

Systematic errors in global air-sea CO2 flux caused by temporal averaging of sea-level pressure

H. Kettle, C. J. Merchant

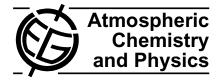
► To cite this version:

H. Kettle, C. J. Merchant. Systematic errors in global air-sea CO2 flux caused by temporal averaging of sea-level pressure. Atmospheric Chemistry and Physics, 2005, 5 (6), pp.1459-1466. hal-00295669

HAL Id: hal-00295669 https://hal.science/hal-00295669

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Systematic errors in global air-sea CO₂ flux caused by temporal averaging of sea-level pressure

H. Kettle and C. J. Merchant

School of GeoSciences, University of Edinburgh, West Mains Rd, Edinburgh EH9 3JN, UK

Received: 7 December 2004 – Published in Atmos. Chem. Phys. Discuss.: 28 January 2005 Revised: 8 April 2005 – Accepted: 22 May 2005 – Published: 15 June 2005

Abstract. Long-term temporal averaging of meteorological data, such as wind speed and air pressure, can cause large errors in air-sea carbon flux estimates. Other researchers have already shown that time averaging of wind speed data creates large errors in flux due to the non-linear dependence of the gas transfer velocity on wind speed (Bates and Merlivat, 2001). However, in general, wind speed is negatively correlated with air pressure, and a given fractional change in the pressure of dry air produces an equivalent fractional change in the atmospheric partial pressure of carbon dioxide (pCO_{2air}). Thus low pressure systems cause a drop in pCO_{2air}, which together with the associated high winds, promotes outgassing/reduces uptake of CO₂ from the ocean. Here we quantify the errors in global carbon flux estimates caused by using monthly or climatological pressure data to calculate pCO_{2air} (and thus ignoring the covariance of wind and pressure) over the period 1990-1999, using two common parameterisations for gas transfer velocity. Results show that on average, compared with estimates made using 6 hourly pressure data, the global oceanic sink is systematically overestimated by 7% (W92) and 10% (WM99) when monthly mean pressure is used, and 9% (W92) and 12% (WM99) when climatological pressure is used.

1 Introduction

An important challenge in the science of climate is to develop quantitative understanding and prediction of the uptake of atmospheric carbon dioxide by the oceans. Measurements of atmospheric carbon dioxide and oxygen concentrations in combination with knowledge of fossil fuel burning (Keeling and Garcia, 2002) give an estimate of global ocean uptake of carbon dioxide. Global ocean uptake can also be estimated

Correspondence to: H. Kettle (H.Kettle@ed.ac.uk)

directly by calculating local air-sea gas transfer and integrating this gas transfer in time and space (Takahashi et al., 1997, 2002). The latter approach requires a high degree of quantitative understanding of gas-transfer processes and knowledge of the controls on the physical and biological factors that determine the imbalance in the partial pressure of carbon dioxide across the air-sea interface. Recent work (Bates and Merlivat, 2001; Chapman et al., 2002), has quantified how shortterm variability in wind-speed significantly affects integrated gas transfer. Here, we extend that insight to the comparable effects of short-term changes in sea-level pressure. In particular, we demonstrate how neglecting or averaging these pressure variations in time can lead to systematic errors in flux computations.

The flux (F) of CO₂ across the air-sea interface is described by:

$$F_t = (ks(pCO_{2sea} - pCO_{2air}))_t.$$
(1)

where F_t is the flux integrated over a time period t, k is the gas transfer velocity, s is the solubility of CO₂ in sea water and pCO_{2sea} and pCO_{2air} are the partial pressures of CO₂ in the ocean and atmosphere respectively. The difference in these latter two variables determines the direction for the exchange, and k controls the transfer rate. The magnitude of the transfer rate is controlled by the thickness of the boundary layer which is a function of near surface turbulence and diffusion. Thus, the transfer rate is determined by the state of the sea surface: by wave age, fetch, wind speed, the prevalence of bubbles, boundary layer stability and naturally occurring surfactants (e.g. Woolf, 1997; Monahan and Spillane, 1984; Liss and Merlivat, 1986; Asher and Wanninkhof, 1998). It is highly unlikely, therefore, that only one physical variable can completely determine the spatial scales and environmental conditions necessary to predict k. Despite this, many empirical relationships for k in practical use are solely functions of wind speed as this is an influential and easily obtainable parameter. Three commonly used wind functions are the piecewise linear relation (Liss and Merlivat, 1986), the quadratic relation (Wanninkhof, 1992; Nightingale et al., 2000), and the cubic relation (Wanninkhof and McGillis, 1999). In this study we use the Wanninkhof (1992; W92) and the Wanninkhof and McGillis (1999; WM99) relations.

When non-linear functions are used, the time-averaging period of the wind speed data becomes important. Bates and Merlivat (2001) showed, using data from a site near Bermuda, that the air-sea CO_2 flux is up to three times greater if hourly wind data are used rather than daily averaged values. Similar work, using model results on a global scale rather than localised data, by Chapman et al. (2002) for dimethylsulfide (DMS) fluxes showed that DMS emission fluxes were often 10-60% higher when using 20-minute rather than monthly averaged wind speeds (using the Liss and Merlivat (1986) relationship for k). These errors arise because in the non-linear gas transfer relationships, periods of higher wind-speeds contribute disproportionately to the timeintegrated flux, and if the wind speed is averaged this effect is lost. When monthly averaged wind data are used, different equations for k are required. For example the quadratic (W92) and cubic (WM99) relations have a short-term (or steady wind) version, in addition to a long-term version that relies on the assumption that wind speed follows a Rayleigh probability density function. Wanninkhof et al. (2002) found that although the Rayleigh distribution is a reasonable assumption for global winds, significant regional deviations from this distribution exist. Consequently these researchers recommend avoiding time-averaged winds, and instead computing the time averages of the higher moments needed for the non-linear relationships.

Thus, to calculate air-sea CO₂ fluxes it is preferable to use short-term wind data. But other variables in the flux equation also change over time: solubility is affected by timevarying sea surface temperature and salinity (SST and SSS); pCO_{2sea} is affected by the evolution in time of complex biological and physical processes; and pCO_{2air} is affected by the meteorologically-driven air pressure and the water vapour pressure just above the air-sea interface. In a recent analysis of data collected in the Southern Ocean, Fransson et al. (2004) found that there is significant diurnal variability in pCO_{2sea} in this region and recommend that estimates of CO₂ sources/sinks in areas and seasons with strong diurnal cycles in temperature and productivity should account for this short term variability. In this study, we assess the effect of including the time variation of pCO_{2air}. This variable is controlled, in large part, by air pressure, which is a readily available and robust parameter. Moreover, wind and pressure are meteorologically related variables. Weather systems that bring about large changes in wind speed are characterized by large changes in the pressure field. Using short-term wind data to calculate k (as recommended) with long-term pressure data for pCO_{2air} (as is generally done in modelling studies) ignores this co-variation.

Atmospheric pCO_2 changes over time according to changes in air pressure, such that

$$pCO_{2air} = x(P - SVP).$$
⁽²⁾

where x is the atmospheric molar fraction of CO_2 in air, P is atmospheric pressure and SVP is the saturation vapour pressure of water at SST. If we consider a given time period (e.g., one month) over which changes in the ambient air pressure cause variations in pCO_{2air}, and consider the case when pCO_{2sea} is equal to the mean value of pCO_{2air} over this time period. Then if the wind blows at a steady speed over this period, the net flux will be zero, because the outgassing (which occurs when pCO_{2sea}>pCO_{2air}) and uptake (when $pCO_{2sea} < pCO_{2air}$) of CO_2 are equal in magnitude. However, if wind speed is negatively correlated with air pressure such that wind speeds are higher when air pressure is low, the times during which pCO_{2air} < pCO_{2sea} will generate larger fluxes (due to the increased wind speed) than those when $pCO_{2air} > CO_{2sea}$: i.e. there will be more outgassing of CO₂ from the ocean than there is uptake. Nonetheless, if we were to use an average value for pCO2air over this period then we would still (wrongly) compute a net flux of zero, since the excess of outgassing caused by the negative co-variation of wind and pressure would not be captured. Conversely, if wind and pressure were positively correlated this would promote uptake of CO_2 by the oceans, uptake that would similarly not be captured by monthly averaged calculations. In general, pCO_{2air} is higher than pCO_{2sea} and wind and pressure are negatively correlated, so the wind-pressure co-variation - while not causing net outgassing - will tend to reduce the amount of uptake. In this paper, we quantify the magnitude of this systematic effect for the global oceans.

2 Data

To assess the effects of wind-pressure co-variability on calculations of global CO₂ fluxes we make use of the monthly climatology (Takahashi et al., 2002; Gurney et al., 2002) made available on the w.w.w. from the Lamont-Doherty Earth Observatory of Columbia University. This dataset will henceforth be referred to as Taka02. From Taka02 we use monthly fields for SST (from the World Ocean database, 1998 (www. nodc.noaa.gov/OC5/wod98.html)), SSS, pCO_{2sea}, pCO_{2air} and pressure given for the reference year 1995. Short term (six-hourly) wind and air pressure data are taken from the ECMWF ERA-40 2.5° gridded reanalysis data (http://www. ecmwf.int/research/era/) over the 10 year period 1990–1999. Annual mean fields for the ERA wind and pressure data are shown in Fig. 1.

3 Method

In order to work on a common grid, we linearly interpolate Taka02 from its 4° latitude by 5° longitude grid to the ERA

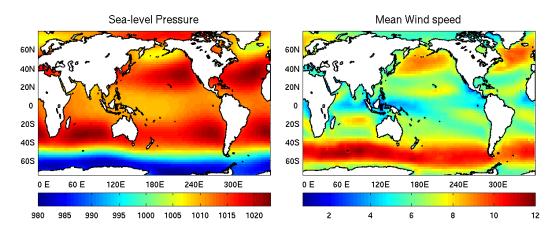


Fig. 1. Climatological ECMWF ERA-40 data for sea-level pressure (mb) and wind speed (ms⁻¹) for 1990–1999.

2.5° grid. The various terms in Eq. (1) are then computed as follows. We use both the W92 and the WM99 parameterisations for the gas transfer velocity (k_{W92} and k_{WM99}) with six-hourly wind speed (ERA) data:

$$k_{\rm W92} = 0.31 \, u_{10}^2 (Sc/660)^{-1/2} \tag{3}$$

$$k_{\rm WM99} = 0.0283 \, u_{10}^3 (Sc/660)^{-1/2} \tag{4}$$

where k is in cm hr⁻¹, u_{10} is wind speed at 10 m (m s⁻¹), and *Sc* is the dimensionless Schmidt number calculated from:

$$Sc = 2073.1 - 125.62 \text{ SST} + 3.628 \text{ SST}^2 - 0.0432 \text{ SST}^3$$
 (5)

using Taka02's climatological monthly SST (°C). The Schmidt number is the viscosity of sea water divided by the molecular diffusion coefficient of CO₂ in water. Solubility (in mol atm $^{-1}$ m $^{-3}$) is calculated according to Weiss (1974) using SST and SSS data from Taka02. pCO_{2sea} values are taken directly from Taka02. ECMWF pressure data are used to calculate percentage changes in pressure from Takahashi's monthly climatology at six hourly intervals. Dalton's Law states that the total pressure of a gas is equal to the sum of the partial pressures of its components. Thus, when air pressure changes, so too must the partial pressures of the component gases. Consequently, the percentage change in pressure equals the percentage change in pCO_{2air}. Since water vapour is another component gas, any independent changes in the water vapour pressure will also affect pCO_{2air}. Just above the air-sea interface, the air is assumed to be saturated, so the water vapour partial pressure is the saturation vapour pressure (SVP) - given by Weiss and Price (1980) and then converted to mb:

$$SVP_{Taka} = 1013.25 \exp\left[24.4543 - 67.4509 \frac{100}{SST_k} - 4.8489 \ln\left(\frac{SST_k}{100}\right) - 0.000544 SSS\right]$$
(6)

where SST_k is SST in Kelvin. In this study we use Taka02 for SST and SSS, and thus SVP_{Taka} is a monthly gridded variable. Assuming that the molar fraction of CO_2 in dry air (*x* in Eq. 2) remains constant, we then calculate 6 hourly values of pCO_{2air} from 6 hourly air pressure data according to:

$$pCO_{2air\,6h} = pCO_{2air\,Taka} \frac{P_{6h} - SVP_{Taka}}{P_{Taka} - SVP_{Taka}}$$
(7)

where the subscripts Taka and 6h refer to Taka02 data and 6 hourly data respectively. In order to isolate the effects of different pressure averaging on estimated net CO_2 fluxes, all other variables remain the same between evaluations. We then consider the following three cases:

- 1. pCO_{2air} calculated using 6 hourly pressure data (Eq. 7)
- 2. pCO_{2air} calculated using monthly pressure data (Eq. 7 with the substitution P_{6h} =monthly mean of P_{6h})
- 3. pCO_{2air} taken directly from Takahashi's climatology

In all cases we use six-hourly wind speed so that the short term flux Eqs. (3) and (4) can be used rather than their long term equivalents. Thus all calculations are performed at sixhourly intervals. We can then see the results of time averaging air pressure in isolation. To calculate mass fluxes over regional to global areas, each cell is weighted by its area.

The covariance of wind and pressure is calculated for each cell over the whole 10 year period as:

$$\operatorname{cov}(u_{10}, P) = \langle u_{10}P \rangle - \langle P \rangle \langle u_{10} \rangle$$
 (8)

where u_{10} and *P* are wind and pressure time series for all 10 years, and <> denotes the mean value over these 10 years.

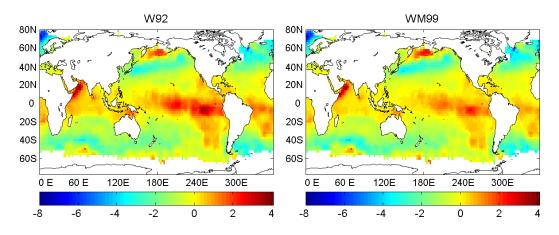


Fig. 2. Mean annual air-sea net flux 1990-1999 (mol $CO_2 m^{-2} yr^{-1}$). Flux is calculated using 6 hourly wind and pressure data and then averaged over the 10 years for both gas transfer parameterisations. White regions indicate sea ice.

Table 1. Mean global mass flux $(PgCyr^{-1})$ computed using 6 hourly winds and k_{WM99} and k_{W92} for different air pressure time averaging periods over 1990–1999, and 1995 (Taka02 reference year). Regions of sea ice are removed. Errors are the overestimates of the oceanic sink strength caused by monthly and climatological averaging (mon. av. and clim. av.) of pressure data.

Averaging Period	1990–1999		1995	
	W92	WM99	W92	WM99
6 hourly	-1.60	-1.91	-1.65	-2.16
Monthly	-1.72	-2.08	-1.77	-2.36
Clim.	-1.74	-2.13	-1.79	-2.41
Error (mon. av.)	0.12	0.17	0.12	0.20
Error (clim. av.)	0.14	0.22	0.14	0.25
% Error (mon. av.)	7.2%	9.7%	7.3%	9.3%
% Error (clim. av.)	8.6%	11.5%	8.5%	11.6%

4 Results

4.1 Mean Global Fluxes

Six-hourly pressure and wind speed data from 1990 to 1999 are used to construct a global 10 year climatology of net CO_2 flux for the 3 different cases of pressure time-averaging stated above using both gas transfer parameterisations. The mean net flux fields over this time period, calculated using 6 hourly wind and pressure data (i.e. case 1) are shown in Fig. 2. Regions affected by sea ice are shown in white and these are discounted in subsequent flux calculations when they are actually ice covered. The figure shows the main sources (red) of CO_2 are in the Northern Pacific, around the equator and the Arabian Sea. The main sink areas (blue) are the Norwegian Sea, the North Atlantic, the Northern Pacific and the Southern Ocean. The plots show that using the 2 different gas transfer parameterisations does not affect the

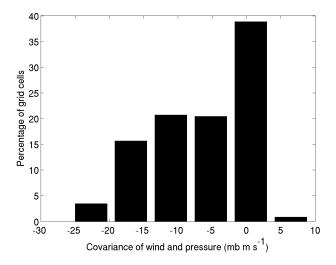


Fig. 3. Covariance of wind and pressure for all grid cells across the global oceans from 1990–1999.

general pattern of flux but just the magnitude. The computed global mean mass fluxes over this time period (1990–1999) are given in Table 1 along with our computed global fluxes for 1995 which is the reference year for Taka02.

Looking at Table 1 it is immediately apparent that the choice of the gas transfer parameterisation makes a large difference to global flux values, a result previously observed by other researchers – for example, Boutin et al. (2002), Wanninkhof et al. (2002) and Takahashi et al. (2002). We can directly compare our 1995 net fluxes computed with climatological pCO_{2air} with those of Takahashi et al. (2002) since the only differences are the wind speed datasets (NCEP/NCAR compared with ECMWF) and the computation of the gas transfer velocity, k. Takahashi et al. (2002) use the long-term W92 and WM99 formulations with mean monthly wind speeds, whereas we use the short-term formulation with

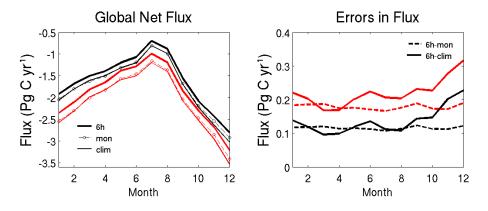


Fig. 4. Net air-sea CO_2 flux as a function of time of year. Red and black lines represent WM99 and W92 gas transfer parameterisations respectively.

six hourly wind speeds. Our values of -1.79 and -2.41 Pg C yr⁻¹ (W92 and WM99 respectively) give 11% and 24.5% less oceanic uptake than Takahashi et al. (2002) values of -1.81 and -3.00 Pg C yr⁻¹. These differences are similar to those reported for 1995 by Wanninkhof et al. (2002), in which monthly mean wind speeds gave oceanic uptakes of -2.2 and -3.3 Pg C yr⁻¹ (W92 and WM99) i.e. 5% and 26% more oceanic uptake than those computed using 6 hourly wind speeds (-2.1 and -2.6 Pg C yr⁻¹). These results highlight the importance of using short-term wind data.

Turning our attention to the systematic differences caused by pressure averaging, Table 1 shows in all cases, that increasing the pressure averaging time period leads to increasingly large values of ocean sink strength. Thus, ignoring the covariation of wind and pressure leads to a systematic bias in calculations of flux. Figure 3 shows a histogram of the wind-pressure co-variation for each grid cell across the global oceans over the period 1990-1999, indicating a predominantly negative correlation over the majority of the ocean surface during this period. That the sink is weaker if the wind-pressure covariation is included (i.e. using the sixhourly data) is consistent with the argument given in the Introduction. If we consider the most accurate global flux estimate to be that calculated using six-hourly wind and pressure data then the mean percentage errors in global fluxes caused purely by using different pressure averaging time periods are 7.2% and 9.7% (monthly; W92 and WM99) and 8.6% and 11.5% (climatological; W92 and WM99). The direction of the effect is such as to further reduce the calculated global uptake compared to the Taka02 value. These results indicate that the calculations of global net flux of CO₂ are sensitive to pressure averaging. Next, we examine how these flux errors are distributed in time and space.

4.2 Temporal distribution of flux errors

Figure 4 shows how the monthly mass fluxes vary with time of year, gas transfer parameterisation and pressure averag-

ing time period. Globally, there is a strong annual cycle in the net flux with the sink strength decreasing in the northern summer due to the seasonal temperature and biological effect on pCO_{2sea}. This seasonal flux pattern was also observed by Boutin et al. (2002) and found to be dominated by the pronounced seasonal variation of the global outgassing flux. The errors incurred through using monthly pressure data are fairly constant throughout the year, however, those due to using climatological pressure increase over October to December, indicating a difference in the climatological pressure field used by Taka02 and that calculated from ERA 1990–1999 pressure data.

4.3 Spatial distribution of flux errors

Figure 2 shows that net air-sea CO₂ flux is very spatially variable. Since storms which cause high negative wind-pressure covariation are also spatially variable we would expect the errors caused by using monthly or climatological pressure to show a strong spatial variation. When the differences between fluxes calculated from monthly averaged values of 6 hourly pressure data and from actual 6 hourly pressure are examined we can see the effect of ignoring the windpressure covariation directly (Fig. 5). When fluxes computed with climatological pressure are compared to those from 6 hourly pressure we are also looking at differences between the ECMWF ERA-40 pressure data and the Atlas of Surface Marine Data (1994) pressure data used by Taka02. Since we are only examining the period 1990-1999 it is possible that these 2 climatological pressure fields may have important differences. However, differences in climatological pressure fields are not the focus of this study therefore we will only examine the spatial distribution of flux errors caused by monthly averaging of air pressure. The left and middle plots in Fig. 5 show the mean errors (1990–1999) in the flux fields created by using monthly averaged pressure rather than 6 hourly for the 2 different gas transfer parameterisations. The plot on the right shows the 10 yr wind-pressure covariance

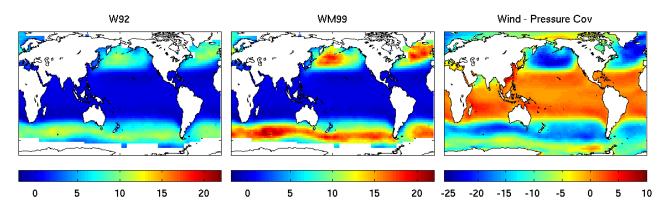


Fig. 5. Left and middle plot: Mean errors $(10^{-2} \text{mol C m}^{-2} \text{ yr}^{-1})$ in flux fields caused by using monthly pressure averaging (1990–1999) for W92 and WM99 gas transfer parameterisations. White cells indicate sea ice. Right plot: Wind-pressure covariance for 1990–1999 (mb m s⁻¹).

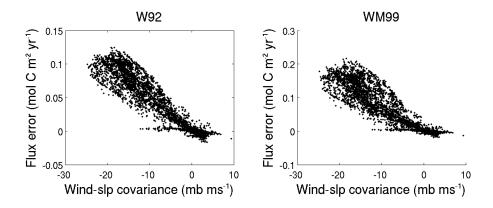


Fig. 6. Relation between flux error caused by monthly averaging of pressure (i.e. the difference between the 6 hourly and monthly flux fields) averaged over 1990–1999, and the wind-pressure covariance for W92 and WM99.

field which is seen to correspond strongly with the errors in the net flux fields. This relationship is shown more explicitly in Fig. 6 which shows the mean flux error against the windpressure covariance for each grid cell for both gas transfer parameterisations (cells under sea ice at any time in the year are discounted). There is a lot scatter in these plots due to the wide range of pCO_{2sea} , SST and SSS values over grid cells with the same wind-pressure covariance. However, the relationship between flux error and wind-pressure covariance is still clear.

5 Discussion

A limitation of all the gas transfer parameterisations available is that they have been compared with laboratory and field fluxes only for wind speeds up to about 20 m s^{-1} . The W92 parameterisation was developed using natural-¹⁴C disequilibrium and bomb-¹⁴C inventory methods (Wanninkhof, 1992), and the field data (Gas Ex-98 cruise) used to derive the short term WM99 parameterisation were mostly measured at

wind speeds of around 6 m s^{-1} with no measurements higher than 15 m s^{-1} (Wanninkhof and McGillis, 1999). The six hourly ERA wind speeds used here are only above 15 m s^{-1} on one occasion over the 10 year period and we have simply extrapolated the *k* equations beyond the range of the calibration data for this data point. However, the ERA wind speeds are low because they are already averaged over time (six-hourly) and space (2.5° grid cell). Since the CO₂ eddy covariance and wind speed measurements used to derive the WM99 gas transfer relationship are hourly averages at a point in space, we have already introduced averaging errors by using 6-hourly ERA wind data.

A further limitation of the method used here – a sensitivity analysis with respect to the timescales on which pressure data are included – is the neglect of variations in SST, SSS and pCO_{2sea} data. Variability in these parameters, of course, is a major component of variability in flux over a wide range of timescales. We have not considered the potential effect of sub-daily variability (or covariability) of these parameters on SVP and solubility: for example, the diurnal response of SST and subsurface mixing to the wind speed (demonstrated by Murray et al., 2000 and Stuart-Menteth et al., 2003). We have also not accounted for the effects of precipitation. Recently Ho et al. (2004) demonstrated that short, intense rain events enhances gas exchange in the oceans. However, for much of the ocean for most of the time, such effects are expected to be smaller than those we highlight here.

For the reference year 1995, Wanninkhof et al. (2002) found that using climatological wind speed data, (with a Rayleigh distribution) rather than six-hourly reanalysis wind speeds to calculate the gas transfer velocity led to an overestimate in global ocean sink strength of 26% (using WM99) or 5% (using W92). Our results, for the same year, show that using climatological pressure data rather than ERA six-hourly pressure data, over estimates the global ocean sink by a further 12% (WM99) and 9% (W92). Pressure is a robust and widely available variable, and is generally output from climate models at the same resolution as wind speed. Therefore, it is easily incorporated into high frequency flux computations, allowing these errors to be eliminated with little additional computational expense.

6 Conclusions

Many researchers have highlighted the importance of using short-term wind speed data to calculate CO₂ fluxes. Here we show that short-term variations in atmospheric pCO₂ caused by fluctuations in pressure are also of significance. The predominantly negative correlation of air pressure and wind speed over the global oceans causes a bias in the net flux towards outgassing from the ocean. Using monthly averaged pressure data to calculate atmospheric pCO₂ ignores this bias and leads to an over estimate of the oceanic sink strength. Using climatological pCO_{2air} data not only ignores this bias but also introduces errors caused by differences in the climatological and actual pressure fields. Globally this means that the amount of CO_2 taken up by the oceans is overestimated by about 0.12 or $0.17 \text{ Pg C yr}^{-1}$ (7 or 10%; W92 or WM99) if mean monthly pressure data is used, and 0.14 or $0.22 \text{ Pg C yr}^{-1}$ (9 or 12%; W92 or WM99) if climatological pressure is used. To better estimate the strength of the oceanic CO₂ sink, we therefore recommend that both shortterm wind speed and air pressure data are used in future flux computations.

Acknowledgements. This research has been funded by the Centre for observation of Air-Sea Interactions and fluXes (CASIX), a UK Natural Environment Research Council (NERC) Centre of Excellence in Earth Observation (contribution no. 33). Wind and sea level pressure data were taken from ECMWF ERA-40 reanalyses obtained on behalf of ECMWF from the British Atmospheric Data Centre (BADC).

Edited by: M. Heimann

References

- Atlas of Surface Marine Data: CD-ROM NODC-56, Ocean Climate Laboratory, NOAA, Washington, D.C., 1994.
- Asher, W. and Wanninkhof, R.: Transient tracers and air-sea gas transfer, J. Geophys. Res., 103, 15 939–15 958, 1998.
- Bates, N. R. and Merlivat, L.: The influence of short-term wind variability on air-sea CO₂ exchange, Geophys. Res. Lett., 28, 3281–3284, 2001.
- Boutin, J., Etcheto J., Merlivat L., and Rangama, Y.: Influence of gas exchange coefficient parameterisation on seasonal and regional variability of CO₂ air-sea fluxes, Geophys. Res. Lett., 29 (8), art. no. 1182, doi:10.1029/2001GL013872, 2002.
- Chapman, E. G., Shaw, W. J., Easter, R. C., Bian, X, and Ghan, S. J.: Influence of wind speed averaging on estimates of dimethylsulfide emission fluxes, J. Geophys. Res., 107, D23, 4672, doi:10.1029/2001JD001564, 2002.
- Fransson, A., Chierici, M., and Anderson, L. G.: Diurnal variability in the oceanic carbon dioxide system and oxygen in the Southern Ocean surface water, Deep Sea Res., Part II, 51, 2827–2839, 2004.
- Gurney, K. R., Law, R. M., Denning, A. S., Rayner, P. J., Baker, D., Bousquet, P., Bruhwiler, L., Chen, Y.-H., Ciais, P., Fan, S., Fung, I. Y., Gloor, M., Heimann, M., Higuchi, K., John, J., Maki, T., Maksyutov, S., Masarie, K., Peylin, P., Prather, M., Pak, B. C., Randerson, J., Sarmiento, J., Taguchi, S., Takahashi, T., and Yuen, C. W.: Towards robust regional estimates of CO₂ sources and sinks using atmospheric transport models, Nature, 415, 626– 630, 2002.
- Ho, D. T., Zappa C. J., McGillis, W. R., Bliven, L. F., Ward, B., Dacey, J. W. H., Schlosser, P., and Hendricks, M. B.: Influence of rain on air-sea gas exchange: Lessons from a model ocean, J. Geophys. Res., 109, C08S18, doi:10.1029/2003JC001806, 2004.
- Keeling, R. F. and Garcia, H. E.: The change in oceanic O2 inventory associated with recent global warming, Proc. Natl. Acad. of Sci., 99, 7848–7853, 2002.
- 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-Menard, P. and Reidel, D., Norwell, Mass., pp. 113–127, 1986.
- Monahan, E. C. and Spillane, M. C.: The role of whitecaps in airsea gas exchange, in: Gas Transfer at Water Surfaces, edited by: Brutsaert, W., Jirka, G. H., and Reidel, D., Norwell, Mass., pp. 495–504, 1984.
- Murray, M. J., Allen, M. R., Merchant C. J., Harris, A. R., and Donlon, C. J.: Direct observations of skin-bulk SST variability, Geophys. Res. Lett., 27 1171–1174, 2000.
- 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. Cycles 14, 373–387, 2000.
- Stuart-Menteth, A. C., Robinson, I. S., and Challenor, P. G.: A global study of diurnal warming using satellite-derived sea surface temperature, J. Geophys. Res. 108 (C5), 3155, doi:10.1029/2002JC001534, 2003.
- Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tillbrook, B., Bates, N., Wanninkhof, R., Feely, R. A., Sabine, C., Olafsson, J., and Nojiri, Y.: Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal bio-

logical and temperature effects, Deep Sea Res., Part II, 49, 1601–1622, 2002.

- 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 CO₂: an estimate based on measurements of sea-air pCO2 difference, Proc. Natl. Acad. Sci., 94, 8292–8299, 1997.
- Takahashi, T., Olafsson, J., Goddard, J., Chipman, D. W., and Sutherland, S. C.: Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: a comparative study, Global Biogeochem. Cycles, 7, 843–878, 1993.
- Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, J. Geophys. Res., 97, C5, 7373–7382, 1992.

- Wanninkhof, R. and McGillis, W. R.: A cubic relationship between air-sea CO₂ exchange and wind speed, Geophys. Res. Lett., 26, 13, 1889–1829, 1999.
- Wanninkhof, R., Doney, S. C., Takahashi, T., and McGillis, W. R.: The effect of using time-averaged winds on regional air-sea CO₂ fluxes, in: Gas Transfer at Water Surfaces, Geophysical Monograph, 127, AGU, 2002.
- Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem., 2, 203–215, 1974.
- Weiss, R. F. and Price, B. A.: Nitrous-oxide solubility in water and seawater, Mar. Chem., 8, 347–359, 1980.
- Woolf, D. K.: Bubbles and their role in gas exchange, in: The Sea Surface and Global Change, edited by: Duce, R. A. and Liss, P. S., pp. 173–205, Cambridge University Press, New York, 1997.