

GENERALIA

The carbon dioxide problem. An interdisciplinary survey

Editorial note. The following article completes the interdisciplinary survey on the carbon dioxide problem published in the July issue of *Experientia* (36/7, 1980). H.M.

The effect of the ocean on the global carbon cycle

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Summary. The fate of fossil fuel CO_2 in the ocean is discussed and a comparison is made with the natural oceanic cycle of carbon. The oceanic share of fossil fuel carbon, presently about 40%, will decrease in the future. Much of the fossil fuel carbon will remain in the atmosphere, and will stay there for many centuries. In the long run, however, the ocean will bring to an end the fossil fuel excursion of atmospheric CO_2 – firstly by dissolution as bicarbonate and ultimately by burial in ocean sediments.

Introduction

About 150 Gt of C have been released into the atmosphere as CO_2 by man's burning of fossil fuel (coal, oil, gas) over the last 100 years (Rotty, 1980), and about 40% of it presently reside in the ocean. However, the ultimate capacity of the ocean to withdraw this CO_2 from the atmosphere is much larger: if the atmosphere were chemically equilibrated with the entire volume of the ocean, the ocean's share of the fossil-fuel CO_2 would be 80%, and it would still be larger, if enough time were given for equilibration with ocean sediments. Thus, the ocean will take up most of the fossil-fuel CO_2 in the long run, whereas its actual capacity before such time is a dynamic feature which is determined by the kinetics of the said equilibration processes.

The ocean's present share of 40%, as well as predictions of future shares, have been arrived at on the basis of geochemical ocean models (Keeling, 1973). It is unfortunate in this context that the global balance of fossil-fuel CO_2 cannot be closed because, on top of fossil-fuel burning, man has also disturbed the terrestrial biosphere, which at the present time presumably acts as an additional net source of atmospheric CO_2 (Hampicke, 1980). Thus, it is impossible to determine directly the present share of the ocean, i.e., essentially the difference between the total released and the

amount remaining in the atmosphere, which could have served as an independent check on the ocean model results. In fact, the ocean models have been challenged on the basis of claims that the biosphere is indeed a net source of C of a magnitude which the available ocean models clearly cannot accommodate (Woodwell and Houghton, 1977), and the apparent discrepancy has induced a search for a 'missing sink' (Zimen, 1979).

On the background of this somewhat uncertain situation, I shall in this article discuss the general oceanic geochemistry of C. This discussion will outline the foundations of the said ocean models. It will become evident that the possibility of a major oceanic missing sink is remote. Furthermore some obvious consequences for the future of fossil-fuel C in the environment will become apparent. Anybody interested in additional details has at his disposal an abundance of literature on the oceanic part of the CO_2 problem (e.g., Andersen and Malahoff, 1977; SCOPE 13, 1979; Broecker et al., 1979), which is so called primarily because of an expected CO_2 -induced change in global climate (Bach, 1980; Elliot and Machta, 1979).

Oceanic geochemistry of carbon

Carbon reservoirs. Figure 1 gives a schematic view of the various carbon reservoirs in nature, with the

global amounts of C in each reservoir. The C buried in ocean sediments represents by far the largest amount. Next is C inorganically dissolved in the ocean, which still greatly exceeds in amount any of the other reservoirs. The amount of organic oceanic carbon is a few percent of that inorganically dissolved. Most of the organic fraction is of low reactivity (Mopper and Degens, 1979); therefore its action on the environmental C cycle is slow. I shall discuss the relevant processes in the atmosphere-ocean-sediment system below. For the sake of simplicity, I shall not consider biospheric processes except where they directly affect the system.

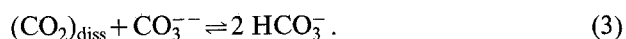
Chemical equilibria in the ocean. Inorganically dissolved C in the ocean is determined in its amount and chemical speciation by equilibration with atmospheric CO_2 above and with sedimentary C below (Pytkowicz and Small, 1977), as is schematically shown in figure 2. At the atmosphere-ocean interface the equilibrium is a solubility equilibrium for CO_2 :

$$(\text{CO}_2)_{\text{diss}} = a(T) \times (\text{CO}_2)_{\text{atm}} \quad (1)$$

The solubility a is of order unity and it decreases with increasing temperature T . At the water-sediment interface, a solid phase of carbonate sustains a certain concentration of dissolved carbonate ions. Neglecting minor effects such as variations in the concentration of calcium ions, the equilibrium at the interface of the first order can be written as:

$$(\text{CO}_3^{--})_{\text{diss}} = L(p). \quad (2)$$

The dependence of the equilibrium concentration L on the hydrostatic pressure p , i.e., on depth (and to a lesser extent on temperature), is such that the equilibrium concentration of dissolved carbonate ions at abyssal depths of the ocean is more than twice that of shallow water areas (Broecker et al., 1979). Dissolved CO_2 and carbonate ions finally combine to form bicarbonate ions:



Thus, in total, CO_2 dissolves carbonate to form bicarbonate. The actual equilibria are such that about 90% of the total dissolved inorganic C is bicarbonate and at most 1% is dissolved CO_2 , and that the total dissolved C ($\Sigma \text{CO}_2 = (\text{CO}_2)_{\text{diss}} + \text{HCO}_3^- + \text{CO}_3^{--}$) amounts to about 2 moles/ m^3 of seawater. (Usually the equilibria $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{--} + 2 \text{H}^+$ and their apparent dissociation constants are considered (Pytkowicz and Small, 1977).)

The equilibration according to equations (1)–(3) is a slow process, because, as figure 2 indicates, it requires the transport of dissolved C back and forth between water surface and sediment. Whereas the undisturbed ocean naturally has had time to approach such an equilibrium, this is not at all the case for the fossil-fuel

C. Rather, fossil-fuel CO_2 , on entering the surface ocean, does react according to equation (3), but without carbonate ions being replenished by sediment dissolution, i.e., with equilibrium (2) being inoperative. Therefore, a depletion of carbonate ions occurs which limits the amount of bicarbonate that can be formed. Consequently, when the rising atmospheric CO_2 partial pressure induces a net atmosphere-ocean transfer of CO_2 , the resulting fractional change in total dissolved inorganic C is much smaller than that in the atmospheric partial pressure. This is commonly expressed by the so-called Revelle, or buffer, factor R (Keeling, 1973; Broecker et al., 1979)

$$R \equiv \left(\frac{\delta \text{CO}_2}{\text{CO}_2} \right)_{\text{atm}} / \left(\frac{\delta \Sigma \text{CO}_2}{\Sigma \text{CO}_2} \right)_{\text{diss}}, \quad (4)$$

where δ stands for a small change. The average value of the Revelle factor for present-day ocean surface water is about 10 (Takahashi, 1979). Equation (4) implies chemical equilibrium between the atmospheric air and the water, as well as an absence of carbonate dissolution or precipitation (which is often stated as constancy of alkalinity, where carbonate alkalinity

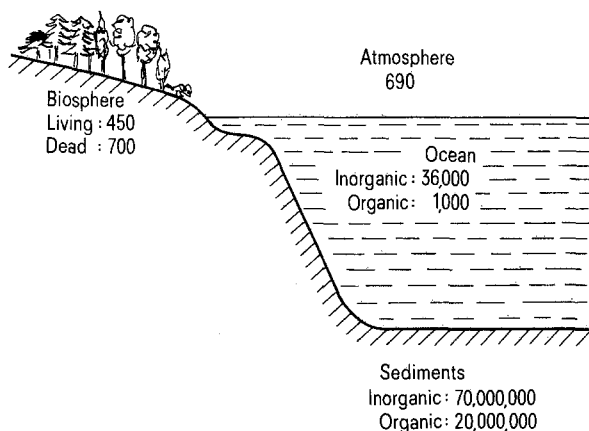


Fig. 1. Global amounts of C (in Gt C; 1 Gt = 10^{12} kg = $8.33 \cdot 10^{13}$ moles C) for the major C reservoirs in nature: atmosphere, biosphere, ocean, and sediments. Data from Holland (1978), except for organic C in the ocean (Mopper and Degens, 1979). Inorganic carbon in sediments is mostly CaCO_3 . The amount of juvenile C in the earth is supposed approximately to equal that in sediments (Holland, 1978).

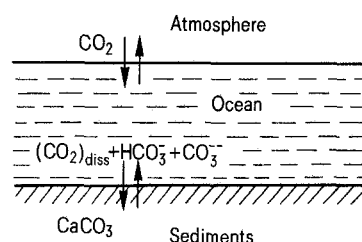


Fig. 2. Schematic equilibration of inorganically dissolved C in the ocean with atmospheric CO_2 and CaCO_3 in oceanic sediments.

$=\text{HCO}_3^- + 2\text{CO}_3^{2-}$ (Pytkowicz and Small, 1977)). It should be noted that the depletion of carbonate ions which occurs when fossil-fuel CO_2 shifts the equilibrium (3) renders the water more apt to dissolve carbonate.

The general relationship between atmospheric CO_2 partial pressure and total dissolved inorganic carbon in chemical equilibrium is shown in figure 3 for a wide range of atmospheric partial pressures. Some numerical values are listed in table 1. 1 m^3 of present-day ocean surface water contains about 135 times the amount of C contained in 1 m^3 of atmospheric air (this is the reason the oceanic C reservoir is so large). However, even an increase in atmospheric partial pressure by a considerable factor will induce only a modest increase in ΣCO_2 above its present value.

The picture changes if enough time is allowed for the replenishment of carbonate ions (equation (2)). Reaction (3) is then no longer limited, and the ocean is able to take up huge amounts of extra CO_2 . This is often referred to as the buffering, or neutralization, action of the ocean.

Oceanic carbonate sedimentation and dissolution. The undisturbed ocean approaches the equilibria (1)–(3) in a dynamic fashion. C becomes incorporated into carbonate shells and organic tissues that are being

formed in the surface waters, and falls as a rain of particulates into the depths of the ocean. Most of this material is redissolved, but some of it gets buried in the sediments. As for carbonate, the ocean is supersaturated in respect to the carbonate ion equilibrium (2) at the surface and undersaturated at great depths (Broecker et al., 1979). This results from both the previously mentioned pressure effect on this equilibrium and from the particulate rain of organic matter, which is reconverted to CO_2 by oxidative decomposition in deeper water and during early sediment diagenesis; here the CO_2 renders the water more corrosive. Consequently, there exists in the ocean a fairly well defined horizon (the calcite compensation depth, or CCD), which separates carbonate-containing sediments above the CCD from carbonate-free sediments below it (Berger, 1977). The depth of the CCD varies between about 3000 m (Pacific) and 5000 m (Atlantic), the differences in depth being due to the deep water circulation. These depths, as the term CCD implies, are those for calcitic carbonate, while for carbonate of aragonitic structure, which is less stable thermodynamically, shallower depths apply. In fact, in certain areas of the Pacific, aragonite dissolution occurs at depths as shallow as a few hundred meters. Dissolution starts as soon as the water is undersaturated with carbonate ions; the depths where saturation is 100% delineate a saturation horizon (Berger, 1977). However, for dissolution to be at all appreciable, substantial undersaturation is necessary. It is for this reason that the compensation depths lie considerably below the saturation horizon, and that they are, in fact, dynamic features: they are found at those depths where the rate of carbonate dissolution just equals the supply. Even at the compensation depths, dissolution is quite slow (Berger, 1977).

In all, there is a delicate balance between carbonate sedimentation and dissolution in the ocean today. About half the net carbonate deposition occurs in the Atlantic, where the deeper waters are less corrosive (Broecker and Takahashi, 1977). Large amounts are deposited on tropical and subtropical shelves, whereas higher latitude shelf sediments have much less carbonate (Hay and Southam, 1977). It has even been argued that the present shelf sedimentation is higher than average, because the space on the shelves made available by the sea level rise after the last glacial age is being filled in (Hay and Southam, 1977).

Because of the supersaturation of the water, dissolution of present shallow-water carbonate sediments does not occur. Supersaturation is greatest in tropical waters (about 5-fold) and least in high-latitude waters (about 2-fold). The saturation horizons, and even more so the depths at which dissolution becomes quite noticeable, are found at considerable depths everywhere in the oceans, i.e., depths below those easily

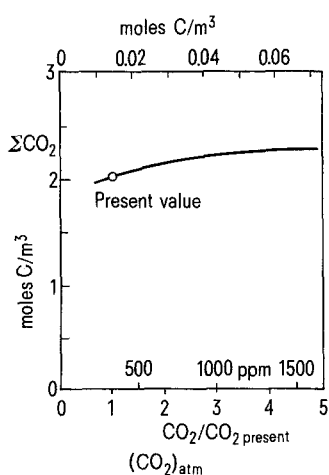


Fig. 3. Concentration of total inorganic dissolved C in the ocean versus atmospheric CO_2 concentration. Atmospheric CO_2 is given in multiples of present value, in ppm, and in moles/ m^3 . Calculated from data for the Revelle factor in Takahashi (1979).

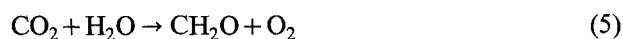
Table 1. Apparent CO_2 solubilities in average ocean surface water for selected atmospheric CO_2 partial pressures ((moles C/m^3)_{water}/(moles C/m^3)_{air}), after Takahashi (1979)

$p\text{CO}_2$ (ppm)	$\Sigma\text{CO}_2/(\text{CO}_2)_{\text{atm}}$	$\delta\Sigma\text{CO}_2/\delta(\text{CO}_2)_{\text{atm}}$ ^b
330 ^a	135	13.5 ^c
660	72	5.5
1320	38	2.2

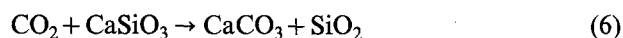
^a Present value; ^b equal to the slope in figure 3; ^c this means that in ocean water in equilibrium with the atmosphere the fossil-fuel C concentration is 13.5 times that in the atmosphere.

accessible to ocean surface waters (Broecker et al., 1979). On this basis it can be concluded that buffering of CO_2 excursions by carbonate dissolution as explained above is indeed a slow process and in particular is not effective now for the present fossil-fuel excursion of CO_2 . A hint of caution is needed, because some dissolution presumably occurs even in shelf sediments, where it is fostered by certain microenvironments, such as in areas of oceanic upwelling (Berger, 1977), or by the presence of high magnesian calcites that are still more reactive than aragonite (Wollast and Reinhard-Derie, 1977). However, considering the rates and areas involved, and the fact that nature will tend to anneal the most reactive spots, it appears that such effects must be small on a global scale.

Geological regulation. The sources of the abundant C present in ocean sediments (figure 1) are the release of CO_2 by volcanoes, and the weathering of terrestrial carbonate minerals (Holland, 1978). The carbonate is dissolved as bicarbonate and carried by rivers to the ocean where it is finally redeposited as CaCO_3 . The volcanic CO_2 source is compensated for by the burial of biogenic organic matter in ocean sediments, according to:



where the organic matter is represented as carbohydrates, CH_2O . However, the sedimentary record (figure 1) says that only about 20% of the total C in ocean sediments has been deposited as organic C. This fraction amounts to less C than the volcanic source supplies. Apparently, therefore, part of the volcanic CO_2 is transformed to carbonate. The reaction is $\text{CO}_2 + \text{Ca}^{++} + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{H}^+$. A compensatory reaction for supplying the Ca^{++} and consuming the H^+ is provided from the weathering of igneous rocks, in the form of such conversions as feldspars to clays (Holland, 1978). The resulting CO_2 fixation can, in a very generalized form, be written as:



where CaSiO_3 is a constituent of the rocks undergoing weathering, and the reaction products CaCO_3 and SiO_2 are deposited in ocean sediments. Some of the Ca^{++} originates from hydrothermal processes in areas of active sea floor spreading (Holland, 1978). It is believed that the true mineralogical equilibria for which equation (6) is a shorthand ultimately regulate the partial pressure of CO_2 in the atmosphere. One may look at both processes (5) and (6) as being closed cycles, as the reaction products may eventually become reexposed to weathering or volcanic decomposition following geodynamic cycling of the sediments. The pertinent time scale here is of the order of 10^8 years (Garrels and Perry, 1974). It is

estimated that about half the C in the earth has undergone such recycling (figure 1) (Holland, 1978).

The two processes (5) and (6) also act on the fossil-fuel CO_2 . Although their rates are small, they will in the long run transfer the fossil-fuel CO_2 to the oceanic sediments. Process (5) is controlled by biospheric activity, and process (6) by weathering, both of which may be increased by elevated atmospheric CO_2 partial pressures. However, a driving factor in the actual weathering is the enhanced CO_2 partial pressure in soils and in groundwater that is brought about by root respiration and plant decay (Holland, 1978). Therefore, elevated atmospheric CO_2 partial pressures will not speed up weathering per se, but may do so indirectly by promoting biospheric activity, which in turn might lead to increased soil CO_2 levels.

Cycling of carbon

The steady-state cycle. In this section I intend to outline the undisturbed cycling of C in the ocean-atmosphere-sediment system. The undisturbed cycle can serve as a background against which the anthropogenic perturbation can be judged. To simplify the picture, a closed, steady-state cycle is postulated. This means that for each reservoir input and output fluxes have to be completely balanced. Some of these fluxes are quite uncertain, but this does not affect any of the general conclusions.

The cycle is shown in figure 4. The individual fluxes are listed and explained in table 2. The net fluxes are all less than 1 Gt/year. From the flux, F , between any two reservoirs and the amount, M , (figure 1) in any of the two, a turnover, or replacement, time can be calculated by $\tau = M/F$ (Holland, 1978). In this way one finds that the addition of crustal C (0.3 Gt/year) replaces the C of the ocean, atmosphere, and biosphere combined about every 150,000 years, and the C addition by rivers (0.7 Gt/year) replaces the ocean-

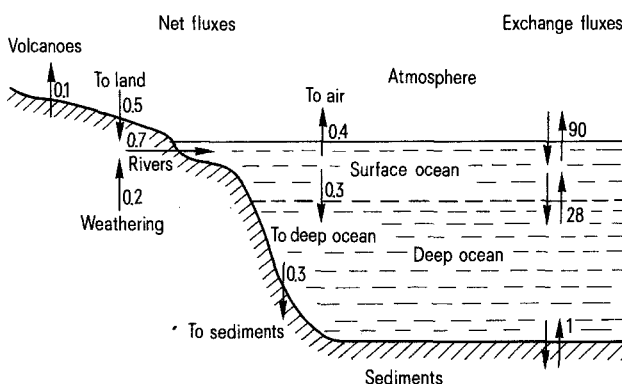


Fig. 4. Steady-state C cycle in the atmosphere-ocean-sediment system. Net fluxes (left) and exchange fluxes (right) are in Gt C per year. Fluxes are listed in table 2. For reservoir sizes see figure 1. Ocean surface layer is about 7% of the total ocean volume (i.e. ~ 250 m average depth).

Table 2. The steady-state carbon fluxes of figure 4

	Gt/year	Explanation	Source
a) Net fluxes			
Volcanoes	0.1	CO ₂ exhalation of volcanoes, etc.	Holland (1978)
Weathering	0.2	Continental weathering of carbonate rocks	Holland (1978)
Rivers	0.7	Dissolved and suspended carbon load of rivers (bicarbonate ~0.4, organic ~0.3)	Hay and Southam (1977)
To land	0.5	Net transfer from the atmosphere, mostly through the biosphere, about 0.2 Gt/year used in weathering	By continuity
To air	0.4	Net CO ₂ release from the ocean to the atmosphere	By continuity
To deep ocean	0.3	Net transfer from surface ocean to deep ocean	By continuity
To sediment	0.3	Net carbon burial in oceanic sediments, mostly on the shelf, continental slope, and in the North Atlantic	Holland (1978), Pytkowicz and Small (1977), Hay and Southam (1977)
b) Exchange fluxes			
Atmosphere-ocean	90	Global rate of CO ₂ gas exchange over atmosphere-ocean boundary	Broecker et al. (1979, 1980)
Surface ocean-deep ocean	28	Downward flux is 25 Gt/year in dissolved and ~3 Gt/year in particulate form, return flow is entirely in dissolved form, 0.3 Gt/year escapes dissolution and forms the net flux to the sediments	Keeling (1973), Broecker et al. (1979), Bolin (1977)
Deep ocean-sediment	~1	Gross sedimentation, and redissolution of CaCO ₃ and organic matter at the ocean floor	Berger (1977)

ic C about every 50,000 years. Turnover by the net fluxes is thus quite slow.

The internal, or exchange, fluxes are very much larger: about 90 Gt of C are annually exchanged between the atmosphere and ocean surface waters, i.e. dry vacations in the atmosphere for any C atom last on the average only about 8 years. Thus, atmosphere and surface ocean are very much linked together. Equilibrium, however, only exists in the global average. In reality, a few percent of the exchange flux form an internal cycle of net oceanic release in the lower and uptake in the higher latitudes, with appropriate meridional return flows in both the atmosphere and ocean. This cycle results because, as a response to the meridional gradient in temperature, dissolved oceanic CO₂ is out of equilibrium with atmospheric CO₂ (eq. (1)) regionally (Keeling, 1968; Broecker et al., 1979).

Within the ocean, mixing is quite fast down to a depth of a few hundred meters. The wind can stir the water to a depth of about 50 m within a few days, and mixing beyond this depth is accomplished by seasonal convective overturning, i.e., within 1 year. The 90 Gt/year atmosphere-ocean exchange rate is enough to lead to chemical equilibrium between the air and the convective ocean surface layer in about 2 years (Keeling, 1973). There is thus a chemical near-equilibrium between atmospheric air and an oceanic surface layer perhaps 250 m deep. Because mixing farther down is considerably slower, it is often useful to divide the ocean into a surface layer and the remaining, deeper ocean. Such a division is shown in figure 4. The mixing into the deeper ocean is also of a convective nature. It is concentrated in certain parts of the ocean, mostly at higher latitudes, and is intermittent.

C transport from the ocean surface layer into the deep ocean amounts annually to about 25 Gt in dissolved form with an additional 3 Gt of particulates. About 90% of the latter are redissolved in the deep ocean or at the ocean floor, and 10% are buried in sediments. Thus, within any full cycle between surface and deep ocean, only about 1 in every 100 C atoms is lost to the sediments. An amount about three times as large (1 Gt/year) is deposited but is subsequently redissolved. The larger part of the back flow is by carbonate dissolution below the carbonate compensation depth, and this part is presumably returned fairly quickly. The other extreme is carbonate originally deposited above the saturation horizon, but subsequently subjected to dissolution, either by being brought to deeper depths by gravitational sediment flow or sea floor subsidence, or as a consequence of a temporal change in the carbonate chemistry of the water (Berger, 1977).

Natural excursions. It is now certain that major climatic events such as glacial periods have induced changes in the C cycle of figure 4. Changes are documented in the sedimentary record, where variations such as in carbonate compensation depth through geologic time can be detected (Berger, 1977). Less certain are indications of a smaller atmospheric CO₂ partial pressure during the last glacial age, that have recently been deduced from measurements in air inclusions in Antarctic ice (Delmas et al., 1980). The causes for the changes are not understood, but changes in oceanic circulation pattern, adjustments of the biosphere, and altered weathering are possibilities. It has been argued that the system is at present not in a steady state, but is still recovering from the excursion during the last glacial episode (Hay and

Southam, 1977). The long time constants in the cycle make this a real possibility. Changes in the deep-water oceanic circulation will bring about a slow readjustment through induced changes in the general carbonate saturation pattern. Changes in the near-surface circulation will lead to excursions of shorter duration that are caused by induced changes in the global pattern of solubility disequilibrium over the air-sea boundary (Bacastow, 1977). Natural excursions of the system which might induce noticeable variations in atmospheric CO_2 partial pressure at various time scales have thus to be expected, and the steady-state assumption made in figure 4 is indeed to some extent arbitrary.

The fossil-fuel CO_2 excursion

Present situation. The atmospheric CO_2 partial pressure has risen by about 15% since the last century and, if most of the presently known recoverable fossil fuels are burned, a total increase of several times the natural level (~ 290 ppm) is to be expected. Fossil-fuel burning has been rising by 3–4% per year on the average over the last few decades, and the atmospheric CO_2 partial pressure is now rising by about 0.3%/year (Rotty, 1980; Baes et al., 1977).

The present release of fossil-fuel CO_2 amounts to about 5 Gt of C annually. This rate is large compared with all net fluxes in the C cycle of figure 4, but much smaller than the exchange fluxes atmosphere-ocean and surface ocean-deep ocean (figure 4, right). It is therefore clear that removal of fossil-fuel CO_2 from the atmosphere does occur by these exchange fluxes, whereas the effect of any of the other fluxes in figure 4 must be minor: the atmospheric perturbation (about 15%) is small enough for perturbation of the steady-state fluxes of figure 4 to be estimated by presuming the perturbation to be first order (it should in reality be rather less); such perturbation, e.g. for river transport, amounts to only 0.1 Gt/year (i.e., 15% of 0.7 Gt/year). The biosphere is excluded in figure 4 because this article only deals with the effect of the ocean on fossil-fuel CO_2 . The atmosphere-biosphere exchange, i.e. the rate of photosynthesis, is in fact comparable to that of atmosphere-ocean exchange, but the present net flux is uncertain (Hampicke, 1980).

It is now easy to get a feeling for the actual oceanic share of the total fossil fuel C burned so far: the ocean surface layer in figure 4, being in chemical near-equilibrium with the atmosphere, contains at present per unit volume about 13.5 times the amount of fossil-fuel C held in atmospheric air (table 1). Taking the depth as 250 m, the fossil-fuel C content of this layer is one third that of the atmosphere (ocean: $250 \text{ m} \times 13.5 \times \text{ocean area}$; atmosphere: 8000 m equivalent standard pressure height \times global area. If the near-equilibrium prevailed throughout the entire

ocean, the above mentioned hypothetical 80% oceanic share would result). To bring the oceanic share of the total to the estimated actual 40%, evidently an amount of fossil-fuel C equal to that in the surface layer must be present in the deep ocean. This is a reasonable postulate in view of intermediate and deep water renewal in the ocean.

It is useful to express the total fossil-fuel C in the ocean as an equivalent subvolume, V_{eff} , of the ocean, which is in chemical equilibrium with the atmosphere, i.e., V_{eff} being defined by:

$$\int_V \Delta \Sigma \text{CO}_2 \times dV = (\Delta \Sigma \text{CO}_2)_{\text{eq}} \times V_{\text{eff}} \quad (7)$$

where $\Delta \Sigma \text{CO}_2$ = fossil-fuel portion of total dissolved inorganic C, and the integration is over the volume of the ocean. The task of determining the fossil-fuel C can thus be reduced to finding V_{eff} . In passing it should be noted that it is impossible to determine the oceanic fossil-fuel C content by integrating the left-hand side of equation (7), because $\Delta \Sigma \text{CO}_2$ is at most about 1.5% of ΣCO_2 (eq. (4), i.e., 15% CO_2 partial pressure excess divided by the Revelle factor), which is too small a value to be specified with any certainty.

The lesson from this is two-fold: The amount of fossil-fuel C in the ocean can indeed not be determined directly. On the other hand, the assumption of a chemical near-equilibrium for the surface water is justified, and the assessment thus only requires the determination of the equivalent volume V_{eff} . This can be achieved in one of two ways, either

- by evaluating the effect of the ocean as a sink for an atmospheric constituent for which a complete global balance can be set up, or, preferably (Roether, 1979),
- by evaluating the oceanic distribution of a constituent for which this distribution can be reliably measured.

The most used constituents are the radionuclides ^{14}C and tritium (^3H), of which ^{14}C has both a natural component and one that has arisen from nuclear weapon testing, whereas tritium is virtually all of nuclear-weapon origin. Commonly, this information is employed to calibrate a simple ocean mixing model, such as that in figure 5, and the so-calibrated model is then run for fossil-fuel C; figure 5 in essence is a further abstraction of figure 4.

The most reliable determination to date is the one of Broecker et al. (1980) who subdivided the global ocean area and for each subarea determined the equivalent subvolume by comparison with the well-known oceanic distributions of tritium and the nuclear-weapon component of ^{14}C . The nuclear-weapon nuclides and fossil-fuel C have sufficiently similar oceanic distributions, so that only minor corrections are required to go from one to the other (see also Weiss et al., 1979). The result is an oceanic

uptake of about 35% of the total fossil-fuel C released. This figure excludes sedimentation of fossil-fuel C, as well as carbonate dissolution, which would lead to an enhanced oceanic uptake of fossil-fuel C. Both effects should be small, as should be evident from the above discussions of the undisturbed C cycle. Allowing for small effects, 40% fossil-fuel uptake by the ocean should be a reasonable estimate. Its uncertainty should not be very much larger than $\pm 25\%$ (i.e., $40 \pm 10\%$ uptake).

Predictions. Predictions of future atmospheric CO_2 partial pressures naturally depend on assumed fossil-fuel energy growth rates. Whatever the actual scenario, however, the rôle of the ocean can be specified by predicting the equivalent volume, V_{eff} , of equilibration with the atmosphere (eq. (7)), and by this the ocean-borne fraction of fossil-fuel C.

If the equivalent volume is unchanged, there remains the effect of the decreasing capacity of the ocean to dissolve extra CO_2 , which can be calculated from the data in table 1. The result is that the oceanic share of the total fossil-fuel C will decrease from its present 40% to about 30% if the atmospheric CO_2 partial pressure reaches twice its natural value, and to about 20% after another doubling in partial pressure. (The share is calculated by reducing the uptake into the equivalent ocean volume V_{eff} by the factor

$$\frac{\Delta \Sigma \text{CO}_2}{\Delta (\text{CO}_2)_{\text{atm}}} \times \left(\frac{\Delta (\text{CO}_2)_{\text{atm}}}{\Delta \Sigma \text{CO}_2} \right)_{\text{present}},$$

$\Delta \Sigma \text{CO}_2$ and $\Delta (\text{CO}_2)_{\text{atm}}$ being the fossil-fuel components, and the present ratio being 13.5 (table 1). The atmospheric rise in CO_2 partial pressure will therefore steepen not only because of the presumed increase in fossil fuel consumption but also because an increasingly larger fraction of the total fossil-fuel C

will remain air-borne. Eventually fossil-fuel reserves must approach exhaustion, and the atmospheric CO_2 partial pressure will finally start to drop. The ocean's share will then increase owing to mixing of fossil-fuel C into the deep ocean. (A tendency for effectively deeper mixing will begin when and if fossil-fuel consumption levels off.) However, the action of the ocean will be slow because it will, at this point, be in virtual chemical equilibrium with the atmosphere to a considerable depth (perhaps 1000 m). Recirculation of the deep waters of the world ocean occurs on a time scale of about 1000 years (Broecker, 1979), and a period of time of this order is therefore required to complete the mixing.

A quantitative account beyond these statements is difficult because eventually two things will, or may, happen:

- The onset of carbonate dissolution in shelf and continental slope sediments, which will allow more fossil-fuel C to enter the ocean. This effect is expected to become noticeable at an atmospheric CO_2 partial pressure about 3-fold the present one. Reduced carbonate formation, presumably with a much lower partial pressure threshold, might add a minor effect;
- a possible change in oceanic circulation as a response to a CO_2 -induced change in global climate, which would affect the equivalent volume, V_{eff} . A change might also lead to a transitory exchange of surface and deep water, with an uncertain net effect on the atmospheric partial pressure. An induced change on the carbonate saturation pattern would bring a long-term effect. Furthermore, a general warming of the surface waters would induce a rise in CO_2 partial pressure.

While the effect of changes in oceanic circulation is uncertain, carbonate dissolution and a slow-down or virtual stop in fossil-fuel consumption will tend to diminish the air-borne fraction of CO_2 . Carbonate dissolution will occur in the deep waters and in higher-latitude shelf areas; tropical and subtropical shelves will presumably be immune to carbonate dissolution (Broecker et al., 1979). It has been estimated that enough carbonate is accessible in deep sea sediments to neutralize all fossil-fuel C that is now thought to be at all recoverable economically (Broecker and Takahashi, 1977). This neutralization will be a slow process because not only the mixing of fossil-fuel C into deeper water but also the neutralization itself is slow. It is furthermore expected to decelerate, because the top layer of the sediments will become exhausted of carbonate, and benthic sediment mixing will have to become involved for a further carbonate supply (Peng and Broecker, 1978). Mixing down into the deep waters of the ocean and subsequent neutralization will eventually lower the atmospheric CO_2 partial pressure to less than twice the present value. The neutralization follows equation (3), i.e., the fossil-fuel

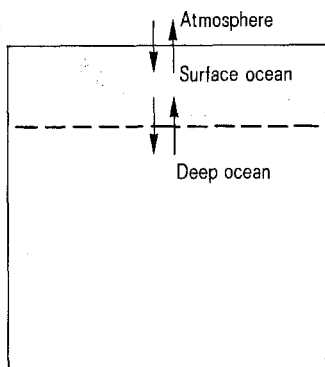


Fig. 5. The two-box ocean mixing model as it is commonly employed to calculate uptake of fossil-fuel CO_2 in the ocean (e.g. Keeling, 1973; Baes et al., 1977; Machta, 1973). The arrows stand for first-order exchange between the reservoirs. In the model of Oeschger et al. (1975) the deep water box is filled by diffusive transport from the surface box rather than by first-order exchange, which gives the model more desirable response characteristics.

CO₂ will be transformed into dissolved bicarbonate. It should be noted that the terrestrial biosphere at this stage will be of minor importance in determining the atmospheric partial pressure of CO₂.

Available model calculations (Keeling, 1973; Bacastow and Keeling, 1979) greatly simplify the situation (i.e., unchanged oceanic circulation, and prescribed fossil-fuel use and carbonate dissolution). They predict peak atmospheric CO₂ partial pressures of about 7 times the present value 200 years from now, and a relaxation time of about 1000 years.

The enhanced bicarbonate content of the world ocean will finally be subject to long-term geological cycles. If the natural turnover time were essentially unaltered, one would predict a relaxation time of the order of 100,000 years. The geological cycle brings atmospheric CO₂ back to its natural level.

The general oceanic fate of fossil-fuel CO₂ is thus understood. Much of the detail, however, is left for further assessment. One line of research that is at present being initiated is on interactive atmosphere-ocean models that would include the feed-back effect of enhanced atmospheric CO₂ partial pressures on the oceanic circulation. A more specific account of carbonate dissolution could be incorporated into such models.

Conclusions

The present oceanic share of the total fossil-fuel C burned so far amounts to about 40%. Although future research will refine this figure, a major revision is unlikely. With increasing fossil-fuel use over the next 100–200 years, as predicted in common energy scenarios (Rotty, 1980), the oceanic share will decrease to about 20%. The oceanic uptake of CO₂ from the atmosphere will then be so slow that the atmospheric CO₂ partial pressure will stay high, at several times the present level, for several centuries, even after fossil-fuel burning has virtually ceased. The maximum CO₂ partial pressure will therefore primarily depend on the total of fossil-fuel burned and much less so on the rates of burning, and it will constitute an environmental burden for many generations to come. The situation can be paraphrased by the statement that the expected fossil-fuel burning will occur on a time scale much faster than nature's control on atmospheric CO₂ – so that, should control become desirable, it will have to be of a socio-economic nature. Once the atmospheric CO₂ partial pressure has risen to a few times its natural value, ocean surface water will become sufficiently corrosive to dissolve carbonate from higher-latitude shelf sediments. Such dissolution, via chemical neutralization of dissolved CO₂, will bring a moderate decrease in atmospheric partial pressure. (The environmental side-effects on marine life are uncertain.) A further decrease in partial pressure will have to await recirculation of the deep

waters of the ocean and carbonate dissolution from deep ocean sediments; these processes require a period of time on the order of 1000 years. Most of the fossil-fuel C will then be converted to oceanic dissolved bicarbonate. Beyond this stage, the cycle of rock weathering and sedimentation will take control; after several hundred thousand years, atmospheric CO₂ will have lost its memory of the fossil-fuel burning episode, and only the sedimentary record will be able to tell of the fossil-fuel CO₂ excursion.

- Andersen, N.R., and Malahoff, A., ed., 1977. The fate of fossil-fuel CO₂ in the oceans. Plenum, New York.
- Bacastow, R., 1977. Influence of the southern oscillation on atmospheric carbon dioxide; in: The fate of fossil-fuel CO₂ in the oceans, p.33–43. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Bacastow, R.B., and Keeling, C.D., 1979. Models to predict future atmospheric CO₂ concentrations; in: Carbon dioxide effects research and assessment program, p.72–90. Ed. W.P. Elliot and L. Machta. US Department of Energy, Washington DC.
- Bach, W., 1980. Climatic effects of increasing atmospheric CO₂ levels. *Experientia* 36, 796–806.
- Baes, C.V., Goeller, H.E., Olson, J.S., and Rotty, R.M., 1977. The global carbon dioxide problem. *Am. Scient.* 65, 310–320.
- Berger, W.H., 1977. Carbon dioxide excursions and the deep-sea record; in: The fate of fossil-fuel CO₂ in the oceans, p.505–542. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Bolin, B., 1977. Modelling the oceans and ocean sediments and their response to fossil-fuel carbon dioxide emissions; in: The fate of fossil-fuel CO₂ in the oceans, p.81–95. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Broecker, W.S., 1979. A revised estimate for the radiocarbon age of North Atlantic deep water. *J. geophys. Res.* 84, 3218–3226.
- Broecker, W.S., and Takahashi, T., 1977. Neutralization of fossil-fuel CO₂ by marine calcium carbonate; in: The fate of fossil-fuel CO₂ in the oceans, p.213–241. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Broecker, W.S., Takahashi, T., Simpson, H.J., and Peng, T.-H., 1979. Fate of fossil-fuel carbon dioxide and the global carbon budget. *Science* 206, 409–418.
- Broecker, W.S., Peng, T.-H., and Engh, R., 1980. Modeling the carbon system. *Radiocarbon* 22, in press.
- Delmas, R.J., Ascencio, J.-M., and Legrand, M., 1980. Polar ice evidence that atmospheric CO₂ 20,000 years BP was 50% of present. *Nature* 284, 155–157.
- Elliot, W.P., and Machta, L., ed., 1979. Carbon dioxide effects research and assessment program. Report Conf. 770385. US Department of Energy, Washington, DC.
- Garrels, R.M., and Perry, Jr, E.A., 1974. Cycling of carbon, sulfur, and oxygen through geologic time; in: The sea, vol. 5, p.303–336. Ed. E.D. Goldberg. J. Wiley, New York.
- Hampicke, U., 1980. The effect of the atmosphere-biosphere exchange on the global carbon cycle. *Experientia* 36, 776–781.
- Hay, W.W., and Southam, J.R., 1977. Modulation of marine sedimentation by the continental shelves; in: The fate of fossil-fuel CO₂ in the oceans, p.569–604. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Holland, H.D., 1978. The chemistry of the atmosphere and oceans, table 6–7. J. Wiley, New York.
- Keeling, C.D., 1968. Carbon dioxide in surface oceans waters. 4. The global distribution. *J. geophys. Res.* 73, 4543–4553.
- Keeling, C.D., 1973. The carbon dioxide cycle: Reservoir models to depict the exchange of atmospheric carbon dioxide with the oceans and landplants; in: Chemistry of the lower atmosphere, p.251–329. Ed. S.I. Rasool. Plenum, New York.
- Machta, L., 1973. Prediction of CO₂ in the atmosphere; in: Carbon and the biosphere, p.21–31. Ed. G.M. Woodwell and E.V. Pecan. US Atomic Energy Commission, Washington DC.
- Mopper, K., and Degens, E.T., 1979. Organic carbon in the ocean: nature and cycling; in: The global carbon cycle, p.293–316. Ed. B. Bolin, E.T. Degens, S. Kempe and P. Ketner. Wiley, New York.

- 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.
- Peng, T.-H., and Broecker, W.S., 1978. Effect of sediment mixing on the rate of calcite dissolution by fossil-fuel CO₂. *Geophys. Res. Lett.* 5, 349–352.
- Pytkowicz, R.M., and Small, L.F., 1977. Fossil-fuel problem and carbon dioxide: an overview; in: *The fate of fossil-fuel CO₂ in the oceans*, p. 7–31. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Roether, W., 1979. Use of oceanic tracers to determine the uptake of excess CO₂ into the ocean; in: *Man's impact on climate*, p. 109–114. Ed. W. Bach, J. Pankrath and W.W. Kellog. Elsevier, Amsterdam.
- Rotty, R.M., 1980. Past and future emission of CO₂. *Experientia* 36, 781–783.
- Scope 13 'The global carbon cycle'. Ed. B. Bolin, E.T. Degens, S. Kempe and P. Ketner. J. Wiley, New York.
- Takahashi, T., 1979. Carbon dioxide chemistry in ocean water; in: *Carbon dioxide effects research and assessment program*, p. 63–71. Ed. W.P. Elliot and L. Machta. US Department of Energy, Washington DC.
- Weiss, W., Roether, W., and Dreisigacker, E., 1979. Tritium in the North Atlantic ocean: inventory, input and transfer into the deep water; in: *Behaviour of tritium in the environment*, p. 315–336. International Atomic Energy Agency, Vienna.
- Wollast, R., and Reinhard-Derie, D., 1977. Equilibrium and mechanism of dissolution of Mg-calcites; in: *The fate of fossil-fuel CO₂ in the oceans*, p. 479–493. Ed. N.R. Andersen and A. Malahoff. Plenum, New York.
- Woodwell, G.M., and Houghton, R.A., 1977. Biotic influences on the world carbon budget; in: *Global chemical cycles and their alterations by man*, p. 61–72. Ed. W. Stumm. Dahlem Konferenzen, Berlin.
- Zimen, K.E., 1979. The carbon cycle, the missing sink, and future CO₂ levels in the atmosphere; in: *Man's impact on climate*, p. 129–137. Ed. W. Bach, J. Pankrath and W.W. Kellog. Elsevier, Amsterdam.

SPECIALIA

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The structure of a novel antitumor antibiotic, saframycin A

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Summary. A structure is assigned to saframycin A, a novel antitumor antibiotic from *Streptomyces lavendulae* No.314, on the basis of ¹³C NMR-spectral data.

Streptomyces lavendulae is the well-known source of the classic antibiotic streptothricin¹. During the course of screening for new antibiotics which are active against the established cell line L1210 mouse leukemia, we found that a strain of *Streptomyces lavendulae*, designated No.314, exhibited cytotoxicity against a line of tumor cells in addition to the production of streptothricin. Satellite antibiotics named mimosamycin and saframycin A to E were obtained from the organic solvent extract of the cultured filtrate². Among these antibiotics, the structure of mimosamycin [C₁₂H₁₁N₃O₄] was determined as 2,6-dimethyl-7-methoxy-3,5,8-trioxo-2,3,5,8-tetrahydroisoquinoline (1)^{3,4}. The structures of 2 major antibiotics, saframycin B [C₂₈H₃₁N₃O₈] and C [C₂₉H₃₃N₃O₉] were determined as 2 and 3, respectively, by an X-ray crystallographic study and ¹³C NMR-spectral data⁵.

The present communication is concerned with the structural elucidation of saframycin A (4) which possesses the highest antitumor activity among these satellite antibiotics against mouse leukemia L1210 and P388⁶.

It was also reported that saframycin A (4) was found to bind to DNA and to inhibit both DNA and RNA syntheses⁷.

The physical constants of saframycin A (4), a yellow amorphous powder (cold ether), are as follows: m.p. 122–126 °C (ether), [α]_D +18.2° (MeOH); C₂₉H₃₀N₄O₈; mass spectrum m/e (%): 562 (M⁺, 8), 462 (M–100, 30), 243 (83), 220 (100), 218 (54); UV λ_{max}^{MeOH} nm (log ε): 267 (4.34), 370 (inf.); CD (MeOH): 278 nm (Δε –28.5); IR ν_{max}^{CHCl₃} cm^{–1}: 3400, 1716, 1685, 1660, 1615.

The ¹H NMR-spectrum (CDCl₃, 100 MHz) showed signals at δ1.90 (s), 1.98 (s), 2.24 (s), 2.30 (s), 4.04 (2×s) for 6 methyl groups. The ¹³C NMR-data (CDCl₃) revealed the nature of all the methyl groups [δ8.8 (2×C–CH₃), 24.3 (COCH), 41.7 (N–CH₃), 61.0 and 61.1 (2×OCH₃)] and displayed the characteristic 6 pairs of signals at δ128–187 due to the quaternary aromatic and carbonyl carbons, and an unusual signal at δ116.7 (s) (table). The above spectroscopic data indicate that saframycin A (4) must have the same carbon skeleton as saframycin B (2) and C (3).

Comparison of the empirical formula of saframycin A (4) with that of saframycin B (2) [C₂₈H₃₁N₃O₈] suggests that 1 cyano group is substituted for 1 hydrogen atom of 2. This assignment was substantiated by the ¹³C NMR-spectrum (δ116.7). However, in the IR-spectrum, no absorption band was observed in the C≡N region.