Tellus
SERIES B
CHEMICAL
AND PHYSICAL
METEOROLOGY
PUBLISHED BY THE INTERNATIONAL METEOROLOGICAL INSTITUTE IN STOCKHOLM

Tellus (2009), 61B, 372–384
Printed in Singapore. All rights reserved

TELLUS

Reconciliation of excess ^{14}C-constrained global CO_2 piston velocity estimates

By TOBIAS NAEGLER*, *Institut für Umweltphysik, INF 229, D-69120 Heidelberg, Germany*

(Manuscript received 12 December 2007; in final form 3 November 2008)

ABSTRACT

Oceanic excess radiocarbon data is widely used as a constraint for air–sea gas exchange. However, recent estimates of the global mean piston velocity $\langle k \rangle$ from Naegler et al., Krakauer et al., Sweeney et al. and Müller et al. differ substantially despite the fact that they all are based on excess radiocarbon data from the GLODAP data base. Here I show that these estimates of $\langle k \rangle$ can be reconciled if first, the changing oceanic radiocarbon inventory due to net uptake of CO_2 is taken into account; second, if realistic reconstructions of sea surface Δ^{14}C are used and third, if $\langle k \rangle$ is consistently reported with *or* without normalization to a Schmidt number of 660. These corrections applied, unnormalized estimates of $\langle k \rangle$ from these studies range between 15.1 and 18.2 cm h^{-1}. However, none of these estimates can be regarded as the only correct value for $\langle k \rangle$. I thus propose to use the 'average' of the corrected values of $\langle k \rangle$ presented here (16.5 ± 3.2 cm h^{-1}) as the best available estimate of the global mean unnormalized piston velocity $\langle k \rangle$, resulting in a gross ocean-to-atmosphere CO_2 flux of 76 ± 15 PgC yr^{-1} for the mid-1990s.

1. Introduction

Human activities have altered the ^{14}C-to-C ratio (expressed as Δ^{14}C) in oceanic dissolved inorganic matter (DIC) and the ocean's radiocarbon inventory since the onset of the industrial revolution in the 18th century. Two major anthropogenic perturbation processes can be distinguished: first, due to fossil fuel combustion and land-use change, mankind released large amounts of CO_2 into the atmosphere. Since the increase of atmospheric CO_2 concentrations, the ocean acts as a sink for anthropogenic CO_2 emissions. Apart from small fractionation effects, the anthropogenic atmosphere-to-ocean CO_2 flux carries the same Δ^{14}C signature as atmospheric CO_2. Consequently, net uptake of (anthropogenic) CO_2 by the ocean increases the oceanic radiocarbon inventory. Note, however, that uptake of CO_2 is expected to have a minor effect on Δ^{14}C of DIC, as atmospheric and sea surface Δ^{14}C differ by only a few percent and the anthropogenic increase in DIC is small compared with the total DIC inventory in the ocean. As an additional effect of the emission of (radiocarbon-free) fossil fuel derived CO_2 into the atmosphere, atmospheric Δ^{14}C started to significantly decrease since the late 19th century (Suess, 1955; Reimer et al., 2004). As a consequence of this so-called Suess effect, Δ^{14}C in the gross atmosphere-to-ocean CO_2 flux (and thus the gross $^{14}CO_2$ flux itself) is decreasing. The Suess effect 'alone' therefore results in decreasing Δ^{14}C in DIC in the upper ocean and a decreasing oceanic radiocarbon inventory. Since the mid-20th century, a second anthropogenic perturbation is superimposed on both the effects of net CO_2 uptake and the Suess effect—atmospheric nuclear bomb tests between 1945 and 1980 released large amounts of radiocarbon into the atmosphere, causing a strong increase in atmospheric Δ^{14}C in the 1950s and 1960s. This 'bomb' radiocarbon has subsequently been taken up by the ocean (and the terrestrial biosphere), perceivable in the strong increase in Δ^{14}C in DIC since pre-bomb times, in particular in the surface ocean, and a corresponding increase in the ocean radiocarbon inventory (Druffel and Linick, 1978; Druffel and Griffin, 1993; Broecker et al., 1985; Key et al., 2004; Peacock, 2004).

Most studies on anthropogenic disturbances of the ocean radiocarbon inventory focused on radiocarbon inventory changes since the onset of atmospheric nuclear weapon tests. These inventory changes are often imprecisely named as 'bomb' radiocarbon, thus neglecting the consequences of both the Suess effect and the net CO_2 uptake. In this paper, I distinguish between 'excess' radiocarbon (labelled with an index E) which denotes changes in the $^{14}CO_2$ flux F^{14}, $^{14}CO_2$ partial pressure $p^{14}CO_2$, Δ^{14}C and ^{14}C inventory I^{14} since the pre-bomb reference state (here, defined by the average state of these quantities in the 1940s i.e. the average between 1940 and 1949):

$$Q^E(t) = Q(t) - Q_{PB}, \tag{1}$$

*Correspondence.
e-mail: tobias.naegler@iup.uni-heidelberg.de
DOI: 10.1111/j.1600-0889.2008.00408.x

where Q represents the quantity studied (I^{14}, F^{14}, $p^{14}CO_2$, $\Delta^{14}C$) and the index PB denotes the pre-bomb reference state. The excess radiocarbon inventory defined in that manner corresponds to the 'bomb' radiocarbon as used in most previous studies. Furthermore, I use the term 'anthropogenic' radiocarbon (index A), which refers to respective changes in the ocean carbon and radiocarbon state since pre-industrial times (i.e. since the 18th century).

Changes in the oceanic radiocarbon state (I^{14} or $\Delta^{14}C$ in DIC) are caused by an excess radiocarbon flux $F^{14,E}$ across the air–sea interface, which itself depends on the intensity of air–sea gas exchange (expressed by the piston velocity k). As a consequence, observations of the oceanic excess radiocarbon inventory $I^{14,E}$ or the excess $\Delta^{14}C^E$, respectively (Broecker et al., 1985,1995; Key et al., 2004; Peacock, 2004), provide important constraints on the piston velocity k (Broecker et al., 1985; Wanninkhof, 1992), which have been re-assessed in detail in several studies in recent years. Using a straight forward approach (similar to eq. (15) below), Naegler et al. (2006) calculate a global mean piston velocity $\langle k \rangle$ of $16.7 \pm 2.9\,\mathrm{cm\,h^{-1}}$ based on ocean excess radiocarbon inventory estimates for the time of the Geochemical Ocean Sections Study (GEOSECS) in the 1970s (Peacock, 2004) and for the time of the World Ocean Circulation Experiment (WOCE) in the 1990s (Key et al., 2004). A key point in their analysis is the reconstruction of a (zonal mean) sea surface $\Delta^{14}C$ history, based on GEOSECS and WOCE sea surface $\Delta^{14}C$ data from Broecker et al. (1995) and Key et al. (2004). Sweeney et al. (2007) improve the method of Rubin and Key (2002) and Key et al. (2004) to separate the excess radiocarbon component from the pre-bomb background $\Delta^{14}C$. They use an inverse approach to estimate the spatio-temporal distribution of $\Delta^{14}C$ in their ocean general circulation model (OGCM), which best matches the combined set of ocean radiocarbon observations in the GLODAP data base (Key et al., 2004). They then employ a similar approach as Naegler et al. (2006): with the help of their reconstructed sea surface $\Delta^{14}C$ time-series and a formulation similar to eq. (15), Sweeney et al. (2007) obtain a value of $\langle k \rangle = 14.6 \pm 4.7\,\mathrm{cm\,h^{-1}}$. The ocean inversion setup of Krakauer et al. (2006) directly estimates the value of $\langle k \rangle$ ($20.0 \pm 3.0\,\mathrm{cm\,h^{-1}}$), which allows for an optimal match between the simulated excess radiocarbon and the observations from the GLODAP data base. Finally, Müller et al. (2008) use their OGCM in a forward mode to optimize the piston velocity to optimally match the GLODAP observations. They obtain an estimate for $\langle k \rangle$ of $15.9 \pm 3.4\,\mathrm{cm\,h^{-1}}$.

Although one might argue that there is no significant discrepancy between these estimates within the uncertainties given, these different results for $\langle k \rangle$ are somewhat surprising, in particular, given the fact that all four studies use the excess radiocarbon data ($\Delta^{14}C^E$ resp. $I^{14,E}$) from the GLODAP data base (Key et al., 2004) as constraints. Systematic biases in the original constraints therefore can be excluded as explanation for the discrepancies between these studies. Consequently, a closer analysis of methodological differences between these studies is worthwhile to reveal possible pitfalls associated with the use of excess radiocarbon constraints in gas exchange studies.

Here, I analyse several possible sources of systematic biases in estimates of $\langle k \rangle$, based on excess radiocarbon observations: first, it is difficult to clearly separate the excess radiocarbon component from pre-bomb anthropogenic changes in the oceanic radiocarbon inventory. Therefore, it is necessary to estimate the pre-bomb anthropogenic radiocarbon perturbance to quantify this possible bias in the reconstructed excess $\Delta^{14}C$ and $I^{14,E}$ and the resulting $\langle k \rangle$ (Section 2.2). Second, Peacock (2004), Key et al. (2004) and Sweeney et al. (2007) do not use the observed DIC concentration when calculating $I^{14,E}$ from the $\Delta^{14}C$ observations (S. Peacock, R. Key, C. Sweeney, personal communication, 2007). They thus do not take into account the increase in DIC due to net uptake of CO_2 since pre-bomb times. Thus, it is required to quantify the effect of net CO_2 uptake (and thus increasing DIC) on the ocean radiocarbon inventory and to calculate an appropriate correction for the ocean excess radiocarbon inventories given by Peacock (2004), Key et al. (2004) and Sweeney et al. (2007), therewith quantifying the consequences for estimates of ⟨k⟩ constrained by $I^{14,E}$. The effect of net CO_2 uptake on the excess ^{14}C inventory is quantified with two alternative approaches presented in Sections 2.2 and 2.3. Third, reconstructions of the sea surface $\Delta^{14}C^{oce}$ (Section 2.4) play a crucial role in the approaches from Wanninkhof (1992), Naegler et al. (2006) and Sweeney et al. (2007). Biases in $\Delta^{14}C^{oce}$ directly affect estimates of $\langle k \rangle$, as also shown in Section 2.4. Furthermore, different definitions of the global average—for ice free ocean regions only or for the entire ocean surface—result in slightly different estimates for $\langle k \rangle$ (Section 2.6). And finally, estimates of the global mean piston velocity in Krakauer et al. (2006), Sweeney et al. (2007) and Müller et al. (2008) are normalized to a Schmidt number of 660 (Section 2.7), whereas estimates from Naegler et al. (2006) are not normalized to any Schmidt number. These different normalizations significantly hamper comparability of the different estimates of k.

2. Methods

2.1. Some definitions

According to Stuiver and Polach (1977), the $\Delta^{14}C$ signature of a sample is defined as

$$\Delta^{14}C_S = \frac{A_S^{14} \times \left(1 - 2(0.025 + \delta^{13}C_S)\right)}{A_R^{14}} - 1 \tag{2}$$

$$= \frac{A_S^{14} \times f_N^{13}}{A_R^{14}} - 1, \tag{3}$$

where A_R^{14} denotes 95% of the radiocarbon OxA I standard activity (0.95×0.238 Bq gC^{-1}). A_S^{14} and δ^{13} C_S are the measured

^{14}C activity (in Bq gC^{-1}) and δ^{13}C signature, respectively, of the sample. $f_N^{13} = (1 - 2 \times (0.025 + \delta^{13}C_S))$ is the δ^{13}C normalization factor. Note that δ^{13}C and Δ^{14}C throughout the text are not meant to be given in ‰, but as a small number e.g. 17‰ = 0.017.)

The sample activity A_S^{14} is related to the dimensionless ^{14}C-to-C atom ratio R_S^{14} in the sample by

$$A_S^{14} = \frac{\lambda \times N_A}{m_C} \times R_S^{14}. \tag{4}$$

Here, m_C is the molar mass of carbon (12.011g mol^{-1}), λ the radiocarbon decay constant (3.8332×10^{-12} s^{-1}) and N_A the Avogadro number (6.02×10^{23} mol^{-1}). We thus obtain from eq. (3):

$$\Delta^{14}C_S = \frac{\lambda \times N_A}{m_C \times A_R^{14}} \times f_N^{13} \times R_S^{14} - 1 \tag{5}$$

$$\leftrightarrow$$

$$R_S^{14} = \frac{m_C \times A_R^{14}}{\lambda \times N_A \times f_N^{13}} \times (\Delta^{14}C_S + 1) \tag{6}$$

$$= \frac{f}{f_N^{13}} \times (\Delta^{14}C_S + 1), \tag{7}$$

with $f = (m_c \times A_R^{14})/(\lambda \times N_A) = 1.176 \times 10^{-12}$ (dimensionless). For δ^{13}C values typically found in DIC ($0.0015 = 1.5$‰), f_N^{13} is 0.947.

Equation (7) now allows to calculate the amount of radiocarbon (I^{14}, in mol ^{14}C) in a sample from the amount of carbon in the sample (I^C, in mol C) and the sample's isotopic signatures $\delta^{13}C_S$ and $\Delta^{14}C_S$, as it holds that

$$I^{14} = R_S^{14} \times I^C \tag{8}$$

2.2. *Components of the oceanic ^{14}C inventory*

A rough estimate of the oceanic radiocarbon inventory I^{14} and its anthropogenic perturbation due to changing atmospheric Δ^{14}C and the net uptake of (anthropogenic) CO_2 by the ocean can be obtained from available oceanographic data as follows: first, the total radiocarbon inventory I^{14} (in mol) can be calculated from the total amount of dissolved inorganic carbon in the ocean (I^C, in mol) and the average Δ^{14}C signature in DIC (see eqs. (7) and (8)).

$$I^{14} = f \times (\Delta^{14}C + 1) \times I^C. \tag{9}$$

Note that—just for clarity—I neglect fractionation at the air–sea interface as well as the δ^{13}C normalization f_N^{13} in Δ^{14}C and radioactive decay of ^{14}C throughout the text. However, these corrections have been taken into account in all calculations.

In a second step, I separate I^C and Δ^{14}C into a pre-industrial (natural) component (P) and the anthropogenic perturbation (A):

$$I^C = I_P^C + I_A^C, \tag{10}$$

$$\Delta^{14}C = \Delta^{14}C_P + \Delta^{14}C_A. \tag{11}$$

If the small product $I_A^C \times \Delta^{14}C_A$ is neglected, it follows from eqs. (9) to (11) that

$$I^{14} = \underbrace{f \times (\Delta^{14}C_P + 1) \times I_P^C}_{I^{14,P}} + \underbrace{f \times \Delta^{14}C_A \times I_P^C}_{I_\Delta^{14,A}} + \underbrace{f \times (\Delta^{14}C_P + 1) \times I_A^C}_{I_{CO_2}^{14,A}} \tag{12}$$

Here, the first term (labelled $I^{14,P}$) refers to the oceanic pre-industrial radiocarbon inventory. The second term (labelled $I_\Delta^{14,A}$) is the anthropogenic oceanic radiocarbon inventory change caused by changing atmospheric Δ^{14}C (Suess effect and bomb radiocarbon; unfortunately, the effects of both processes cannot easily be separated). The third component ($I_{CO_2}^{14,A}$) describes the ocean radiocarbon inventory change due to net uptake of CO_2 by the ocean. As mentioned above, the excess radiocarbon in the ocean is defined as the difference between the ocean radiocarbon inventory at time t (>1940 s) and the average inventory in the 1940s

$$I^{14,E} = I^{14}(t) - I^{14}(1940s) \tag{13}$$

$$= I_\Delta^{14,E} + I_{CO_2}^{14,E}. \tag{14}$$

If $I_{CO_2}^{14,A}$ and $I_\Delta^{14,A}$ can be estimated for both the pre-bomb period (1940s) as well as the time of the WOCE ocean survey (mid-1990s), the excess components $I_{CO_2}^{14,E}$ and $I_\Delta^{14,E}$ can be calculated from the difference between the respective $I^{14,A}$ for the mid-1990s and the 1940s.

To evaluate the components of I^{14} in eq. (12), I used values of I_A^C, I_P^C, $\Delta^{14}C_A$ and $\Delta^{14}C_P$ as summarized in Table 1A: I_P^C is taken from Prentice et al. (2001), $\Delta^{14}C_P$ and $\Delta^{14}C_A$ for 1995 from Key et al. (2004). The I_A^C value for 1995 has been published by Sabine et al. (2004). I_A^C for 1950 is estimated from the I_A^C(1995) value and the assumption that 46% of the total anthropogenic CO_2 uptake until 1995 occurred before 1945. This assumption is consistent with results from a series of ocean models (Enting et al., 1994). The global average $\Delta^{14}C_A$(1940s) value (-1.0 ± 1.0‰) is a 'guesstimate' based on the fact that the sea surface Δ^{14}C decrease between the onset of the atmospheric Suess effect (late 19th century) and the 1940s as observed in corals did not exceed 8‰ (Druffel and Linick, 1978; Druffel and Griffin, 1993) and the assumption that the Suess effect in DIC decreased linearly to an invasion depth of 1000 m

Table 1. (A) Estimates of the natural (pre-industrial, index P) and anthropogenic (index *A*) global DIC inventory (I^C, in PgC) and global average Δ^{14}C signature in DIC (in ‰). (B) Estimates of the natural and anthropogenic components of the ocean radiocarbon inventory in the 1940s ('pre-bomb') and in 1995 (WOCE ocean survey) and the change between the 1940s and 1995 ('excess')

Quantity	⟨1940s⟩ ('pre-bomb')	1995 (WOCE)	1995 − ⟨1940s⟩ ('excess')
(A)			
I^C_A	38 000 ± 1000	38 000 ± 1000	0
$\Delta^{14}C_P$	−152 ± 10	−152 ± 10	0
I^C_A	53 ± 10	118 ± 19	65 ± 21
$\Delta^{14}C_A$	−1.0 ± 1.0	17 ± 5	17.5 ± 5
(B)			
$I^{14,P}$	19 000 ± 1200	19 000 ± 1200	0
$I^{14,A}_\Delta$	−19 ± 19	327 ± 97	346 ± 98
$I^{14,A}_{CO_2}$	23 ± 4	51 ± 8	27 ± 9
Total $I^{14,A}$	4 ± 20	378 ± 97	374 ± 98

Note: The numbers given here are based on eq. (12) and the I^C and Δ^{14}C values given above in part (A). For the definition of $I^{14,P}$, $I^{14,A}_{CO_2}$ and $I^{14,A}_\Delta$ see Section 2.2. Units are in 10^{26} atoms of ^{14}C. Note that cross-correlations between Δ^{14}C and I^C add an uncertainty of less then 10%. Note further that by definition I^C_P, $\Delta^{14}C_P$ and $I^{14,P}$ are constant in time.

on the global average. This 'guesstimate' is corroborated by results from a box-diffusion model (Oeschger et al., 1975) which give a global average $\Delta^{14}C_A$(1940s) value of −0.8‰ in the entire ocean. However, the uncertainty of $\Delta^{14}C_A$(1940s) is set to 100% in my calculation. Uncertainties of the global average $\Delta^{14}C_P$ and $\Delta^{14}C_A$ are based on the uncertainties given in Key et al. (2004). The uncertainty estimate for I^C_A is chosen to be on the same order of magnitude as the difference between the I^C_A value given by Prentice et al. (2001) and I^C_A calculated from the GLODAP data set (Key et al., 2004).

2.3. *Effect of the net CO_2 uptake*

Alternatively to the approach presented in the previous section, the contribution of $I^{14,E}_{CO_2}$ to the oceanic excess radiocarbon inventory can be estimated as follows: the excess radiocarbon inventory $I^{14,E}$ is the temporally (since the 1940s) and spatially integrated excess radiocarbon flux $F^{14,E}$, which in turn depends on the piston velocity k, the solubility L, and the excess $^{14}CO_2$ partial pressure difference $\Delta p^{14}CO_2^E$ between atmosphere and ocean surface. Note that most of the quantities used in the following equations (in particular oceanic and atmospheric pCO_2 and R^{14}) depend on the location **x** and on time t. However, for the sake of simplicity, the (**x**,t) dependence is omitted in the equations. The brackets ⟨⟩ denote the global annual mean value of the quantity in question.

$$I^{14,E} = \int F^{14,E}\,\mathrm{d}S\,\mathrm{d}t = \int k \times L \times \Delta p^{14}CO_2^E\,\mathrm{d}S\,\mathrm{d}t \tag{15}$$

$$\approx \langle k\rangle \times \langle L\rangle \times \int \Delta p^{14}CO_2^E\,\mathrm{d}S\,\mathrm{d}t, \tag{16}$$

with

$$\Delta p^{14}CO_2 = pCO_2^{\mathrm{atm}} \cdot R^{14}_{\mathrm{atm}} - pCO_2^{\mathrm{oce}} \cdot R^{14}_{\mathrm{oce}} \tag{17}$$

$$\Delta p^{14}CO_2^E = \Delta p^{14}CO_2 - \langle \Delta p^{14}CO_2\rangle_{1940s}. \tag{18}$$

Here, pCO_2^{oce} and pCO_2^{atm} denote the CO_2 partial pressure in the sea surface and atmosphere, respectively. R^{14}_{oce} and R^{14}_{atm} are the ^{14}C-to-C ratios in sea surface DIC and atmospheric CO_2. As it generally holds that $pCO_2^A \neq pCO_2^O$, eqs. (16)–(18) implicitly include the effect of net uptake of CO_2 by the ocean on the oceanic excess radiocarbon inventory.

Note that in this approach, spatial and temporal cross-correlations between k, L, and $\Delta p^{14}CO_2$ are neglected, as they only provide second-order effects of the corrections for ⟨k⟩ discussed. This can be seen as follows: the product ⟨k⟩ × ⟨L⟩ × ⟨$\Delta p^{14}CO_2$⟩ is of the order of 10% smaller than the (spatially integrated) product of the full fields, as can be tested with the available k, L, and $\Delta p^{14}CO_2$ fields. Thus, the *corrections* for ⟨k⟩ due to net CO_2 uptake estimated here also will be biased by approx. 10%. However, as these corrections themselves are of the order of 10% (Section 3), the resulting absolute error of the corrected ⟨k⟩ due to negligence of cross-correlations will be of the order of 1% and thus negligible.

The excess radiocarbon component driven by changes in atmospheric Δ^{14}C *alone*, $I^{14,E}_\Delta$, can be calculated by setting $pCO_2^{\mathrm{oce}} = pCO_2^{\mathrm{atm}}$ in eq. (17). Equations (16)–(18) thus become

$$I^{14,E}_\Delta \approx \langle k\rangle \times \langle L\rangle \times \int \Delta p^{14}CO_2^{E,NU}\,\mathrm{d}S\,\mathrm{d}t \tag{19}$$

with

$$\Delta p^{14}CO_2^{NU} = pCO_2^{\mathrm{atm}} \times \left(R^{14}_{\mathrm{atm}} - R^{14}_{\mathrm{oce}}\right) \tag{20}$$

$$\Delta p^{14}CO_2^{E,NU} = \Delta p^{14}CO_2^{NU} - \left\langle \Delta p^{14}CO_2^{NU}\right\rangle_{1940s}. \tag{21}$$

Here the label 'NU' stands for 'no CO_2 uptake'. From eqs. (14), (16) and (19), it further follows that

$$\frac{I^{14,E}_{CO_2}}{I^{14,E}_\Delta} = \frac{\int \Delta p^{14}CO_2^E\,\mathrm{d}S\,\mathrm{d}t}{\int \Delta p^{14}CO_2^{NU,E}\,\mathrm{d}S\,\mathrm{d}t} - 1. \tag{22}$$

The integrals in eq. (22) now can be evaluated using the reconstructed pCO_2^{atm}, pCO_2^{oce}, R^{14}_{atm} and R^{14}_{oce} fields from Naegler et al. (2006). Equation (22) thus allows to estimate the contribution of the excess radiocarbon inventory component due to net CO_2 uptake, $I^{14,E}_{CO_2}$, relative to the component due to changing atmospheric Δ^{14}C, $I^{14,E}_\Delta$. Note that this approach does not require

any knowledge of the piston velocity k and thus circumvents problems stemming from the uncertainty in k.

2.4. Atmosphere–sea surface excess $\Delta^{14}C$ gradient

If we assume that the excess $p^{14}CO_2$ gradient across the air–sea interface is proportional to the excess $\Delta^{14}C$ gradient between atmospheric CO_2 and sea surface DIC, that is,

$$\Delta p^{14}CO_2^E \propto \Delta(\Delta^{14}C^E), \tag{23}$$

it follows from eqs. (1) and (16) that

$$\langle k \rangle \propto \frac{1}{\int \Delta(\Delta^{14}C^E)\,\mathrm{d}S\,\mathrm{d}t} \tag{24}$$

$$\propto \frac{1}{\int \left[\Delta(\Delta^{14}C) - \Delta(\Delta^{14}C)_{PB}\right]\,\mathrm{d}S\,\mathrm{d}t}. \tag{25}$$

As $\Delta(\Delta^{14}C) = \Delta^{14}C_{atm} - \Delta^{14}C_{oce}$, it follows that with

$$\langle k \rangle \propto \frac{1}{\int \left[\Delta^{14}C^E_{atm} - \Delta^{14}C^E_{oce}\right]\,\mathrm{d}S\,\mathrm{d}t}. \tag{26}$$

$\langle k \rangle$ depends on the reconstruction of sea surface $\Delta^{14}C_{oce}$. Although eq. (23) implicitly assumes that $pCO_2^{atm} = pCO_2^{oce} =$ const. (which is not true), the evaluation of the integrals in eq. (25) resp. eq. (26) for different reconstructions of sea surface $\Delta^{14}C$ allows a first-order estimate of the resulting differences for $\langle k \rangle$.

The consequences of different reconstructions of sea surface $\Delta^{14}C$ during the bomb-era in Naegler et al. (2006) and Sweeney et al. (2007) have been tested with the original sea surface $\Delta^{14}C$ reconstructions from these two publications.

2.5. Estimate of the global mean sea surface $\Delta^{14}C$

The global mean sea surface $\Delta^{14}C$ for the mid-1990s of 62‰ has been calculated from the gridded sea surface $\Delta^{14}C$ data from the GLODAP database (Key et al., 2004). For the time of the GEOSECS survey (1972–1978), however, no gridded sea surface $\Delta^{14}C$ is available, but only the $\Delta^{14}C$ data at the individual GEOSECS stations (Broecker et al., 1995). To estimate the global mean sea surface $\Delta^{14}C$ for the mid-1970s from the GEOSECS data, I proceeded as follows: first, I binned all available GEOSECS sea surface $\Delta^{14}C$ data in each ocean basin (Atlantic, Pacific and Indian Oceans) into 10° latitudinal bins and calculated the (spatially unweighted) average of all $\Delta^{14}C$ values for each bin. I then assumed that each 10° average in each ocean basin well represents the actual average sea surface $\Delta^{14}C$ in that particular ocean region. Finally, I calculated an area-weighted global average of these zonal averages. The resulting global average sea surface $\Delta^{14}C$ for the mid-1970s (GEOSECS) is 98‰. The uncertainty of this method is discussed in Section 4.3.

2.6. Sea ice coverage

As already noted by Sweeney et al. (2007), consideration or negligence of the sea ice cover of ocean areas significantly affects the resulting spatial integrals and spatial averages: for example, the average transfer velocity *over the ice-free ocean* (as calculated in Krakauer et al., 2006; Naegler et al., 2006; Sweeney et al., 2007) is approximately 3% higher than the average transfer velocity over the entire ocean surface (neglecting ice coverage), which is presented, for example, by Müller et al. (2008). In the present study, all globally averaged quantities $\langle Q \rangle$ are defined for the ice-free ocean only, that is, it holds that

$$\langle Q \rangle = \frac{\int_S (1 - f_{ice}(\vec{x})) \cdot Q(\vec{x})\,\mathrm{d}S}{\int_S (1 - f_{ice}(\vec{x}))\,\mathrm{d}S}, \tag{27}$$

where f_{ice} is the monthly mean climatological fraction of ocean area covered by sea-ice from (Orr et al. 2000, based on Walsh, 1978 and Zwally et al., 1983). Annual means are always calculated by averaging over 12-monthly mean values.

2.7. Schmidt number normalization

The piston velocity k is often parametrized in dependence on wind speed u and the (dimensionless) Schmidt number Sc (see for example Wanninkhof, 1992):

$$k = a_q \times u^2 \times \left(\frac{Sc}{660}\right)^{-0.5}. \tag{28}$$

As the Schmidt number Sc depends on the gas in question, also k is gas specific. To allow for a scaling of gas transfer velocities for different gases, k is often normalized to a Schmidt number of 660:

$$k_{660} = k \times \left(\frac{Sc}{660}\right)^{0.5} = a_q \times u^2. \tag{29}$$

An estimate of the average $\langle k_{660} \rangle$-to-$\langle k \rangle$ ratio allows for the conversion of $\langle k_{660} \rangle$ to $\langle k \rangle$ and vice versa. For this purpose, the Schmidt number for sea water is calculated according to the formulation of Wanninkhof (1992), using the sea surface temperature climatology from Locarnini et al. (2006). $\langle k \rangle$ and $\langle k_{660} \rangle$ are calculated according to eqs. (28) and (29) using climatologies of wind fields from the NCEP and ECMWF re-analyses (Kalney et al., 1996; Gibson et al., 1997). Additionally, I used the piston velocity fields as used in the OCMIP-2 study (Orr et al., 2000). The resulting average $\langle k_{660} \rangle$-to-$\langle k \rangle$ ratio is 1.10 ± 0.10, which was used to normalize $\langle k \rangle$ respectively (resp.) denormalise $\langle k_{660} \rangle$, for example in Table 2.

3. Results

Table 1B summarizes the estimates of the pre-industrial radiocarbon inventory in the ocean and the different components of the anthropogenic perturbation. It should be emphasized that these numbers here merely illustrate the order of magnitude of

Table 2. Originally published and, if necessary, corrected estimates of the global mean unnormalized resp. normalized piston velocities $\langle k \rangle$ and $\langle k_{660} \rangle$ (in cm h^{-1}).

publication	ocean excess ^{14}C	original publication		corrected (this work)		
	constraints	$\langle k \rangle$	$\langle k_{660} \rangle$	$\langle k \rangle$	$\langle k_{660} \rangle$	corrections
Wanninkhof (1992)	B85, B86	21.9 ± 3.3	(24.1 ± 3.6)	17.5 ± 3.3	19.2 ± 3.6	
Naegler et al. (2006)	P04, K04	16.7 ± 2.9	(18.4 ± 3.1)	16.9 ± 2.9	18.5 ± 3.1	P, C
Krakauer et al. (2006)	K04	(18.1 ± 2.7)	20.0 ± 3.0	18.2 ± 2.7	20.0 ± 3.0	no correction
Sweeney et al. (2007)	K04, S07	(13.3 ± 4.3)	14.6 ± 4.7	15.1 ± 4.3	16.6 ± 4.7	Δ, C
Müller et al. (2008)	B95, P04, K04	(15.6 ± 3.0)	17.2 ± 3.3	16.1 ± 3.0	17.7 ± 3.3	I
average		$15.9 \pm 3.2 \pm 2.1$	$17.5 \pm 3.5 \pm 2.3$	$16.5 \pm 3.2 \pm 1.3$	$18.2 \pm 3.6 \pm 1.4$	

Note: Values in brackets in the 'original publication' columns are calculated from the assumption that $\langle k_{660} \rangle = 1.1 \cdot \langle k \rangle$ (see text). Units are cm h^{-1}. Note that the uncertainty estimates of the corrected $\langle k \rangle$ resp. $\langle k_{660} \rangle$ are chosen to be identical with the original estimates. The 'average' row takes into account only the studies from Naegler et al. (2006), Krakauer et al. (2006), Sweeney et al. (2007) and Müller et al. (2008). The first uncertainty estimate in the 'average' row is the average uncertainty of $\langle k \rangle$ (resp. $\langle k_{660} \rangle$) of these four studies, whereas the second uncertainty estimate is the standard deviation of all $\langle k \rangle$ (resp. $\langle k_{660} \rangle$) estimates in each column. References: B85: Broecker et al. (1985), B86: Broecker et al. (1986), B95: Broecker et al. (1995), P04: Peacock (2004), K04: Key et al. (2004), S07: Sweeney et al. (2007). Corrections: P: pCO_2 correction, C: net CO_2 uptake, Δ: reconstruction of sea surface Δ^{14}C, I: sea ice cover.

the different components. However, an update of the excess ^{14}C inventory estimates from Peacock (2004) and Key et al. (2004) corrected for the uptake of anthropogenic CO_2 is presented below in Section 4.1.

The global natural radiocarbon inventory I^{14} is estimated to be $(19\,000 \pm 1200) \times 10^{26}$ atoms of ^{14}C. Before the onset of strong atmospheric nuclear bomb tests and the subsequent rise of atmospheric Δ^{14}C in the 1950s, the ocean had lost up to $(19 \pm 19) \times 10^{26}$ atoms of ^{14}C due to the decrease of atmospheric Δ^{14}C (Suess effect). However, at the same time, the ocean has gained $\approx (23 \pm 5) \times 10^{26}$ atoms ^{14}C due to the net uptake of (anthropogenic) CO_2. Thus in the 1940s, the anthropogenic radiocarbon inventory in the ocean was approx. $(4 \pm 20) \times 10^{26}$ atoms of ^{14}C.

In the mid-1990s (at the time of the WOCE ocean survey), the ocean had gained $(327 \pm 96) \times 10^{26}$ atoms ^{14}C due to changing atmospheric Δ^{14}C—mainly caused by atmospheric nuclear weapon testing and the subsequent increase of atmospheric Δ^{14}C. The anthropogenic radiocarbon inventory due to net CO_2 uptake up to the 1990s was of the order of $(50 \pm 10) \times 10^{26}$ atoms of ^{14}C. So the inventory change between 1950 and the mid-1990s—the 'excess' radiocarbon inventory according to the definition above—is estimated to $(346 \pm 98) \times 10^{26}$ atoms ^{14}C due to the increase in atmospheric Δ^{14}C and $(27 \pm 9) \times 10^{26}$ atoms of ^{14}C due to net CO_2 uptake. Thus, approx. 7% ± 3% of the total ocean radiocarbon inventory change between pre-bomb times and the mid-1990s has to be attributed to the net uptake of CO_2.

This finding is corroborated by the alternative approach (Section 2.3 and eq. (22)), presented in Fig. 1a, which shows $\Delta p^{14}CO_2$ and $\Delta p^{14}CO_2^{NU}$ according to eqs. (17) and (20), respectively; $\Delta p^{14}CO_2$ (which includes oceanic CO_2 uptake) always exceeds $\Delta p^{14}CO_2^{NU}$ (which assumes that $pCO_2^{atm} = pCO_2^{oce}$). The same is true for the 'excess' $^{14}CO_2$ partial pressure differences (i.e. $\Delta p^{14}CO_2^{E} > \Delta p^{14}CO_2^{E,NU}$, Fig. 1b) and the integrated excess partial pressure differences (Fig. 1c). Figure 1d finally illustrates the ratio $I_{CO_2}^{14,E}/I_{\Delta}^{14,E}$ (eq. (22)): in the mid-1970s, the excess ^{14}C inventory component due to net CO_2 uptake $I_{CO_2}^{14,E}$ made up approx. 3% of the excess radiocarbon inventory component ($I_{\Delta}^{14,E}$) driven by changing atmospheric Δ^{14}C. However, in the mid-1990s, this fraction has increased to 8%, in good agreement with the estimate above (7% ± 3%, see Section 2.2 and Table 1).

Figures 2a and b show the reconstructed time-series of the global mean sea surface Δ^{14}C from Naegler et al. (2006) and Sweeney et al. (2007) and the resulting excess Δ^{14}C gradient between atmosphere and sea surface. Estimates of global average sea surface Δ^{14}C and—as a consequence— the excess $\Delta^{14}C^{E}$ gradient between atmosphere and sea surface differ by up to 25‰ between Naegler et al. (2006) and Sweeney et al. (2007), in particular in the 1970s. Pre-bomb sea surface Δ^{14}C, as well as sea surface Δ^{14}C for the 1990s, however, agree well. Figure 2c illustrates that the temporally integrated excess Δ^{14}C through the mid-1990s for Sweeney et al. (2007) is approximately 5% larger than in the case of Naegler et al. (2006).

The effects of the Schmidt number normalization are shown in Table 2, which gives an overview over originally published and corrected estimates of $\langle k \rangle$ resp. $\langle k_{660} \rangle$. To facilitate the comparison, all published and corrected values are presented as both $\langle k \rangle$ *and* $\langle k_{660} \rangle$, with $\langle k_{660} \rangle = 1.10 \times \langle k \rangle$ (see Section 2.7).

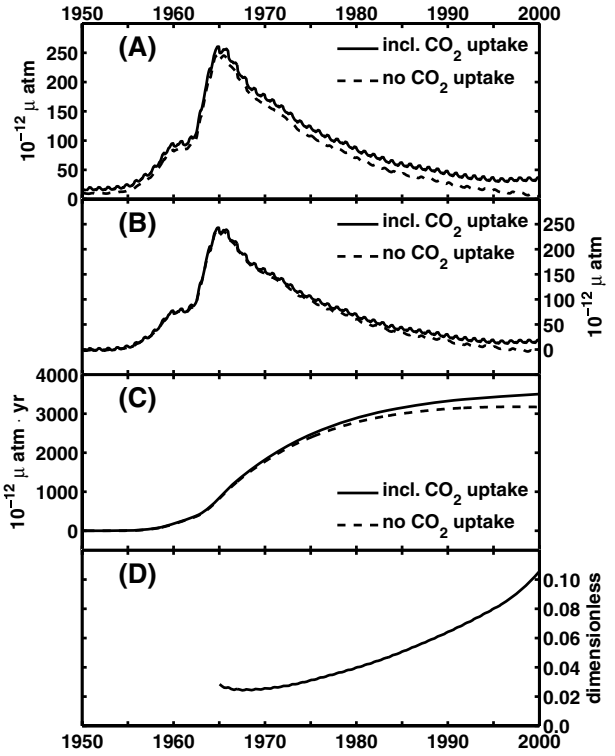

Fig. 1. (a) Global average atmosphere—sea surface $\Delta p^{14}CO_2$. Solid line: $\Delta p^{14}CO_2^U$ (eq. (17)) including net uptake of CO_2. Dashed line: $\Delta p^{14}CO_2^{NU}$ (eq. (20)), neglecting net uptake of CO_2. (b) As in panel (a), but *excess* $\Delta p^{14}CO_2$ (eqs. (18) and (21)). (c) Temporally integrated excess $\Delta p^{14}CO_2$ from Panel (b). (d) $I^{14,A}_{CO_2}/I^{14,A}_{\Delta}$ as in eq. (22).

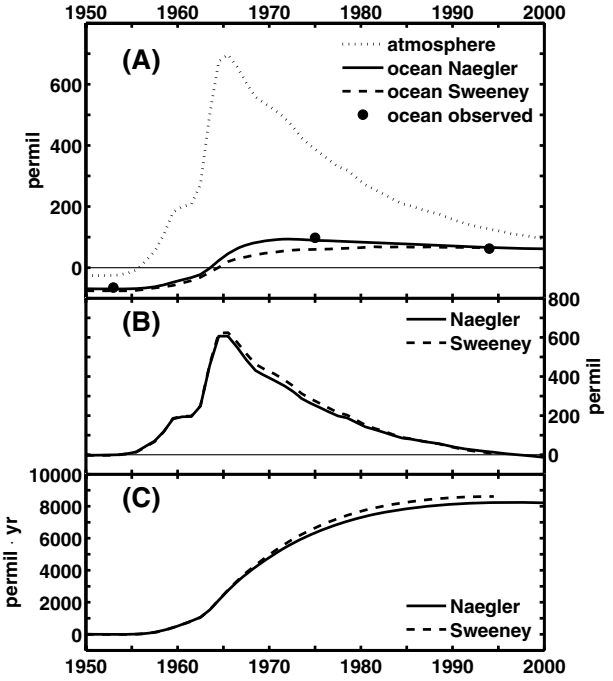

Fig. 2. (a) Global average observed atmospheric $\Delta^{14}C$ (dotted line) and reconstructions of global average sea surface $\Delta^{14}C$ from Naegler et al. (2006) (solid line, based on Hesshaimer, 1997; Naegler, 2005) and Sweeney et al. (2007) (dashed line). Observed global mean sea surface $\Delta^{14}C$ (filled black circles) for 1953 (−65‰) resp. 1994 (62‰) are from the gridded natural resp. total $\Delta^{14}C$ map from the GLODAP data base (Key et al., 2004). The global average sea surface $\Delta^{14}C$ for 1975 (98‰) is calculated from the single surface $\Delta^{14}C$ measurements during the GEOSECS survey (also from the GLODAP data base, original data from Stuiver and Östlund, 1980; Östlund and Stuiver, 1980; Stuiver and Östlund, 1983 and Broecker et al., 1985). (b) Resulting excess $\Delta^{14}C$ gradient between atmosphere and sea surface for Naegler et al. (2006) and Sweeney et al. (2007). (c) Temporally integrated excess $\Delta^{14}C$ gradient for Naegler et al. (2006) and Sweeney et al. (2007).

4. Discussion

4.1. *Effect of increasing DIC on observation-based estimates of* $I^{14,E}$ *and* $\Delta^{14}C^E$

The Key et al. (2004, based on the method of Rubin and Key, 2002) as well as the Peacock (2004) and the Sweeney et al. (2007) studies estimate the ocean excess $\Delta^{14}C$ and the ocean excess ^{14}C inventory $I^{14,E}$ in three (resp. four) steps: first, correlations are found between the observed $\Delta^{14}C$ and oceanographic tracers in water masses assumed *not* to be contaminated by *bomb* radiocarbon. In a second step, these radiocarbon tracer relationships from uncontaminated water masses are assumed to hold also in the upper ocean where the uptake of bomb radiocarbon already led to an increase in $\Delta^{14}C$. This assumption allows to reconstruct the *natural* $\Delta^{14}C$ in water masses contaminated by bomb radiocarbon. Third, the excess $\Delta^{14}C$ is calculated as the difference between the actually observed $\Delta^{14}C$ and the reconstructed natural $\Delta^{14}C$ background. Finally, the excess radiocarbon inventory $I^{14,E}$ is calculated from the reconstructed excess $\Delta^{14}C$ and the observed DIC concentration. In all previous studies, DIC concentrations are assumed to be constant in time ($I^C_A = 0$ in eq. (12)). The estimates of the oceanic excess radiocarbon inventory from Peacock (2004), Key et al. (2004) and Sweeney et al. (2007) therefore comprise of only the component $I^{14,E}_{\Delta}$ driven by changing atmospheric $\Delta^{14}C$, but not the component $I^{14,E}_{CO_2}$ (see eq. (12)).

As illustrated in Fig. 1 and Table 1B, neglecting increasing DIC concentrations as in Key et al. (2004), Peacock (2004) and Sweeney et al. (2007) results in an underestimation of the oceanic excess radiocarbon inventory at the time of GEOSECS (mid-1970s) of approx. 3% and at the time of WOCE (mid-1990s) of approx. 8%. Consequently, these $I^{14,E}$ estimates should be corrected upwards by the respective amount. For $I^{14,E}$ published by Peacock (2004) and Key et al. (2004), these corrections result in an excess inventory estimate for the mid-1970s of 252×10^{26} atoms of ^{14}C (including the corrections for missing ocean areas proposed by Naegler et al., 2006); for the mid-1990s, the corrected excess

radiocarbon inventory is 383×10^{26} atoms of ^{14}C (again including the Naegler et al., 2006 corrections). The Sweeney et al. (2007) estimate of $I^{14,E}$ (343×10^{26} atoms of ^{14}C) for the 1990s has to be corrected to 370×10^{26} atoms of ^{14}C. The uncertainties of these estimates are on the order of 10% (Naegler et al., 2006). In contrast to the estimates of $I^{14,E}$, no corrections due to increasing DIC have to be applied to the reconstructed excess Δ^{14}C fields, as the Δ^{14}C signature of DIC depends only weakly on the net CO_2 exchange.

4.2. Natural versus pre-bomb state of ocean ^{14}C

The methods of Rubin and Key (2002), Key et al. (2004) and Peacock (2004) clearly define 'excess' radiocarbon with respect to a point in time *before* any bomb radiocarbon entered the ocean, that is *before* the atmospheric Δ^{14}C significantly increased over the pre-bomb value. However, Δ^{14}C in DIC has not only been affected by the uptake of bomb radiocarbon from the mid-1950s on, but Δ^{14}C started to *decrease* due to the Suess effect since the late 19$^{\text{th}}$ century. Therefore, it is necessary to discuss how far the ocean Suess effect is taken into account by the approaches from Rubin and Key (2002), Key et al. (2004) and Peacock (2004) and then to estimate the bias introduced by a particular 'reference year', that is, the year for which the 'natural' radiocarbon distribution is assumed to be well represented by the reconstructed natural distribution from Peacock (2004) and Key et al. (2004).

Peacock (2004) assumed that the bomb ^{14}C signal penetrated into the ocean up to a similar depth as CFC-11. She then used simulated CFC-11 concentrations to distinguish between water masses contaminated with bomb ^{14}C and bomb ^{14}C free water masses. In her study, the penetration depth of the bomb signal ranges between approx. 400 and 1600 m. Rubin and Key (2002) defined their uncontaminated water masses by depth (>600 m) and tritium concentration (<0.1 TU). Tests with a one-dimensional box diffusion ocean model (Oeschger et al., 1975) forced with the observed atmospheric Δ^{14}C and CO_2 concentration show an average Suess effect in 1954 (change in Δ^{14}C with respect to average Δ^{14}C 1850–1890) of less than 0.2‰ below 600 m (not shown). Consequently, water masses defined as 'bomb radiocarbon free' by both Rubin and Key (2002) and Key et al. (2004) probably are also not measurably affected by the ocean Suess effect. Thus, in principle, the natural ^{14}C–tracer correlations used to reconstruct natural Δ^{14}C in these studies can be assumed to represent the pre-Suess effect state of the ocean. Note, however, that Rubin and Key (2002) recalibrated their correlation between natural Δ^{14}C and potential alkalinity to match observed sea surface Δ^{14}C in the 1950s. Consequently, whereas it is reasonable to assume that the natural Δ^{14}C from Peacock (2004) rather represents the ocean state in the late 19$^{\text{th}}$ century, the Δ^{14}C background from Rubin and Key (2002) resp. Key et al. (2004) could reflect a point in time somewhat closer to the 1950s.

All studies discussed here (Krakauer et al., 2006; Naegler et al., 2006; Sweeney et al., 2007; Müller et al., 2008) assume that the excess ^{14}C data represent the change in ocean radiocarbon since the 1940s resp. early 1950s. If the background ^{14}C data, however, rather represents the ocean state in the 19th century, these studies slightly overestimate the true pre-bomb Δ^{14}C in the upper ocean and thus slightly underestimate the change in ocean ^{14}C between pre-bomb times and GEOSECS (1970s) resp. WOCE (1990s). Again, the magnitude of this bias can be estimated with a box-diffusion model (Oeschger et al., 1975), which shows a Suess effect at the sea surface of 8‰ in 1954. This result is consistent with coral data from Druffel and Linick (1978) and Druffel and Griffin (1993): coral Δ^{14}C exhibits a decrease in sea surface Δ^{14}C between the late 19$^{\text{th}}$ century and 1954, which does not exceed 8‰. The Suess effect in the 1950s averaged over the entire ocean is less than 1‰ in the box diffusion model. However, if we want to assess the effect of the 1950s Suess effect on the assumption that the observed ^{14}C excess represent the changes since pre-bomb times, it is more appropriate to calculate the average Suess effect only in water masses contaminated by the bomb signal (i.e. the upper ≈800 m of the ocean), where the average (simulated) pre-bomb Suess effect is on the order of 4‰–5‰. Thus, if one identifies the observed 'natural' ^{14}C from Peacock (2004) and Key et al. (2004) with the pre-bomb ^{14}C distribution, one might underestimate the true change in oceanic Δ^{14}C since pre-bomb times by up to 5‰. This bias is smaller than the uncertainties associated with the natural Δ^{14}C–tracer correlation used to reconstruct the natural sea surface Δ^{14}C signature. As a consequence, for most applications, it is reasonable to identify the 'natural' Δ^{14}C from both Key et al. (2004) and Peacock (2004) with the pre-bomb state in the 1940s and early 1950s, but to keep the small possible bias of up to 5‰ in the back of one's mind.

For the excess radiocarbon inventory, the estimate of the pre-bomb anthropogenic radiocarbon inventory of $4 \pm 20 \times 19^{26}$ atoms ^{14}C (Table 1B) can be regarded as a measure for the error introduced by the choice of the 1940s as pre-bomb reference. The bias in the reported excess radiocarbon inventory estimates from Peacock (2004) and Key et al. (2004) (as corrected in Naegler et al., 2006 and in this paper) due to uncertainties in the reference year for the methods of Rubin and Key (2002), Peacock (2004) and Sweeney et al. (2007), thus, are negligible.

4.3. Reconstruction of sea surface Δ^{14}C for GEOSECS

Peacock (2004) has doubted the representativeness of GEOSECS sampling stations for zonal (or global) mean excess ^{14}C distribution: she has shown that simulated column inventories of CFC-11 and anthropogenic CO_2 sampled at the GEOSECS stations overestimate the global mean column inventory of these tracers. As the time horizon of excess ^{14}C falls between the time horizons of CFC-11 and anthropogenic CO_2,

she concluded that also the excess ^{14}C column inventories at the GEOSECS stations overestimate the global mean oceanic excess ^{14}C column inventory.

To test whether the global mean sea surface $\Delta^{14}C$ estimated here from the GEOSECS data for the mid-1970s (Section 2.5) is also biased, simulated sea surface $\Delta^{14}C$ for the GEOSECS era from two OGCMs (ORCA2, Rodgers et al., 2004, and Bern3D, Müller et al., 2008) were used: simulated sea surface $\Delta^{14}C$ was sampled at the same locations and in the same year as the GEOSECS observations (ORCA2) resp. in 1975 (Bern3D). From these simulated 'station data', a global average sea surface $\Delta^{14}C$ was calculated in exactly the same manner as from the individual GEOSECS data. Additionally, the global average sea surface $\Delta^{14}C$ was calculated from the entire global simulation field of $\Delta^{14}C$. The global mean sea surface $\Delta^{14}C$ calculated from the individual (simulated) 'sample' results is 5‰ (ORCA2) resp. 2‰ (Bern3D) *lower* than the global average sea surface $\Delta^{14}C$ calculated from the full field. As this bias is very small, it can be concluded that the global average sea surface $\Delta^{14}C$ of 98‰ obtained from the GEOSECS data for 1975 as described in Section 2.5 well represents the actual global average at that time and does not require any further corrections.

This result seems to be at odds with the results from Peacock (2004) who has shown that the global excess ^{14}C inventory calculated from the excess ^{14}C column inventories at the GEOSECS stations *overestimate* the true global inventory. However, there is one important difference between this analysis here and Peacock (2004): here, the analysis focuses on *sea surface* $\Delta^{14}C$, whereas Peacock (2004) has analysed the ^{14}C *column* inventory. Sea surface excess $\Delta^{14}C$ and the excess ^{14}C inventory are not necessarily correlated. This can be seen if we consider two ocean regions, which differ only by the strength of the vertical mixing but not by the atmospheric excess ^{14}C forcing nor the efficiency of the air–sea gas exchange. In the region of weak vertical mixing, excess ^{14}C taken up from the atmosphere is trapped at the surface, resulting in a strong increase in sea surface $\Delta^{14}C$. As the excess ^{14}C flux into the ocean depends on the excess $\Delta^{14}C$ gradient between atmosphere and sea surface, high sea surface $\Delta^{14}C$ results in a weak excess ^{14}C flux across the air–sea interphase and consequently in a small excess ^{14}C inventory. In contrast, in the region with strong vertical mixing, excess ^{14}C is effectively mixed downwards into the deep ocean, resulting in a weak increase in sea surface $\Delta^{14}C$, a strong excess ^{14}C gradient between atmosphere and sea surface and a resulting strong excess ^{14}C flux and inventory. Thus, if differences in the excess ^{14}C distribution in two ocean regions is entirely controlled by vertical mixing, sea surface excess $\Delta^{14}C$ and the excess ^{14}C column inventory are *negatively* correlated. In contrast, if the vigorousness of the gas exchange is the controlling difference between both regions, sea surface $\Delta^{14}C$ and the ^{14}C inventory are positively correlated. This explanatory approach has been verified by results of a box-diffusion model (Oeschger et al., 1975), which show exactly the behaviour described above. Thus, the results from Peacock (2004) and the results presented here are entirely consistent with each other.

As demonstrated in eq. (26), a correct reconstruction of the temporal evolution of sea surface $\Delta^{14}C$ is crucial to determine $\langle k \rangle$, in particular when using the methods of Naegler et al. (2006) and Sweeney et al. (2007). Figure 2 illustrates that the global mean sea surface $\Delta^{14}C$ from Naegler et al. (2006) matches well the available observations for 1953 (pre-bomb, −65‰), 1975 (GEOSECS, 98‰) and 1995 (WOCE, 62‰). Sea surface $\Delta^{14}C$ from Sweeney et al. (2007) also matches the pre-bomb and the WOCE data point, however, $\Delta^{14}C$ for the GEOSECS era is too low by up to 24‰. This finding is qualitatively corrobated by the fact that Sweeney et al. (2007) admit that their GEOSCES ocean excess radiocarbon inventory (225×10^{26} atoms of ^{14}C) might be biased towards lower values by up to 10%, which is an inherent consequence of their method. In their inverse approach to estimate sea surface $\Delta^{14}C$, Sweeney et al. (2007) assume that the time history of the excess radiocarbon flux is proportional to the time history of the atmospheric excess $\Delta^{14}C$. They thus neglect the effect of increasing sea surface $\Delta^{14}C$ on the excess ^{14}C flux. Consequently, they overestimate the contribution of the flux in later years to their excess radiocarbon inventory (and $\Delta^{14}C$) relative to the early years of their integration period (1954–1995). As their 1990s sea surface Δ^{14} is very well constrained by the WOCE observations, they consequently underestimate $\Delta^{14}C$ in the 1970s. Sea surface $\Delta^{14}C$ from Naegler et al. (2006) agrees well with the observations (Fig. 2a) and can be regarded as the reference in this study. Therefore, the relative difference between the integrated excess $\Delta^{14}C$ gradient from Naegler et al. (2006) and Sweeney et al. (2007) (5% in 1995, see Fig. 2c) is a measure for the underestimation of $\langle k \rangle$ by Sweeney et al. (2007) due to the underestimation of the sea surface $\Delta^{14}C$ in the 1970s.

4.4. Consequences for estimates of ⟨k⟩

Note that all estimates of $\langle k \rangle$ presented in this section are *not* normalized to any Schmidt number, except where otherwise indicated. This choice is arbitrary; I might as well have normalized all piston velocities to $Sc = 660$ (which is done, for comparability, in Table 2).

The global mean piston velocity estimate given by Krakauer et al. (2006) ($20.0 \pm 3.0\,\mathrm{cm\,h^{-1}}$) is normalized to $Sc = 660$. Thus, the de-normalized value of $\langle k \rangle$ is $18.2 \pm 2.7\,\mathrm{cm\,h^{-1}}$. Note, that the result from Krakauer et al. (2006) does *not* require a correction for the negligence of net CO_2 uptake, as they use excess $\Delta^{14}C$ fields as constraints which are, in contrast to the excess ^{14}C inventory $I^{14,E}$, only affected by net CO_2 uptake in a minor way.

In contrast, the gas exchange study from Naegler et al. (2006) relied on the excess radiocarbon inventory numbers from Peacock (2004) for GEOSECS and Key et al. (2004) for WOCE. As discussed above, these estimates of $I^{14,E}$ have to be corrected upwards by approx. 3% for the mid-1970s resp. 8% for the

mid-1990s due to net CO_2 uptake. Consequently, $\langle k \rangle$ has to be corrected accordingly. However, due to an error in the water vapour-pressure correction of atmospheric pCO_2 in Naegler et al. (2006) and a re-calculation of the CO_2 solubility according to Weiss (1974), results from Naegler et al. (2006) require an additional downward correction of 7%. These corrections nearly cancel each other; they result in a global mean piston velocity $\langle k \rangle$ of 16.9 ± 2.9 cm h^{-1} (Table 2). Gas exchange coefficients a_q given in Naegler et al. (2006) also require an upward correction of 1%, whereas the normalized gas exchange coefficients a_q^N from Naegler et al. (2006) are only affected by the pCO_2^{atm} correction mentioned above but not by the correction of $I^{14,E}$. They thus have to be corrected downwards by 7%.

The global mean piston velocity estimate given by Sweeney et al. (2007) (14.6 ± 4.7 cm h^{-1}) is normalized to a Schmidt number of 660. As in the case of Naegler et al. (2006), the excess radiocarbon inventory estimate used by Sweeney et al. (2007) has to be corrected upward by 8% to account for net uptake of CO_2. Furthermore, the bias in reconstructed sea surface Δ^{14}C requires an additional upward correction of 5%. Both corrections and the Schmidt number de-normalization result in an estimate of $\langle k \rangle$ of 15.1 ± 4.3 cm h^{-1} (Table 2).

Estimates of the global mean piston velocity from Müller et al. (2008) are normalized to a Schmidt number of 660. Müller et al. (2008) took into account the ocean excess radiocarbon component due to net CO_2 uptake. Consequently, no respective correction is required. However, I correct the $\langle k \rangle$ from Müller et al. (2008) by a factor of 1.03 to take into account the fact that Müller et al. (2008) define $\langle k \rangle$ for the entire ocean (and not only the ice-free ocean, as Naegler et al., 2006, Krakauer et al., 2006 and Sweeney et al., 2007). Taking these corrections into account, the corrected estimate of $\langle k \rangle$ for Müller et al. (2008) is 16.1 ± 3.0 cm h^{-1} (Table 2).

4.5. Global mean piston velocity in Wanninkhof (1992)

From the excess radiocarbon data of the GEOSECS cruises in the 1970s, Broecker et al. (1986) estimated a global average CO_2 invasion rate $F_{CO_2}^{AO}$ (i.e. gross CO_2 flux from atmosphere to ocean) of 20.0 mol m^{-2} yr^{-1}) at a global excess radiocarbon inventory of 289 × 10^{26} atoms ^{14}C (Broecker et al., 1985). From this estimate of $F_{CO_2}^{AO}$, Wanninkhof (1992) calculated a global mean piston velocity of 21.9 cm h^{-1} (his eq. (A3)):

$$\left\langle F_{CO_2}^{AO} \right\rangle = \langle k \rangle \times \langle L \rangle \times \left\langle pCO_2^A \right\rangle \quad (30)$$

$$\Leftrightarrow$$

$$\begin{aligned} \langle k \rangle &= \frac{F_{CO_2}^{AO}}{\langle L \rangle \times \left\langle pCO_2^A \right\rangle} \\ &= \frac{20 \frac{\text{mol}}{\text{m}^2 \cdot \text{yr}}}{33.2 \frac{\text{mol}}{\text{m}^3 \text{atm}} \times 314 \times 10^{-6} \text{atm}} \\ &= 1918 \frac{\text{m}}{\text{yr}} = 21.9 \frac{\text{cm}}{\text{h}} \end{aligned} \quad (31)$$

Note that $\langle k \rangle = 21.9$ cm h^{-1} from eq. (31) is the physically active piston velocity controlling the CO_2 uptake and is thus *not* normalized to a Schmidt number of 660.

Note further that Wanninkhof (1992) uses a global mean solubility L of 0.0324 mol kg^{-1} atm^{-1} (erroneously given in units of mol L^{-1} atm^{-1} in his paper, R. Wanninkhof, personal communication, 2007). As the global mean sea surface density is 1.025 kg L^{-1}, this corresponds to L = 33.2 mol m^{-3} atm^{-1}. Wanninkhof (1992) choose a global mean sea surface pCO_2 of 314 μatm. This corresponds to an atmospheric CO_2 mixing ratio of 324 μmol mol^{-1}, which is approximately the average atmospheric CO_2 mixing ratio during the invasion of excess radiocarbon into the ocean between the increase of atmospheric Δ^{14}C in 1954 due to atmospheric nuclear bomb tests and the GEOSECS survey in the mid-1970s.

The $\langle k \rangle$ estimate from Wanninkhof (1992) now requires two corrections: first, the estimate of the oceanic excess radiocarbon inventory of 289 × 10^{26} atoms of ^{14}C is too high in the light of recent studies (Peacock, 2004; Naegler and Levin, 2006) and this work. Including the corrections for net CO_2 uptake, the best estimate of the GEOSECS excess radiocarbon inventory is 252 × 10^{26} atoms ^{14}C (see Section 4.1), 15% lower than the estimate of Broecker et al. (1985) used by Wanninkhof (1992). Second, the global mean CO_2 solubility calculated from the sea surface temperature and salinity (Antonov et al., 2006; Locarnini et al., 2006) and the parametrization from Weiss (1974) is 0.0361 mol L^{-1} atm^{-1}, 9% higher than the estimate used by Wanninkhof (1992). Both factors yield a corrected estimate of $\langle k \rangle$ for Wanninkhof (1992) of 17.5 cm h^{-1}.

4.6. Resulting best estimate of $\langle k \rangle$

If all the necessary corrections are applied, the corrected, unnormalized estimates of $\langle k \rangle$ from Wanninkhof (1992), Naegler et al. (2006), Krakauer et al. (2006), Sweeney et al. (2007) and Müller et al. (2008) agree very well within their uncertainties (see Table 2). I am thus confident that the remaining differences do not reflect any (correctable) systematic shortcomings, but merely (uncorrectable) methodological differences between the different approaches due to different ocean models as well as different Schmidt number, pCO_2, solubility, water vapour pressure and/or sea-ice fields applied in these studies. Combining the results from all four studies based on the GLODAP data (Naegler et al., 2006; Krakauer et al., 2006; Sweeney et al., 2007; Müller et al., 2008), the average of all corrected $\langle k \rangle$ values (16.5 ± 3.2 ± 1.3 cm h^{-1}) can be regarded to best represent our knowledge of excess radiocarbon constraints on air–sea gas exchange. The first uncertainty given here is the average uncertainty of these four corrected $\langle k \rangle$s, whereas the second uncertainty is the standard deviation of all four corrected estimates of $\langle k \rangle$ (see Table 2). The (corrected) $\langle k \rangle$ of the Wanninkhof (1992) study has been disregarded in the calculation of the 'best estimate' $\langle k \rangle$, as the Wanninkhof (1992) estimate relies only on

the limited GEOSECS data and is further limited by the coarse (global) resolution of the fields used (see eq. (31)).

4.7. Recommendations for the parametrization of air-sea gas exchange

If we assume a quadratic relationship between the piston velocity k and the wind speed u (Wanninkhof, 1992; Nightingale et al., 2000; Ho et al., 2006), k can be parametrized as follows:

$$k = a_q \times u^2 \times \left(\frac{Sc}{660}\right)^{-0.5}. \tag{32}$$

In the studies by Wanninkhof (1992), Naegler et al. (2006) and Sweeney et al. (2007), the piston velocity scales linearly with the global oceanic excess radiocarbon inventory: $k \propto I^{14,E}$. Formally, we can therefore define a global average piston velocity $\langle k' \rangle$ which is normalized to the ocean excess ^{14}C inventory in 1995:

$$\langle k' \rangle = \frac{\langle k \rangle}{I^{14,E}_{1995}} \tag{33}$$

As Naegler et al. (2006) have shown that the choice of a_q depends on the wind fields used to calculate the piston velocity, for any particular wind field $u(\mathbf{x}, t)$ and any new, revised estimate of the ocean excess radiocarbon inventory in the 1990s, $\langle k \rangle$ (and therewith a_q) should be determined in a way that

$$\begin{aligned}\langle k \rangle &= a_q \times \left\langle u(\mathbf{x}, t)^2 \times \left(\frac{Sc(\mathbf{x}, t}{660}\right)^{-0.5} \right\rangle \\ &= \frac{16.5}{385} \times I^{14,E}_{1995}\end{aligned} \tag{34}$$

or

$$a_q = \frac{16.5}{385} \times I^{14,E}_{1995} \times \frac{1}{\left\langle u(\mathbf{x}, t)^2 \times \left(\frac{Sc(\mathbf{x},t}{660}\right)^{-0.5} \right\rangle}, \tag{35}$$

where $u(\mathbf{x}, t)$ and $Sc(\mathbf{x}, t)$ are the wind and Schmidt number fields used in the calculation. This approach is similar to the approach suggested by Naegler et al. (2006) but more intuitive and thus easier to apply.

Note that the assumption that $\langle k \rangle \propto I^{14,E}$, which underlies eqs. (33)ff is not entirely true: Krakauer et al. (2006) have shown that the excess ^{14}C inventory increases less than proportional with increasing $\langle k \rangle$. Their results allow to estimate the error in a_q, and thus $\langle k \rangle$, if eq. (35) is applied to re-calculate a_q from revised estimates of $I^{14,E}$: If the new $I^{14,E}_{1995}$ value is $\pm 10^{26}$ atoms higher (respectively lower) than the reference value of 385×10^{26} atoms used here, the re-scaled a_q will be too low (respectively too high) by approx. 1.8%. Furthermore it should be noted that Krakauer et al. (2006) have shown that the total excess ^{14}C inventory depends not only on the global mean piston velocity, but also on the exponent n of the relationship between piston velocity and wind speed ($k \propto u^n$), which affects the latitudinal distribution of the piston velocity k. As it can be tested with the approach from Naegler et al. (2006), for the same excess ^{14}C inventory constraints, the global mean piston velocity $\langle k \rangle$ for a linear k–u relationship is approx. 8% higher than for a quadratic relationship, which, in turn, is approx. 7% higher than $\langle k \rangle$ for a cubic relationship. Therefore, eqs. (33)ff can only provide a first estimate of a_q resp. $\langle k \rangle$ in the case that the excess ^{14}C inventory estimate for the mid-1990s should be revised again in the future.

5. Conclusions

Oceanic excess radiocarbon data provide important constraints on air–sea gas exchange. However, a number of sources of systematic biases have to be taken into account.

Net uptake of (anthropogenic) atmospheric CO_2 is a significant source for the oceanic excess radiocarbon inventory: for the time of the WOCE ocean survey in the 1990s, net uptake of CO_2 had contributed approx. 8% to the total oceanic excess radiocarbon inventory, with increasing tendency. As increasing DIC concentrations due to net CO_2 uptake are neglected by Peacock (2004) and Key et al. (2004), their estimates for the ocean excess radiocarbon inventories (updated by Naegler et al., 2006) have to be corrected accordingly. This correction also affects the gas exchange studies by Naegler et al. (2006), Sweeney et al. (2007) and Müller et al. (2008), as these studies rely on excess radiocarbon inventories as constraints.

The pre-bomb background oceanic Δ^{14}C signature reconstructed from oceanographic data (Rubin and Key, 2002; Key et al., 2004; Peacock, 2004) cannot precisely be attributed to a specific year or even decade, but rather represents the ocean radiocarbon signature at some time between the onset of a significant atmospheric Suess effect (late 19$^{\text{th}}$ century) and the rise of atmospheric Δ^{14}C due to atmospheric nuclear bomb testing (early 1950s). However, anthropogenic changes in the oceanic Δ^{14}C until pre-bomb times (1940s) are probably small compared with the uncertainties of the reconstruction of the 'natural' oceanic Δ^{14}C levels. Furthermore, the anthropogenic pre-bomb change in the oceanic radiocarbon inventory (due to the Suess effect and net uptake of CO_2) probably is negligible, as both effects partly cancel each other. Consequently, it is reasonable to identify the 'excess' radiocarbon with the radiocarbon flux and inventory changes since the 1940s.

The surprisingly large spread between the original estimates of the global mean piston velocity from Naegler et al. (2006), Krakauer et al. (2006), Sweeney et al. (2007) and Müller et al. (2008) can be reduced by 60% (see Table 2), if necessary inventory corrections are taken into account, if reconstructed sea surface Δ^{14}C agrees well with the observations, and if the piston velocity is reported in a consistent manner. The estimate of the global mean piston velocity $\langle k \rangle$ from Naegler et al. (2006) has to be slightly corrected upwards from 16.7 to $16.9 \pm 2.9\,\mathrm{cm\,h^{-1}}$. The de-normalized global mean piston velocity based on the original value from Krakauer et al. (2006) ($\langle k_{660} \rangle = 20.0\,\mathrm{cm\,h^{-1}}$) is $\langle k \rangle = 18.2 \pm 2.7\,\mathrm{cm\,h^{-1}}$. The original $\langle k \rangle$

estimate from Sweeney et al. (2007) ($14.6 \pm 4.7\,\mathrm{cm\,h^{-1}}$) has to be corrected (and de-normalized) to $15.1 \pm 4.3\,\mathrm{cm\,h^{-1}}$, whereas the corrected, de-normalized estimate for Müller et al. (2008) is $16.1 \pm 3.0\,\mathrm{cm\,h^{-1}}$ instead of the original $\langle k_{660}\rangle$ of $17.7 \pm 3.0\,\mathrm{cm\,h^{-1}}$. The remaining spread probably reflects methodological differences between these three studies, different ocean models and different boundary conditions not further correctable. As none of the methods adopted by Naegler et al. (2006), Krakauer et al. (2006), Sweeney et al. (2007) and Müller et al. (2008) can be regarded as superior to the other methods, I propose to use the average of the (corrected, non-normalized!) estimates of $\langle k\rangle$ presented here ($16.5\,\mathrm{cm\,h^{-1}}$) as the best estimate of the global mean piston velocity in gas exchange calculations. All original $\langle k\rangle$ estimates discussed here have inherent uncertainties of 3–4 $\mathrm{cm\,h^{-1}}$ (see Table 2). Consequently, the uncertainty of the $\langle k\rangle$ estimate proposed in this study is probably still of similar size; here the average uncertainty of the corrected $\langle k\rangle$ estimates ($3.2\,\mathrm{cm\,h^{-1}}$) is chosen as the uncertainty of the best estimate of $\langle k\rangle$. The global annual gross CO_2 flux resulting from $\langle k\rangle = 16.5\,\mathrm{cm\,h^{-1}}$ is $76 \pm 15\,\mathrm{PgC\,yr^{-1}}$ for the mid-1990s.

6. Acknowledgments

I thank Ingeborg Levin, Robert Key, Synte Peacock, Simon Müller and Rik Wanninkhof for helpful and inspiring discussions. Special thanks to Colm Sweeney and Nir Krakauer whose reviews significantly helped to clarify the manuscript. This work was funded by the German Science Foundation.

References

Antonov, J. I., Locarnini, R. A., Boyer, T. P., Mishonov, A. V. and Garcia, H. E. 2006. *World Ocean Atlas 2005* Volume 2 *(Salinity). NOAA Atlas NESDIS 62*. U.S. Government Printing Office, Washington, D.C., USA.

Broecker, W. S., Peng, T.-H., Östlund, G. and Stuiver, M. 1985. The distribution of bomb radiocarbon in the ocean. *J. Geophys. Res.* **90**(C4), 6953–6970.

Broecker, W. S., Ledwell, J. R., Takahashi, T., Weiss, L. M. R., Memery, L. and co-authors. 1986. Isotopic versus micrometeorologic ocean CO_2 fluxes: a serious conflict. *J. Geophys. Res.* **91**, 10 517–10 527.

Broecker, W. S., Sutherland, S., Smethie, W., Peng, T.-S. and Östlund, G., 1995. Oceanic radiocarbon: separation of the natural and bomb component. *Global Biogeoch. Cycl.* **9**, 263–288.

Druffel, E. R. M. and Griffin, S. 1993. Large variations of surface ocean radiocarbon: evidence of circulation changes in the southwestern Pacific. *J. Geophys. Res.* **98**, 20 249–20 259.

Druffel, E. R. M. and Linick, T. W. 1978. Radiocarbon in annual coral rings of Florida. *Geophys. Res. Let.* **5**, 913–916.

Enting, I. G., Wigley, T. M. L. and Heymann, M. 1994. *Future Emissions and Concentrations of Carbon Dioxide: Key Ocean/Atmosphere/Land Analyses*. Tech. Paper 31, CSIRO Div. of Atmos. Res., Melbourne.

Gibson, J. K., Kallberg, K., Uppala, S., Hernandez, A., Nomura, A. and co-authors. 1997. *ECMWF Re-Analysis, Project Report Series 1: ERA description*. Tech. rep., European Center for Mid-Range Weather Forecast, Reading, GB.

Hesshaimer, V. 1997. *Tracing the Global Carbon Cycle with Bomb Radiocarbon*. PhD Thesis. University of Heidelberg, Heidelberg, Germany.

Ho, D. T., Law, C. S., Smith, M. J., Schlosser, P., Harvey, M. and co-authors. 2006. Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: implications for global parameterizations. *Geophys. Res. Lett.* **33**, L16611, doi:10.1029/2006GL026817.

Kalney, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D. and co-authors. 1996. The NCEP/NCAR 40-year reanalysis project. *Bull. Am. Meteorol. Soc.* **77**, 437–471.

Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R. and co-authors. 2004. A global ocean carbon climatology: results from Global Data Analysis Project (GLODAP). *Global Biogeoch. Cycl.* **18**, doi:10.1029/2004GB002247.

Krakauer, N. Y., Randerson, J. T., Primeau, F. W., Gruber, N. and Menemenlis, D. 2006. Carbon isotope evidence for the latitudinal distribution and wind speed dependence of the air-sea gas transfer velocity. *Tellus* **58B**, 390–417.

Levin, I. and Kromer, B. 2004. The tropospheric $^{14}CO_2$ level in mid-latitudes of the Northern Hemisphere (1959-2003). *Radiocarbon* **463**, 1261–1272.

Levin, I., Kromer, B., Wagenbach, D. and Münnich, K. O. 1987. Carbon isotope measurements of atmospheric CO_2 at a coastal station in Antarctica. *Tellus* **39B**, 89–95.

Locarnini, R. A., Mishonov, A. V., Antonov, J. I., Boyer, T. P. and Garcia, H. E. 2006. *World Ocean Atlas 2005* Volume 1 *(Temperature). NOAA Atlas NESDIS 61*. NOAA, U.S. Government Printing Office, Washington, D.C., USA.

Manning, M. R. and Melhuish, W. H. 1994. Atmospheric ^{14}C record from Wellington. In: *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge, Tenn., USA.

Müller, S. A., Joos, F., Plattner, G.-K., Edwards, N. R. and Stocker, T. F. 2008. Modelled natural and excess radiocarbon - sensitivities to the gas exchange formulation and ocean transport strength. *Global Biogeoch. Cycl.* doi:10.1029/2007GB003065.

Naegler, T. 2005. *Simulating Bomb Radiocarbon: Consequences for the Global Carbon Cycle*. PhD Thesis, University of Heidelberg, Heidelberg, Germany.

Naegler, T. and Levin, I. 2006. Closing the global radiocarbon budget 1945-2005. *J. Geophys. Res.* **111**, D12311, doi:10.1029/2005JD006758.

Naegler, T., Ciais, P., Rodgers, K. and Levin, I. 2006. Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO_2 by the oceans. *Geophys. Res. Lett.* **33**, L11802, doi:10.1029/2005GL025408.

Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S. and co-authors. 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Global Biogeoch. Cycl.* **14**, 373–387.

Oeschger, H., Siegenthaler, U., Schotterer, U. and Gugelmann, A. 1975. A box diffusion model to study the carbon dioxide exchange in nature. *Tellus* **27**, 168–192.

Orr, J., Najjar, R., Sabine, C. and Joos, F. 2000. *Aiotic-HOWTO*. LSCE/CEA Saclay, Gif-sur-Yvette, France. 29 pp.

Östlund, H. G. and Stuiver, M. 1980. GEOSECS Pacific radiocarbon. *Radiocarbon* **22**, 25–53.

Peacock, S. 2004. Debate over the ocean bomb radiocarbon sink: closing the gap. *Global Biogeoch. Cycl.* **18**, doi:10.1029/2003GB002211.

Prentice, I. C., Farquhar, G. D., Fasham, M. J. R., Goulden, M. L., Heimann, M. and co-authors. 2001. The carbon cycle and atmospheric CO_2. In: *Climate Change: The Scientific Basis, the Contribution of WGI of the IPCC to the IPCC Third Assessment Report (TAR)*, (eds. J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden and co-editors.). Cambridge University Press, Cambridge, UK, 183–237.

Reimer, P. J., Baillie, M. G. L., Bard, E., Bayliss, A., Beck, J. W. and co-authors. 2004. Terrestrial radiocarbon age calibration, 0-26 cal kyr BP. *Radiocarbon* **46**, 1029–1058.

Rodgers, K. B., Aumont, O., Madec, G., Menkes, C., Blanke, B. and co-authors. 2004. Radiocarbon as a thermocline proxy for the eastern equatorial Pacific. *Geophys. Res. Lett.* **31**, doi:10.1029/2004GL019764.

Rozanski, K., Levin, I., Stock, J., Falcon, R. E. G. and Rubio, F. 1995. Atmospheric $^{14}CO_2$ variations in the equatorial region. *Radiocarbon* **37**, 509–515.

Rubin, S. and Key, R. M. 2002. Separating natural and bomb-produced radiocarbon in the ocean: the potential alkalinity method. *Global Biogeoch. Cycl.* **16**, doi:10.1029/2001GB001432.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister and co-authors. 2004. The oceanic sink for anthropogenic CO_2. *Science* **305**, 367–371.

Stuiver, M. and Östlund, H. G. 1980. GEOSECS Atlantic radiocarbon. *Radiocarbon* **22**, 1–24.

Stuiver, M. and Östlund, H. G. 1983. GEOSECS Indian Ocean and Mediterranean radiocarbon. *Radiocarbon* **25**, 1–29.

Stuiver, M. and Polach, H. A. 1977. Reporting of ^{14}C data. *Radiocarbon* **19**, 355–363.

Stuiver, M., Reimer, P. J. and Braziunas, T. F. 1998. High-precision radiocarbon age calibration for terrestrial and marine samples. *Radiocarbon* **40**, 1127–1151.

Suess, H. E. 1955. Radiocarbon concentration in modern wood. *Science* **122**, 415–417.

Sweeney, C., Gloor, E., Jacobson, A. R., Key, R. M., McKinley, G. and co-authors. 2007. Constraining global air-sea gas exchange for CO_2 with recent Bomb ^{14}C measurements. *Global Biogeoch. Cycl.* **21**, GB2015, doi:10.1029/2006GB002784.

Walsh, J. 1978. A data set on northern hemisphere sea ice extent, 1953–1976. *Report GD-2: Glaciological data*. World Data Cent. A for Glaciol. (Snow and Ice), Boulder, Colorado.

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

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

Zwally, H. J., Comiso, J., Parkinson, C., Campbell, W., Carsey, F. and co-authors 1983. *Antarctic Sea Ice, 1973-1976: Satellite Passive Microwave Observations*. NASA, USA.