



## Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO<sub>2</sub> by the oceans

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[1] We re-assess the constraints that estimates of the global ocean excess radiocarbon inventory ( $I^E$ ) place on air-sea gas exchange. We find that the gas exchange scaling parameter  $a_q$  cannot be constrained by  $I^E$  alone. Non-negligible biases in different global wind speed data sets require a careful adaptation of  $a_q$  to the wind field chosen. Furthermore,  $a_q$  depends on the spatial and temporal resolution of the wind fields. We develop a new wind speed- and inventory-normalized gas exchange parameter  $a_q^N$  which takes into account these biases and which is easily adaptable to any new estimate of  $I^E$ . Our study yields an average estimate of  $a_q$  of  $0.32 \pm 0.05$  for monthly mean winds, lower than the previous estimate (0.39) from Wanninkhof (1992). We calculate a global annual average piston velocity for CO<sub>2</sub> of  $16.7 \pm 2.9$  cm/hr and a gross CO<sub>2</sub> flux between atmosphere and ocean of  $73 \pm 10$  PgC/yr, significantly lower than results from previous studies. **Citation:** Naegler, T., P. Ciais, K. B. Rodgers, and I. Levin (2006), Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO<sub>2</sub> by the oceans, *Geophys. Res. Lett.*, 33, L11802, doi:10.1029/2005GL025408.

### 1. Introduction

[2] Individual ocean regions are temporally varying sources or sinks of atmospheric CO<sub>2</sub>, depending on factors such as sea surface temperature and salinity, biological activity, or the upwelling of CO<sub>2</sub>-rich waters to the surface. Full thermodynamic equilibrium is thus never reached for CO<sub>2</sub> at the air-sea interface. This yields a permanent flux ( $F$ ) of CO<sub>2</sub> to and from the ocean, which is proportional to the CO<sub>2</sub> partial pressure difference between the sea surface and the atmosphere ( $\Delta p\text{CO}_2$ ), the temperature-dependent solubility ( $L$ ), and the transfer- (or piston-) velocity ( $k$ ). Thus  $F$  can be expressed as

$$F(\vec{x}, t) = k(\vec{x}, t) \cdot L(\vec{x}, t) \cdot \Delta p\text{CO}_2(\vec{x}, t) \quad (1)$$

[3] A global gridded climatology of  $\Delta p\text{CO}_2$  has been derived using in situ measurements [Takahashi *et al.*, 2002], albeit with some gaps, but there remains a fundamental

uncertainty in the determination of the piston velocity  $k$  when calculating the air-sea flux of CO<sub>2</sub>.

[4] Numerous process studies under both controlled conditions (e.g., wind tunnels) and real-world conditions (e.g., tracer releases at sea) have measured the dependency of  $k$  as a function of wind speed  $u$ , but no unified theory exists yet. Commonly accepted relationships for  $k(u)$  assume in sections linear [Liss and Merlivat, 1986], quadratic [Wanninkhof, 1992; Nightingale *et al.*, 2000] or cubic functions [Wanninkhof and McGillis, 1999] of wind speed. The most widely used gas exchange parameterization is the quadratic  $k(u)$  relationship from Wanninkhof [1992]:

$$k(\vec{x}, t) = a_q \cdot u(\vec{x}, t)^2 \cdot (Sc(\vec{x}, t)/660)^{-0.5} \quad (2)$$

where  $Sc$  refers to the Schmidt number.  $a_q$  denotes a global gas exchange scaling parameter, which cannot be measured directly, but has to be calibrated against observations, e.g., the observed ocean excess radiocarbon inventory ( $I^E$ ) [Broecker *et al.*, 1985; Wanninkhof, 1992] (see also section 2). “Excess radiocarbon” refers to human-induced changes in the radiocarbon (<sup>14</sup>C) inventory of the main carbon reservoirs. These changes are caused by the production of <sup>14</sup>C in atmospheric nuclear bomb tests and the release of <sup>14</sup>C by the nuclear industry. As a second, yet smaller effect, the combustion of <sup>14</sup>C-free fossil carbon dilutes the atmospheric <sup>14</sup>C-to-C ratio of CO<sub>2</sub> (the so-called “Suess effect”), causing a <sup>14</sup>C flux from ocean (and biosphere) to the atmosphere.

[5] Ocean <sup>14</sup>C observations performed during the Geochemical Ocean Section Study (GEOSECS) and the World Ocean Circulation Experiment (WOCE) ocean surveys in the 1970s and 1990s respectively, allowed estimations of  $I^E$  for these two periods. From their  $I^E$  estimate based on the GEOSECS data ( $289 \cdot 10^{26}$  atoms <sup>14</sup>C), Broecker *et al.* [1985] inferred a global mean piston velocity of  $\langle k \rangle = 21.9 \pm 3.3$  cm/hr. Wanninkhof [1992] used this estimate of  $\langle k \rangle$  to constrain the parameter  $a_q$  for a quadratic  $k(u)$  relationship ( $0.39$  cm/hr/(m/s)<sup>2</sup>), which has since then been widely used as the standard gas exchange parameterization. (Note that we omit the unit cm/hr/(m/s)<sup>2</sup> for  $a_q$  in the remaining text.) However, two more recent estimates of  $I^E$  for GEOSECS [Peacock, 2004] and WOCE [Key *et al.*, 2004] which are based on improved methods to separate the excess <sup>14</sup>C signal from the natural background suggest lower  $I^E$  and consequently smaller  $\langle k \rangle$  and  $a_q$  values. Naegler and Levin [2006] demonstrated with the help of a simple global <sup>14</sup>C cycle model that these values for  $I^E$  from Peacock [2004] and [Key *et al.*, 2004] (corrected as described below) are consistent with our current knowledge of the global excess <sup>14</sup>C budget, in contrast to the older GEOSECS estimate from Broecker *et al.* [1985], which has served as

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**Table 1.** Characteristics of the Five Wind Speed Climatologies Used in This Study: Global Annual Mean Wind Speeds Over the Ice-Free Ocean ( $\langle u \rangle$  and  $\langle u^2 \rangle$ ), Resulting Gas Exchange Parameter  $a_q$  for Different Temporal and Spatial Resolutions, the Product  $a_q \cdot \langle u^2 \rangle$ , and the Global Annual Mean Piston Velocity  $k$  (Calculated According to Equation (2))<sup>a</sup>

Parameter	Unit	NCEP	ECMWF	SSM/I	QSCAT	ERS12	Mean $\pm \sigma$	$\sigma/\text{Mean}$
$\langle u \rangle$	m/s	6.6	7.0	7.8	7.9	7.3	$7.3 \pm 0.6$	0.08
$\langle u^2 \rangle$	(m/s) <sup>2</sup>	46.9	53.1	65.0	66.4	57.1	$57.7 \pm 8.2$	0.14
$a_q$ (monthly winds, $5^\circ \times 4^\circ$ grid)	(cm/hr)/(m/s) <sup>2</sup>	0.40	0.35	0.29	0.29	0.34	$0.33 \pm 0.05$	0.14
$a_q$ (monthly winds, $1^\circ \times 1^\circ$ grid)	(cm/hr)/(m/s) <sup>2</sup>	0.39	0.34	0.28	0.27	0.32	$0.32 \pm 0.05$	0.14
$a_q$ (daily winds, $1^\circ \times 1^\circ$ grid)	(cm/hr)/(m/s) <sup>2</sup>	0.38	0.33	-	-	-	-	-
$a_q \cdot \langle u^2 \rangle$	cm/hr	18.1	17.9	18.2	18.1	18.4	$18.1 \pm 0.2$	0.01
$\langle k \rangle$	cm/hr	16.6	16.2	16.4	17.3	16.9	$16.7 \pm 0.4$	0.02

<sup>a</sup>Note that for the satellite wind speed data sets (SSM/I, QSCAT and ERS1/2), no daily resolution with full global coverage is available.  $\langle u \rangle$ ,  $\langle u^2 \rangle$ ,  $a_q \cdot \langle u^2 \rangle$  and  $\langle k \rangle$  are calculated from monthly winds on a  $1^\circ \times 1^\circ$  grid.

a reference value for the calibration of the  $k(u)$  relationship [Wanninkhof, 1992]. Consequently, these findings require a revision of the excess  $^{14}\text{C}$  constraints on air-sea gas exchange.

[6] Additional attention has to be paid to biases in available wind speed products which significantly affect the piston velocity  $k$  and consequently the fluxes  $F$ . Wanninkhof [1992] and Wanninkhof *et al.* [2002] already noticed the dependency of the  $k(u)$  parameterization on the temporal resolution of the wind fields. Here we additionally focus on biases introduced by the choice of a particular wind speed data set and a particular temporal and spatial resolution and provide a new approach to calculate unbiased values of  $k$ .

## 2. Methods

[7] The net excess  $^{14}\text{C}$  flux across the ocean surface,  $F_{^{14}\text{C}\text{CO}_2}^E$ , depends on the same piston velocity  $k(u)$  and solubility  $L$  as the flux of  $\text{CO}_2$  (equation (1)), but is driven by the effective (i.e., fractionation-corrected) excess  $^{14}\text{CO}_2$  partial pressure difference  $\Delta p^{14}\text{CO}_2^E$  between atmosphere and ocean. Following Wanninkhof [1992], we assume a quadratic  $k(u)$  relationship (equation (2)). Note that our approach is, however, in principle applicable for any  $k(u)$  relationship which depends on a single scaling parameter. (For the sake of simplicity, we omit the variability in space and time ( $\vec{x}, t$ ) from our notation in what follows.)  $\Delta p^{14}\text{CO}_2^E$  is calculated as the difference between the effective total  $^{14}\text{CO}_2$  partial pressure difference  $\Delta p^{14}\text{CO}_2$  and the effective prebomb (i.e., pre-1945)  $^{14}\text{CO}_2$  partial pressure difference  $\Delta p^{14}\text{CO}_2^{\text{pre}}$ :

$$\Delta p^{14}\text{CO}_2^E = \Delta p^{14}\text{CO}_2 - \Delta p^{14}\text{CO}_2^{\text{pre}} \quad \text{with} \quad (3)$$

$$\Delta p^{14}\text{CO}_2 = R_A^{14} \cdot p\text{CO}_2^A \cdot \alpha_{14}^{A\text{O}} - R_O^{14} \cdot p\text{CO}_2^O \cdot \alpha_{14}^{O\text{A}} \quad (4)$$

where  $R_A^{14}$  and  $R_O^{14}$  are the  $^{14}\text{C}/\text{C}$  isotope ratios in the atmosphere and the surface ocean, respectively.  $p\text{CO}_2^A$  and  $p\text{CO}_2^O$  are the atmospheric and oceanic  $\text{CO}_2$  partial pressure histories,  $\alpha_{14}^{A\text{O}}$  ( $=0.9980^2$ ) and  $\alpha_{14}^{O\text{A}}$  ( $=0.9897^2$ ) are the kinetic fractionation factors for the transfer of  $^{14}\text{CO}_2$  from atmosphere to ocean and vice versa.

[8] As the total excess  $^{14}\text{C}$  inventory in the ocean is equal to the (temporally and spatially) integrated flux of excess  $^{14}\text{C}$  into the ocean, the gas exchange parameter  $a_q$ , crucial in the parameterization for any air-sea gas exchange relation-

ship (equation (2)), can be calculated from the observed excess  $^{14}\text{C}$  inventory  $I^E$  in the ocean at a given reference date  $t_1$ :

$$a_q = \frac{I^E(t_1)}{\int_{t_0}^{t_1} \int_{S_{\text{oce}}} u^2 \left(\frac{S_c}{660}\right)^{-0.5} \cdot L \cdot \Delta p^{14}\text{CO}_2^E \, dS \, dt} \quad (5)$$

where  $t_0$  indicates pre-bomb times (pre-1945) and  $S_{\text{oce}}$  is the surface of the ice-free ocean.  $R_A^{14}$  and  $R_O^{14}$  are calculated from observation-based reconstructions of the zonal mean  $\Delta^{14}\text{C}$  history in the atmosphere and the sea surface from Hesshaimer [1997]. The atmospheric  $p\text{CO}_2$  history has been reconstructed using available records of the atmospheric  $\text{CO}_2$  mixing ratio [Etheridge *et al.*, 1998; Keeling and Whorf, 2004; GlobalView (CDIAC, Oak Ridge, Tennessee; anonymous ftp to ftp.cmdl.noaa.gov)]. The global distribution of  $p\text{CO}_2^O$  for 1995 is taken from Takahashi *et al.* [2002]. The relative increase of  $p\text{CO}_2^O$  between 1945 and 1995 has been estimated with the IPSL Ocean General Circulation Model (J. Orr and J.-C. Dutay, personal communication, 2004). To take into account the uncertainties of global wind speed products and biases due to spatial and temporal averaging, we used five different climatological wind speed data sets (Table 1) from satellite observations (ERS1/2 [Bentamy *et al.*, 1998], QSCAT [Lungu, 2001], SSM/I [Boutin and Etcheto, 1996]) or re-analysis products from numerical weather prediction models (ECMWF [Gibson *et al.*, 1997] and NCEP [Kalnay *et al.*, 1996]) and tested different temporal and spatial resolutions of these wind fields.

[9] Our study is based on the new  $I^E$  estimates from Peacock [2004] for GEOSECS ( $241 \cdot 10^{26}$  atoms  $^{14}\text{C} \pm 25\%$ , multitracer correlation method) and from Key *et al.* [2004] for WOCE ( $313 \cdot 10^{26}$  atoms  $^{14}\text{C} \pm 15\%$ ). Neither the Peacock [2004] nor the Key *et al.* [2004] inventory estimates used data with fully representative global coverage. We corrected the original inventory estimates for these missing ocean areas by estimating the relative contribution of the missing areas to  $I^E$ , using the OPA Ocean General Circulation Model [Rodgers *et al.*, 2004]. With this correction applied,  $I^E$  for the mid-1970s from Peacock [2004] increases to  $245 \cdot 10^{26}$  atoms  $^{14}\text{C}$ . Furthermore, the Key *et al.* [2004] study uses North Atlantic samples from the mid-1980s, whereas the rest of the world ocean was sampled in the 1990s (with a mid-point in 1995). To correct for this

temporal bias in the WOCE data for the North Atlantic, we estimated the increase of  $I^E$  in the North Atlantic between 1985 and 1995 again with the OPA OGCM. The two corrections of the *Key et al.* [2004] inventory estimate result in a total  $I^E$  in the mid-1990s of  $355 \cdot 10^{26}$  atoms  $^{14}\text{C}$ . Due to the consistency of these  $I^E$  values with a totally independent  $^{14}\text{C}$  modelling study [*Naegler and Levin*, 2006], we assume that the real uncertainties of  $I^E$  are smaller than reported by *Peacock* [2004] and *Key et al.* [2004], namely on the order of 10% for both inventories.

### 3. Results and Discussion

[10] Table 1 summarizes the results for the gas exchange parameter  $a_q$  calculated for the different temporally and spatially resolved wind fields. Clearly  $a_q$  cannot be unambiguously constrained by  $I^E$  alone, but depends on a number of factors.

[11] First, due to the non-linear  $k(u)$  relationship and the co-variability of  $\Delta p^{14}\text{CO}_2$ , solubility  $L$ , Schmidt-Number  $Sc$  and wind speed  $u$ ,  $a_q$  depends on the temporal and spatial resolution of the study, with higher resolution implying lower values for  $a_q$ . This effect is more pronounced for interannually varying winds (not shown) than for climatological wind fields (as used in Table 1).

[12] Second, and even more importantly,  $a_q$  depends on the wind field used. We found significant differences between the five different wind speed data sets, leading to a significant uncertainty in  $a_q$ . The five wind speed data sets used here show a standard deviation of 14% in the global annual mean squared wind speed over the ice-free ocean ( $\langle u^2 \rangle$ ) (Table 1), which translates into a spread of similar magnitude in  $a_q \pm 0.32 \pm 0.05$ , calculated on a  $1^\circ \times 1^\circ$  grid and for monthly average wind fields.

[13] However, in contrast to  $a_q$ , the product  $a_q \langle u^2 \rangle$  depends only weakly on the wind fields used; it shows a spread of only about 1.0% around the mean for monthly  $1^\circ \times 1^\circ$  fields (Table 1) and a spread of 2% for the  $5^\circ \times 4^\circ$  resolution (not shown). Thus, the dependence of  $a_q$  on the wind speed data set (and the dependence of  $a_q$  on  $I^E$ ) can be reduced greatly by defining a new wind-speed- and inventory-normalized gas exchange parameter  $a_q^N$ , namely

$$a_q^N \equiv \frac{a_q \cdot \langle u^2 \rangle}{I^E} \Leftrightarrow a_q = a_q^N \cdot \frac{I^E}{\langle u^2 \rangle} \quad (6)$$

[14] As for the product  $a_q \cdot \langle u^2 \rangle$ , but in contrast to  $a_q$ , the parameter  $a_q^N$  depends only weakly on the wind speed product and its resolution. Thus  $a_q^N$  allows us to balance biases in the piston velocity  $k$  introduced by biases in the wind fields. Table 2 summarizes our results for  $a_q^N$ .

[15] Equation (6) now allows us to calculate values of  $a_q$  for each wind speed data set whose global annual mean squared wind speed  $\langle u^2 \rangle$  is known. Furthermore,  $I^E$  in equation (6) can be adapted to future improved estimates of this quantity. In this formulation, uncertainties of each individual estimate of  $a_q$  calculated according to equation (6) for a given wind speed data set originate from uncertainties in  $I^E$  of  $\pm 10\%$ , which translate into uncertainties in  $a_q$  of  $\pm 0.03$ , and from uncertainties in  $a_q^N$ , which are estimated as follows:

**Table 2.** New Normalized Gas Exchange Parameter  $a_q^N$  (Defined in Equation (6)) for Different Spatial Resolutions and for Different  $I^E$  Targets<sup>a</sup>

Temporal Resolution	Spatial Resolution	GEOSECS (1975)	WOCE (1995)
Monthly	$5^\circ \times 4^\circ$	$0.0760 \pm 3\%$	$0.0524 \pm 3\%$
Monthly	$1^\circ \times 1^\circ$	$0.0740 \pm 1\%$	$0.0511 \pm 1\%$
Daily	$1^\circ \times 1^\circ$	$0.0733 \pm 1\%$	$0.0506 \pm 1\%$

<sup>a</sup>The values given are averages ( $\pm 1$  standard deviation) over all five (two in the case of daily winds) wind speed data sets. Units are in  $(\text{cm/hr})/10^{26}$   $^{14}\text{C}$  atoms. Note that the values shown here are calculated from climatological wind fields. However,  $a_q^N$  for the corresponding interannually varying wind fields is virtually identical.

[16] The uncertainty of  $a_q^N$  is dominated by the uncertainty of the integrated  $\Delta p^{14}\text{CO}_2^E$ , which again is dominated by the uncertainty of  $p^{14}\text{CO}_2^O$ . As revealed in a comparison of reconstructed sea surface  $\Delta^{14}\text{C}$  with observations, the uncertainty in the reconstruction is less than 30‰ [*Naegler*, 2005], resulting in a 3% uncertainty in  $R_O^{14}$ . The uncertainty of the reconstructed  $p\text{CO}_2^O$  is difficult to assess, but probably not larger than (globally) 10%. This results in an upper limit of the uncertainty of  $a_q^N$  of 15%, resulting in an overall uncertainty of  $a_q$  due to uncertainties in  $I^E$  and  $a_q^N$  of  $\pm 0.06$  for a specific wind speed data set.

[17] Our revised set of estimates for  $a_q$  for monthly mean winds is systematically lower (up to 40%) than the value from *Wanninkhof* [1992] for long-term averaged winds ( $a_q = 0.39$ , averaging period  $\geq 1$  month). This is primarily because different wind speed estimates and a lower  $I^E$  value were employed in our study, but also because of the low spatial and temporal resolution of *Wanninkhof* [1992] as well as the resulting neglect of correlations between  $L$ ,  $Sc$ ,  $u$ , and  $\Delta^{14}\text{pCO}_2$ . For daily winds that are available only from Numerical Weather Prediction models, we obtain  $a_q = 0.38$  (NCEP) and  $a_q = 0.33$  (ECMWF) (Table 1). Our values are both higher than the value given by *Wanninkhof* [1992] for short-term winds ( $a_q = 0.31$ ), although we would expect lower values due to the lower  $I^E$  used in our study. When estimating  $a_q$  for short term winds, *Wanninkhof* [1992] assumed that the spectrum of short-term wind speeds  $u$  is characterized by a Rayleigh distribution. If this is the case, the ratio  $R = \langle u^2 \rangle / \langle u \rangle^2$  has a characteristic constant value of 1.25, which allows one to extrapolate  $a_q$  for short-term wind speeds from estimates of  $a_q$  for long-term averages. However, as already stated by *Wanninkhof et al.* [2002], the assumption of a Rayleigh distribution does not hold over large areas of the oceans. Consequently,  $R$  is generally lower than 1.25 [*Wanninkhof et al.*, 2002], yielding a too low gas exchange parameter for short-term winds ( $a_q = 0.31$  [*Wanninkhof*, 1992]) compared to  $a_q$  for long-term winds (0.39) and also lower values than our estimates of  $a_q$  for daily averaged winds.

[18] From our new estimates of  $a_q$  we calculate global average values for the piston velocity  $k$  of  $16.7 \pm 2.9$  cm/hr. The uncertainty estimate given here comprises uncertainties in the wind fields, in  $\Delta p^{14}\text{CO}_2$  and in  $I^E$ . Mainly due to the lower ocean excess  $^{14}\text{C}$  inventory used, our value is lower than the previous estimates of  $21.9 \pm 3.3$  cm/hr from *Broecker et al.* [1985] and used by *Wanninkhof* [1992].

[19] Our  $k$  values (short-term winds) are generally higher than the field-based  $k(u)$  relationship from *Nightingale et al.*

[2000], which is adequate for field studies on a local scale. This is probably due to the different scales of the studies, but also due to the neglect of chemical enhancement in our study. However, we believe that results from the excess  $^{14}\text{C}$  method and field studies will converge with increasing resolution of global wind fields.

[20] Although our method does not assume a Rayleigh distribution of wind speeds, it implicitly assumes that the same wind speed distribution is valid everywhere over the ocean (i.e.,  $R = \langle u^2 \rangle / \langle u \rangle^2$  is globally constant). Regional deviations from this assumption cause regional biases in  $k$  [Wanninkhof *et al.*, 2002], which increase with decreasing resolution of the wind fields. Our method therefore tends to underestimate  $k$  in high latitudes and overestimate  $k$  in low latitudes. However, for monthly mean winds, these biases probably do not exceed 5% for the zonal average of  $k$ . This was tested using a method similar to that used by Wanninkhof *et al.* [2002].

[21] When applied to ocean  $\text{pCO}_2$  data [Takahashi *et al.*, 2002] and smoothed atmospheric  $\text{CO}_2$  observations (GlobalView, see above), our new numbers yield a net ocean  $\text{CO}_2$  uptake rate of  $1.57 \pm 0.30 \text{ PgC/yr}$  for 1995, lower than previous estimates based on the same method from Takahashi *et al.* [2002] ( $1.64 \text{ PgC/yr}$ , corrected flux estimates), but still consistent within the uncertainties. At first glance, the small difference between these two estimates is surprising, as Takahashi *et al.* [2002] used the high  $a_q = 0.39$  from Wanninkhof [1992] (and NCEP winds) for their calculations. However, NCEP winds have low  $\langle u^2 \rangle$  and therefore require a high  $a_q$  (Table 1). Thus our  $a_q$  value for NCEP winds is, by chance, close to the value from Wanninkhof [1992], resulting in similar values for the net ocean  $\text{CO}_2$  flux in our study and in that by Takahashi *et al.* [2002]. In contrast, our estimate of the gross  $\text{CO}_2$  exchange between the atmosphere and the ocean ( $73 \pm 10 \text{ PgC/yr}$ ) is  $\approx 20\%$  lower than previous estimates [Broecker *et al.*, 1985] of  $88 \text{ PgC/yr}$ .

#### 4. Conclusions

[22] The observed excess  $^{14}\text{C}$  inventory in the ocean ( $I^E$ ) provides important constraints on air-sea gas exchange. However, uncertainties in the global wind fields and the dependence of the “optimal” gas exchange parameterization on the spatial and temporal resolution of the study complicate the simulation of air-sea fluxes. Consequently, in any gas exchange simulation, the gas exchange parameter  $a_q$  has to be carefully chosen depending on the wind speed data set used (and its resolution) in order to calculate an unbiased piston velocity. In our study, we introduce a new wind-speed- and inventory-normalized gas exchange parameter  $a_q^N$ . Once the value of  $a_q^N$  is tabulated for a given spatial and temporal resolution, the gas exchange parameter  $a_q$  can easily be adjusted to any wind speed data set and any estimate of the ocean excess  $^{14}\text{C}$  inventory to allow the calculation of an unbiased global mean piston velocity. As we rely on recent  $I^E$  estimates [Peacock, 2004; Key *et al.*, 2004] which are lower than the values previously used to constrain air-sea gas exchange [Broecker *et al.*, 1985], our study yields significantly lower values (20–40%) for the gas exchange parameter  $a_q$  for long-term averaged winds, the global annual mean piston velocity  $k$  and the gross

atmosphere-ocean  $\text{CO}_2$  exchange than previous studies [Broecker *et al.*, 1985; Wanninkhof, 1992].

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