Modeling Air-sea Exchange of Carbon Dioxide.

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1. Introduction

Air-sea exchange of slowly dissolving gases is mostly estimated by means of the transfer-velocity relations based on the Liss and Merlivat, and the Wanninkhof studies, that offer integration of many data sets, and seems satisfactory integrations of these data, although with substantial scatter (MacIntyre et al, 1995). However the small transfer rates implied by these relations indicate that in the natural environment fluxes and concentrations will often not be in the equilibrium, implicitly assumed when employing the transfer velocity relations. Such non-equilibrium between flux and concentrations is most likely to occur coastal areas and/or in areas with strong biological activity, where rapid changes over space and time may occur in both the water and air concentrations of the trace gas species considered. Within the OMEXI project such highly variable CO_2 concentrations in the marginal waters are reported by e.g. Keir et al (1997).

2. Model development

To study the behaviour of the air-sea flux for such inhomogeneous and non-stationary conditions, we have developed a diffusion model considering the 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:

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + W\frac{\partial C}{\partial z} = -\frac{\partial\, Flux}{\partial z} - a(C - C_{eq}),$$

$$Flux = WC + \langle w'c' \rangle - D\frac{\partial C}{\partial z}$$

In these equations $\alpha(C-C_{eq})$ accounts for the buffer effect in the water, with C_{eq} being the CO_2 concentration in equilibrium with the total dissolved inorganic carbon. Average values are indicated by capital letters, while lower case letters are used to describe the turbulent part of the variables. In the air α is zero and 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 expressions, described my Liss and Merlivat and Wanninkhof (McIntyre et al, 1995). 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. The model solves for the flux-concentrations between an upper and a lower boundary, corresponding typically to the levels for the water and the air inlets for the concentration measurements in an experimental situation. Model estimates of the flux response to concentration changes are illustrated by for a Gaussian change in the water concentration at the lower boundary for CO_2 in Figures 1 (Kjeld, 1998).

The exchange coefficients in the literature (McIntyre et al, 1995) have been shown to be consistent with exchange coefficient for the interfacial processes based on the flow exchange model (Kjeld, 1998)

3. Work in the first year of OMEXII phase 2.

Within the first year of OMEXII, 2 a the final phase on a PhD project focused on the exchange modelling, as described in section 2, has been conducted. The project report is presently being finalised (Kjeld, 1998).
In the context of this project the surface exchange of CO_2 and other trace gases has been modelled and compared with those exchange rates predicted by the transfer coefficients for characteristic pCO_2 variations as reported in OMEXI (Keir et al, 1996).

Simultaneously field data from the first OMEXII-1 cruises on pCO2 has been received from 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 modelling work has been conducted within the framework of Task I.2 and II.7, while so far only data from Task II.7 have been considered The modelling of the field data is slightly behind schedule because the modelling development has gone slightly slower than anticipated.

Within the context of OMEXII, the participants have participated in several workshops, notably the OMEX workshops in the fall of 1997 in Paris and the Lisbon workshop in the spring of 1998. The participants have as well participated in the EC workshops air-sea exchange at NILU in June 1997 and on Green house gases in Orvieto in November 1997 (Larsen, 1997,Liss et al, 1997,Larsen et al, 1997)

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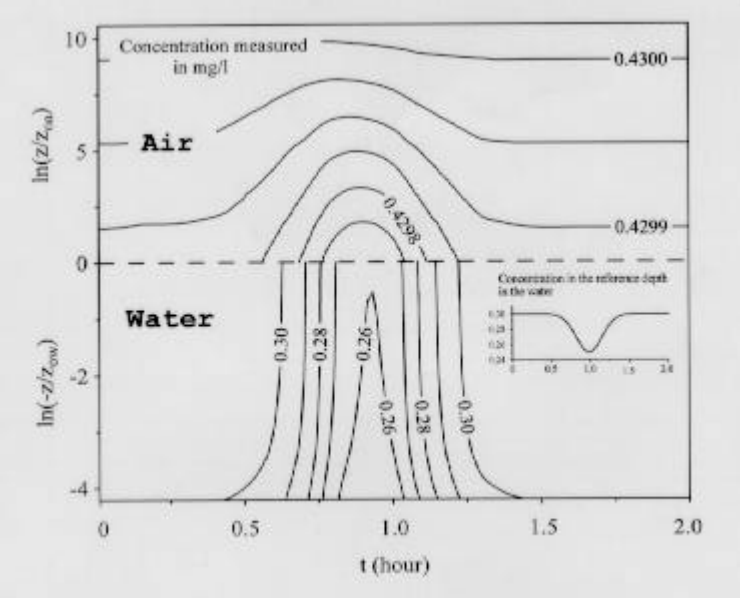

Figure 1. Air and water concentration response to a Gaussian concentration perturbation at 6 meters depth.