequilibria in the subtropical NE Atlantic by planktonic metabolism under the ocean skin, *Geophys. Res. Lett.*, 32, L08606, doi:10.1029/2004GL022120, 2005.

Dachs, J., Calleja, M. L., Duarte, C. M., del Vento, S., Turpin, B., Polidori, A., Herndl, G. J., and Agustí, S.: High atmosphere-ocean exchange of organic carbon in the NE subtropical Atlantic, *Geophys. Res. Lett.*, 32, L21807, doi:10.1029/2005GL023799, 2005.

Donelan, M. A.: Air-sea interaction, in: *The Sea*, edited by: Le Mehaute, B. and D. M. Hanes, Ocean Engineering Science, Wiley-Interscience, Hoboken, New Jersey, Vol. 9, 239–292, 1990.

Duarte, C. M. and Prairie, Y. T.: Prevalence of heterotrophy and atmospheric CO<sub>2</sub> emissions from aquatic ecosystems, *Ecosystems*, 8, 862–870, 2005.

Frankignoulle, M.: Field-measurements of air sea CO<sub>2</sub> exchange, *Limnol. Oceanogr.*, 33, 313–322, 1988.

Frew, N. M.: The role of organic films in air-sea gas exchange, in: *The Sea Surface and Global Change*, edited by: Liss, P. S. and Duce, R. A., Camb. Univ. Press, Cambridge, New York, 121–171, 1997.

Frew, N. M., Goldman, J. C., Dennett, M. R., and Johnson, A. S. Impact of phytoplankton-generated surfactants on air-sea gas-exchange, *J. Geophys. Res.-Oceans*, 95, 3337–3352, 1990.

Frew, N. M., Nelson, R. K., McGillis, W. R., Edson, J. B., Bock, E. J., and Hara, T.: Spatial variations in surface microlayer surfactants and their role in modulating air-sea exchange, in: *Gas Transfer at Water Surfaces*, edited by: Donelan, M. A., Drennan, W. M., Saltzman, E. S., and Wanninkhof, R., Washington DC, USA, 153–159, 2002.

Gašparović, B. and Čosović, B.: Distribution of surface-active substances in the Northern Adriatic Sea, *Mar. Chem.*, 75, 301–313, 2001.

Gašparović, B. and Čosović, B.: Surface active properties of organic matter in the north Adriatic Sea, *Estuar. Coast. Shelf S.*, 58, 555–566, 2003.

**BGD**

5, 4209–4233, 2008

---

## Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Gašparović, B., Plavšić, M., Čosović, B., and Reigstad, M.: Organic matter characterization and fate in the subarctic Norwegian fjords during late spring/summer period, *Estuar. Coast. Shelf S.*, 62, 95–107, 2005.

5 Gašparović, B., Plavšić, M., Čosović, B., and Saliot, A.: Organic matter characterization in the sea surface microlayers in the subarctic Norwegian fjords region, *Mar. Chem.*, 105, 1–14, 2007.

Goldman, J. C., Dennet, M. R., and Frew, N. M.: Surfactants effects on air-sea gas exchange under turbulent conditions, *Deep-Sea Res.*, 35, 1953–1970, 1988.

10 Guérin, F., Gwenaël, A., Serça, D., Delon, C., Richard, S., Delmas, R., Tremblay, A., and Varfalvy, L.: Gas transfer velocities of CO<sub>2</sub> and CH<sub>4</sub> in a tropical reservoir and its river downstream, *J. Marine Syst.*, 66, 161–172, 2007.

Hartman, B. and Hammond D. E.: Gas exchange in San Francisco Bay, *Hydrobiologia*, 129, 59–68, 1985.

15 Hunter, K. A. and Liss, P. S.: Organic sea surface films, in: *Marine Organic Chemistry*, edited by: Duursma, E. K. and Dawson, R., Elsevier, Amsterdam, 259–298, 1982.

Jähne, B. and Haußecker, H.: Air-water gas exchange, *Annu. Rev. Fluid. Mech.*, 30, 443–468, 1998.

Jähne, B., Munnich, K. O., Bosinger, R., Dutzi, A., Huber, W., and Libner, P.: On parameters influencing air-water exchange. *J. Geophys. Res.*, 92, 1937–1949, 1987.

20 Keeling, R. F.: On the role of large bubbles in air-sea gas exchange and supersaturation in the ocean, *J. Mar. Res.*, 51, 237–271, 1993.

Kremer, J. N., Nixon, S. W., Buckley, B., and Roques, P.: Technical Note: Conditions for using the floating chamber method to estimate air-water gas exchange, *Estuaries*, 26, 985–990, 2003.

25 Kuss, J., Nagel, K., and Schneider, B.: Evidence from the Baltic Sea for an enhanced CO<sub>2</sub> air-sea transfer velocity, *Tellus B*, 56, 175–182, 2004.

Kuss, J. and Schneider, B.: Chemical enhancement of the CO<sub>2</sub> gas exchange at a smooth seawater surface, *Mar. Chem.*, 91, 165–174, 2004.

30 Kuznetsova, M., Lee, C., Aller, J., and Frew, N.: Enrichment of amino acids in the sea surface microlayer at coastal and open ocean sites in the North Atlantic Ocean, *Limnol. Oceanogr.*, 49, 1605–1619, 2004.

Liss, P. S. and Merlivat, L.: Air-sea gas exchange rates: Introduction and synthesis, in: *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by: Buat-Ménard, P., D. Reidel

**BGD**

5, 4209–4233, 2008

---

## Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Publishing Company, Boston, Massachusetts, 113–127, 1986.
- Marino, R. and Howarth, R. W.: Atmospheric oxygen-exchange in the Hudson River – dome measurements and comparison with other natural waters, *Estuaries*, 16, 433–445, 1993.
- Matthews, C. J. D., St Louis, V. L., and Hesslein, R. H.: Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces, *Environ. Sci. Technol.*, 37, 772–780, 2003.
- McGillis, W. R., Edson, J. B., Ware, J. D., Dacey, J. W. H., Hare, J. E., Fairall, C. W., and Wanninkhof, R.: Carbon dioxide flux techniques performed during GasEx-98, *Mar. Chem.*, 75, 267–280, 2001.
- McGillis, W. R., Edson, J. B., Zappa, C. J., Ware, J. D., McKenna, S. P., Terray, E. A., Hare, J. E., Fairall, C. W., Drennan, W., Donelan, M., DeGrandpre, M. D., Wanninkhof, R., and Feely, R. A.: Air-sea CO<sub>2</sub> exchange in the equatorial Pacific, *J. Geophys. Res.*, 109, C08S02, doi:10.1029/2003JC002256, 2004.
- McKenna, S. P. and McGillis, W. R.: The role of free-surface turbulence and surfactants in air-water gas transfer, *Int. J. Heat Mass Tran.*, 47, 539–553, 2004.
- Nightingale, P. D., Liss, P. S., and Schlosser, P.: Measurements of air-sea gas transfer during an open ocean algal bloom, *Geophys. Res. Lett.*, 27, 2117–2120, 2000a.
- Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cy.*, 14, 373–387, 2000b.
- Smedman, A., Högström, U., Bergström, H., Rutgersson, A., Kahma, K. K., and Pettersson, H.: A case study of air-sea interaction during swell conditions, *J. Geophys. Res.*, 104, 25 833–25 851, 1999.
- Takahashi, T., Feely, R. A., Weiss, R., Wanninkhof, R. H., Chipman, D. W., Sutherland, S. C., and Takahashi, T. T.: Global air-sea flux of CO<sub>2</sub>: an estimate based on measurements of sea-air *p*CO<sub>2</sub> difference, *P. Natl. Acad. Sci. USA*, 94, 8292–8299, 1997.
- Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R. A., Sabine, C., Olafsson, J., and Nojiri, Y.: Global sea-air CO<sub>2</sub> flux based on climatological surface ocean *p*CO<sub>2</sub>, and seasonal biological and temperature effects, *Deep-Sea Res. Pt. II*, 49, 1601–1622, 2002.
- Tseng, R. S., Viechnicki, J. T., Skop, R. A., and Brown, J. W.: Sea-to-air transfer of surface-active organic-compounds by bursting bubbles, *J. Geophys. Res.-Oceans*, 97, 5201–5206, 1992.

**BGD**

5, 4209–4233, 2008

---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Wanninkhof, R.: Relationship between wind-speed and gas-exchange over the ocean, *J. Geophys. Res.-Oceans*, 97, 7373–7382, 1992.

Wanninkhof, R. and Knox, M.: Chemical enhancement of CO<sub>2</sub> exchange in natural waters, *Limnol. Oceanogr.*, 41, 689–698, 1996.

5 Wanninkhof, R., Ledwell, J. R., and Broecker, W. S.: Gas-exchange wind-speed relation measured with sulfur-hexafluoride on a lake, *Science*, 227, 1224–1226, 1985.

Wanninkhof, R. and McGillis, W. R.: A cubic relationship between air-sea CO<sub>2</sub> exchange and wind speed, *Geophys. Res. Lett.*, 26, 1889–1892, 1999.

10 Weiss, R. F.: Carbon dioxide in water and seawater: The solubility of a non ideal gas, *Mar. Chem.*, 2, 203–215, 1974.

Zemmelink, H. J., Houghton, L., Sievert, S. M., Frew, N. M., and Dacey, J. W. H.: Gradients in dimethylsulfide, dimethylsulfoniopropionate, dimethylsulfoxide, and bacteria near the sea surface, *Mar. Ecol.-Prog. Ser.*, 295, 33–42, 2005.

15 Zutic, V., Cosović, B., Marcenko, E., Bihari, N., and Krsinic, F.: Surfactant production by marine-phytoplankton, *Mar. Chem.*, 10, 505–520, 1981.

**BGD**

5, 4209–4233, 2008

---

**Organic matter  
modulation of air-sea  
CO<sub>2</sub> gas exchange**

M. Ll. Calleja et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

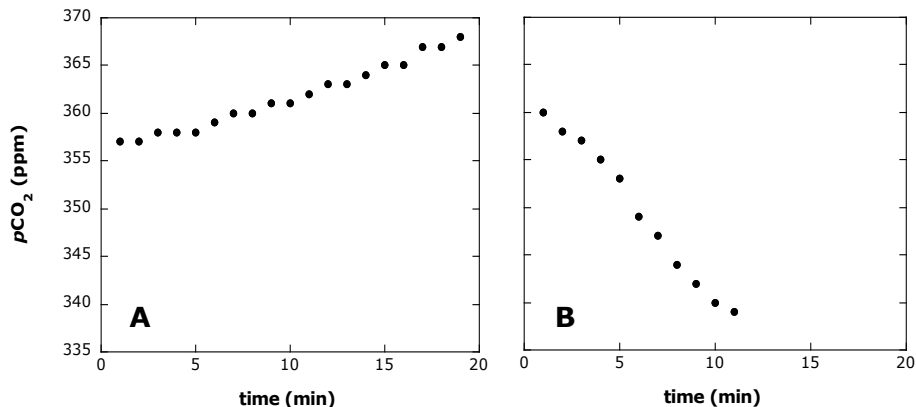
Printer-friendly Version

Interactive Discussion



Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.



**Fig. 1.** Two examples of the linear correlation between  $p\text{CO}_2$  (ppm) inside the bell and time (min) obtained by the direct chamber measurements of air-sea CO<sub>2</sub> exchange at (a) the Atlantic Ocean and (b) the Southern Ocean.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

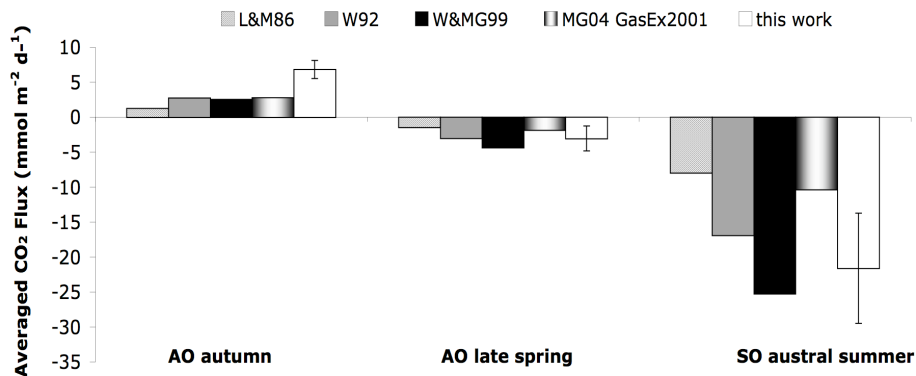
Printer-friendly Version

Interactive Discussion



Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.



**Fig. 2.** Comparison of regional and seasonal averaged air-sea CO<sub>2</sub> measured fluxes within this work ( $\pm$ SE), with fluxes inferred from the wind-speed parameterizations of Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and McGillis et al. (2004). AO means Atlantic Ocean, and SO means Southern Ocean.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

Navigation: Left Arrow, Right Arrow, Double Left Arrow, Double Right Arrow

Back Close

Full Screen / Esc

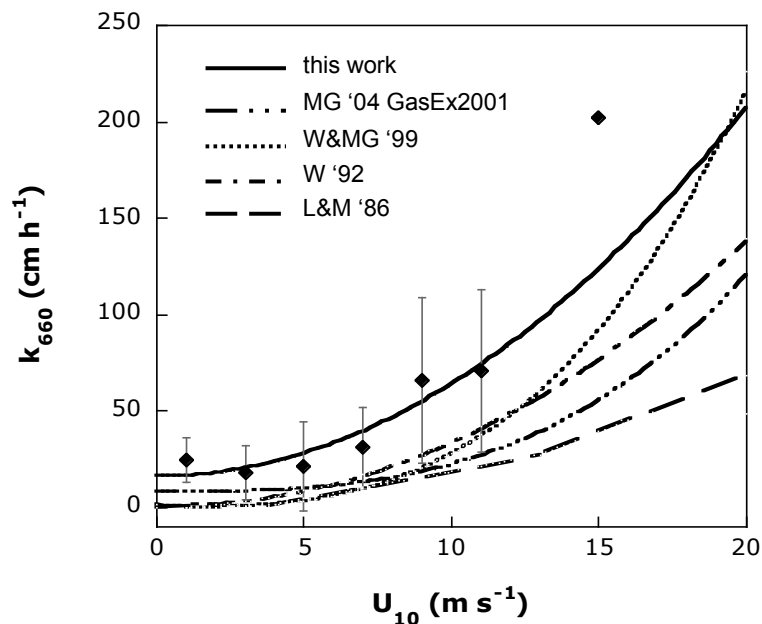
Printer-friendly Version

Interactive Discussion



## Organic matter modulation of air-sea CO<sub>2</sub> gas exchange

M. Ll. Calleja et al.



**Fig. 3.** The relationship between the apparent gas transfer velocities ( $k_{660}$ ) derived from this study and wind speed ( $U_{10}$ ). Diamond symbols represent  $k_{660}$  values averaged ( $\pm$  SD) by bins of  $2 \text{ m s}^{-1}$  of  $U_{10}$ . The solid line represents the fitted relationship between gas transfer velocity and wind speed (Eq. 5),  $k(U_{10}) (\text{cm h}^{-1}) = 13.33 (\pm 5.50) + 0.50 (\pm 0.09) (U_{10} (\text{m s}^{-1}))^2$ , ( $R^2 = 0.88$ ,  $P < 0.01$ ).  $k_{660}$  inferred from wind-speed parameterizations of Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and McGillis et al. (2004) are plotted for comparison.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

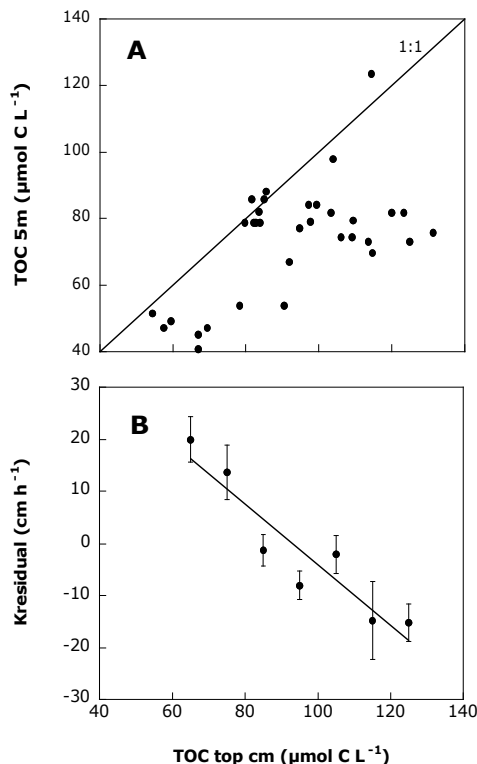
Full Screen / Esc

Printer-friendly Version

Interactive Discussion







**Fig. 4.** (a) The relationship between total organic carbon (TOC) concentration at 5 m depth and that within the top 2 cm of the water surface. The solid line represents the 1 to 1 line; and (b) the relationship between the residuals of the empirically-determined apparent gas transfer velocity in this study and that predicted by wind speed from Eq. (5), and the TOC concentration within the top cm of the water surface. Solid circles represent  $K_{\text{residual}}$  values averaged ( $\pm$ SE) by bins of  $10 \mu\text{mol C L}^{-1}$  of TOC. The solid line represents the fitted linear regression equation:  $K_{\text{residual}} (\text{cm h}^{-1}) = 53.07 (\pm 10.77) - 0.57 (\pm 0.11) \text{ TOC } (\mu\text{mol C L}^{-1})$ ;  $R^2 = 0.84$ ,  $p < 0.01$ .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

