Modelling Air-sea Exchange of Carbon Dioxide

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1. Introduction

Air-sea exchange of carbon dioxide is normally estimated from measurements of the difference of partial pressure across the air- water interface, followed by multiplication with an empirical exchange coefficient, being a function of primarily wind speed and water temperature, with other parameters involved occasionally as well. Estimates of this exchange coefficient however continue to show a disappointing scatter, reflecting uncertainty, both with respect to basic processes as well as about the resulting flux estimates.

Until now the work of the Risø group has concentrated on evaluating the approaches in common use, and on studying the possible influence of advection and turbulent diffusion between the two measuring levels for the ship measurements providing the ΔpCO_2, typically being 5-20 above the water surface, and 3-8 m below the surface. The advection / diffusion processes are most important for the inhomogeneous/instationary concentration fields for CO_2 encountered quite often, but most often in the coastal waters of special interest in the OMEX context. This part of the work has been the focus of a PhD-study, solving numerically the diffusion/ advection equations in the air- and water layers between the measuring levels. This activity has now come to an end provided a number of conclusions: The importance of the diffusivity/advection is for normal conditions negligible for horizontal scales of variation larger than 5 km. For smaller scales of variation a bewildering number of different solutions are derived that are not easily simplified to practical use. These results are basically derives from the importance of the chemical buffer for CO_2; for other trace gases the advection/diffusion is much more important than for CO_2. The strong control of the chemical buffer on the other hand means, that for air-sea CO_2 exchanges over scales of more than a kilometre or so, the main systematic improvement will be derived from estimates of the chemically controlled behaviour of pCO_2 from the water measuring level and up to the surface, where the real air-sea exchange take place. Minor improved can be achieved as well in keeping track of the wind history for the averaging times involved.

In the final part of the project these principles will be used to provided and constrain the air-sea fluxes of CO_2 in co-operation with the other OMEX-partners, primarily based on the pCO_2 data obtained by the partner ULg.

The Risø effort to model the air-sea flux of CO_2 is taking place within the following tasks:
Task I.2: Inorganic Carbon biogeochemistry and atmospheric CO_2 uptake and release.
Task II.7: Air-Sea exchange of CO_2.
Task IV.2: Carbon sources sinks and fates.

2. Model development

The common method for determination of the air-sea exchange of gases is application of the exchange-coefficient method, where the exchange is determined from the difference in concentration between the air and the water, that is:

$$F = k_p \bullet (C_{w0} - b\ C_{a0}), \qquad (1)$$

where C_{w0} and C_{a0} are the concentrations close to the surface at the water and the air respectively. β is the dimensional Ostwall solubility coefficient, $\beta = K_H RT$, with K_H being the Henry's law constant. The gas exchange coefficient, k_p, has been determined empirically and theoretically by several authors. Empirical expressions are found in Liss and Merlivat (1986) and Wanninkhof (1992), while theoretical evaluation are found Coantic (1986) and by the work of Jacobs *et al.* (1999), using surface renewal theory. In general the authors find k_p to grow with wind speed, or u_{*}, in a power between 1 and 2, dependent on the velocity interval and the authors. Also a dependency on the Schmidt number, $Sc = \nu/D$, in the power between -½ and -¾, with a typical value being -2/3. Woolf (1997) relates k_p to the bubble production at the surface in a way that captures the velocity and Sc dependency described above and adds a bubble-dependency related to the solubility of the individual gases. An important fact is that the theoretical results for the magnitude and variation of k_p basically agree with the empirical forms within the scatter to be expected.

There are two sources of uncertainty when using (1), the first is that it is an in principal stationary and homogenous model, that in its formulation does not allow for evaluation of the importance of in-stationary and inhomogeneous flow and concentration fields. By its form (1) presupposes a stationary and homogeneous water mass and a similar stationary and homogeneous air mass. Most data used to estimate k_p one way or the other interpret the world the same way. For laboratory data this assumption can be fulfilled fairly easily, while field data without doubt are influenced by the non-idealities of the real world. Principally, one must assume, that if the water and the air concentrations are measured just below and just above the surface, the calibrated equation (1) will indeed describe the air-sea flux. The second uncertainty, therefore, is associated with how closely the observed concentrations correspond to the surface values, given that they in practice always must measured in a certain depth and a certain height, typically 2-6 m below the surface and 5-15 m above the surface and, given that the measuring situation always will include some non-stationarity and non-homogeneity.

To study the behavior of the air-sea flux for inhomogeneous and non-stationary conditions, we have developed a diffusion model considering vertical diffusion in the water and in the air and the chemical buffer in the water as well the Webb corrections in the air. Basically, the model looks as follows:

$$\begin{aligned} \frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} &= - \frac{\partial\, Flux}{\partial z} - a\,(C - C_{eq})\,, \\ Flux &= WC + < w'c' > - D\frac{\partial C}{\partial z} \end{aligned} \tag{2}$$

In these equations, the term, $\alpha(C-C_{eq})$, accounts for the buffer effect in the water, with α being of the order of the rate constant of dehydration of H_2CO_3 (k_{H2CO3}) or about 10-20 s^{-1} for $C<C_{eq}$ and of the order of the rate constant for hydrolysis of CO_2 (k_{CO2}) or about 0.025-0.04 s^{-1} for $C>C_{eq}$ (Kjeld, 1999). In the air α is zero. Average values are indicated by capital letters, while lower case letters are used to describe the turbulent part of the variables. In the air the mean vertical velocity, W, is derived from the formulation for the Webb correction to the measured/modeled raw turbulence fluxes. The turbulent part of the flux is determined through a turbulence diffusivity-closure. The model is constructed to match the transfer velocity expression if conditions are homogenous and stationary by stipulating the exchange across the interfacial layer to be described by the exchange coefficient expression. This concept is based on that the transfer coefficient method models situations where all the air-water concentration difference is found at the air-water interface, a situation that is most closely approximated for stationary and horizontally homogenous situations. Also, the empirical transfer rates are well in according with transfer rates derived from first principles characteristics of the surface processes (Coantic, 1986) and the work by Jacob et al (1999). The model solves for the flux-concentrations between an upper and a lower boundary, corresponding to the levels for the water and the air inlets for the concentration measurements in an experimental situation.

The model of (2) have been solved for numerous different situations with perturbations of the concentrations at the upper or lower boundaries, with the perturbations typically being formulated as Gaussian perturbations of different horizontal scales.

From the model computations we can draw a number of conclusions (Kjeld, 1999):

For CO_2 the equation for the water is dominated completely by the chemical buffer, meaning that the advection-diffusion terms in the (12) are negligible in the water. On the other hand this means that knowledge about C_{eq} all the way to the surface becomes very important for estimating the surface exchange, if the concentrations are known at some depth. C_{eq} can be estimated from the total Dissolved Inorganic Carbon, DIC, alkalinity, salinity, pH and temperature. In the air, however, the advection-diffusion part is always important for the flux-profile relation ships.

Taking the true exchange rate as given by (1) with the concentration obtained just on either side of the water surface, the exchange rates estimated by (1) by use of concentrations at the typical measuring levels, at ±5-10 m, or by micrometeorological methods. The different flux estimates agree for perturbations of scales larger than 3-5 km. For smaller scales the different estimates start disagrees, with the micrometeorological method being more sensitive, as illustrated from Figure 1. This aspect can be understood in the light of a simplified stationary version of (2):

$$U \frac{\partial C}{\partial x} = - \frac{\partial}{\partial z} \left(WC - k u_* z \frac{\partial C}{\partial z} \right), \qquad (3)$$

where we have parameterised the turbulence flux by use of a standard formulation for the neutral turbulence diffusivity. In the atmospheric surface layer the vertical gradients of both C and W are very small for homogeneous conditions. For W due to the general formulations for a surface layer and for C because the largest gradient will be found in the water, and especially at the water-air interface. Therefore the vertical fluxes determined at a given height in the air can be more sensitive to an advection term on the left hand side (3), than will the flux determined from the differences at the water-air interface, since these differences are typically much larger.

Finally, we mention that for other trace gases, the flux profile relations in the water is more directly sensitive to the advection-diffusion aspects of a concentration perturbation, because the species are non-reactive in the water. In Figure 2, we show as an example the concentration profiles for He and SF_6 at different phases of the perturbation, indicated by an arrow. The horizontal scale of the perturbation is here the same as in Figure 1, 500 m.

3. Work in the second year of OMEX II-II

Within the second year of OMEX II-II the modelling work, summarised in section 2, was concluded as a PhD project (followed by a post-doc continuation). The project report has been defended and accepted at University of Odense, Denmark (Kjeld, 1999).

1. For variations in the ocean CO_2 concentration of length scales larger than a couple of kilometres there is no significant influence on the surface flux from the advection and diffusion of the CO_2 concentration in neither the water nor the air. The reason for this is that the Carbonate buffer controls almost completely the water concentration, irrespective of advection or turbulence diffusion. These fluxes can therefore be computed by one or several of the standard exchange coefficient methods. However, such methods include uncertainties of the order of a factor 2-5 between the lowest accepted values to the largest accepted values.

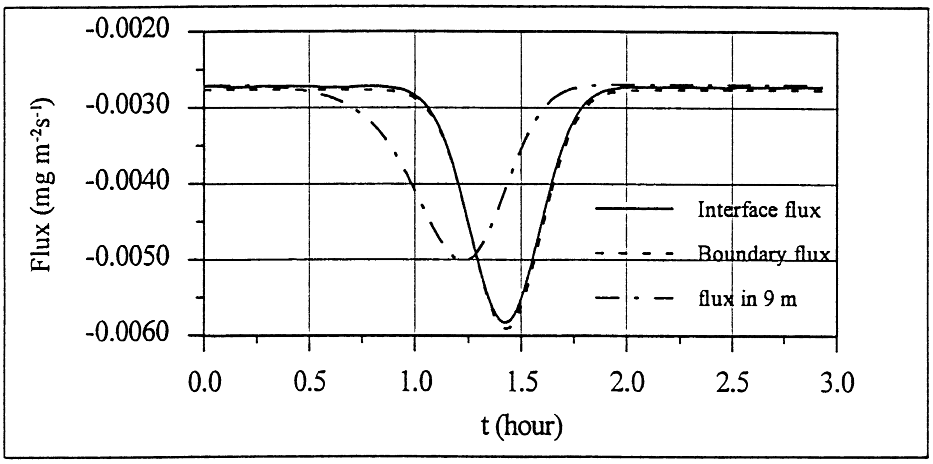

Figure 1. Model computation of the different estimates of the air-water CO_2 flux in response to a Gaussian concentration perturbation at 6-m depth. The perturbation has a horizontal scale of 500 m and is drifting by the measuring position with a wind induced current corresponding to a u* = 0.3 m s^{-1}. The Boundary fluxes are those one would obtain from measurements of the CO_2 concentrations at 6-m depth and 10-m height, while the interface flux is estimated from (1) and the flux at 9 m is estimated from the concentration vertical concentration gradient.

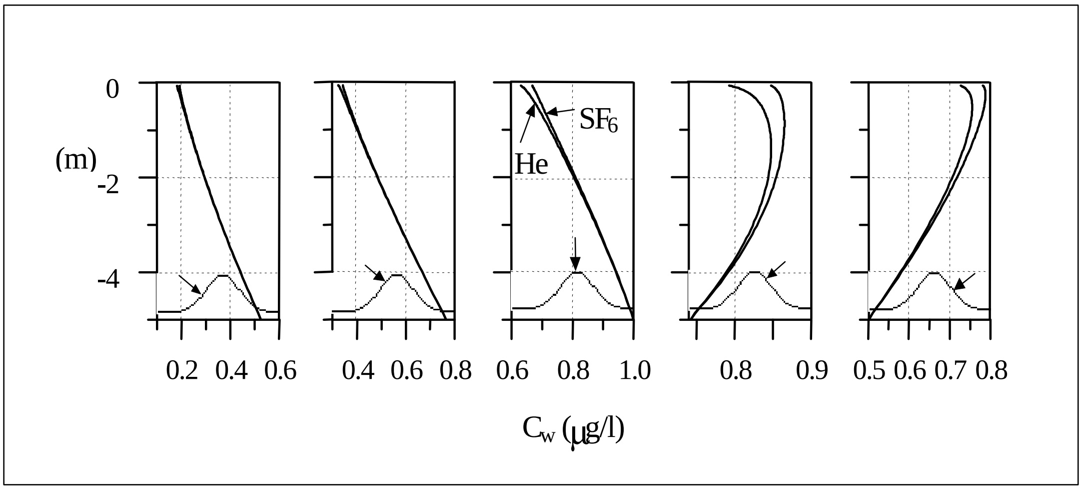

Figure 2. Concentration profiles for He and SF_6 *versus* depth (m) modeled at different phases of a concentration perturbation, with a horizontal length scale of 500 m, drifting by a measuring point with an wind driven current corresponding to an u_* = 0.3 m s^{-1}. The phase along the perturbation when the profile is estimated is indicated by an arrow on the Gaussian form for each profile in the figure.

These uncertainties however can not be explained by the diffusion. They may possibly be associated with the behaviour of the aqueous pCO_2 very close to the surface, and with ill defined experimental conditions.

2. For smaller scales of the variation, less than a kilometre or so, the different processes start interacting. However, generally the micrometeorological derived flux is more likely to deviate from the true interfacial flux, than is the boundary flux.

3. Changes in the water concentration of CO_2, due temperature, alkalinity, salinity *etc.* will create differences between the true interfacial flux and the boundary flux. Therefore it is important to try to extrapolate the CO_2 concentration to the surface taking into account the vertical variation of these

parameters.

4. For other trace gases in the water, the diffusion plays a much large role than for CO_2, since these gases are without a controlling buffer.

Simultaneously field data from the first OMEX II-II cruises on pCO_2, as obtained by the partner ULg (partner number 22) and the transformation of these data to surface fluxes has been initiated. These initial results show very indicate small deviations from the transfer-coefficient predictions only.

The data from the following cruises has obtained from BODC and are being treated:
Belgica BG9714 (Legs B, C, D), *Belgica BG9815* (Legs B, C, D),
Charles Darwin CD110 (Leg B), *Charles Darwin CD114* (Legs A and B),
Meteor M43/2
We intent an integrated presentation of the flux estimates in co-operation with ULg in the fall this year.

The modelling work has been conducted within the framework of **Tasks I.2** and **II.7**. The two tasks to a large extent amount to a similar development from the Risø perspective, since they both demand understanding of the processes responsible for the air-sea exchange in the near surface water and air masses. The modelling of the field data is slightly behind schedule because our modelling development has gone slower than anticipated.

Within the context of OMEX II-II, the participants have attended the annual workshop in Plymouth in April this year. The participants have as well participated in the EC-ENVIRONMENT European Climate Science Conference, Vienna, October 19-23, 1998 and the MAST Meeting on: Air-Sea-Ice Studies, Brussels, January 7-8 1999 (Larsen, 1998, Larsen, 1999)

4. Work to be conducted the coming year

In the coming the developed models will be used to derive the air-sea fluxes of CO_2 from the cruises conducted by partner ULg, and to contribute to the general modeling of the interfacial CO_2 fluxes for the OMEX project.

5. References

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