

3.4.4. Towards a Global Ocean Carbon Model*

by

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ABSTRACT. – The general structure of a three-dimensional model of carbon fluxes in the ocean is described. Using the computed currents of a realistic model of the general oceanic circulation, the components which are relevant to the carbon cycle are transported as dynamically passive properties of the water. As a first step, the transport of inorganic carbon is simulated, neglecting all biological processes. As boundary condition, chemical equilibrium between the surface of the ocean and the atmosphere is assumed; no empirical buffer factors or flux rates are used. The computed distributions of the chemical quantities seem to be realistic within the range of the neglects. The role of winter convection in high latitudes to the uptake capacity of the ocean for excess CO_2 in the atmosphere is demonstrated by two extremal assumptions.

INTRODUCTION

During the past decade, a number of mathematical models have been proposed to describe the storage of CO_2 in the ocean (e.g., Oeschger and Siegenthaler, 1973; Björkström, 1981; Vieceili, 1982). In general, these models describe the ocean as a system of a few linked boxes with known – i.e. tuned to the distribution of other geochemical tracers – flux rates between the boxes. The gas exchange between ocean and atmosphere is parameterized by a linear – sometimes latitude dependent – buffer factor. The transport of CO_2 into the deep waters is often described by a constant coefficient of eddy diffusion in the order of $2 \text{ cm}^2/\text{s}$. An extensive state-of-the-art compilation up to 1981 is given by Björkström et al. (1981). These models can be tuned to give a satisfactorily description of the observed increase of atmospheric CO_2 content within the past century, which can be regarded as a small perturbation of the pre-industrial state. For stronger perturbations, which are expected for the next centuries, the models are less appropriate for a reliable prognosis, because

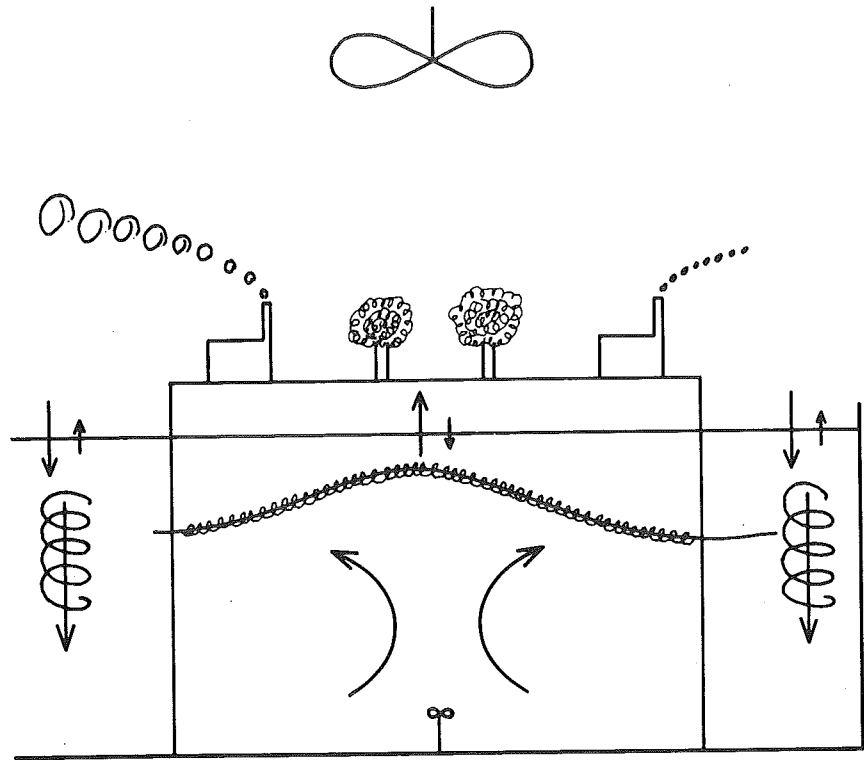
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- the buffer factor changes with increasing CO_2 ,
- if the increased CO_2 creates a climatic change, the circulation of the ocean will change too, changing the flux rates in a way that cannot be determined from today's observations,
- last but not least: the ocean is a continuum; the description by 20 or less boxes is a rather poor representation.

A rough sketch of inorganic carbon fluxes in the ocean is given in Fig.1.



On the continents, the exchange with the biosphere and fossil fuel burning yields sources and sinks of CO_2 . In the atmosphere, strong mixing takes place. The gas exchange at the interface atmosphere-ocean is dependent on the temperature. In the arctic regions, cooling produces deep water, by which CO_2 is transported downwards. In tropical oceans, there is a constant upwelling of CO_2 into the atmosphere. In the inner parts of the ocean, diffusion is small; it is widely accepted that large-scale transports are caused mainly by advection.

A carbon cycle model of the ocean should elucidate essentially three questions:

- (1) how does CO_2 enter the ocean?
- (2) how is it transported into the ocean?
- (3) what are the effects of biological sources and sinks in the ocean?

In this paper, an approach is proposed to answer the first two questions.

1. Dynamics of CO₂-buffering

At present, the ocean contains about half as much of CO₂ as the atmosphere, but about 50 times more dissolved inorganic carbon. It is usual to relate changes of the atmospheric CO₂ content to the sum of the dissolved fractions rather than to the gaseous fraction which is in direct equilibrium with the atmosphere. The uptake capacity of the ocean for excess CO₂ in the atmosphere is much less than would be suggested by assuming proportionality to the present equilibrium values. The reason for this behaviour is, of course, the ability of the carbonate ions to disassociate.

Let us denote by $s = [\text{CO}_2]$ the concentration of undissociated carbon dioxide, $h = [\text{H}^+]$ the concentration of H⁺ ions, P the partial pressure of CO₂ in the atmosphere. In equilibrium, we have $s = \alpha P$, where α is the solubility, dependent on temperature. The law of mass action requires

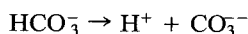
$$[\text{HCO}_3^-] = \frac{K_1}{h} s$$

and

$$[\text{CO}_3^{2-}] = \frac{K_2}{h} [\text{HCO}_3^-]$$

where K_1 , K_2 are the apparent disassociation constants.

The determination of the new equilibrium state, when the atmospheric content is changed, is complicated by the fact that at any disassociation process, for instance



a new hydrogen ion is formed, shifting the equilibrium towards the undissociated fraction, whereas the difference $[\text{CO}_3^{2-}] - [\text{H}^+]$ remains constant. The equilibrium is also influenced by all other molecules that may be subject to disassociation.

The combined effect of the most important disassociating fractions in the ocean is summarized by the alkalinity

$$A = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + \frac{K_w}{h} - h + \frac{B_t}{1 + \frac{h}{K_B}}$$

where K_w , K_B are the disassociation constants of water and borate, and

$$B_t = \text{B(OH)}_3 + \text{B(OH)}_4^-, \quad \text{B(OH)}_4^- = \frac{K_B}{h} \text{B(OH)}_3$$

The alkalinity has the property that it remains constant for any dissoziation process, irrespective of the form of the reaction. Fig. 2 shows the alkalinity as a function of h and temperature, assuming a 300 ppm partial pressure of CO_2 in the atmosphere and measured values of α , B_t , K_1 and K_2 . Consider, for instance, a water body sinking near the pole with low temperature and high CO_2 content, drifting near the bottom towards the equator, heated up after its upwelling, releasing CO_2 to the atmosphere and travelling back near the surface to the pole. During its history, nearly all properties change, but the alkalinity remains constant; it remains on the same isoline of Fig. 2. (In this consideration, biological sources and sinks are ignored.)

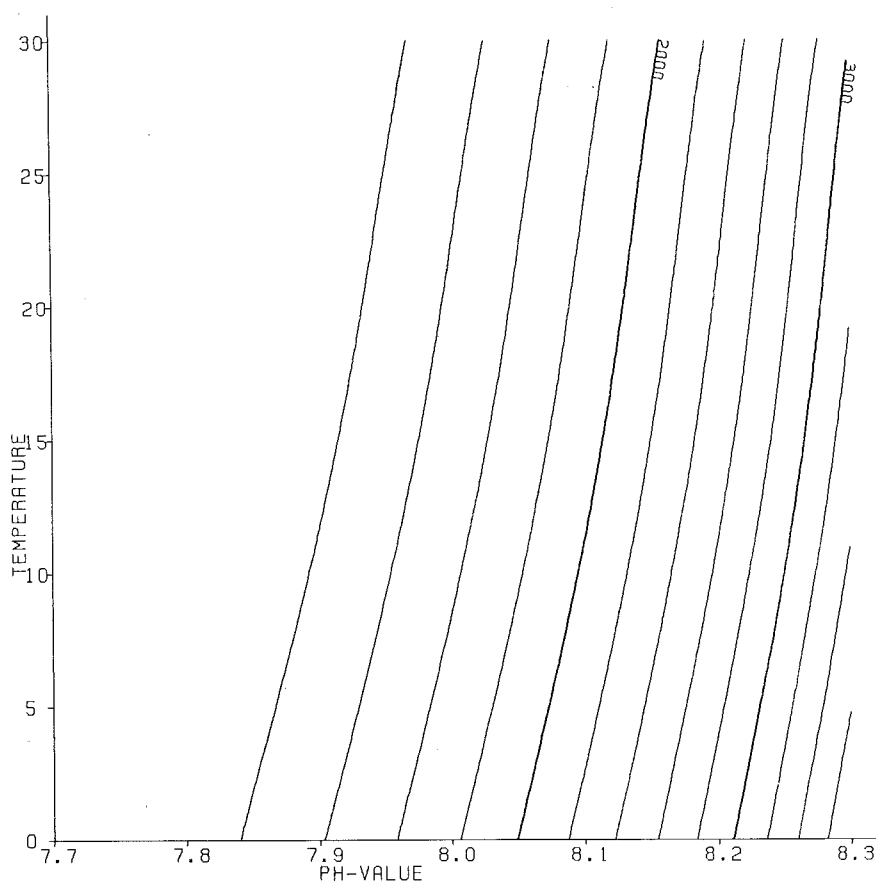


Fig. 2. Alkalinity as function of temperature and pH-value at 300 ppm.

Let us denote by $C = \Sigma \text{CO}_2$ the sum of the concentrations of all carbonate fractions; then we have C and A as functions of s and h

$$A = \left(2 \frac{K_1 K_2}{h^2} + \frac{K_1}{h} \right) s + \frac{K_w}{h} - h + \frac{B_t}{1 + \frac{h}{K_B}}$$

$$C = \left(1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2} \right) s$$

For a small change, caused for instance by increasing atmospheric content, we have

$$dA = \frac{\partial A}{\partial s} ds + \frac{\partial A}{\partial h} dh$$

$$dC = \frac{\partial C}{\partial s} ds + \frac{\partial C}{\partial h} dh$$

As $dA = 0$, we can immediately evaluate the change in C :

$$dC = ds \left(\frac{\partial C}{\partial s} - \frac{\partial C}{\partial h} \frac{\partial A}{\partial s} \left(\frac{\partial A}{\partial h} \right)^{-1} \right)$$

For finite amplitude changes ΔP and ΔC , often an empirical dimensionless integral "buffer-" ("evasion-" or "Revelle-") factor is introduced:

$$\xi = \frac{\Delta P \cdot C}{P \cdot \Delta C} \left(= \frac{\Delta s}{s} \frac{C}{\Delta C} = \frac{\partial C}{\partial s} \left(\frac{\Delta s}{\Delta C} \right)^{-1} \right) \text{ at a given temperature}$$

This factor can be approximately determined by direct measurement (Sundquist et al., 1979). It increases with increasing partial pressure. This shifts the dissoziative equilibrium towards the undissoziated form. For very high CO_2 release (much higher than can be produced by fossil fuel burning), the uptake capacity would be determined only by the physical solubility of CO_2 and would be considerably smaller than the present uptake capacity.

Fig. 3 shows the computed value of ξ for a fixed temperature for partial pressures between 300 and 600 ppm as a function of the pH-value.

As all dissoziation constant are functions of temperature, the buffer factor is a rather complicated function of the temperature. Fig. 4 shows the "differential" buffer factor.

$$\xi' = \frac{dP}{dC} \frac{C}{P}$$

as a function of pH-value and temperature. For fixed pH-value, it decreases monotonically with increasing temperature, as supported, for instance, by Sundquist's data (Sundquist, 1977).

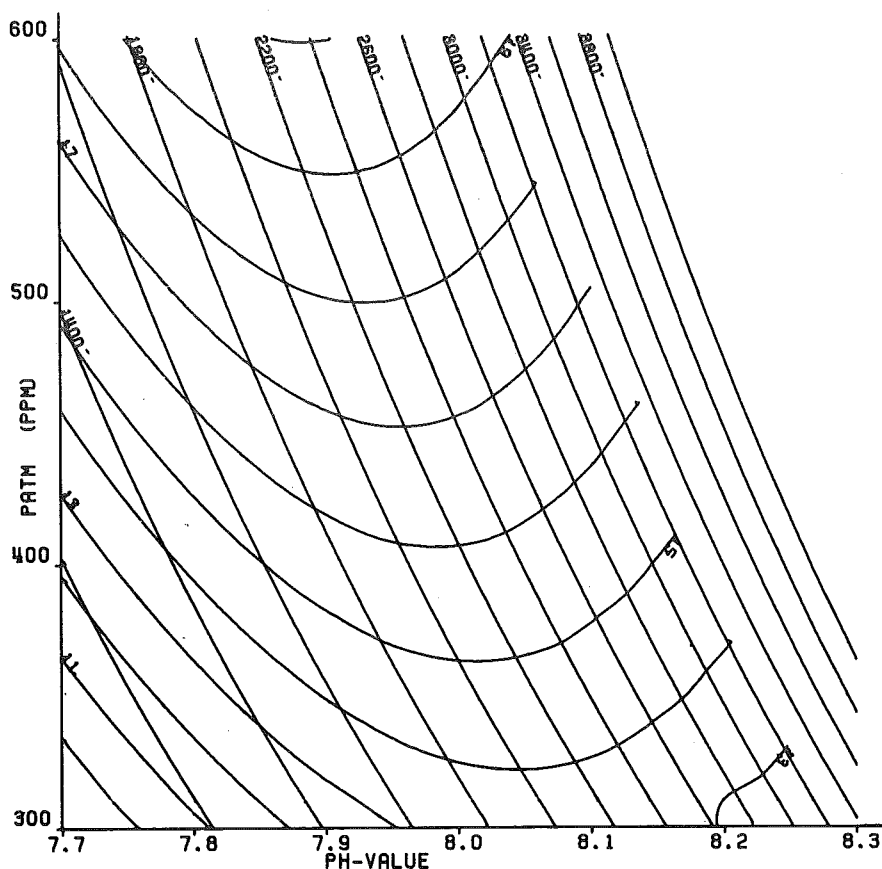


Fig. 3. Integral buffer factor as function of pH-value and atmospheric P_{CO_2} , related to a state of $15^\circ C$ and 300 ppm.

This temperature dependence does not appear so prominent in the effective uptake

capacity $\frac{dC}{dP} = \frac{P}{C} \cdot \frac{1}{\xi}$, since the temperature dependence of ξ' is largely cancelled by the similar temperature dependence of $\frac{P}{C} = \frac{1}{\alpha}$. Fig. 5 shows the marginal uptake capacity for excess carbon in the atmosphere $\frac{dC}{dP}$ together again with the alkalinity. It is strictly

monotonic with respect to the pH-value, its temperature dependence is much weaker. For realistic pH-values, there is a light increase with temperature, as suggested by the buffer factor, whereas the actual carbon content decreases with increasing temperature.

2. The carbon advection model

In the interior of the ocean, the different carbon fractions essentially behave as Lagrangian tracers. An exception may be allowed for particulate fractions, for which an

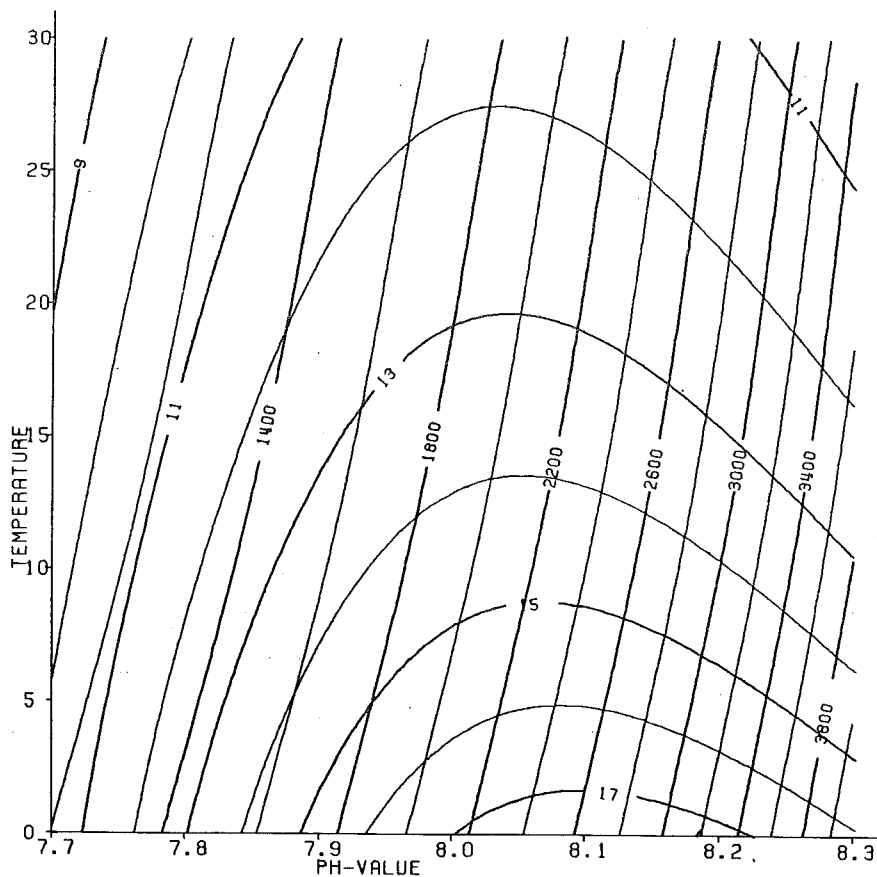


Fig. 4. Differential buffer factor as function of partial pressure and pH-value at 15°C.

explicit buoyancy velocity with respect to the surrounding water should be assumed. Denoting by u_j the components of a given current field, the development of the concentrations c_i of different carbon fractions can be described in general by

$$\partial_t c_i + u_j \partial_j c_i + w_i \partial_z c_i = \Delta(D \Delta c_i) + \text{Interaction}$$

where D denotes any diffusion operator and w_i the specific buoyancy velocity of the carbon fraction under consideration. Mathematically, this is represented by second order differential equations of elliptic type, requiring boundary conditions at all bounds of the domain of computation. The appropriate boundary conditions are of the type

$$\frac{\partial c}{\partial n} = 0 \quad \text{at closed boundaries (coastlines, bottom)}$$

$$\frac{\partial c}{\partial z} = Q \quad \text{at sea surface,}$$

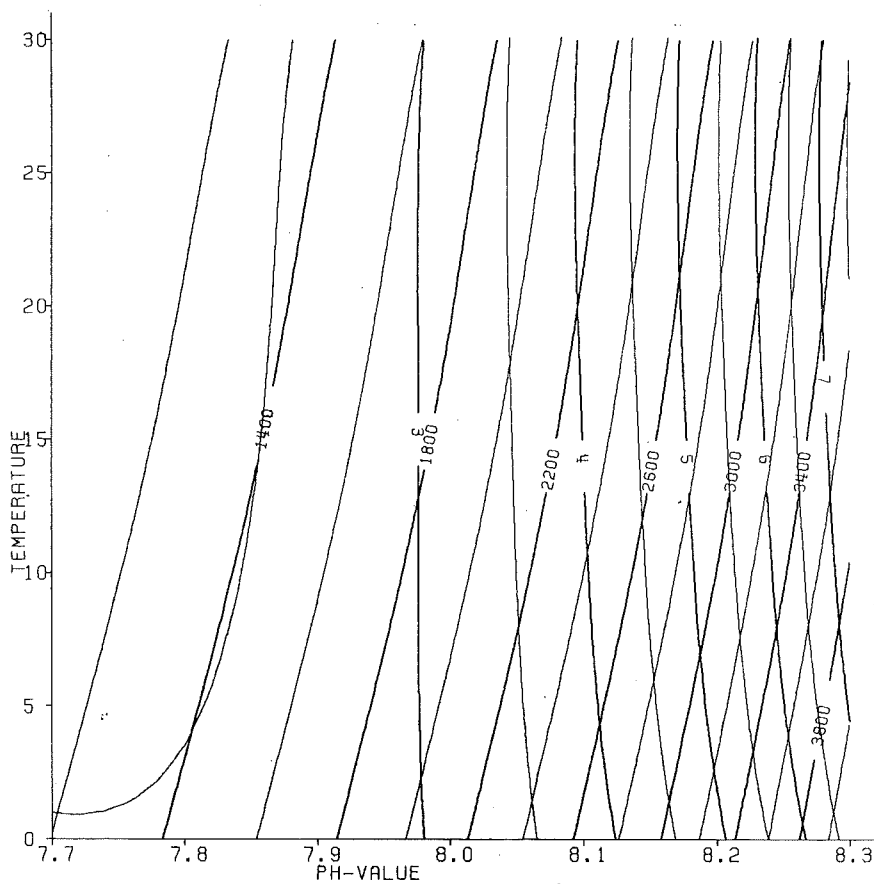


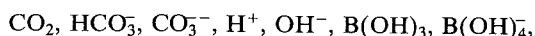
Fig. 5. Effective uptake capacity $\frac{dC}{dP}$ [0.1 mol/l/bar] at 300 ppm.

where Q denotes any flux (prescribed explicitly or computed, for instance, from mass conservation principles). In practice, however, there is a widespread agreement, that diffusion is small in oceanic motion, and that all advection problems should be formulated in a way that is compatible with the assumption.

$$D = 0.$$

With this assumption, we have a system of first order equations which are subject only to initial conditions, but not to boundary conditions. As a compromise between these two extremes, we can assume D to be a depth dependent function, being large within the top mixed layer, allowing for suitable boundary conditions, and being essentially zero below the main thermocline.

In the present state of the model development, we consider only one fraction of carbon, the dissolved inorganic carbon. Regarding only processes within the system



we can assume the alkalinity and the borate as constant throughout the ocean. Then the system is, at a given temperature, completely determined by any of the constituents, the other components following from chemical equilibrium conditions. It is convenient to take

$$C = \text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{--}$$

as the one constituent which is traced, and to derive the other fractions diagnostically. If we look at long term variations, without regard to seasonal variations, it is not necessary to consider the problem of finding an appropriate coefficient of gas exchange between ocean and atmosphere: using a time step of one year, we can assume complete equilibration between the atmosphere and the uppermost layer of the ocean model (100 m). With this assumption, the flux conditions at the sea surface can be formulated as follows:

At the previous time step we have computed for the top layer of the ocean the carbon fractions



The total carbon constant in the upper layer, which has the thickness M , is $M(\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{--}) = C_w$. In the atmosphere, we have given the partial pressure P , which can be transformed into the total atmospheric content C_A . Equilibrium is established by

$$\text{CO}_2 = \alpha P.$$

A change in C_w or C_A at the new time step gives rise to a new equilibrium, which is created under the premises that the alkalinity in the water remains constant, as well as the sum of the carbon contents C_w and C_A . The fulfilment of these conditions leads to a system of nonlinearly coupled algebraic equations, which can be solved easily by a Newton interaction.

As advecting current field, we take the results of a mean range experiment of the general circulation model of the ocean, which is in development at the Max-Planck-Institut of Meteorology in Hamburg (Maier-Reimer et al., 1983). In this experiment, the model was driven by the mean windstress field as compiled by Hellermann (1977) and mean surface fields of temperature and salinity as compiled by Levitus and Oort (1976). With these boundary conditions, the model was run for a century. After that time, an almost stationary state of motion was achieved. Some small changes still occurred in the deep layers, but for the carbon distribution, they may be regarded as irrelevant. Despite some shortcomings of the present state of the model – the winter convection, for instance, is represented rather unsatisfactorily – many basic commonly accepted features of the oceanic circulation are reproduced (as well as can be expected from a model using a grid resolution as coarse as 500 km). Fig. 6 shows the computed surface circulation of the model.

3. Pre-industrial equilibrium state

In the first experiment, we looked at the stationary state that existed in the middle of the

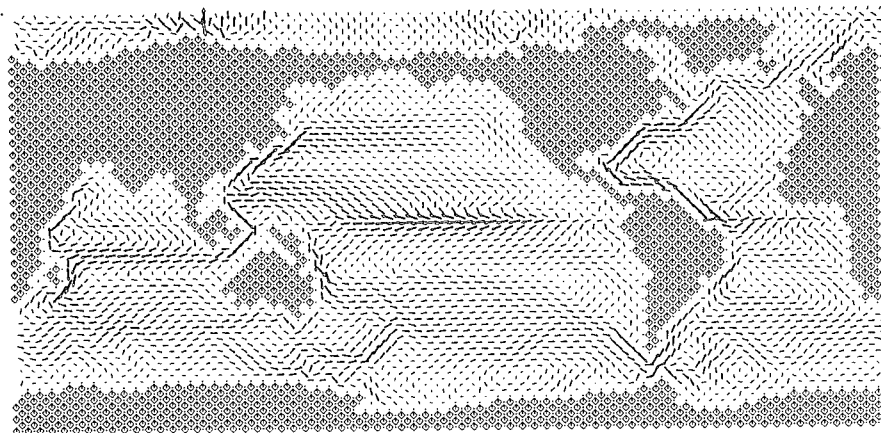


Fig. 6. Absolute velocities in 75 m depth.

past century, before man's activity began to distort the natural equilibrium state. As an estimate of the atmospheric partial pressure at that time we assumed approximately 275 ppm. The other quantities, e.g. the alkalinity or the pH-value are not known. Thus, the pre-industrial state of equilibrium cannot be prescribed, but must be computed as the selfconsistent asymptotic state of a long term run of our model, starting from an optimal guess initial condition. The computed preindustrial state cannot be verified directly. The model can be validated only by continuing the integration with a realistic human input function and by comparing the results with existing modern measurements.

However, as the changes since 1860 are not very great, the 1860-results should not deviate very much from present days observations, except for the partial pressure of CO_2 , which must have increased linearly with the atmospheric content.

Fig. 7 shows some of the properties of such a possible preindustrial state. Panel 7a

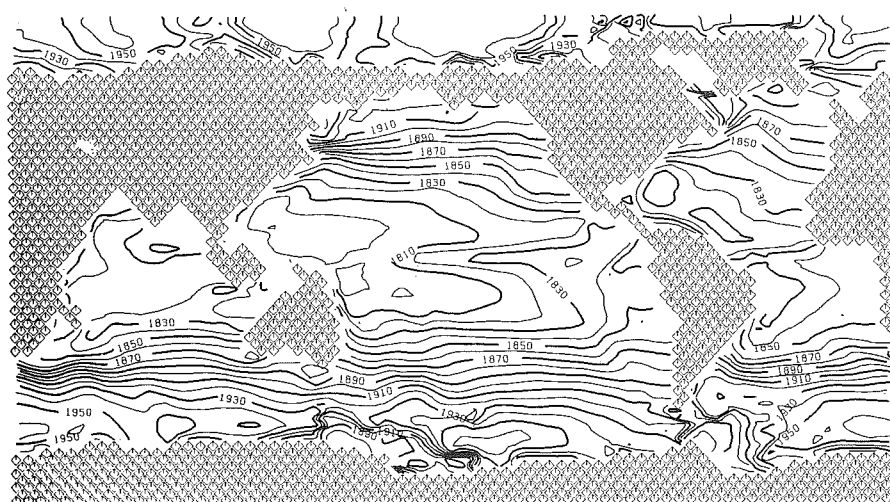


Fig. 7a. Total inorganic carbon 1860 in 75 m [u mol/l].

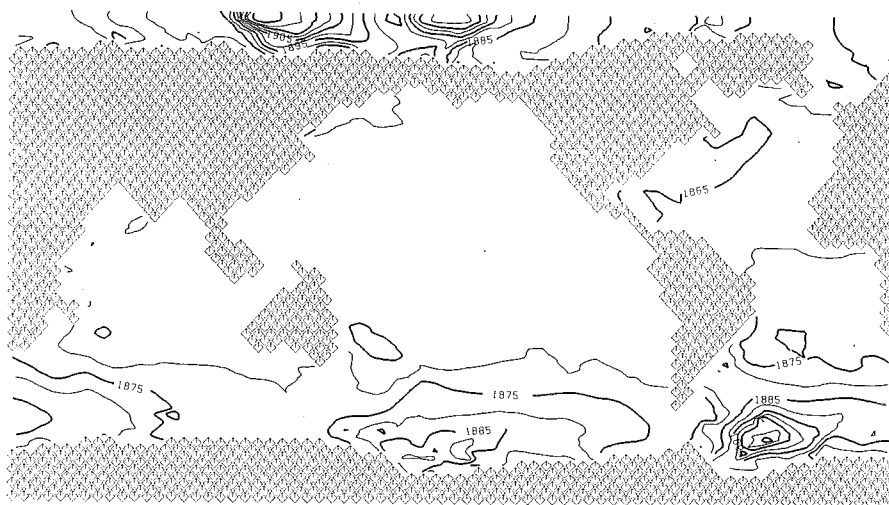


Fig. 7b. Total inorganic carbon 1860 in 1000 m [$\mu\text{mol/l}$].

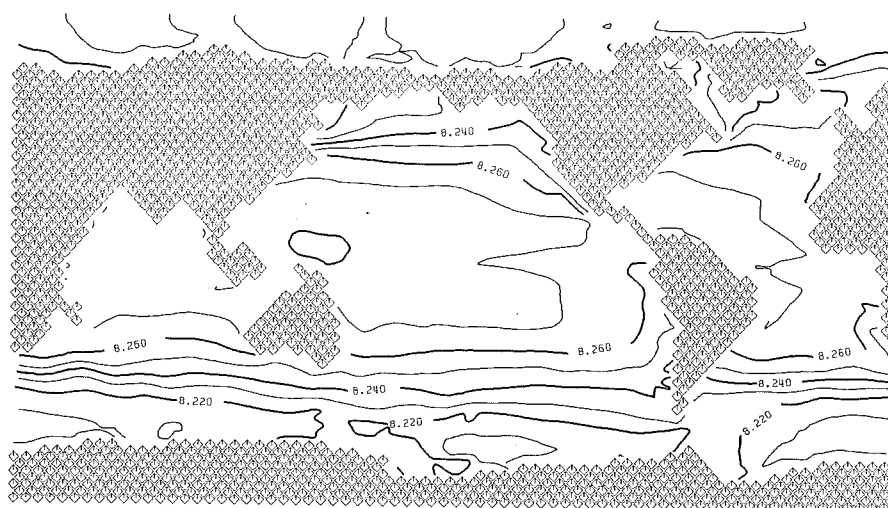


Fig. 7c. Surface pH-value 1860.

shows the surface distribution of total inorganic carbon. The distribution follows closely the distribution of the surface temperature. Minima are seen in the regions of warmest water, the subtropical gyres and the western Pacific, maxima are found in the polar regions. Due to the direct contact with the rather uniform atmospheric distribution at the imposed temperature, the relative variability is relatively small, approximately 10%. In the deeper layers, where at any point water masses from different origins join, the variability is smaller. At 1000 m, for instance, it is less than 2% in most parts of the ocean. However, it is substantially higher at a few locations of deep water formation (Fig. 7b).

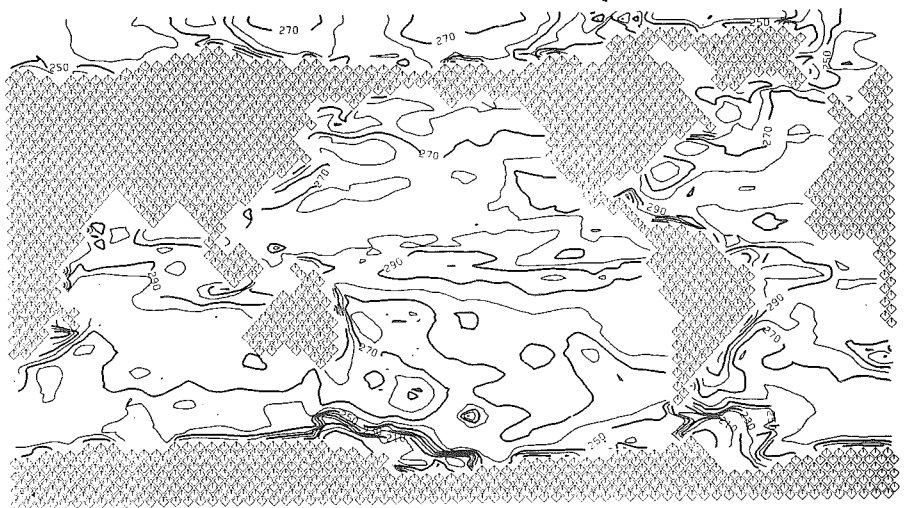


Fig. 7d. Equivalent partial pressure CO_2 1860.

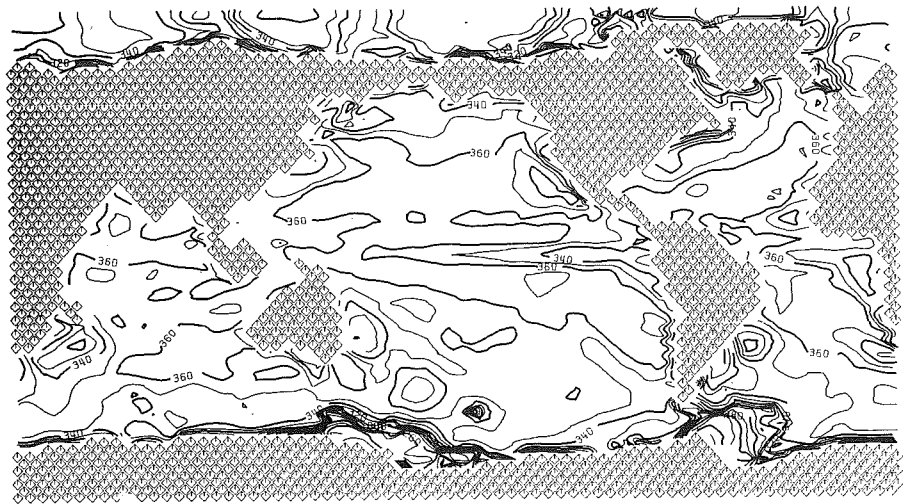


Fig. 7e. 1980.

The structure of the imposed temperature field is also seen in the distribution of the pH-value (Fig. 7c). The model was started with a uniform distribution of pH. In accordance with the temperature dependency discussed in 1., the pH-value is raised in warm water regions and decreased in cold water regions.

The best measurable quantity of the carbon fractions is the partial pressure of CO_2 in the surface waters. This quantity, however, is computed in our model only for an equilibrium state of the top layer of the ocean with the atmosphere and is therefore not of interest for the determination of the non-equilibrium state corresponding to a flux from the atmosphere to the ocean. An equivalent parameter to the non-equilibrium

P_{CO_2} value of the upper ocean can be extracted from our model, however, as the sum of the dissolved CO_2 that is in equilibrium with the atmosphere and the amount of carbon that is exchanged with the atmosphere during one time step, normalized to pressure units. Fig. 7d shows the equivalent surface partial pressure of CO_2 computed according to this definition for the conditions of the year 1860 and Fig. 7e the same for the year 1980.

4. Uptake of excess carbon released into the atmosphere

As mentioned above, the deep water formation of the present version of our circulation model appears to be rather too weak. Consequently, a straightforward application of the advection current field of this model to the problem of CO_2 -storage yields an airborne fraction of 80%, which is unrealistically high. To achieve a more realistic simulation within the framework of the present state of the circulation model, two simple modifications were introduced. In a first experiment, the seasonal mixing was assumed to extend over the two uppermost layers of the model, i.e. over the top 225 m. In a second experiment, the winter convection was simulated by the assumption of complete mixing over regions in which negative vertical components of the temperature gradient occurred during the general circulation model run which was carried out to determine the mean ocean circulation.

As input, we took the numbers compiled by Rotty from industrial CO_2 -production, raised by a "most probable" net biogenic input of one Gt/y. The different storage characteristics are displayed in Fig. 8: Fig. 8b shows the airborne fraction produced by the model without artificial mixing. The resulting airborne fraction is obviously much too high. Fig. 8d shows the result for the experiment in which the convection is controlled by the temperature gradient. Here the airborne fraction has a value slightly less than 50%, a result which would be widely accepted. (It must be emphasized, however, that since we do not know the net biogenic input, the term "observed airborne fraction" must be used carefully). Fig. 8c shows the airborne fraction for the experiment with mixing over the top two layers. The resulting fraction – 65% – also lies within the range of accepted values.

As one of the results of this run, Fig. 9 displays the computed increase of the surface partial pressure of CO_2 between 1860 and 1980. Here again, we see the effect of the imposed temperature field. In the North Polar Basin, which is almost disconnected from the main ocean, the increase is the same as in the atmosphere. The same value is seen in the subtropical gyres. Substantially lower values are found in the upwelling regions, for example at the equator and at the antarctic circumpolar current. In both cases the smaller increase can be attributed to the upwelling of water of old origin, which is relatively poor in CO_2 .

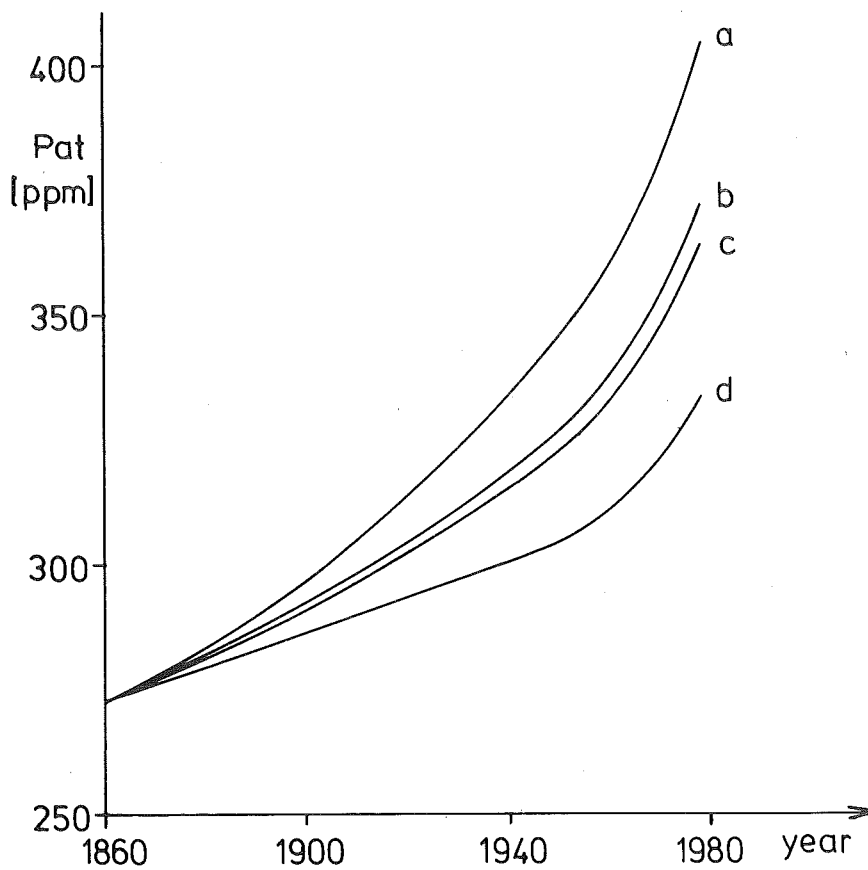


Fig. 8. Increase of atmospheric carbon content.

- a. Integration of input function Rotty's numbers + Gt/y
- b. remained in atmosphere without explicit mixing in the ocean
- c. remained in atmosphere with the deep water formation of the circulation model
- d. remained in atmosphere with neglect of the stabilizing effect of salinity to the stratification.

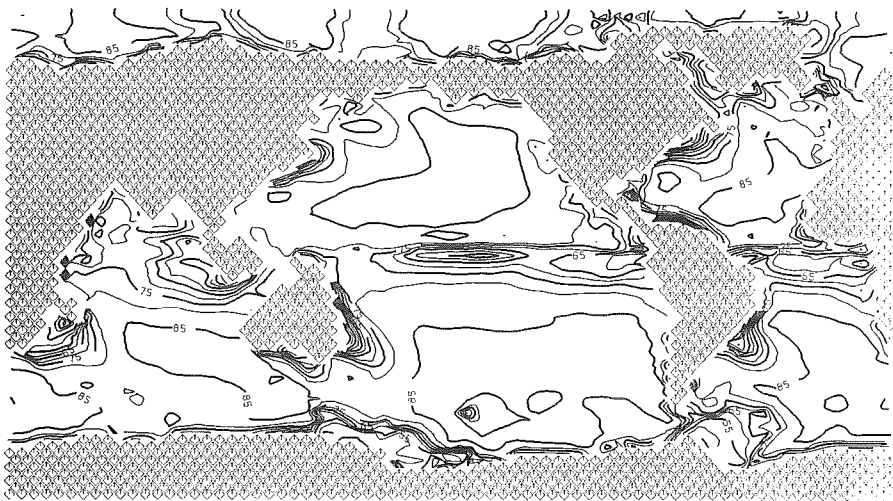


Fig. 9. Increase partial pressure.

ZUSAMMENFASSUNG

Die allgemeine Struktur eines dreidimensionalen Modells der Kohlenstoff-Flüsse im Ozean wird dargestellt. In den errechneten Strömungen eines realistischen Modells der allgemeinen ozeanischen Zirkulation werden die für den Kohlenstoffkreislauf relevanten Komponenten als dynamisch passive Eigenschaften der Wasserkörper transportiert. Als erster Schritt wird bei Vernachlässigung aller biologischer Prozesse der Transport von anorganischem Kohlenstoff simuliert. Als Randbedingung wird chemisches Gleichgewicht zwischen Ozeanoberfläche und Atmosphäre ohne empirisch ermittelte Pufferfaktoren angenommen. Die errechneten Verteilungen der chemischen Größen scheinen angesichts der Vernachlässigungen realistisch. Die Bedeutung der Winterkonvektion in hohen Breiten für die Aufnahmefähigkeit des Ozeans für Überschuß- CO_2 in der Atmosphäre wird an zwei Extremfällen demonstriert.

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