

# *Dynamics of the Surface Ocean—Deep Sea Carbon Exchange in its Relation to the Atmosphere—Surface Ocean Exchange*

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## ABSTRACT

Within the framework of a one compartment surface ocean for total inorganic carbon the adjustment to additional atmospheric carbon is conventionally described by a Revelle buffer factor  $\xi_m$ , which controls the sharing ratio of carbon between atmosphere and the surface ocean. It is suggested in this paper that the surface ocean—deep sea exchange may be formally modelled in a similar fashion by introducing a Revelle buffer factor  $\xi_d$  for the deep sea, such that, together with  $\xi_m$ , the final state distribution ( $t \rightarrow \infty$ ) between atmosphere, surface ocean and deep sea may be described.

The dynamic counterpart to the sharing ratios is obtained by introducing the nonproportionality factors  $\xi_{ma}$ ,  $\xi_{da}$ ,  $\xi_{md}$ ,  $\xi_{dm}$  as parameters into the corresponding set of differential equations. Using the boundaries imposed by final state analysis a one-parameter expression is obtained which may allow a faster carbon uptake than the corresponding linear expressions.

If the terrestrial biota are a substantial source of additional atmospheric carbon, then such a model as suggested may explain a faster uptake of atmospheric carbon by the deep sea, and with it the observed airborne fraction of  $\text{CO}_2$ .

## INTRODUCTION

It is generally recognized that within the framework of a two-compartment ocean, there is a relatively fast equilibration for additional atmospheric carbon dioxide between the atmosphere and the surface ocean and a relatively slow and rate-determining exchange for carbon between the surface ocean and the deep sea. The latter process is still incompletely understood, but a dynamic approach guided by the atmosphere-surface ocean exchange such as suggested below may help to provide an overall dynamic understanding of the processes encountered. At a later stage, one must consider the detailed photosynthesis and degradation processes, including the

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accompanying processes of calcite formation and dissolution, and the transport processes between the layers of different biotic activity and physical chemical transformations, such as have been suggested in the pioneering work of Bacastow *et al.* (1973), Bolin *et al.* (1959), Broecker *et al.* (1971), Broecker (1974) and Keeling (1973). We propose in this paper to describe the dynamic interaction between any two compartments, A and B, with the following nonlinear differential equation or its corresponding linearized form, which show a dramatically different relaxation behaviour from the corresponding linear expression (Kohlmaier *et al.*, 1978; and Rodhe *et al.*, 1979).

$$\frac{dN_a}{dt} = k_{ba}^{(\beta)} N_b^\beta - k_{ab}^{(\alpha)} N_a^\alpha \quad (1)$$

where  $\alpha$  and  $\beta$  are real numbers, as determined by the detailed processes involved,  $k_{ba}^{(\beta)}$  and  $k_{ab}^{(\alpha)}$  are the corresponding rate constants, and  $N_a$  and  $N_b$  are the total carbon masses of the compartments A and B. A convenient form related to the empirical information is obtained by expansion around an assumed stationary state before perturbation by additional  $\text{CO}_2$ .

$$\frac{d(N_a^\circ + \Delta N_a)}{dt} = k_{ba} (N_b^\circ + \beta \Delta N_b) - k_{ab} (N_a^\circ + \alpha \Delta N_a) \quad (2)$$

where

$$k_{ba} \equiv k_{ba}^{(\beta)} N_b^{\circ \beta-1}; \quad k_{ab} \equiv k_{ab}^{(\alpha)} N_a^{\circ \alpha-1}$$

and

$$k_{ba} N_b^\circ = F_{ba}^\circ = F_{ab}^\circ = k_{ab} N_a^\circ \quad (2a)$$

Considering then only the perturbation from the original steady state  $N_a^\circ$  and  $N_b^\circ$ , we may write eq. 2 equivalently:

$$\frac{d\Delta N_a}{dt} = \frac{F_{ba}^\circ}{N_b^\circ} \beta \Delta N_b - \frac{F_{ab}^\circ}{N_a^\circ} \alpha \Delta N_a \quad (3a)$$

or with the exchange times of compartment B with respect to A (and A with respect to B)

$$T_b = N_b^\circ / F_{ba}^\circ \quad \text{and} \quad T_a = N_a^\circ / F_{ab}^\circ$$

we obtain:

$$\frac{d\Delta N_a}{dt} = \frac{\beta}{T_b} \Delta N_b - \frac{\alpha}{T_a} \Delta N_a \quad (3b)$$

Finally we obtain the adjustment time from the above equation, by setting

$$\Delta N_b = -\Delta N_a$$

$$\frac{d\Delta N_a}{dt} = - \left( \frac{\beta}{T_b} + \frac{\alpha}{T_a} \right) \Delta N_a = - \frac{1}{T_{ab}} \Delta N_a \quad (4)$$

with

$$\frac{1}{T_{ab}} = \frac{\beta}{T_b} + \frac{\alpha}{T_a} \quad (5)$$

If  $\alpha$  and  $\beta$  are not equal to one, but, for instance, greater than one, then the adjustment time will become smaller, and the relaxation process will become faster than that obtained from the corresponding linear theory. In most models of the global carbon cycle such nonproportionality factors as  $\alpha$  or  $\beta$  have been used for the exchange between the atmosphere and the surface oceans, whereas the interaction for the surface ocean–deep sea subsystem has been modelled either linearly (Bacastow *et al.*, 1973; Bolin *et al.*, 1959; Bolin *et al.*, 1979; Keeling, 1973) or by eddy diffusion, as suggested by Oeschger *et al.* (1975), or by additional advective or particulate transport (Bolin *et al.* 1959; Bolin *et al.*, 1979; Broecker *et al.*, 1971; Broecker, 1974). We suggest that this exchange may also be modelled by the general form of equation 1. If this, indeed, is a correct assumption, then we may have an explanation for the missing sink of atmospheric carbon: by introducing the nonlinearities or the corresponding nonproportionalities between the surface the ocean and deep sea we obtain an uptake of CO<sub>2</sub> by the deep ocean, which may be much higher than previously postulated in the corresponding two box models.

## 2. DISCUSSION OF THE MODEL

Most models of the global carbon cycle consider explicitly or implicitly an evasion factor  $\xi_m$ , sometimes called the Revelle factor (Bacastow *et al.*, 1973; Keeling, 1973) (slightly different definitions are used in various contexts, see Wagener (1979)). The exchange of carbon between the atmosphere and the surface ocean mixed layer is defined by:

$$\frac{\Delta P_{CO_2}}{P_{CO_2}^o} = \xi_m \frac{\Delta \Sigma [C]}{\Sigma [C]^o} \quad (6)$$

where a relative change in the partial pressure of CO<sub>2</sub> in the atmosphere,  $\Delta P_{CO_2} / P_{CO_2}^o$ , is related to a smaller relative change in the total inorganic carbon concentration in the oceans,  $\Delta \Sigma [C] / \Sigma [C]^o$ , expressed by  $\xi_m > 1$ , and found to be approximately equal to ten for the upper ocean. In a compartment (or box) model, with  $N_a$  being the total mass of carbon in the atmosphere, and  $N_m$  being the carbon mass in the surface ocean, we may then, by integrating over the corresponding volumes, write equivalently:

$$\frac{\Delta N_a^{eq}}{N_a^o} = \xi_m \frac{\Delta N_m^{eq}}{N_m^o} \quad (7)$$

where  $\Delta N_a^{\text{eq}}$  and  $\Delta N_m^{\text{eq}}$  stand for the equilibrated additional carbon.

We should like to introduce a more general definition of the Revelle factor;

$$\frac{\Delta P_{\text{CO}_2}}{P_{\text{CO}_2}^{\circ}} = \xi(z) \frac{\Delta \Sigma[\text{C}]_z}{\Sigma[\text{C}]_z^{\circ}} \quad (8)$$

Here  $\xi(z)$  is taken to depend on the depth  $z$ , since we may expect quite different behaviour of  $\text{CO}_2$  equilibration in different layers of the ocean.  $\xi(z)$  as a function of depth may be, at least in principle, determined from a corresponding equilibration experiment. We may model this dependence by an empirical continuous function  $\xi(z)$  or by a discontinuous distribution, which in the simplest case may be a two-compartment ocean. In the formulation of the compartment theory, we can rewrite eq. 8, by integrating over the corresponding volumes. Introducing two weighted Revelle factors, one for the surface ocean mixed layer  $\xi_m$ , and one for the deep sea,  $\xi_d$  we obtain:

$$\frac{\Delta N_a^{\text{eq}}}{N_a^{\circ}} = \xi_m \frac{\Delta N_m^{\text{eq}}}{N_m^{\circ}} = \xi_d \frac{\Delta N_d^{\text{eq}}}{N_d^{\circ}} \quad (9)$$

The compartment D, including the polar waters as well as the deep sea, may be equilibrated directly or indirectly via the surface ocean as given in Fig. 1. The parameter  $\kappa$  ( $0 < \kappa \leq 1$ ) gives the fraction of the total atmosphere-ocean exchange (FAW) which proceeds via the surface ocean; the parameter  $K$  allows for additional advection such that all fluxes obey complex balancing rather than detailed balancing for  $K = 0$ .

Setting up the differential equations we introduce four nonproportionality factors ( $\xi_{ma}$ ,  $\xi_{md}$ ,  $\xi_{da}$ , and  $\xi_{dm}$ ) which are determined or limited within the concept of final state analysis:

$$\frac{d\Delta N_a}{dt} = k_{ma} \xi_{ma} \Delta N_m - k_{am} \Delta N_a + k_{da} \xi_{da} \Delta N_d - k_{ad} \Delta N_a \quad (10a)$$

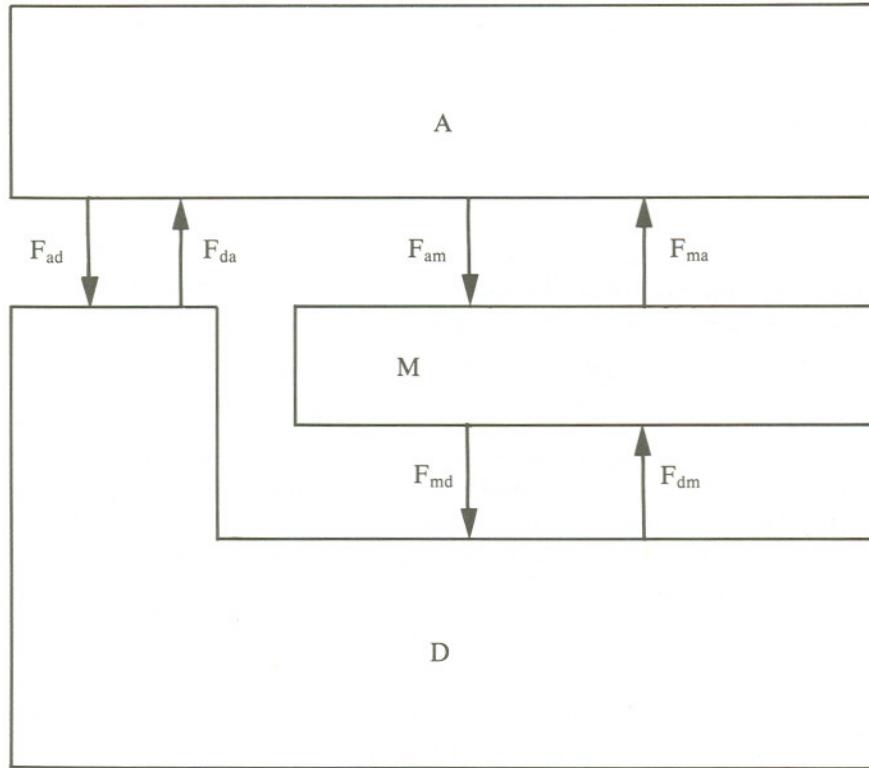
$$\frac{d\Delta N_d}{dt} = k_{md} \xi_{md} \Delta N_m - k_{dm} \xi_{dm} \Delta N_d + k_{ad} \Delta N_a - k_{da} \xi_{da} \Delta N_d \quad (10b)$$

with

$$-\frac{d\Delta N_m}{dt} = \frac{d\Delta N_a}{dt} + \frac{d\Delta N_d}{dt} \quad (10c)$$

after all external inputs have been turned off. If the rate formulation, as given above, has been stated correctly, then this set of differential equations has to fulfill the equilibrium conditions of eq. 9. In the equilibrium case,  $d\Delta N_a^{\text{eq}}/dt$ ,  $d\Delta N_m^{\text{eq}}/dt$  and  $d\Delta N_d^{\text{eq}}/dt$  become zero. Three limiting cases are discussed in the context of the model.

Figure 1: Model for atmosphere–surface ocean–polar water–deep sea exchange.



Legend to Fig. 1

$$F_{am}^{\circ} = k_{am} N_a^{\circ} = \kappa FAW - (1 - \kappa) K$$

$$F_{ma}^{\circ} = k_{ma} N_m^{\circ} = \kappa FAW + (1 - \kappa) K$$

$$F_{ad}^{\circ} = k_{ad} N_a^{\circ} = (1 - \kappa) FAW + (1 - \kappa) K$$

$$F_{da}^{\circ} = k_{da} N_d^{\circ} = (1 - \kappa) FAW - (1 - \kappa) K$$

$$F_{md}^{\circ} = k_{md} N_m^{\circ} = FMD - (1 - \kappa) K$$

$$F_{dm}^{\circ} = k_{dm} N_d^{\circ} = FMD + (1 - \kappa) K$$

$$FAW = \frac{1}{2} (F_{am}^{\circ} + F_{ma}^{\circ} + F_{ad}^{\circ} + F_{da}^{\circ})$$

$$FMD = \frac{1}{2} (F_{md}^{\circ} + F_{dm}^{\circ})$$

$$N_m^{\circ} = \kappa N_m^{\max} ; N_d^{\circ} = N_d^{\min} + (1 - \kappa) N_m^{\max}$$

Case I:  $\kappa = 1, K = 0$ ; implying  $k_{ad} = k_{da} = 0$ ; all carbon is exchanged via the mixed layer. Applying the stationary assumption we find from eq. (10a):

$$\frac{\Delta N_a^{\text{eq}}}{N_a^{\circ}} = \xi_{ma} \frac{\Delta N_m^{\text{eq}}}{N_m^{\circ}}; \xrightarrow{\text{eq. (9)}} \xi_{ma} = \xi_m \quad (11a)$$

and thereby:

$$\frac{1}{T_{am}} = k_{am} + \xi_m k_{ma} \quad (11b)$$

Typical values of the rate constants for the three cases discussed are contained in table 1; using these data we find a response time  $T_{am}$  of about 1 year. Applying the stationarity condition to eq. (10b) we find:

$$\xi_{md} \frac{\Delta N_m^{\text{eq}}}{N_m^{\circ}} = \xi_{dm} \frac{\Delta N_d^{\text{eq}}}{N_d^{\circ}}; \xrightarrow{\text{eq. (9)}} \frac{\xi_{md}}{\xi_{dm}} = \frac{\xi_m}{\xi_d} \quad (11c)$$

This equation gives a relation between the mixed layer and the deep sea only, since no relation to the atmosphere is contained. If  $\xi_m = \xi_d = \xi$ , then any value for  $\xi_{md} = \xi_{dm}$  will fulfill the second part of eq. (9). An agreement with the box-diffusion model of Oeschger *et al.* (1975) may be reached, when the relative deep ocean uptake capacity  $\theta$  ( $\theta = h_d/h_m$ ) is related to the nonproportionality factor  $\xi_{md}$  (Siré *et al.*):

$$\xi_{md} = \frac{a \theta}{k_{md}} \quad (12)$$

Using the rate constants of Table 1 and  $a = 0.037 \text{ yr}^{-1}$  ( $a$  is the integrated growth coefficient) then the three values for  $\xi_{md} = 5.2, 8.0$  and  $10.9$  are obtained depending on whether the biota are considered a mild sink, neutral, or a mild source (corresponding to  $\varepsilon = -0.1; 0$  and  $+0.1$ ).

Case II:  $\kappa = 0.75; K = 0$ ; modelling the polar regions as part of the deep sea. Applying the stationarity condition to eq. (10a) we obtain:

$$\frac{\Delta N_a}{N_a^{\circ}} = \xi_{ma} \frac{\Delta N_m}{N_m^{\circ}} \quad \text{and} \quad \frac{\Delta N_a}{N_a^{\circ}} = \xi_{da} \frac{\Delta N_d}{N_d^{\circ}} \quad (13)$$

The above relations together with eq. 9 imply:

$$\xi_{ma} = \xi_m; \xi_{da} = \xi_d \quad (14)$$

Again as above in case I, we obtain from eq. (10c):  $\xi_{md}/\xi_{dm} = \xi_m/\xi_d$ . According to eq. (12) and Table 1,  $\xi_{md}$  becomes smaller by  $23.3/21.1$  for the same surface ocean-deep sea flux, while an additional flux via the polar waters is obtained.

Case III:  $\kappa = 0.75, K = 20 \text{ Gt C/a}$ ; detailed (pairwise) balancing is no longer maintained, while complex balancing for the steady state is still considered. If allowance is made for the observed fact that there is relatively more release of  $\text{CO}_2$  than uptake in

the midlatitudes, and that the opposite situation exists in the polar regions, the fluxes and rate constants as given in table 1 may arise. Again here, as in case II, all three compartments are coupled directly. The equilibrium condition of eq. (9), however, cannot be maintained because of the disparity of opposing fluxes. This leads to the result that the effective buffer factors are different from the ones assumed in eq. (9).

Table 1:  
Calculation of rate constants for three cases of flux partitioning

	$k_{am}$	$k_{ma}$	$k_{ad}$	$k_{da}$	$k_{md}$	$k_{dm}$
$K = 0$	$\frac{1}{8.8}$	$\frac{1}{11.7}$	0	0	$\frac{1}{31.1}$	$\frac{1}{1250}$
$\kappa = 1$	$\frac{1}{11.7}$	$\frac{1}{11.7}$	$\frac{1}{35}$	$\frac{1}{1890}$	$\frac{1}{23.3}$	$\frac{1}{1260}$
$K = 20$	$\frac{1}{12.7}$	$\frac{1}{10.8}$	$\frac{1}{28}$	$\frac{1}{2520}$	$\frac{1}{28}$	$\frac{1}{1080}$
$\kappa = 0.75$						

$$N_a^o = 700 \text{ Gt C, FAM} = 80 \text{ Gt C/a}$$

$$N_m^{\max} = 933 \text{ Gt C, FMD} = 30 \text{ Gt C/a}$$

$$N_d^{\min} = 37,500 \text{ Gt C (all data with reference to 1975)}$$

scaling parameter :

$$0 < \kappa \leq 1$$

$$K = 20 \text{ Gt C/a}$$

### 3. RESULTS AND CONCLUSIONS

Based on a consistent set of nonlinear (nonproportional) equations with the boundary conditions of stationarity for Revelle equilibration for the surface ocean as well as for the deep sea, we have presented a simple dynamic model, which may allow for a much faster adjustment to additional  $\text{CO}_2$ , than the *ab initio* linear box-models. The size of the surface ocean mixed layer can be described in this model by its physical boundary, the thermocline, and need not be expanded to a 5- to 7- fold reservoir size (Bacastow *et al.*, 1973; Keeling, 1973). Calculations show that, for a N 4,4% growth in carbon input into the atmosphere, the remaining airborne fraction is about 56%. Calculations are at present extended to include the detailed terrestrial biosphere.

The author is aware that a more sophisticated general transport equation concept is needed to settle the question of the fate of the additional atmospheric  $\text{CO}_2$ . However, this simple model may help to stimulate more theoretical and empirical

research in the direction of surface ocean–deep sea exchange. Decisions on future energy alternatives will depend not only on technological and economical feasibility, but also on the environmental impact. In that sense, with a new coal technology emerging it will be important to know how much of the CO<sub>2</sub> emitted into the air can ultimately be absorbed by the largest sink, for carbon dioxide, the deep sea.

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#### REFERENCES

- Bacastow, R., and Keeling, C.D. (1973). Atmospheric Carbon Dioxide and Radiocarbon in the Natural Carbon Cycle: II. Changes from A.D. 1700 to 2070 as Deduced from a Geochemical Model. In Woodwell, G.M., and Pecan, E.V. (Eds.) Carbon in the Biosphere. AEC Symposium Series 30: 86–135, NTIS. US Dept. Commerce, Springfield, Virginia.
- Bolin, B., and Erikson, E. (1959). Changes in the Carbon Dioxide Content of the Atmosphere and Sea due to Fossil Fuel Combustion. In Bolin, B. (Ed.) The Atmosphere and the Sea in Motion 130–142, The Rockefeller Int. Press. New York.
- Bolin, B., Degens, E.T., Kempe, S., and Ketner, P. (1979). The Global Carbon Cycle. SCOPE Report No 13., John Wiley New York: 491 pages.
- Broecker, W.S. (1974). Chemical Oceanography. Harcourt Brace Jovanovich, New York: 214 pages.
- Broecker, W.S., Li, Y.-H., and Teng, T.-H. (1971). Carbon Dioxide–Man's Unseen Artifact. In Hood, D.W. (Ed.) Impingement of Man on the Oceans. 287–324, Wiley Interscience, New York.
- Keeling, C.D. (1973). The Carbon Dioxide Cycle. In Rasool, S. (Ed.) Chemistry of the Lower Atmosphere. 251–329, Plenum Press, New York.
- Kohlmaier, G.H., Fischbach, U., Kratz, G., and Siré, E.O. (1978). A non-linear interaction model between land biota and the atmosphere. In Williams, J. (Ed.) Carbon Dioxide, Climate and Society. IIASA Proceedings. 111–119, Pergamon Press, Oxford.
- Kohlmaier, G.H. (in Press). Elementary Dynamic Control Mechanisms of Pools and Fluxes within Global Biogeochemical Cycles as applied to the Carbon Cycle. Submitted to Ecological Modelling.
- 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.
- Rodhe, H., and Björkström, A. (1979). Some consequences of non-proportionality between fluxes and reservoir contents in natural systems. *Tellus*, 31, 269–278.
- Siré, E.O., Kratz, G., Fischbach, U., Bröhl, H., and Kohlmaier, G.H. (1980). Analytische Diskussion des Austauschs von Kohlendioxid zwischen Atmosphäre und Ozean an Hand eines Advektions-Diffusions-Modells, submitted and accepted by Berichte der Bunsengesellschaft für Physikalische Chemie., Darmstadt, W.-Germany.
- Wagener, K., (1979). The Carbonate System of the Ocean. In Bolin, B., Degens, E.T., Kempe, S., and Ketner, P. (Eds.) The Global Carbon Cycle. SCOPE Report No 13, 251–258, John Wiley, New York.