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Evidence for surface organic matter modulation of air-sea CO_2 gas exchange

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Abstract. Air-sea CO_2 exchange depends on the air-sea CO_2 gradient and the gas transfer velocity (k), computed as a function of wind speed. Large discrepancies among relationships predicting k from wind suggest that other processes also contribute significantly to modulate CO_2 exchange. Here we report, on the basis of the relationship between the measured gas transfer velocity and the 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, confirming previous observations. The potential role of total surface organic matter concentration (TOC) on gas transfer velocity (k) was evaluated by direct measurements of air-sea CO_2 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_2 fluxes, for a given air-sea CO_2 partial pressure gradient and wind speed below $5\,\mathrm{m\,s^{-1}}$, 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 results support previous evidences that consideration of the role of organic matter in modulating air-sea CO_2 exchange may improve flux estimates and help avoid possible bias associated to variability in surface organic concentration across the ocean.

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1 Introduction

The role of air-sea exchange as a sink for atmospheric CO_2 is assessed through a major concerted international effort to examine CO_2 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_2 uptake and release by the ocean for a better understanding of climate change feedback mechanisms. The calculation of air-sea CO_2 flux (FCO_2) is typically based on an indirect bulk method where data sets of global distributions of surface water CO_2 partial pressure, increasingly available (Takahashi et al. 1997, 2002), and wind speed (U) are used as model input variables. Fluxes are commonly determined from the bulk formula:

$$FCO_2 = k \times S \times \Delta pCO_2 \tag{1}$$

where ΔpCO_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 ΔpCO_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, b; 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 assumption considers wind as the main driving kinetic parameter. However, as Zappa et al. (2007) demonstrated recently, wind is only a proxi of turbulence at the aquatic boundary layer (and thus of k). 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 more research is needed to gauge the effects of other processes that are not controlled by wind speed in modulating gas transfer kinetics. Among these are the effects of waves traveling faster than winds (Smedman et al., 1999), microbreaking of small-scale waves altering the surface roughness (Zappa et al., 2004), hydrostatic increase of the CO$_2$ partial pressure in bubbles (Keeling, 1993), and abundance of organic surfactants in the surface microlayer (Frew, 1997). These processes occurring in the air-sea interface have been recognized by oceanographers to affect gas transfer velocity.

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). In the presence of surface films, near-surface turbulence is suppressed and k can be significantly reduced at a given wind speed (Jähne et al., 1987). This effect has been previously documented to be particularly important under low wind conditions (Frew et al., 2002). 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 tracer techniques which are not able to describe the patchiness of organic matter in the ocean, 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$_2$ 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$_2$ 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. Thus, the use of the chamber method allowed us the examination of organic matter patchiness among sites where gas transfer velocity was measured.

2 Sampling and methods

2.1 Location

Water samples within the top cm of the sea surface and CO$_2$ 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 (between 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 m s^{-1}. And one measurement alone was possible at higher (15.9 m s^{-1}) wind speeds.

2.2 Instrumentation

Determination of water surface CO$_2$ partial pressure (pCO$_2w$) and atmospheric CO$_2$ partial pressure (pCO$_2a$) was performed using a high-precision (±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 1.25×9 Membrane Contactor, Celgard) with an effective surface area of 0.5 m^2, a total volume of 52 ml and a 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 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 CO$_2$ and N$_2$ containing a CO$_2$ molar fraction of 541 ppm, which revealed an accuracy of ±1 ppm in the determinations of pCO$_2$. All pCO$_2$ measurements were corrected for water vapor pressure and temperature, and final results reflected pCO$_2$ 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 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 μmol C L^{-1} and 2 μmol C L^{-1}, provided by D. A. Hansell and Wenhao 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 10m (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

The floating chamber method (Frankignoulle, 1988) 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 CO₂ 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 (minutes) and spatial (below m², i.e. the area covered by the chamber) resolution scales.

The chamber, consisting in a plastic circular cone (volume 16 L, surface 0.12 m^{-2}) 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 avoid-
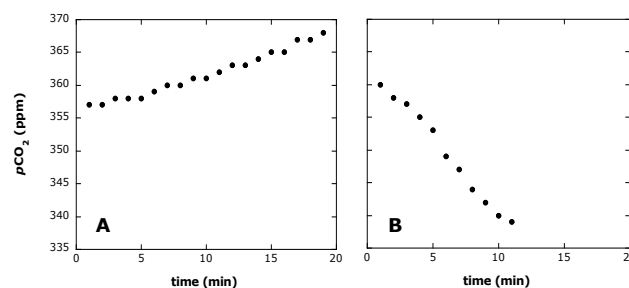

Fig. 1. Two examples of the linear correlation between pCO₂ (ppm) inside the bell and time (min) obtained by the direct chamber measurements of air-sea CO₂ exchange at (**A**) the Atlantic Ocean and (**B**) the Southern Ocean.

ing the creation of artificial turbulence (Guérin et al., 2007). The readings of pCO₂ inside the chamber were acquired every minute during 10–20 min, and CO₂ fluxes (FCO₂) were computed from the slope of the linear regression (R²averaged 0.93±0.01) of pCO₂ 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 pCO₂ 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), which 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 showing that air turbulence inside the chamber 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). This becomes more important at very low wind speeds (<1 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 m s^{-1} and measurements were achieved under rough oceanic water masses.

Despite previously described discrepancies, the chamber technique has been previously reported to agree with other

direct methods within 10-30% (Borges et al 2004a, 2004b). Also, a recent comparison of CO$_2$ fluxes obtained by the use of the chamber and the eddy covariance technique showed little discrepancies between both methods (Guérin et al., 2007). However, these agreements have only been observed in coastal waters and reservoirs, and our measurements are performed at the open ocean, so the gas transfer velocities estimated here could still be controversial.

2.4 Calculation of the transfer velocity (k)

The CO$_2$ flux is derived by:

$$FCO_2 = -\frac{1}{A}\frac{V}{RT}\frac{dpCO_2}{dt} \qquad (2)$$

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 $dpCO_2/dt$ is derived from the slope of the linear change of pCO_2 against time (t) inside the chamber headspace.

Combining Eqs. (1) and (2) empirical air-water CO$_2$ gas transfer velocity, k_{emp}, was estimated by:

$$k = -\frac{1}{A}\frac{V}{RT}\frac{dpCO_2}{dt}\frac{1}{S \times (pCO_{2w} - pCO_{2a})} \qquad (3)$$

where S is the CO$_2$ solubility in seawater at in situ conditions calculated from water Temperature and Salinity according to Weiss (1974) and pCO_{2w} and pCO_{2a} are the measured partial pressure of CO$_2$ in the water surface and in the atmosphere respectively. Resulting k was then normalized to a Schmidt number of 660, corresponding to CO$_2$ in seawater at 20°C, by assuming that k is proportional to Sc^{-n}:

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

where $n=1/2$ for $U_{10} \geq 5$ m s^{-1} and $n=2/3$ for $U_{10} < 5$ 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 pCO_2 against time and averaged 3.3 (± 0.7) cm h^{-1}.

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 μg Chl a L^{-1}) to very oligotrophic and unproductive waters in the Subtropical NE Atlantic Ocean (0.05 μg Chl a L^{-1}), with an
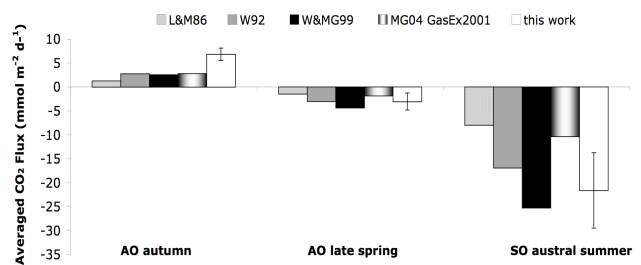

Fig. 2. Comparison of regional and seasonal averaged air-sea CO$_2$ measured fluxes within this work ($\pm$SE), with fluxes inferred from the wind-speed parameterizations of Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and McGillis et al. (2004). AO means Atlantic Ocean, and SO means Southern Ocean.

intermediate situation in the upwelling waters of the NW African Coast of the Subtropical Atlantic Ocean (3.5 μg Chl a L^{-1}). Sampled surface waters ranged from strongly under-saturated in CO$_2$ (189 μatm) in the Southern Ocean, to waters super-saturated (419 μatm) relative to atmospheric equilibrium in the upwelling system; from the coldest waters (-0.26°C) to very warm ones (27.07°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).

Observed TOC values ranged between 54 and 131 μmol 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$4.5 m s^{-1}; Table 1) than in the Atlantic Ocean (5.6$\pm$1.9 m s^{-1}; Table 1).

High wind speeds over the cold nutrient-rich polar waters, with high biological activity and low pCO_2 values render them a strong sink for atmospheric CO$_2$ (Takahashi et al., 1997). Accordingly, the measurements we performed during the austral summer (February) at South of 60°C latitudes identified a strong net uptake of atmospheric CO$_2$ with a water surface pCO_{2w} as low as 189 μatm, and measured air to sea fluxes averaging -21.6 ± 27.4 mmolC m^{-2} d^{-1} (SD, Table 1), or ±8.4 mmolC m^{-2} d^{-1} (SE, 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 CO$_2$ sink during late spring, with CO$_2$ fluxes averaging -3.1 ± 5.1 mmolC m^{-2} d^{-1} (SD, Table 1), or ±1.7 mmolC m^{-2} d^{-1} (SE, Fig. 2) and as a net CO$_2$ source to the atmosphere during autumn, with CO$_2$ fluxes averaging 6.8$\pm$6.4 mmolC m^{-2} d^{-1} (SD, Table 1), or ±1.3 mmolC m^{-2} d^{-1} (SE, Fig. 2). Our flux results are consistent with the direction of those reported for the same geographical zone using climatological surface ocean pCO_2 and seasonal, biological and temperature effects (Takahashi et al., 2002).

Table 1. Regional and seasonal averaged ($\pm$SD) air-sea CO_2 gradients (ΔpCO_2), water Temperature (SST), Salinity, CO_2 fluxes (FCO$_2$), gas transfer velocities (k_{660}), wind speeds (U_{10}) and organic carbon concentration in the top cm's (TOC) measured or estimated within this work, for the different sites and sampling periods.

Site	Sampling period	ΔpCO_2 (μatm)	SST (°C)	Salinity (ppt)	FCO$_2$ (mmol C m^{-2} d^{-1})	k_{660} (cm h^{-1})	U_{10} (m s^{-1})	TOC (μmol C L^{-1})
Atlantic Ocean	autumn	35.5$\pm$13.9	25.1$\pm$1.7	36.8$\pm$0.5	6.8$\pm$6.4	21.4$\pm$19.5	5.0$\pm$1.9	101$\pm$17
Atlantic Ocean	late spring	-11.7 ± 12.8	22.4$\pm$1.4	36.9$\pm$0.4	-3.1 ± 5.1	37.2$\pm$24.8	8.0$\pm$1.9	103$\pm$10
Southern Ocean	austral summer	-56.7 ± 58.5	1.3$\pm$1.0	33.8$\pm$0.3	-21.6 ± 27.4	75.1$\pm$58.3	7.8$\pm$4.5	69$\pm$11

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 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 where 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 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 and the closest calculated fluxes. Similar differences, of 30–50% between short-term CO_2 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_2 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_2 fluxes should necessarily be found on discrepancies between the empirically determined gas transfer velocity and that parameterized from wind speed.

Bin-averaged and row 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 gas transfer velocities obtained were consistently higher than those predicted from wind using non-intrusive methods. The reason for the difference in magnitude might refers to the difference in average conditions affecting gas exchange over different spatial and tem-
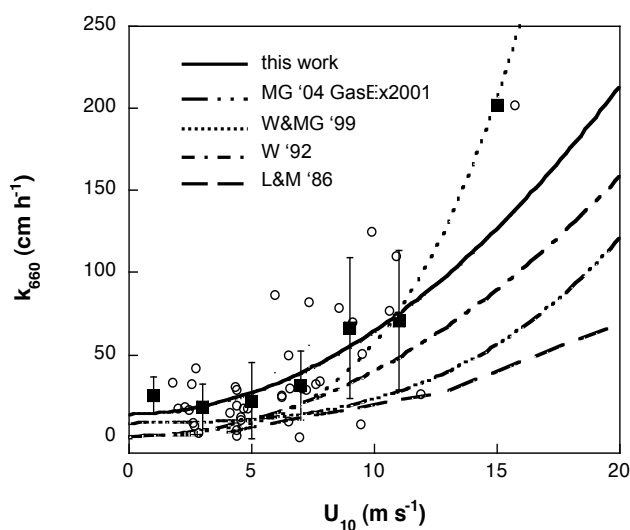
Fig. 3. The relationship between the apparent gas transfer velocities (k_{660}) derived from this study and wind speed (U_{10}). Open circles represent individual k_{660} estimated values from each measurement. Solid square symbols represent k_{660} values averaged ($\pm$SD) by bins of 2 m s^{-1} of U_{10}. The solid line represents the fitted relationship between gas transfer velocity and wind speed (Eq.5), $k(U_{10})$ (cm h^{-1})=13.33 ($\pm$5.50)+0.50 ($\pm$0.09) $(U_{10}$ (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.

poral scales. Whereas the floating chamber technique used yields estimates applicable to small time and spatial resolution, those from the literature taken for comparison average the gas exchange process over larger time and spatial scales. The high k values could also be artificially enhanced by unnatural turbulence generated by the chamber pressure, although this method's artifact should just affect measurements performed at low wind speeds (Marino and Howarth, 1993; Matthews et al., 2003).

Thus gas transfer velocities reported here are treated as apparent values and shouldn't be directly extrapolated outside the small scales applicable to the rates.

The relationship between the empirically-determined gas transfer velocity, k_{emp}, and wind speed was statistically analyzed (see Table 2), and we found the best fit to be described by the regression equation

Table 2. Correlation functions between; the estimated gas transfer velocity (k_{660}, cm h^{-1}) and the wind speed at 10 m height (U_{10}, m s^{-1}) based on unbinned and bin-averaged data over winds of 2 m s^{-1}; and the calculated residuals of gas transfer velocity (k_{res}, cm h^{-1}) and the organic carbon content at the top cm's of the water surface (TOC, μmolC L^{-1}) based on unbinned and bin-averaged data over TOC of 10 μmol L^{-1}.

		Function	Equation	r^2	p	n
k_{660} vs. U_{10} (all U_{10} range)	Unbinned	Linear	$k_{660}=-17.38(\pm10.15)+9.00(\pm1.48)U_{10}$	0.49	<0.0001	40
		Power	$k_{660}=7.37(\pm5.72)+0.65(\pm0.09)U_{10}^2$	0.60	<0.0001	40
		Exponential	$k_{660}=6.23(\pm1.93)e^{0.18(\pm0.10)U_{10}}$	0.62	<0.0001	40
	U_{10}-Bin average*	Linear	$k_{660}=5.94(\pm10.57)+5.48(\pm1.53)U_{10}$	0.76	0.0231	6
		Power	$k_{660}=13.33(\pm5.50)+0.50(\pm0.09)U_{10}^2$	0.88	0.0055	6
		Exponential	$k_{660}=14.89(\pm1.30)e^{0.14(\pm0.04)U_{10}}$	0.76	0.0240	6
k_{660} vs. TOC (U_{10}<5 m s^{-1}	Unbinned	Linear	$k_{res}=47.38(\pm10.86)-0.54(\pm0.11)TOC$	0.59	0.0002	18
	TOC-Bin average	Linear	$k_{res}=50.41(\pm10.13)-0.57(\pm0.10)TOC$	0.86	0.0028	7

* k_{660} value derived at >12 m s^{-1} was not considered in the fit to avoid strong bias derived from a single observation.

$$k(U_{10})(\text{cmh}^{-1}) = 13.33(\pm5.50)+ \quad (5)$$
$$0.50(\pm0.09)(U_{10}(\text{ms}^{-1}))^2(R^2 = 0.88, P<0.01)$$

Note that bin-average data points shown in Fig. 3 represent k_{emp} average values estimated from 3 or more observations ($n=3$–11), but the data point at >12 m s^{-1} represents just one observation alone. To avoid strong bias derived from a single observation that data value was not considered in the fit. 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 cm h^{-1}). We also observed that at low wind speeds (U_{10}<5 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 m s^{-1}, and a high gas transfer value at zero wind (8.2 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).

At low winds, surfactants are known to particularly modulate gas exchange because of dampening of waves and turbulence (Frew, 1997; McKenna and McGillis, 2004). 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 μmol 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 m s^{-1}). This enrichment can be 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 (≥ 90 μmol C L^{-1}) estimates of apparent gas transfer velocities, are significantly lower than those found at lower TOC content (<90 μmol C L^{-1}). This pattern suggests that organic content is damping sea surface turbulence leading to lower gas transfer rates at a wide range of wind speeds (up to 12 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 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_{emp}, and that predicted from wind alone, $k_{Residual}=k_{emp}-k(U_{10})$] and the organic carbon content at the top cm's. To avoid bias between different techniques and models, we use the trend
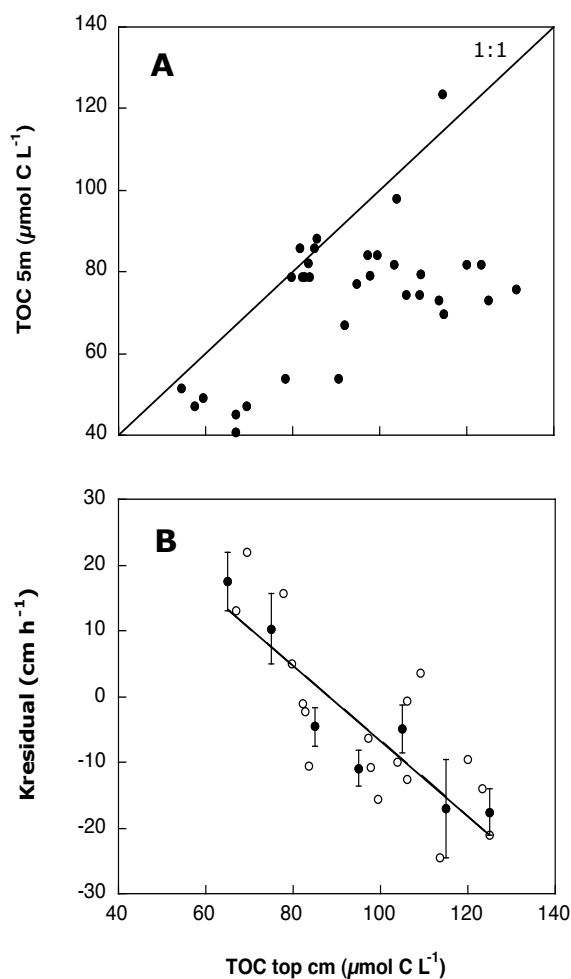
Fig. 4. (A) The relationship between total organic carbon (TOC) concentration at 5 m depth and that within the top 2 cm of the water surface. The solid line represents the 1 to 1 line; and **(B)** the relationship between the residuals of the empirically-determined apparent gas transfer velocity in this study and that predicted by wind speed from Eq. (5), and the TOC concentration within the top cm of the water surface at wind speeds below $5\,\mathrm{m\,s^{-1}}$. Open circles represent individual k_{residual} estimated from each measurement. Solid circles represent K_{Residual} values averaged ($\pm$ SE) by bins of $10\,\mu\mathrm{mol\,C\,L^{-1}}$ of TOC. The solid line represents the fitted linear regression equation: $K_{\mathrm{residual}}\,(\mathrm{cm\,h^{-1}}){=}53.07\,(\pm10.77){-}0.57\,(\pm0.11)\,\mathrm{TOC}\,(\mu\mathrm{mol\,C\,L^{-1}})$; $R^2{=}0.84$, $p{<}0.01$.

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_{emp} and $k(U_{10})$, and hence subtracted when calculating k residuals.

The dependency of the residuals of k with TOC content in the top cm were analyzed at different wind regimes, and we found the residuals to be strongly and significantly negatively correlated with TOC in the top cm of the ocean surface at wind speeds below $5\,\mathrm{m\,s^{-1}}$ ($R^2{=}0.86$, $p{<}0.01$, Fig. 4b; Table 2), indicating that low TOC in surface waters could

lead to faster gas fluxes than predicted from wind alone at those low wind regimes. According to this pattern, at surface waters with TOC content higher than $93\,\mu\mathrm{mol\,C\,L^{-1}}$ (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. Because the absolute k values obtained in this work could be artificially enhanced due to method limitations, our result cannot really be considered as quantitative, and don't aim to provide empirical relationship to derived k_{660} versus TOC, but to bring evidences of the significant suppressing effect of surface TOC concentration on gas exchange in the open ocean.

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 there is 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 Ćosović, 2001) and autochthonous production by phytoplankton (Gašparović et al., 2005). Accordingly, high release rates of organic carbon by phytoplankton are 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 allocthonous 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 Ćosović 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 Ćosović 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 $5\,\mathrm{m\,s^{-1}}$ a TOC content higher than $93\,\mu\mathrm{mol\,C\,L^{-1}}$ in surface layer waters will have suppressive effects on 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 $1\,\mathrm{mg\,L^{-1}}$, corresponding to an organic carbon content of around $90\,\mu\mathrm{mol\,C\,L^{-1}}$, during the productive spring season (Frew et al., 2002; Fig. 1a). Despite the trend being the same, Frew et al. (2002) observed smaller k changes over a greater TOC range than those derived from our observations. Differences in the magnitude and TOC ranges affecting k could be explained by the fact that k reduction measured in our work is dependent on the bulk TOC concentration of the surface top cm, whereas that measured by Frew et al. (2002) depends on the excess of microlayer surfactant relative to that in the underlayer water. As surfactants are just a percentage of the bulk TOC concentration, the whole TOC effect must be masking the pure surfactant effect investigated by Frew et al. (2002). Thus, there should be other processes, apart from surfactants, accounting for the whole TOC effect on suppressing gas transfer velocity. 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 yields low surface $p\mathrm{CO}_2$/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 CO$_2$ fluxes in TOC-poor unproductive areas, which are often net sources of CO$_2$ (Duarte and Prairie, 2005; Takahashi et al., 2002), could be larger than previ-

ously 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; 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 CO$_2$ sources to the atmosphere than previously thought. Moreover, oligotrophic regions are characterized by a small $p\mathrm{CO}_2$ gradient between water and air and by low wind speeds conducive to a major contribution of organic matter on modulating air-sea CO$_2$ fluxes.

This imply that substantial errors in flux computations may be incurred if generic k-wind relationships are employed for the purpose of computing global air-sea 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 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 CO$_2$ fluxes, which has been identified as one of the major challenges of research in this area (McGillis et al., 2001, 2004; Nightingale et al., 2000b).

In summary, the results presented here, 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$_2$ gas fluxes al low and intermediate wind speeds ($<5\,\mathrm{m\,s^{-1}}$), confirming previous suggestions (Frew et al., 2002, 2004). 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$_2$ 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$_2$ sink and the impact of changes in ocean ecosystems on this process.

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