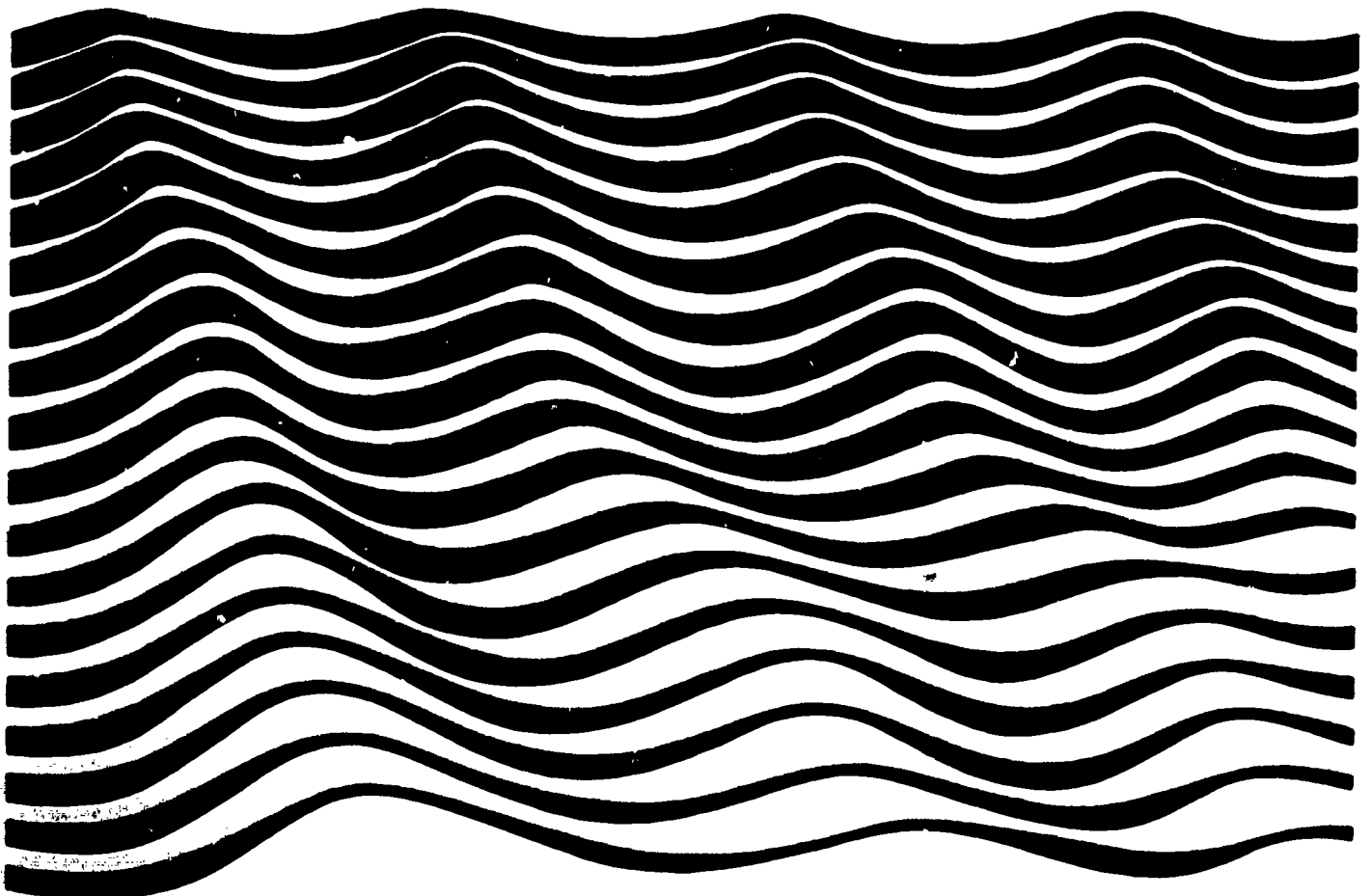


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in marine science 34

The carbon budget of the oceans

Report of SCOR
Working Group 62
Unesco,
Paris, 12-13 November 1979



Unesco 1980

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PREFACE

This series, the Unesco Technical Papers in Marine Science, is produced by the Unesco Division of Marine Sciences as a means of informing the scientific community of recent developments in oceanographic research and marine science affairs.

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I. INTRODUCTION

The SCOR Working Group 62 on the carbon budget of the oceans had its first meeting in Paris, France at Unesco Headquarters, on 12-13 November 1979. Members in attendance were : M. Whitfield (UK); F. Millero (USA) ; H. Geshger (Sweden) ; S. V. Smith (USA) ; P.J. Le B. Williams (UK) and E.D. Goldberg (USA), Chairman. Absent were J. Edmond (USA), R. Ginsburg (USA) and E.A. Romankovitch (USSR). In addition, some members of Working Group 44, which was meeting the following two days, attended the sessions : R. Chesselet (France); J. Prospero (USA) ; R.A. Duce (USA) ; S. Tsunogai (Japan) ; W. Seiler (Federal Republic of Germany). The meeting of SCOR committees "back to back" proved especially rewarding to Working Group 62 which gained substantial inputs from this procedure. Clearly, such a tactic will be successful where the Working Groups have some common interests.

The carbon budget of the earth is of great concern to many scientists today, especially those involved in the study of the implications to the environment of man-mobilized carbon dioxide through fossil fuel combustion and through the destruction and burning of terrestrial biomass. There are several recent volumes and many recent papers dedicated to formulation of models of the carbon budget; the oceans play a significant role in all such models. Briefly the situation may be summarized as follows : approximately 1.60×10^{11} tons of carbon have been released to the atmosphere by the burning of fossil fuel ; the present release rate is about 5×10^9 tons yr^{-1} . About 50% of the carbon released is believed to be present in the atmosphere and 40% is believed by chemical oceanographers to be in the oceanic CO_2 pool. The chemical oceanographers suggest that an increase in the terrestrial biosphere accounts for the remaining 10%. However, terrestrial biologists suggest that there has been net terrestrial biosphere reduction equivalent to 20 to 100% of the fossil fuel release. In other words, the terrestrial biosphere may actually be a substantial CO_2 source, rather than a sink. The Working Group recognized that neither reviewing the present literature nor rewriting the conventional wisdom on the role of the oceans in the carbon budget would be especially fruitful. Instead they posed the question "What are other sinks for carbon in the ocean that may be significant and which have been over-looked or played down?", "What measurements should be made to evaluate the importance of such sinks?" and "What ancillary measurements might be made to more clearly define the ocean's role in the carbon cycle?".

2. THE ELEMENTAL CARBON SINK

The annual burning of biomass has been estimated by Seiler and Grutzen (Seiler and Grutzen, 1980) to be between 5 and 9×10^9 tons per year. This results from slash/burn agriculture, forest fires both natural and man-started, industrial and domestic wood burning and the burning of agricultural wastes. As a consequence, between 0.1 and 1.5×10^9 tons of elemental carbon are produced.

This charcoal is accumulated in part in the soils and in part is transported by rivers and by air to marine, glacial and lacustrine sediments, where it is refractory to biological degradation. In principle, such sediments maintain a historical record of the extents and type of biomass burning.

The carbon is essentially removed from the short term cycle of the element. Further, the elemental carbon pool may accommodate some of the excess carbon produced by fossil fuel burning.

The yearly fluxes of the carbon are poorly known and the burning record can be developed by analyses of carbon in coastal marine and lacustrine sediments which receive the burning debris from wide areas. Thus, a systematic programme of analysis of carbon in sediments, emphasizing the area between 30° N and 30° S, but including deposits accumulating material from the temperate and boreal forests is proposed

Secondly, present day biomass burning can be measured by remote sensing techniques from satellites. Such satellite studies must be accompanied by ground truth surveys of the burnt areas where the biomass burnt per unit area and the net carbon dioxide flux per unit area can be obtained. Further, investigations on the fate of the unburnt carbon is important for the carbon budget. Since many countries will be involved in the biomass burning, a co-ordinated programme can be effectively implemented by an international agency.

The development of novel but simple analytical techniques for the measurement of elemental carbon is needed. Present methods are time-consuming and cumbersome.

3. INFLUENCE OF THE OCEANIC BIOSPHERE

The carbon dioxide utilization rates of the marine biota are estimated to be around 25×10^{15} g C yr⁻¹ (Whittaker and Likens, 1973) of which about 24×10^{15} g C yr⁻¹ is attributed to planktonic processes and about 1×10^{15} g C yr⁻¹ to the benthic and estuarine ecosystems. These rates are of the same order of magnitude as the production of carbon dioxide, as a consequence of anthropogenic processes. This enables the transport of significant amounts of carbon to some biomass or detritus reservoir. The most important consideration is the size of the pools themselves. The oceanic and benthic ecosystems will be considered separately because of the great difference in the turnover rates of the primary products in the system (See Fig. 1).

The phytoplankton biomass is turned over in a time scale of weeks, most of which (i.e., 90%) appears to be recycled within the mixed layer. Transport of particulate detritus from the euphotic zone to the deep ocean appears to be in the order of 3-10% of primary plankton production (i.e., about 1×10^{15} g C yr⁻¹). This could be a significant term in the overall net dioxide budget. Presumably, it would be linked to primary production and one needs to look for evidence of increases in primary production. There is no historical

evidence for any such increase. It is not immediately apparent how one could obtain such data. From a mechanistic point of view, it is difficult to identify a process, linked to the increased input of carbon dioxide into the atmosphere, which could give rise to an enhanced phytoplankton production in oceanic regions. The details of the argument are as follows:

In the oceans the ΣCO_2 concentration is sufficiently high (mixed layer content : $580 \times 10^{15} \text{ g C}$) in comparison with the estimated annual plankton production ($25 \times 10^{15} \text{ g C yr}^{-1}$) that it will never place a limitation on total production. Plankton crops at any one point in time rarely exceed 10% of total annual production, so that the maximum amount of carbon dioxide locked up in the plankton cycle is about 1% of the total mixed layer ΣCO_2 pool. Assuming that dissolved free- CO_2 is the immediate carbon dioxide source for plankton photosynthesis, it will inevitably reduce the free dissolved CO_2 reservoir. However a rough calculation suggests that even during peak periods of production ($50 \mu \text{g C fixed l.}^{-1} \text{ hr}^{-1}$) photosynthesis would reduce the free CO_2 pool by less than $0.4 \mu \text{g C l.}^{-1}$ (i.e., $< 0.1\%$). Over periods of days, the sustained rates of net production would reduce the free CO_2 by less than $0.3 \mu \text{g C l.}^{-1}$. Thus, neither the CO_2 pool nor the free CO_2 concentration appear to offer a control mechanism on oceanic plankton production which in its turn could result in an enhancement of organic sedimentation rate.

Three other storage reservoirs exist : phytoplankton biomass, particulate organic carbon and dissolved organic carbon. In the mixed layer of the ocean they probably amount to $5 \times 10^{14} \text{ g C}$, $2 \times 10^{15} \text{ g C}$ and $3 \times 10^{16} \text{ g C}$ respectively. The accuracies of these values are probably above the average of those used in global carbon budgeting. The plankton biomass term is about 10% of the annual fossil fuel carbon input and cannot therefore over all of the years have accumulated anything but an insignificant portion of the total anthropogenic carbon dioxide production ($1.25 \times 10^{17} \text{ g C}$, Wong, 1978). The other two reservoirs and especially the dissolved organic carbon reservoir, are of sufficient size to account for a significant proportion of the net carbon dioxide production, however this would call for changes in the biochemistry of the processes giving rise to dissolved and particulate organic carbon in response to the changes in the chemical environment. The immediate chemical changes in the oceans due to the uptake of anthropogenic carbon dioxide are restricted to a small increase in the total carbon dioxide pool and a very small change in pH. It is difficult to foresee how these very minor chemical changes could provide a mechanism for the increased accumulation of dissolved organic material.

4. SEAWEED AS A CO_2 SINK

Three possible roles may be assigned to seaweed as a sink for CO_2 :

1. may be significant as a net carbon sink;
2. may also be an important short-term sink which transfers its contents "surreptitiously" to the oceanic CO_2 pool;
3. may act as a control valve on the direct transfer of CO_2 from the atmosphere to the oceanic CO_2 pool. This component, in general terms, consists of attached benthic plants (both seagrasses and macroalgae), which will henceforth be referred to as seaweed.

Figure 1 represents data from Whittaker and Likens (1963) in a format convenient for considering plant biomass, primary production and turnover time (i.e., the ratio of biomass to primary production). The cumulative fossil-fuel carbon input and the input rate are shown as "biomass" and "production" respectively, for comparison. The accumulated fossil carbon input is approximately 10% of the global plant biomass and the present input rate is about 6% of the global primary production.

Most terrestrial ecosystems (A-N, Fig. 1) exhibit relatively high biomass and have turnover times of several years. By contrast, most oceanic ecosystems (O-S, Fig. 1) exhibit low biomass and have turnover times of only a few weeks. Among the marine ecosystems, there are two interesting exceptions to this generality. The "algal bed and reef" ecosystem (R) and the estuarine ecosystem (S) have the highest biomass among the marine ecosystems, which have turnover times of about one year. Attached plants are important components of both these ecosystems and hence they may be called "seaweed ecosystems". The primary production of these seaweed ecosystems is only a small fraction of the oceanic primary production.

Ecosystems with a high turnover are not effective carbon sinks, because the carbon has no reservoir in which to accumulate. Thus, the forests on land are more effective sinks than grasslands. By analogy, the seaweed ecosystems are a more effective carbon sink than the planktonic ecosystems (see the previous section for a discussion of the plankton).

The reservoir size of these ecosystems is inadequately known, and the figures of Whittaker and Likens must be regarded as very uncertain estimates. Despite this uncertainty, it appears that seaweed biomass and annual production are in the neighborhood of 10^9 tons carbon. This figure is 20% of the present annual fossil-fuel carbon input and half the estimated storage in oceanic CO_2 .

The fate of this material is uncertain. Very little seaweed seems to be directly grazed. Some enters the foodweb as detritus, but much becomes deposited in sediments. Either broadcast dispersal of the detritus away from production sites or burial of the seaweed as localized clumps renders detection and quantification of this carbon sink a difficult task.

One can argue that the biological economy of the seaweed ecosystems "could not afford" to lose the bulk of the seaweed to the sediments. This is not necessarily so. Figure 1 demonstrates that the primary production of the seaweed ecosystem is a relatively small fraction of the primary production of even the continental shelf ecosystem (Q), a planktonic ecosystem encompassing the seaweed system. Emery (1960) constructed an organic carbon budget for the southern California continental borderland and suggested that attached algae there account for only about 4% of the total primary production. Thus, the buried detritus from seaweed may represent a substantial carbon sink in the world oceans.

Let us consider the role of seaweed as a short-term sink transferring carbon to the oceanic CO_2 pool. Undoubtedly some of the seaweed carbon is

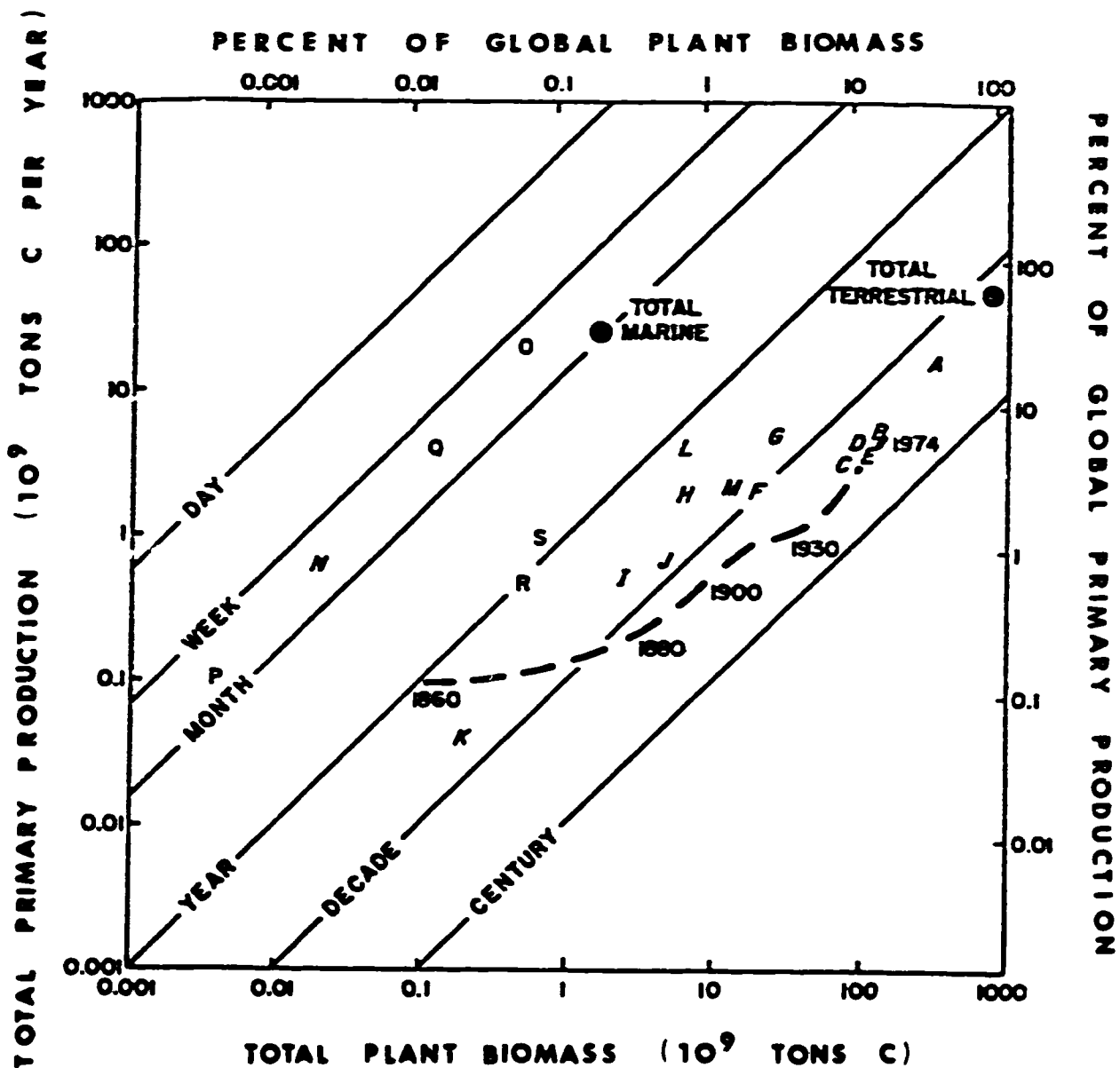


Figure 1. Primary production, biomass, and turnover time for the carbon in the biosphere. Adapted from Whittaker and Likens (1973). Coding as follows: Italic letters (A-N) indicate terrestrial ecosystems and remaining letters (O-S) indicate marine ecosystems. A - tropical rain forest; B - tropical seasonal forest; C - temperate evergreen forest; D - Temperate deciduous forest; E - boreal forest; F - woodland and shrubland; G - Savanna; H - temperate grassland; I - tundra and alpine meadow; J - desert scrub; K - rock, ice, and sand; L - cultivated land; M - swamp and marsh; N - lake and stream; O - open ocean; P - upwelling zones; Q - continental shelf; R - algal bed and reef; S - estuaries.- The cumulative fossil carbon input and the input rates are shown for comparison

consumed as detritus. To the extent that the detritus consumption occurs at or near the production site, the seaweed production is part of a local CO_2 cycle between water and biota, with no net impact on the CO_2 balance. However, seaweed is often well removed from its production site before it is totally consumed. Seaweed which grows near the surface, drifts to deep water, and is consumed there, functions as a temporary sink moving CO_2 out of the mixed layer and into deep water.

The data are unavailable to evaluate the importance of this CO_2 transfer process relative to direct carbon storage. One "advantage" of such carbon transfer over direct storage as organic residue is that direct storage sequesters some amount of limiting nutrients, whereas the advective transfer pathway liberates the nutrients back to the ocean for continued cycling.

We come now to the final role postulated here for seaweed ecosystems in carbon transfer. Global estimates of CO_2 transfer across the air-sea interface are based on data collected from the open ocean to construct worldwide box models. The consideration of transfer rates does not address the coastal regions which may have high seaweed production, and hence a substantial depression of the CO_2 partial pressure.

Withdrawing only 0.2 moles $\text{CO}_2 \text{ m}^{-3}$ from seawater halves the CO_2 partial pressure. The data in Figure 1 for seaweed primary production are equivalent to approximately 0.2 moles $\text{CO}_2 \text{ m}^{-3} \text{ day}^{-1}$. It is now possible to establish some notions of expected CO_2 utilization by organic carbon production.

Typically seaweed grows in water less than 5 metres deep, although some species of kelp grow to depths of 25 metres. Water exchange times of a few hours up to a few days might typify fairly open water settings, whereas sheltered environments might harbour waters for many days. It can be calculated that a CO_2 draw-down of 0.2 moles m^{-3} , or even more, is not unreasonable. Thus a CO_2 partial pressure depression to 150 ppm by seaweed production is entirely plausible.

Such P_{CO_2} anomalies are not encountered in the open ocean. Broecker et al. (1979) CO_2 suggest that the average oceanic anomaly is about 8 ppm. Localized high anomalies as might be created by the CO_2 draw-down of seaweed could greatly influence the rate at which the oceans take up CO_2 ; thus this P_{CO_2} depression is yet one more manner in which seaweed influences the oceanic CO_2 sink.

The biomass of many of the seaweeds is highly seasonal. In addition there is evidence, both locally and worldwide, for massive long-term fluctuations in the area covered by algae and grass beds. The time-scale of this fluctuation is of the order of years to decades, superimposed on the seasonal biomass fluctuations, so the carbon storage capacity of this reservoir is highly variable. Because the carbon reservoir is relatively small, although potentially significant, any globally significant biomass variation will be represented by very strong amplification in the seaweed reservoir. Such information may be retrievable from relatively crude historical records. The variation of this reservoir is not likely to have been responsive to CO_2 increases in the

atmosphere and oceans, but this variation may nonetheless partially account for our uncertainty about carbon sinks.

Nutrient limitation of this seaweed biomass accumulation does not appear to be an immediately relevant issue in evaluating the importance of the seaweed biomass reservoir. It has been observed that the growth of the marine organic carbon reservoir could be proportional to human discharges of limiting nutrients which may have been in rough proportion to the CO_2 loading. There are some other points of resiliency in this nutrient limitation as well. Biochemical utilization of the seaweed in part liberates the potentially limiting nutrients and leaves behind a carbon-rich residue. Often the seaweed represents a relatively minor part of the total ecosystem production, which may be dominated by high production, high-turnover phytoplankton. Hence, seaweed biomass burial may be a locally insubstantial drain on the nutrient reservoirs. Finally, the process of seaweed biomass fluctuation is a demonstrable event which pre-dates the industrial carbon input and is at least implicitly "covered" in extant nutrient budgets. If more careful inspection of data on seaweed biomass and biomass fluctuation continues to suggest this reservoir to be significant as a global carbon sink, then the extant budgets of limiting nutrients may need to be modified accordingly.

This potential importance of the seaweed carbon sink suggests three related lines of research :

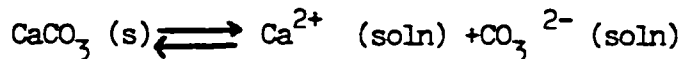
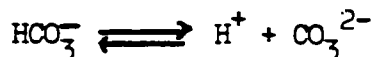
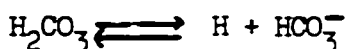
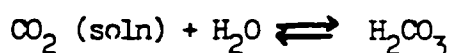
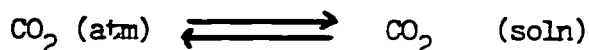
1. Effort should be devoted to a global inventory of the present area of algae and seagrass beds and evidence for long-term variation of these beds. This evaluation of historical changes can probably be accomplished in large part from both published and unpublished data, in particular historical archives of air photographs. Air photographs, satellite remote sensing and limited ground-truth surveys should be used for assessment of present seaweed areas. The only way seaweed carbon can be important to the global carbon inventory is if the changes in this reservoir are relatively large.

2. The data on biomass and productivity should be evaluated, to insure that they are properly weighted on a global scale.

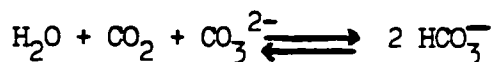
3. The fate of the seaweed biomass should be carefully examined, to determine whether this biomass indeed does represent a significant carbon sink or merely a closed carbon re-cycling loop.

5. INORGANIC RESPONSES OF THE OCEAN TO INCREASES IN ATMOSPHERIC CO_2

Most CO_2 models assume that the amount of atmospheric CO_2 taken up by the ocean is involved in the following chemical reactions:



The total CO_2 in solution is increased when the atmospheric CO_2 increases. The concentration of HCO_3^- increases at the expense of CO_3^{2-} ,



The carbonate alkalinity ($\text{HCO}_3^- + 2 \text{CO}_3^{2-}$) remains constant. If the process continues long enough, the solid CaCO_3 (in its various forms) will begin to dissolve with a consequent increase in alkalinity. Since most surface waters are normally supersaturated with common shell material, most models do not consider the reactions of CO_2 with solid CaCO_3 in assessing the short and medium term response of the oceans to changes in atmospheric CO_2 .

5.1. Basic data

Thermodynamic data (Millero, 1979) on homogeneous equilibria are adequate for modelling purposes and the equilibrium relationship between $\Delta \Sigma \text{CO}_2$ and ΔCPCO_2 (i.e., the Revelle factor) can be accurately assessed. Solubility data at 1 atm. for magnesium-calcites in equilibrium with sea water are in reasonable agreement (e.g., see summary by Morse et al., 1980). The data for aragonite (Morse et al., 1980) are not in good agreement and long equilibration times probably associated with structural rearrangements can cause problems. Refinement of these solubility data is required, particularly at low temperatures and also at high pressures.

Dissolution rates of calcite and aragonite require further study as do the rates of hydration and dehydration of gaseous CO_2 . In particular, it will be important to ascertain the degree of undersaturation required before calcium carbonate dissolution can occur at significant rates in cold and temperate surface waters. These investigations would constitute refinements to the response characteristics of the system but are unlikely to involve major changes in the parameters used in modelling.

5.2. Direct measurements in surface waters of response of oceanic system to increasing P_{CO_2}

Investigations are required in which transient tracer (e.g., tritium) and nutrient (e.g., nitrate) concentrations are used together with CO_2 data to assess the net uptake of $\Delta \Sigma CO_2$ from the atmosphere. Initial measurements along these lines (Chen and Millero, 1979 ; Chen and Pytkowicz, 1979) suggest that the ocean surface layers are following atmospheric PCO_2 changes quite closely. Similar procedures should also be used to follow the rapid downwelling of high latitude water to intermediate depths with the consequent transport of $\Delta \Sigma CO_2$, (see Broecker et al., 1979). Estimates are required of the net flux of $\Delta \Sigma CO_2$ by this mechanism in comparison with advective (dispersive) fluxes in tropical and temperate waters. Long term monitoring of mixed layer CO_2 levels and the status of the CO_2 system in selected sites is required to follow the response of the surface waters to changes in PCO_2 and, in shelf-waters, to show whether this response involves the dissolution of carbonate minerals.

5.3. Influence of P_{CO_2} increases on solubility of carbonate phases

5.3.1. Shallow water dissolution

When dissolution of $CaCO_3$ solid phases occurs the response is likely to be noticed first in aragonite and high magnesium calcite ($> 8\%$ magnesium) phases in high latitude and temperate shelf-seas, (Whitfield, 1974). More information is required on the distribution of aragonite and high magnesium calcite phases in such seas and on their potential role as a sink for fossil fuel CO_2 . Indications of contemporary corrosion of carbonate phases in shallow waters (Alexandersson, 1976, 1978) deserve further investigations. It is important to ascertain whether such sites are associated with regions of high productivity and/or with excursions to low ambient temperatures. Studies of the status of the CO_2 system are required in the interstitial waters in sites where dissolution is indicated from morphological evidence. A close watch should be kept on temperate and polar shelf seas for signs of corrosion of deposited $CaCO_3$ since calculations show that such waters should approach the saturation limit for high magnesium calcite and aragonite (and possibly calcite) when P_{CO_2} increases to two or three times its present value (Whitfield, 1974). Temperate shelf-seas in the Northern hemisphere are also likely to experience some degree of eutrophication over the next few decades.

5.3.2. Deep water dissolution

It has been generally assumed that in the long term (millenia), oceanic circulation patterns will allow atmospheric PCO_2 changes to lower the pH of deep waters so that dissolution of $CaCO_3$ can occur, thus providing a mechanism with a large buffer capacity which can act as a long term sink for anthropogenic CO_2 . Recent measurements of the penetration of tritium into the deep ocean (see summary by Broecker, et al., 1979) suggest that, at high latitudes, water equilibrated with the atmosphere may move rapidly to depths in excess of 1000 m. It is important to assess whether such rapid penetration of $\Delta \Sigma CO_2$

is likely to cause CaCO_3 dissolution on a significant scale in the short or medium term (decades or centuries). In assessing such effects, we again come up against the problem of studying the status of the CO_2 system in the interstitial waters of sediments. It is also necessary to investigate the source and nature of the material accumulating in the vicinity of the lysocline and to estimate the fluxes of settling material. Relationships between atmospheric CO_2 levels, estimated from ice cores, and the preservation record of calcitic and aragonitic tests in deep sea cores should be investigated in more detail to clarify the historical links between these parameters.

5.4. Recommendations

5.4.1. Further direct measurements should be made of the extent of undersaturation required for the dissolution of naturally occurring calcium carbonates. Particular emphasis should be placed on conditions representative of the environment at possible dissolution sites (i.e., temperatures less than 10°C at atmospheric pressure and also at pressures of several hundred atmospheres).

5.4.2. Coherent studies involving transient tracers, nutrient balance and CO_2 status measurements should be made in areas of active downwelling to assess the extent of removal of fossil fuel CO_2 . Attempts should be made to improve the method used by Chen (Chen and Millero, 1979; Chen and Pytkowicz, 1979) to separate the inorganic and organic contributions to $\Delta \Sigma \text{CO}_2$ in ocean waters.

5.4.3. A few select monitoring sites should be established in temperate and high latitude shelf seas and in the open ocean to follow the oceanic uptake of excess CO_2 and to ascertain the extent of involvement of solid buffer mechanisms. Measurements of PCO_2 , CO_2 and carbonate alkalinity should be made.

5.4.4. Studies (both theoretical and observational) should be undertaken to establish the extent to which rapidly downwelling waters are able to affect significant changes in the depth of the lysocline.

6. TRACERS FOR STUDIES OF ATMOSPHERE-OCEAN EXCHANGE

In the past and up to now carbon-14, tritium and radon isotopes have been used as tracers for atmosphere/ocean interactions. Carbon-14 has mainly provided apparent ages of sea water, the true ages, (relative to ocean surface) being masked by internal mixing to varying extents. Radon has provided an independent tool for determining gaseous exchange rate across the sea surface. Tritium, being bomb produced, represents a transient state and will continue to give valuable information on the atmospheric-ocean exchange. Since radioactive decay takes place, measurements of both the parent tritium and the stable daughter helium-3 make it possible to treat bomb tritium as a tracer with conservative properties. Krypton-65 is also a transient tracer, which is being introduced to the oceans.

Argon-39 being a steady state tracer with a half-life of 270 years, would be a valuable complement to carbon-14 apparent age determination since it will respond in a different way to internal mixing processes in the oceans. Argon-39 would therefore be of great value for evaluations of the true frequency distribution of age in the sea.

The objective of tracer studies in the oceans is to be able to construct a model for the oceanic components of its carbon dioxide cycle, making it possible to predict future uptake. The model should be based on the true frequency distribution of age (relative to the surface) of water in the oceans. This frequency distribution has to be assessed from tracer work of the past, present and future.

7. THE HISTORY OF THE ATMOSPHERIC CO₂ CONTENT

Measurements of the CO₂ content of the air occluded in ice cores indicate a lower atmospheric CO₂ content during last glaciation (of the order of 200 ppm., Oeschger, personal communication) than during the Holocene (around 300 ppm).

Attempts to find CO₂ concentration oscillations from the ocean sedimentary record should be sought. Combined with the ice core record on the atmospheric CO₂ content, they may contribute to the understanding of the oceans role in controlling the atmospheric CO₂ content.

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