Environmental Science and Engineering
Subseries: Environmental Science

Series Editors: R. Allan • U. Förstner • W. Salomons

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(Eds.)

Transport at the Air-Sea Interface

Measurements, Models and Parametrizations

With 127 Figures and a CD-ROM

Springer

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ISSN 1863-5520
ISBN 10 3-540-36904-x **Springer Berlin Heidelberg New York**
ISBN 13 978-3-540-36904-2 **Springer Berlin Heidelberg New York**

Library of Congress Control Number: 2007931824

Springer is a part of Springer Science+Business Media
springeronline.com

Cover design: deblik, Berlin
Production: A. Oelschläger
Typesetting: Camera-ready by the Editors
Printed on acid-free paper 30/2132/AO 543210

Preface

The sea surface represents the interface between the ocean and the atmosphere. As the interface is approached from either the atmospheric or ocean side, the transport mechanisms are shifted from turbulent to diffusive diffusion. Hence the viscous boundary layers at both sides of the water surface represents the major resistance to the transport of energy, mass and impulse between atmosphere and ocean. This has implications for the composition of the atmosphere and has gained importance especially for radiatively (climate)-active gases such as CO_2, CH_4, N_2O and DMS. But also, the transport of gases across the interface is significant for the fate and the atmospheric/marine budgets of many man-made pollutants, in particular of volatile organic compounds and mercury.

The two key variables which are required for the determination of the gas exchange fluxes are the partial pressure difference of the considered gas at the sea surface, and the gas exchange transfer velocity k. Partial pressure differences are either obtained from measurements in the surface water and in the atmosphere or from biogeochemical models. Whereas our knowledge about the partial pressure difference distributions, in particular for CO_2, has increased considerably during the past years, the choice of an appropriate transfer velocity is still a matter of controversy. This is because the transport mechanisms across the free, wind-driven water surface are still only known superficially. This is not surprising because both the experimental investigation as well as the modeling is very challenging.

Experimental techniques and modeling efforts have evolved separately with little quantitative comparisons. Recently, refined measurement techniques have advanced which allows researchers to gain novel insights into the boundary layer processes. Likewise, computer simulations have improved significantly both in terms of resolution and model complexity. This has made it feasible to compare model output of realistic boundary

conditions to actual measurements. Through these comparisons, models can be verified, leading to a deepening of our knowledge of the transport of energy and mass between ocean and atmosphere. Only by linking experimental measurements with computer models, can our understanding of air-sea interactions be enhanced. In turn, through insights into the underlying transport processes, physically sound parameterizations can be found. Better parameterizations are needed in order to improve global models of our climate and predict climatic change.

In order to bridge the gap between current models and measurements, as well as spark new ideas for novel simulation and experimental efforts, an "International Workshop on Transport at the Air Sea Interface" was organized by the editors of this volume. The focus of the workshop was on small scale processes directly at the interface. The workshop took place at the University of Heidelberg from September 6–8, 2006. Leading scientist from around the world came together and focused on different aspects of the transport across the air-water interface. The current state of the art of research was presented and current and future research interests and problems were discussed.

The program of the workshop is listed after this preface. This volume contains peer reviewed, extended and updated versions of selected talks that also reflect the discussions during the workshop. The editors cordially thank all reviewers for their detailed responses and their efforts to improve the quality of the papers.

Christoph Garbe
Robert Handler
Bernd Jähne

Heidelberg,
April 2007

Contributions to "International Workshop on Transport at the Air-Sea Interface"

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Herlina
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1

The Impact of Different Gas Exchange Formulations and Wind Speed Products on Global Air-Sea CO_2 Fluxes

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Abstract Significant advances have been made over the last decade in estimating air-sea CO_2 fluxes over the ocean by the bulk formulation that expresses the flux as the product of the gas transfer velocity and the concentration difference of aqueous CO_2 over the liquid boundary layer. This has resulted in a believable global monthly climatology of air-sea CO_2 fluxes over the ocean on a 4° by 5° grid [38]. It is shown here that the global air-sea CO_2 fluxes are very sensitive to estimates of gas transfer velocity and the parameterization of gas transfer with wind. Wind speeds can now be resolved at sufficient temporal and spatial resolution that they should not limit the estimates, but the absolute magnitudes of winds for different wind products differ significantly. It is recommended to use satellite-derived wind products that have the appropriate resolution instead of assimilated products that often do not appropriately resolve variability on sub-daily and sub-25-km space scales. Parameterizations of gas exchange with wind differ in functional form and magnitude but the difference between the most-used quadratic relationships is about 15%. Based on current estimates of uncertainty of the air-water CO_2 concentration differences, the winds, and the gas exchange-wind speed parameterization, each parameter contributes similarly to the overall uncertainty in the flux that is estimated at 25%.

1.1 Introduction

In order to determine the role of the ocean in the global cycles of climate-relevant gases such as carbon dioxide (CO_2), the flux of these gases across the air-sea interface must be quantified. The ocean sequesters 20-30% of the excess CO_2 produced by fossil-fuel burning, thereby mitigating the greenhouse effect [19]. The projected future amount of CO_2 in the atmosphere is thus critically dependent on the amount of exchange between the ocean and atmosphere. Quantifying the air-sea gas CO_2 is, therefore, a major research objective of various international global change research programs.

C.S. Garbe, R.A. Handler, B. Jähne (eds.): Transport at the Air Sea Interface
pp. 1-23, 2007,

Global air-sea gas flux estimates of slightly soluble gases are routinely determined from the product of the concentration gradient of the gas in question across the liquid boundary layer and the gas transfer velocity,

$$F = k\Delta C = kK_o\Delta pC \tag{1.1}$$

Equation (1.1) is often referred to as the bulk formulation where F is the flux [mol m^{-2} day^{-1}]; k is the gas transfer velocity [m d^{-1}]; ΔC is the concentration gradient [mol m^{-3}]; K_o is the solubility [mol m^{-3} atm^{-1}]; and ΔpC is the partial pressure (or fugacity) difference across the air-water interface [atm^{-1}]. The ΔC and ΔpC are often approximated from measurements in the surface ocean mixed layer at 1-5 m depth and in air well above the interface. While this bulk formulation is frequently used in this form, there are known issues with these approximations that are discussed elsewhere [26, 29]. One of the most referenced global applications utilizing this approach is the global air-sea CO_2 flux estimate of Takahashi et al. [38] based on a monthly global climatology of the partial pressure difference of CO_2 and ΔpCO_2.

Here I will focus on how uncertainty in the gas transfer velocity, in particular, its relationship with wind speed, affects the global CO_2 flux. First, a brief background is provided on determination of the gas transfer velocity in wind-wave tanks and in the field, and the functional relationship of gas transfer to wind speed. The sensitivity of the global CO_2 flux estimates to changes in wind, ΔpCO_2, and functional dependence on wind is shown. The issue of applying gas transfer velocities derived from other trace gases to CO_2 exchange is presented. The impact of the recent reassessment of the inventory of excess-^{14}C in the ocean is assessed. Excess-^{14}C is the ^{14}C produced by nuclear bomb tests corrected for dilution by ^{14}C-free fossil fuel emissions. Henceforth, the excess-^{14}C is referred to as bomb-^{14}C. The effect of high-resolution satellite wind speeds on the gas exchange wind speed relationship is discussed. The paper concludes with a brief summary of current estimates of interannual variability in CO_2 flux.

1.2 Discussion

1.2.1 A Summary of Gas Exchange Wind Speed Relationships

Gas transfer velocities have been determined in many field and wind-wave tank experiments. The laboratory studies benefit from full experimental control, but scaling considerations and possible artifacts due to the limited size and configuration of the experimental setups have raised questions about the applicability of the wind-wave tank results to the open ocean with respect to the absolute magnitude of the derived relationship of gas exchange with wind speed [16]. The work in wind-wave tanks has

shown a strong dependence of gas exchange with wind. A notable finding is that there are distinct regimes in gas exchange and wind speed that are delineated by wave state [5]. Over smooth surfaces there is a weak dependence of gas exchange with wind that closely follows theoretical considerations of transfer across a smooth wall [9]. Once capillary and capillary-gravity waves form, the linear dependency strengthens appreciably. The onset of breaking waves enhances the gas transfer and gas transfer shows a solubility dependence with gases of lower solubility, showing a stronger enhancement. The transitions from smooth to rough surfaces and to breaking waves occur at wind speeds of about 3 and 13 m s^{-1}, respectively, depending on cleanliness and configuration of the tank. In field studies this clear delineation is not seen because of wind speed variability on short time scales, and variable thresholds for onset of capillary waves and breaking waves in the natural environment. Liss et al. [25] provide a comprehensive review of the status of air-sea gas exchange research in the 1980s.

Because of limitations of wind-wave tank studies, most empirical gas exchange-wind speed relationships are either derived from observations over the ocean or scaled to such studies. Initial studies over the ocean were performed using the ^{222}Rn disequilibrium method. The results showed no discernable trend with wind [36]. Factors that cause the absence of a clear correlation include experimental shortcomings of insufficient sampling at a particular location over the averaging time for the ^{222}Rn deficit method (four days) and inability to quantify losses and gains of ^{222}Rn in the mixed layer [23]. Use of deliberate tracers, in particular, the dual tracer technique with sulfur hexafluoride (SF_6) and the light isotope of helium (^{3}He), has proven to be a powerful approach to assess gas transfer in the coastal and open ocean [18, 32, 43]. Several, but not all, of the limitations of the ^{222}Rn are circumvented using injected tracers into the surface mixed layer. Major advantages of the dual tracer technique over the ^{222}Rn deficit method include the ability to do the studies in shallow coastal seas, ease of quantifying losses other than gas exchange, and the Lagrangian nature of the approach.

Using other gases as proxies for air-sea CO_2 transfer velocity works well for transfer over the smooth or turbulent interface in the absence of wave breaking since the gas transfer velocities can be scaled to their Schmidt number, which is defined as the kinematic viscosity of water divided by the molecular diffusion coefficient of the gas in question in water, according to

$$\frac{k_{CO_2}}{k_x} = \left(\frac{Sc_{CO_2}}{Sc_x}\right)^{-2/3} \quad \text{for smooth surfaces } \left(U_{10} \lessapprox 3 \text{ m s}^{-1}\right) \quad (1.2)$$

and

$$\frac{k_{CO_2}}{k_x} = \left(\frac{Sc_{CO_2}}{Sc_x}\right)^{-1/2} \quad \text{for wavy surfaces} \quad (1.3)$$

While these dependencies are well established based on theoretical and experimental considerations [10, 20], it is important to consider that the interrelationships will break down under conditions of bubble entrainment. This is of particular concern when the results of the dual tracer technique using the gases ^{3}He and SF_6 that have very low solubilities are used to estimate the exchange of CO_2 which has a higher solubility. Comparisons in the field at low to intermediate winds have confirmed that results can be scaled using a $Sc^{-1/2}$ dependence [32], but laboratory and theoretical considerations suggest that Schmidt number normalized gas transfer velocities of SF_6 and ^{3}He are appreciably higher than CO_2 transfer at high winds due to bubble exchange [1, 44].

The effect of solubility for a particular pair of gases has been included in the Schmidt number parameterization through an apparent Schmidt number dependence [2] but this is seldom applied when converting the tracer results to CO_2 exchange. For example, Ho et al. [18] suggest a parameterization of

$$k_{600} = 0.266 \cdot U_{10}^2 \tag{1.4}$$

based on a dual deliberate tracer study in the open ocean near New Zealand. The k_{600} is the gas transfer velocity, k, normalized to a Schmidt number of 600 according to Eq. (1.3). As shown in Fig. 8 of [1], the apparent Schmidt number for the combination of ^{3}He and CO_2 decreases monotonically from -0.5 to -0.65 over a wind speed range from 5 to 25 m s^{-1}. Accounting for this change would lead to a dependence for CO_2 that can be well approximated by:

$$k_{CO_2,600} = 0.230 \cdot U_{10}^2 \tag{1.5}$$

The 15% difference in coefficients is relatively small considering the differences in the relationships discussed below. However, a change in the coefficient from 0.266 to 0.23 will decrease the global uptake of CO_2 by 15%. The adjustment procedures are strictly only applicable for situations where the gases are far from equilibrium. More work needs to be done in these comparisons [2], but it is clear that comparison of exchange rates of gases with differing solubilities must be done with some caution.

To estimate global air-sea CO_2 flux, constraints on the global gas transfer velocities are critical. While these constraints can be obtained from atmospheric measurements of CO_2 along stable carbon isotopes, or N_2/O_2 ratios [4], they are commonly obtained from the inventory of bomb-^{14}C in the ocean [6, 7]. This method takes advantage of the rapid increase of $^{14}CO_2$ in the atmosphere in the 1960s due to testing of thermo-nuclear devices. The atmospheric ^{14}C anomaly is followed as it penetrates into the ocean.

One of the first invasion rate estimates, I [mol m^{-2} yr^{-1}], was derived from optimizing for inventory and surface concentration of bomb-^{14}C in a multi-box ocean model for time dependent inventories and surface concentrations [6]. Wanninkhof [40] used this estimate, along with an inferred

quadratic functional dependence with wind, to obtain a global parameterization of gas exchange with wind speed. The gas transfer velocity, k, was determined from I through

$$k = \frac{I}{K_o \cdot \mathrm{pCO}_{2,a}} \tag{1.6}$$

where $\mathrm{pCO}_{2,a}$ is the partial pressure of CO_2 in air. In this case, the invasion rate of CO_2 was assumed equivalent to that of $^{14}CO_2$, and the average mixing ratio of CO_2 in the atmosphere in 1964, at the peak of nuclear bomb testing, was used. A global average wind speed normalized to 10-m height (U_{10}) of 7.4 m s^{-1} from ship-based observations [13] yields the relationship

$$k_{av} = 0.39 \cdot U_{10,av}^2 \left(\frac{660}{Sc}\right)^{1/2} \tag{1.7}$$

where k_{av} is the global average gas transfer velocity and $U_{10,av}$ is the global average wind speed. This parameterization, when used in models to estimate air-sea gas fluxes, leads to consistent estimates of changing ocean bomb-^{14}C inventories. This is, in part, due to the fact that many of the older general circulation models are tuned to or validated with the same bomb-^{14}C inventories in the ocean.

The original global bomb-^{14}C inventory estimate did not lend itself to determine regional gas transfer rates because of difficulties accounting for transport of ^{14}C once it entered the ocean. The basin-wide invasion rates [6] are quite similar, and the wind speeds for each basin are similar enough to prevent obtaining meaningful discrete points for different oceans except for the Red Sea [8]. Therefore, while the global gas transfer velocity could be estimated from the invasion rate [6], the functional form of the relationship between gas exchange and wind had to be obtained by other means.

Three functional forms have been commonly used in combination with the bomb-^{14}C constraint:

- linear with a non-zero intercept [6, 39];
- quadratic [40]; and
- cubic [27, 41].

The linear relationship was proposed, in part, because the evidence of any other reasonable functional dependence was lacking from field observations. A quadratic dependence was suggested since this was the approximate dependence observed in wind-wave tanks [40]. Moreover, wind stress scales with U_{10}^2, and some theories suggest that gas exchange scales with stress. Monahan was one of the original proposers of a cubic dependence of gas exchange and wind speed [30]. In this formulation, it is implicitly assumed that bubbles have a controlling role on air-sea gas transfer. Several improvements of these global empirical parameterizations have been

developed that include boundary layer stability criteria [12, 15], and both bubble-mediated exchange and exchange over the air-water interface [3].

An important advance over the last decade has been the improved wind speed measurements over the ocean from active and passive microwave sensors on earth-orbiting satellites. These measurements provide coverage of much of the ocean surface, once or twice a day, at a resolution of 25 km. Besides offering, for the first time, comprehensive measurements in the remote ocean, the measurements also provide a good estimate of the variability in wind speed. The variability of the wind affects the calculated k for non-linear dependencies of gas exchange with wind [40, 42]. Wanninkhof [40] proposed different dependencies for steady or "short-term" wind and for "long-term" averaged winds assuming that long-term averaged winds followed a Rayleigh wind speed frequency distribution. While both long-term and short-term dependencies were assumed quadratic with wind, the coefficients of proportionality differed by 26%. It was known that wind speed distributions vary by location and by averaging time, but lack of winds at high resolution prevented an exact solution.

With the remotely sensed winds it is now possible to determine gas transfer velocities without needing to assume a particular wind speed distribution curve. Average gas transfer velocities can be expressed as

$$k_{\mathrm{av},660} = a \sum \frac{u^n}{s} = a \cdot {}^nM \tag{1.8}$$

where $k_{\mathrm{av},660}$ is the average transfer velocity for a Schmidt number of 660; a is a coefficient of proportionality; s is the number of wind speed measurements, $n = 2$ for the quadratic dependence and $n = 3$ for the cubic dependence; and ${}^nM$ is the n^{th} moment that is sometimes expressed as $\langle u^n \rangle$. Changing sea surface temperature (SST) over the period of determination will affect the gas transfer as well through the temperature dependency of the Schmidt number correction $({}^{660}/_{\mathrm{Sc}})^{1/2}$ (see Eq. (1.7)), which is non-linear as well. However, using the average SST over the time period of investigation will cause a bias of less than 5%.

1.2.2 The Sensitivity of Global Air-Sea CO_2 Flux

The uncertainty in the global air-sea CO_2 flux determined from the bulk flux method is estimated at +22, -19% [38], but this error estimate is primarily associated with the estimated uncertainty in the ΔpCO_2 field and likely an underestimate of the true error. An illustration of the sensitivity of the global CO_2 flux can be obtained from varying the wind, ΔpCO_2, and the functional dependence by an amount that approximates its uncertainty and determining the resulting change in flux. For this exercise we obtained the winds, sea surface temperatures, and ΔpCO_2 from the monthly global CO_2 climatology [38] and used as default the gas exchange wind speed formulations $k_{660} = 0.31 \cdot {}^2M$ or $k_{660} = 0.0283 \cdot {}^3M$ to take

into account the monthly variability of the wind in each pixel. For this exercise the ^2M and ^3M were determined from the six-hour NCEP winds for 1995 re-gridded from the original 2° by 2° grid to the 4° by 5° grid of the Takahahsi monthly global CO_2 climatology as used in [42]. The results of these changes are shown in Table 1.1. Changes in wind speed have a pronounced effect, especially for a cubic dependency. The functional dependency itself can change the flux two-fold. It is also of note that while many of the proposed relationships have a zero intercept, there is little evidence to support this premise. Turbulence and instabilities near the water surface induced by (diurnal) heating and shear [28] are believed to cause a finite gas transfer at low or no wind. This has lead to a reformulation of gas transfer to $k = b + a \cdot U_{10}^n$ where b is referred to as a "background" gas transfer velocity. McGillis et al. [27] suggest a value of $b = 3.2$ cm hr^{-1}. Including this term and adjusting the coefficient a to meet the bomb-^{14}C constraint leads to a decrease in the ocean uptake of 11-15%. This is because, on average, the ocean releases CO_2 at lower winds when the "background" transfer plays a more important role and because the relationships with a non-zero intercept yield lower k at higher winds in order to meet the bomb-^{14}C constraint.

1.2.3 The Impact of Updated Oceanic Bomb-^{14}C Inventories

Using the bomb-^{14}C invasion into the ocean to determine the gas transfer velocity requires knowledge of the time evolution of the atmospheric ^{14}C and the oceanic ^{14}C inventories on a regional basis, and the ^{14}C levels in the surface ocean. Several approximations have been made to estimate the global gas transfer velocity in this manner with poorly quantified effect on the final results. In particular, the means of extrapolation of sparse field measurements has led to uncertainties in the estimate of the ocean ^{14}C inventory. Considerable effort has been put into improving the global bomb-^{14}C inventory that has yielded revised global oceanic bomb-^{14}C based gas transfer estimates. The largest current shortcoming is the uncertainty in the partial pressure of $^{14}CO_2$ in seawater, $p^{14}CO_2sw$, which controls the "back flux" of $^{14}CO_2$. This term is increasingly significant because the atmosphere and ocean are reaching equilibrium with respect to $^{14}CO_2$. In the estimates below, most of the differences in calculated gas transfer rates can be associated with differences in inventory estimates and calculation methods.

The first estimates of the global inventory of bomb-^{14}C in the ocean in the 1980s were based on interpolating relatively few measurements in each ocean basin [6]. Separation of the bomb-^{14}C contribution from the natural background was problematic [35]. The estimates were also subject to interpolation errors and differences in interpolation schemes.

A simple box model used in the original analysis [6] could roughly reproduce the observed surface values and basin inventories obtained dur-

Table 1.1. Sensitivity of global air-sea CO_2 fluxes to changes in wind speed, ΔpCO_2, and wind speed formulation (in Pg C yr^{-1}).

Variable	Adjustment	$k = 0.31 \cdot {}^2M$	$k = 0.0283 \cdot {}^3M$
Wind[a]	+1 m/s (U_{av} = 8.1 m/s)	–1.86 (17%)[b]	–2.58 (34%)
	0 m/s (U_{av} = 7.1 m/s)	–1.59	–1.93
	–1 m/s (U_{av} = 6.1 m/s)	–1.31 (–18%)	–1.4 (–27%)
ΔpCO_2[c]	+1 µatm	–1.38 (–13%)	–1.75 (–9%)
	0 µatm	–1.59	–1.93
	–1 µatm	–1.79 (13%)	–2.12 (10%)
k[d]	+20% (a = 0.37, 0.0339)	–1.90 (19%)	–2.32 (20%)
	0% (a = 0.31, 0.0283)	–1.59	–1.93
	–20% (a = 0.25, 0.0226)	–1.26 (–21%)	–1.55 (–20%)
k[e]	linear = $2.88 \cdot U_{10}$	–1.02 (–36%)	
	quadratic = $0.31 \cdot {}^2M$	–1.59	
	cubic = $0.0238 \cdot {}^3M$	–1.93 (20%)	
k[f]	linear = $3.2 + 2.46 \cdot U_{10}$	–0.92 (–11%)	
	quadratic = $3.2 + 0.26 \cdot {}^2M$	–1.39 (–14%)	
	cubic = $3.2 + 0.0238 \cdot {}^3M$	–1.67 (–15%)	

[a] Change wind speed for each monthly 4° by 5° pixel by 1 or -1 m/s. The winds are six-hour NCEP winds for 1995 re-gridded from the original 2° by 2° grid to a 4° by 5° grid (Doney, pers. com.). The resulting global average winds U_{av} are listed in parentheses.

[b] Percent difference from the standard case.

[c] Change ΔpCO_2 for each monthly 4° by 5° pixel by 1 or -1 µatm.

[d] Change coefficient a in $k = a \cdot {}^2M$ or $k = a \cdot {}^3M$ for each monthly 4° by 5° pixel by the listed amount. The change in a for a quadratic or cubic dependence, respectively, is listed in parentheses.

[e] Change functional dependence of k as listed.

[f] Include a finite "background" gas transfer at low winds.

ing the GEOSECS cruises and offered a means to project future ^{14}C concentrations in the ocean (Figure 1.1). The controversy about the bomb-^{14}C inventory in the ocean and resulting global ^{14}C constraint started when the inventory values [6] were put in question by an independent stratospheric ^{14}C constraint and a global mass balance [17]. In this analysis, the ocean inventory was approximately 25% less for 1974 than the original estimate [6].

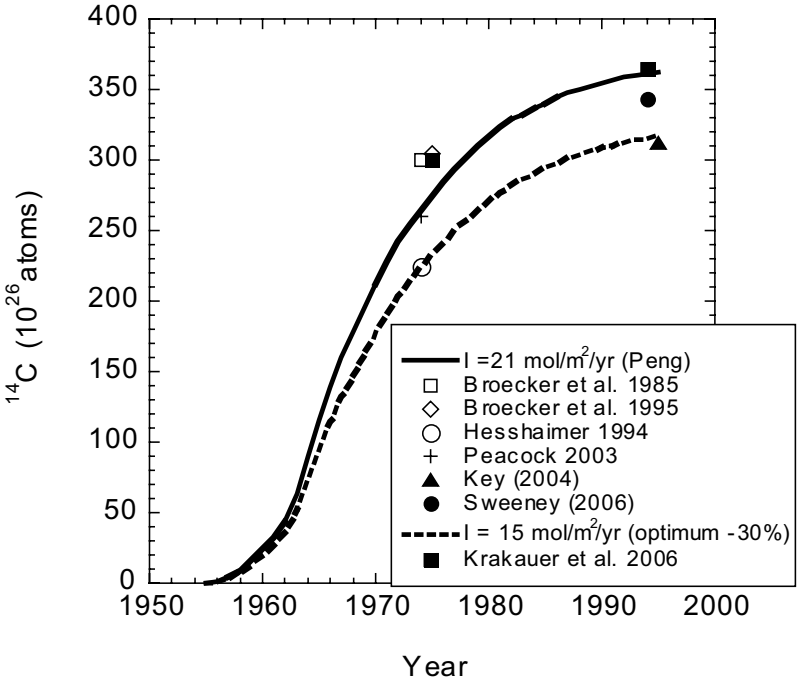

Figure 1.1. Change in bomb-^{14}C inventory over time. The solid line is the result of the box model optimized for basin-wide ^{14}C inventories and surface concentrations [6] as recently rerun by Peng (pers. com.). The dashed line is the model run where the invasion rate, I, was decreased by 30%. The points are the model and data-based estimates listed in Table 1.2.

This was followed by an analysis which suggested the results could be reconciled if a more sophisticated ocean model was used [11]. A more rigorous observation based ^{14}C inventory was performed for the mid-1970s using a model and chlorofluorocarbon (CFC) inventories to estimate the distribution of bomb-^{14}C in the ocean [34]. This estimate was 15% lower than the original estimates [6, 7]. The comparison of estimates based on data from the 1970s is complicated by the rapid rise of ^{14}C in the ocean during this time (Fig. 1.1), the multi-year expeditions that were used to determine the inventories, and the inconsistent estimates of the inventories cited in various publications. Of note is that the original optimized ocean model results [6] fall below the estimates of global inventory (see Fig. 1.1) but that this run is in good agreement with the more recent ocean bomb-^{14}C estimate [34]. For comparison, a model run using the same model as in [6] with an evasion rate 30% below the optimum is also provided.

Currently, inventories are estimated for two time periods from large hydrographic surveys that were conducted in the 1970s (the Geochemical