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The Interaction of Global Biochemical Cycles

Workshop Chairmen:
B. Moore, III
University of New Hampshire

M.N. Dastoor
Jet Propulsion Laboratory

January 15, 1984

NASA
National Aeronautics and Space Administration
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
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Abstract

The global biosphere is an exceedingly complex system. To gain an understanding of its structure and dynamic features, it is necessary not only to increase our knowledge about the detailed processes but also to develop models of how global interactions take place. Our attempts to analyze the detailed physical, chemical and biological processes in this context need to be guided by an advancement of our understanding of the latter. It is necessary to develop a strategy of data gathering that serves both these purposes simultaneously.

The following papers deal with critical aspects in the global cycles of carbon, nitrogen, phosphorus and sulfur in detail as well as the cycle of water and the flow of energy in the earth's environment. The objective of the report is to set partly the foundation for the development of mathematical models that allow exploration of the coupled dynamics of the global cycles of carbon, nitrogen, phosphorus, sulfur, as well as energy and water flux. We state this objective with the recognition that a scientifically rigorous model -- one that captures the bulk of the interactions and resulting dynamics in a way faithful to the heterogeneity embedded within these cycles -- is beyond our current collective ability. Yet, we believe that it is not too early to begin developing a framework designed to help us consider the behavior of these interactions and their implications for global biogeochemical cycles.
Preface

The Biospheric Research Program (formerly Global Biology) deals with the understanding the fundamental aspects of biospheric dynamics as revealed by the interaction of the biota and the global environment. This program serves as the biological component of the U.S. Habitability initiative which addresses the impacts of change on the physical, chemical, and biological processes of the global environment affecting the long-term "habitability" of the earth.

Technological advancements over the last five years have considerably strengthened the potential for a science of the biosphere. Satellite and aircraft remote sensing, coupled with ground-based research, provides both the tools and the means for assessing the extent, rate, and significance of changes in the biosphere, while also measuring specific processes that can yield insight into fundamental aspects of global dynamics. Computer systems can now store and process the prodigious amounts of data that such a research effort will gather. Theoretical models provide a means for integrating the data and designate gaps in existing knowledge, while reflecting current levels of understanding.

Within such a framework, the Biospheric Research Program requires a major modeling effort to integrate data in a meaningful manner. Such data include biogeochemical cycling, global vegetation/biomass, land use changes, nutrient fluxes, and atmospheric and oceanic processes. Extensive field investigations correlate ground process measurements with remote sensing data needed for regional and global extrapolation.

Initially, the program rationale, scope, and research strategy were defined by a science working group (NASA TM #85629) convened by the Life Sciences Division within the Office of Space Science and Applications. In the continuing refinement and formulation of research elements within the Biospheric Research Program, NASA seeks advice from the scientific community at large. These proceedings represent the conclusions and recommendations of a workshop specifically addressing the problems in modeling the biosphere. A comprehensive review of the present state of knowledge of global biogeochemical cycling was not the intent of the workshop; participants were charged with the formulation of gaps in our understanding and research priorities. These workshop results will serve as a guide to NASA in the implementation of the long-term Biospheric Research.

The Biospheric Research program office wishes to acknowledge the excellent and timely contributions by the workshop participants and extend sincere appreciation to all.

Mitchell B. Rambler, Ph.D.
Biospheric Research Program
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INTERACTIONS OF GLOBAL BIOGEOCHEMICAL CYCLES - AGENDA

Westpark Hotel, Rosslyn, Virginia
April 10-13, 1983
SUNDAY EVENING, APRIL 10, 1983:

4:30 - 6:00 pm  REGISTRATION AND WORKSHOP CHECK-IN  
                 (Shenandoah Room)

5:00 - 6:30 pm  Social Hour

6:30 - 8:00 pm  Dinner

8:00 - 9:00 pm  Featured Speaker:  
                 Bert Bolin, University of Stockholm  
                 "Global Biogeochemical Cycles"

MONDAY, APRIL 11, 1983:

8:00 am          --- COFFEE AVAILABLE --- (Club Room)

8:20 - 8:30 am   Introduction/Conference Business

8:30 am - 12:30 pm  SESSION I: THE CARBON CYCLE  
                     (Chairman: Bert Bolin)

8:30 - 8:45       Introductory Remarks

8:45 - 9:30       Overview of the Carbon Cycle  
                   (William Emanuel, Oak Ridge National Laboratory)

9:30 - 10:00     Floor Discussion

10:00 - 10:30    --- BREAK ---

10:30 - 11:00    Terrestrial Interactions  
                 (William Schlesinger, Duke University)

11:00 - 11:30    Ocean Interactions  
                 (Bruce Peterson, Marine Biology Laboratory)

11:30 - 12:00    Atmosphere Interactions  
                 (Jim Hansen, Goddard Institute for Space Studies)

12:00 - 12:30    Floor Discussion

12:30 - 2:00 pm  --- LUNCH --- (on own)

x
SESSION II: PHOSPHORUS AND SULFUR CYCLES  
(Chairman: Daniel Botkin, University of California, Santa Barbara)

2:00 - 6:15 pm  
2:00 - 2:15 pm Introductory Remarks  
2:15 - 3:00 pm Overview of Sulfur Cycle  
   (Robert Garrels, University of Southern Florida)  
3:00 - 3:45 pm Overview of Phosphorus Cycle  
   (Phillip Froelich, Florida State University)  
3:45 - 4:15 pm Floor Discussion  
4:15 - 4:30 pm BREAK  
4:30 - 5:00 pm Atmosphere Interactions, Sulfur  
   (Ronald Prinn, Massachusetts Institute of Technology)  
5:00 - 5:30 pm Terrestrial Interactions, Phosphorus  
   (Abraham Lerman, Northwestern University)  
5:30 - 6:15 pm Floor Discussion  
6:15 pm END OF FIRST DAY'S SESSIONS  

TUESDAY, APRIL 12, 1983:  
8:00 am --- COFFEE AVAILABLE --- (Club Room)  
8:20 - 8:30 am Introduction/Conference Business  
8:30 am - 12:45 pm SESSION III: THE NITROGEN CYCLE:  
   (Chairman, Constant Delwiche, Univ. of California-Davis)  
8:30 - 8:45 am Introductory Remarks  
8:45 - 9:30 am Overview of the Nitrogen Cycle  
   (Michael McElroy, Harvard University)  
9:30 - 10:00 am Floor Discussion  
10:00 - 10:30 am --- BREAK ---
10:30 - 11:00  Atmosphere Interactions  
(Joel S. Levine, Langley Research Center)

11:00 - 11:30  Terrestrial Interactions  
(Peter Vitousek, Univ. of North Carolina)

11:30 - 12:00  Ocean Interactions  
(Richard W. Eppley, Scripps Institute of Oceanography)

12:00 - 12:30  Floor Discussion

12:30 - 2:00 pm  --- LUNCH --- (on own)

2:00 - 6:15 pm  SESSION IV: ENERGY AND WATER CYCLES  
(Chairman: Harold J. Morowitz, Yale University)

2:00 - 2:15  Introductory Remarks

2:15 - 3:00  Overview of the Energy and Water Cycles  
(David Miller, University of Wisconsin)

3:00 - 3:30  Floor Discussion

3:30 - 4:00  --- BREAK ---

4:00 - 4:30  Terrestrial Interactions  
(Hank Shugart, Oak Ridge National Laboratory)

4:30 - 5:00  Ocean Interactions  
(Moustafa Chahine, Jet Propulsion Laboratory)

5:00 - 5:30  Atmosphere Interactions  
(Jagadish Shukla, NASA/Goddard Space Flight Center)

5:30 - 6:15  Floor Discussion

6:15 pm  END OF SECOND DAY'S SESSIONS

7:00 pm  --- BANQUET ---  
(The Vantage Point Restaurant)
SESSION V: SCIENTIFIC ISSUES AND NASA PROGRAM PLANS

Chairman: Berrien Moore, University of New Hampshire
Co-Chairman: Minoo Dastoor, JPL
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12:00 Noon

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UNKNOWN AND RESEARCH PRIORITIES:

BIOGEOCHEMICAL CYCLES
THE ATMOSPHERE

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Not enough is currently known about the sources, fluxes, and atmospheric budget of a large number of biogenic gases, or about the ultimate capabilities of needed remote sensing and in situ measurements to define a set of recommendations in specific terms. However the direction in which we recommend starting can be outlined relatively clearly. In order of priority, we recommend that NASA:

(1) Investigate the sources and fluxes of biogenic gas contributing to the S, C, and N cycles.

(2) Investigate role of the atmosphere as an integrator to infer locations and strengths of sources and sinks.

(3) Investigate energy and water cycles.

(4) Determine changes in deposition of solar energy.

I. SOURCES AND FLUXES OF BIOGENIC GASES

A. Nitrogen and Carbon Species

Fundamental deficiencies exist in our understanding of the sources and fluxes of biogenic gases into the atmosphere, the biological parameters (i.e., soil temperature, moisture, oxygen level, acidity, etc.) that control or modulate these fluxes, and the perturbations due to anthropogenic activities on the production of these gases. Many of these gases have important effects on the composition and photochemistry/chemistry of the troposphere (CH_4, CO, non-methane hydrocarbon, and biogenic NMHC, NH_3, NO), the stratosphere (N_2O, biogenic sulfur species and halocarbons) and on climate (CO_2, CH_4, N_2O, NH_3). Hence, due to research programs dealing with the troposphere, stratosphere, and climate, knowledge of the fluxes of these biogenic species is clearly relevant to NASA's on-going research program objectives. Yet, in general, determination of biogenic fluxes is not included in NASA's on-going atmospheric science programs.
Sources and fluxes of biogenic gases can be determined by controlled laboratory experiments and by field measurements. Field measurements of biogenic fluxes include field chamber measurements and very fast response detectors. Extrapolating from the controlled laboratory environment or microscale field environment to the global scale is not an easy task and requires considerable care. Once global sources are determined they will be used as input parameters in the photochemical models of the troposphere and stratosphere and in climate models.

Some specific questions to be addressed include:

1. N\(_2\)O: What are the biogenic processes that led to the production of N\(_2\)O in the ocean and on land? What is the ocean vs. land source strength of N\(_2\)O? How are anthropogenic activities perturbing the ocean and land production of N\(_2\)O?

2. NH\(_3\): What are the biogenic sources of NH\(_3\)? How are anthropogenic activities, i.e., fertilizers, perturbing the biogenic production of NH\(_3\)?

3. NO: What is the biogenic source strength of NO? How much of the biogenic NO is oxidized before it enters the atmosphere?

4. CH\(_4\): What are the processes that lead to the formation of anoxic fresh water habitats and what is the global extent of such habitats? How much of the biogenic-produced CH\(_4\) is oxidized before it enters the atmosphere?

5. CO\(_2\): What are the biogenic source and sink strengths for CO\(_2\)? What are the roles of the biosphere and oceans in controlling and modulating the atmospheric CO\(_2\) budget?

6. Non-Methane Hydrocarbons (NMHC): What is the global source strength of the various NMHC species? Are NMHC fluxes varying due to anthropogenic perturbations?

7. Low Molecular Weight Halocarbons: What role does biology play in the production of various low molecular weight halocarbons, e.g., methyl chloride, methyl bromide and methyl iodide?

B. Sulfur Species

Even though, from a global metabolism point of view, a significant portion of the sulfur chemical cycle occurs in the oceans, important transformations do occur in the atmosphere that impact terrestrial habitats in significant ways. In general, sulfur that contains gases is quite easily subjected to anthropogenic influences. In order to assess such anthropogenic perturbations, one needs to estimate the nature of the natural sources and their fluxes.

The oxidized atmospheric sulfur gases SO, SO\(_2\) are presumed to be of both natural and anthropogenic origin. It is generally believed that about
half of the source strength of \( \text{SO}_2 \) is produced by fossil fuel burning, the other half being arrived at by the oxidation of the reduced sulfur gases \( \text{H}_2\text{S}, (\text{CH}_3)_2\text{S}, \text{CS}_2, \text{etc.} \), in the atmosphere. Hence, the following tasks arise:

(1) Identify sources of \((\text{CH}_3)_2\text{S}, \text{CS}_2, \text{OCS}, \text{H}_2\text{S}, \text{etc.}\), and determine sensitivity of emissions to environmental parameters (light, moisture, temperature, etc.)

(2) Determine oxidation mechanisms of the reduced gases \((\text{CS}_2, (\text{CH}_3)_2\text{S}, \text{etc.})\) and measure their reaction rates

(3) Determine global, spatial and temporal distribution in "clean" air

(4) Identify and quantify important heterogeneous oxidation mechanisms for \( \text{SO}_2 \) in "polluted" and "clean" air

(5) Develop global models with sufficient resolution to include spatially heterogeneous sources and sinks

II. ROLE OF THE ATMOSPHERE

Can the question of source and sinks be approached from the gradients in atmospheric concentration of particular gases via inverse techniques? More specifically, how are the atmospheric distributions of biogenic gases related to the fluxes at the Earth’s surface? Can the atmospheric distributions be used to infer source and sink strengths and locations?

Sources and sinks of biogenic gases are difficult to obtain from local flux measurements, because of spatial and temporal heterogeneity and possible disturbance of the source by the measurement technique. However, it may be possible to infer the surface fluxes from the free atmosphere distribution of the gases, since the latter are determined by the sources and sinks together with the mixing effects of the atmospheric general circulation and in some cases chemical reactions in the atmosphere. With the help of models which account for the atmospheric mixing and chemical reactions, it should be possible to infer information on the surface sources and sinks. In the case of gases such as \( \text{N}_2\text{O}, \text{CH}_4 \) and \( \text{CO}_2 \), the rate of reactions in the lower atmosphere is so slow that only atmospheric mixing need be accounted for.

An example of this approach is provided by the modeling of the atmospheric \( \text{CO}_2 \) distribution by Fung et al. (see their paper, following) where they show the computed seasonal amplitude of surface air \( \text{CO}_2 \) illustrating the expected correlation of the atmospheric variations with the biospheric sources. In this case, determination of the net primary productivity of the biosphere source will depend upon improved definition of the seasonality of the biospheric uptake and release.

The measurements required to carry out this approach are accurate observations of the spatial distribution of the gases of interest, e.g., \( \text{N}_2\text{O}, \text{CH}_4, \text{CO}_2, \) and \( \text{SO}_2 \). The measurements need to be made at several times during the year to define seasonal variations, because the general
circulation and most expected sources change seasonally. The spatial scale of measurements would normally need to be at least regional, and in many cases global coverage is desirable. The greatest difficulty may be attainment of an adequate precision of measurement of the gas abundances to define the existing spatial inhomogeneities. In the case of CO₂, the need is for accuracy within a few tenths of a part per million; Keeling has shown that this is possible with careful calibration, and measurements at several stations are underway. However, even in this case the distribution of stations is not sufficient to define the terrestrial biospheric source/sink strength. Systematic observations of other variable biogenic trace gases have not yet been initiated.

III. ATMOSPHERIC WATER AND ENERGY

1. Objective: To understand storage and transport processes in the atmosphere.

2. Data needed about the following:
   (a) Evaporation from oceans and land
   (b) Atmospheric water vapor
   (c) Cloud water content
   (d) Cloud distribution
   (e) Precipitation
   (f) Skin surface temperature
   (g) Height and structure of Pbl

IV. SOLAR ENERGY FLUXES

1. Objective: To understand regional and local changes in solar energy deposition, and atmospheric energy budget

2. Data needed about the following:
   (a) Surface albedo
   (b) Cloud distribution and opacity
   (c) Atmospheric thermal structure
   (d) Atmospheric composition
THE TERRESTRIAL BIOTA

Unknowns and Research Priorities

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The research issues are divided into two broad areas: (1) terrestrial vegetation and biogeochemical fluxes and (2) terrestrial vegetation and climate.

I. TERRESTRIAL VEGETATION AND BIOGEOCHEMICAL FLUXES

A. Classification

All biogeochemical studies involving the terrestrial biosphere include the recognition of pools of elements on land and transfers to/from these pools. Because land ecosystems form a heterogeneous surface, these pools are best estimated by careful "point" studies in recognized units multiplied by the mapped area of such units. At present there is a relatively large body of the former information for most ecosystems, but much uncertainty and disagreement about how to approach the latter. Present schemes include mapping by vegetation, soil and life zone (climatic) units.

Recommendation. Preliminary studies should examine the correlation of parameters such as albedo and surface moisture to particular vegetation and life zone types. Then, satellite measurement of these parameters at a scale of 0.5m x 0.5m units could be used to calculate the area of classes of the terrestrial biosphere. While we see no need to favor a classification based on vegetation, life zones or soils, we suspect that the correlations of remote sensing parameters will be better with the former two schemes.
B. Land-Use

The combined characteristics of vegetation type and land use effect the storage levels of carbon, nitrogen, phosphorus and sulfur. Alteration in vegetation will release elements if the change is to a system of lower biomass and lower soil organic matter, or will store carbon if the change is to a system with more mass, as for example the establishment of forest on formerly cultivated land. Changes in land use are important in the global carbon balance because they determine the largest part, and perhaps all, of the net exchange of carbon between land and atmosphere. The same kind of documentation is needed for the calculation of changes in the storage of N, P, and S, as well as C.

Recommendation. In determining the pattern of land use, NASA should pursue three questions simultaneously: what systems were converted, to what, when?

C. The Effects of Land-Use and the Role of Partitioning Elemental Transformations

It is known that the gross fluxes of C, N, and S mobilized by land clearing are large — larger than the river flux on a global scale, larger (for N) than fertilizer use. Erosion is also substantially increased, altering the fluxes of P and other elements with sedimentary cycles. If the bulk of material mobilized is simply redistributed on land, the contribution to global fluxes will be minor. Similarly, if it is lost to the atmosphere in unreactive gas (N₂), its global effects will be nil. However, to the extent either erosion (for most elements) or leaching (for N and S) is important, then substantial consequences for aquatic and for marine ecosystems could occur; and to the extent this material is lost to the atmosphere in reactive forms (N₂O, NO, CH₄, CO, various forms of sulfur), its effect on the atmosphere (and downwind terrestrial or marine systems) also could be substantial.

Decomposition (carbon dynamics) controls the partitioning of N and to a large extent S; N and P availability in return can affect carbon dynamics. Carbon dynamics are particularly important in controlling (together with soil water) the oxidation/reduction status of soils, which control the proportion of N and S lost to leaching (as NO₃ and SO₄) and various gaseous fluxes. Soil organic matter remaining also strongly influences erosive losses of sedimentary elements.

The other side of the transformation occurring on land clearing is the rebuilding of element pools during succession reforestation. An understanding of where the rate of revegetation is limited by element dynamics (particularly by N and P) and in what regions each is important would be most helpful.

Recommendation. We have relatively little information on how these changes in terrestrial element reservoirs are partitioned. Developing such information will require developing a more thorough understanding of what regulates element transformations and how the cycles of the major elements interact. Techniques are now available which allow point measurements of the fluxes of C, N, and S from terrestrial systems. The problem is that these processes
are so variable both spatially and temporarily as to make generalization from point measurements difficult.

We should determine the controls of pathways of element transformations in particular, intensively studied sites, and a concurrent program of environmental monitoring (especially of soil moisture).

II. TERRESTRIAL VEGETATION AND CLIMATE

A. Heat and Moisture

The climate on earth and the distribution of terrestrial vegetation zones are mutually dependant on each other. We wish to be able to determine how external factors (e.g., solar radiation) or internal features of the climate system (e.g., concentration of radiatively active gases such as CO₂) may change climate and the terrestrial biosphere. In this context the ability to describe the processes of interaction in the transition zone occupied by plants is essential. This must be done on a space scale that is useful in making use of GCMs for climate modeling and experimentation. The characteristic time scale we are concerned with is that of the response time of the plant/soil system to external factors and climatic change particularly, i.e., one to several hundred years or more if concerned with soil changes.

Recommendation. We need to determine the characteristic features of the existing terrestrial vegetation zones that determine fluxes of heat and moisture. For instance, seasonal variations of albedo of different vegetation zones as function of season is one important such parameter to be determined. The systematic recording of key parameters during exceptional (stress) conditions of the biomes would also be of interest.

B. Ecosystem Boundaries

Ecosystem boundaries are particularly sensitive to changes in climate and other variables. Some of these boundaries are clearly identifiable by remote sensing means and their movement can be used as indirect indicators of change.

Recommended Boundaries to Monitor:

1. Taiga – tundra boundary
2. Taiga – prairie boundary
3. Sphagnums marsh – forest boundary
4. Desert – savannah boundary
5. Snow and ice line on seasonal basis
6. Greening and blossoming (pollen) times for selected ecosystems

7. Sea-water transition for selected bodies on a seasonal basis

8. Algal blooms on a seasonal basis for selected bodies of water

The interpretation of this information and the argumentation of the information by more refined means will make possible the interpretation of gross features of climate. Moreover, when interpreted in terms of more direct information on climate (temperature and rainfall) the interpretation will help identify the effects of other variables such as acid precipitation, insolation and (possibly) atmospheric constituents of recent origin.
THE OCEAN

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I. RESEARCH QUESTIONS

The research questions are divided into the following six areas: Continental runoff, estuaries and coastal zone, atmosphere-surface ocean fluxes, surface ocean mixed layer, deep sea, and benthic boundary layer plus sediments.

A. Continental Runoff

1. Can NASA quantify the water vapor flux from oceans to continents to constrain river fluxes?

2. What are the pre-anthropogenic fluxes of C, N, P, S plus other essential elements in rivers? What are the perturbed fluxes? What are chemical forms of the anthropogenic inputs? What is the fate of the various chemical forms of C, N, P, and S carried by rivers?

B. Estuaries and Coastal Zone

1. What fractions of the fluxes of essential elements are trapped in estuaries and deltas, and how has human perturbation affected the fraction trapped?
2. How important are deltas in trapping material fluxes? There is little C:N:P:S data in deltaic sediments and little information on diagenesis in this sediment type. In addition, a synthesis of information on C:N:P:S ratios is needed for coastal and deep sea sediments.

C. Atmosphere-Surface Ocean Fluxes

1. What is rain-out and dry deposition on surface ocean of essential elements? Is atmospheric transport of NOₓ to the ocean significant?

2. What are the fluxes of volatile N and S from the ocean to the atmosphere? These calculations depend on models which require data on wind stress and sea surface roughness. Can NASA generate global wind stress maps on 3 day resolution? There may be a need to calibrate Rn-222 and physical models of stagnant film.

D. Surface Ocean

1. Color scanners can map chlorophyll and could be useful for resolution of questions concerning the time and space scales of phytoplankton patchiness and biological-physical interactions.

2. Can abiotic "color" be subtracted, so turbid coastal waters can be assayed for chlorophyll as well?

3. What is relationship between spatial differences in oceanic ecology and the chemistry of vertical particulate fluxes (i.e., C:N:P:S fluxes and CaCO₃/C organic fluxes). Which ecosystems produce fecal pellets as contrasted to smaller particles?

4. Does overfishing affect the vertical particle fluxes or their chemistry through changing the structure of the marine food web?

E. Deep-Sea

1. Are volatile compounds being produced in the O₂-minimum zone?

2. It is critically important to follow the the time course of penetration of tracers into the upper thermocline over time scales of decades to get oceanic mixing and circulation rates. Are there NASA technologies which could assist in the development of improved estimates in the distribution of important transient tracers such as ¹⁴C, ³⁴S, ³⁹Ar, freons?

3. What are the long-term feedbacks between deep-water nutrient chemistry, surface productivity and climate?
F. Benthic Boundary Layer and Sediments

1. What are the burial rates and elemental exchange fluxes of C, N, S, and P across the benthic interface?

2. What is the production of $\text{N}_2\text{O}$, $\text{NO}$, $\text{N}_2$ (total denitrification) and sulfate reduction in sediments, especially slope sediments intersecting the $\text{O}_2$ minimum zone?

3. What is the rate of benthic denitrification in hemipelagic sediments under coastal-upwelling zones? Is it the missing fixed-N sink in the oceans? Are significant volatile sulfur fluxes associated with this denitrification environment?

4. What are elemental burial ratios (C:N:P:S) in marine sediments?

II. RESEARCH PRIORITIES

The committee realized that not all of these areas could receive equal attention and also that not all were of equal relevance for NASA's Global Biology Program. A few questions that appear to be of critical importance for NASA could be chosen. We have taken a start at such a listing.

1. How has man altered the chemistry of continental runoff and oceanic precipitation? What consequences have these changes for the biota of the coastal zone and open oceans?

2. What are the emissions of $\text{N}_2\text{O}$ and $\text{NO}$, and the volatile sulfur gases ($\text{DMS}$, $\text{COS}$, $\text{CS}_2$) from the coastal and open ocean areas?

3. Because of NASA's expertise in remote sensing of surface meteorologic conditions such as wind speed, it would appear most reasonable for NASA to sponsor and participate in an attempt to calibrate surface gas exchange measures using tracers such as radon. Improvements in these techniques would aid calculations of $\text{CO}_2$, $\text{N}_2\text{O}$ and $\text{DMS}$ fluxes across the air-sea interface.

4. What are the rates of oceanic denitrification and $\text{N}$-fixation? Can the oceans compensate for a fixed nitrogen deficiency by increased $\text{N}$-fixation or is the ocean dependent on variable inputs of nitrogen from continental runoff?

5. The question of errors in estimation of total open ocean primary productivity deserves careful attention because the cycles of C, N, P and S are intimately associated with the biotic processes of photosynthesis and respiration. Even the fluxes of the volatiles $\text{DMS}$ and $\text{N}_2\text{O}$ may be closely related to the rates of total production and decomposition of organic matter in the water column.
INTRODUCTORY PAPER

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A science that chooses the globe as its fundamental biogeophysical unit faces extraordinary conceptual difficulties. The questions that can be asked about biology at this level are not immediately obvious. Nor is it clear how to formulate theories, or experiments for a biological (biochemical) system of this size. From the viewpoint of physical sciences, the scale is not particularly grand; geophysics, meteorology and astrophysics often measure systems of planetary magnitude and larger. Yet, since considering biological systems on a planetary scale is new, initially it might seem that we lack the paradigms for understanding ecosystem dynamics at this level.

The primary dictum of global biology is that energy flows and matter cycles. The first part of this statement is a consequence of the second law of thermodynamics. Energy must move from low entropy sources to high entropy sinks; any sustained reversal of this direction of flow will result in a violation of one of the most universal constructs that has emerged within science. The second part of the original statement, dealing with the global cycling of matter, also follows from the laws of physics but in a less well understood way, which it would do well to clarify.

A closed system is defined as one through which there is no flow of matter. The surface of the earth approximates such a system, although the hydrogen leak and arrival of cosmic debris are not negligible on a geological time scale. In any case, an abstract closed system conserves atoms but allows for variation in molecular composition and spatial distribution. When electromagnetic energy flows into a closed system, its subsequent flux is determined by the spectral distribution of the radiation and the molecules present in the system. Energy which enters the system can be converted into chemical potential, heat, or macroscopic configurational energy, which is largely gravitational in the case of the earth. For chemical or gravitational energy the second law's tendencies toward degradation limit the accumulation and result in a constant flux from these low entropy forms to the higher entropy form of thermal energy. The flow of heat from the system to a thermal sink is the final stage in energy processing.
All closed systems with an energy flux from a source, whose spectral distribution is very different from the system's own black body distribution, are subject to an energy pumping to high levels of chemical potential and a second law relaxation to thermal levels. This takes the form of a matter flux from lower potential forms to those at a higher potential, at either a microscopic or macroscopic level. The return flow to the ground state then completes the cycle. The existence of geochemical cycles is the inevitable result of the energy flow in a closed system. In a planet devoid of life this can be seen in high and low chemical potential compounds such as those observed on Mars. When biota are present they are of necessity involved in the flows giving rise to biogeochemical cycles. The form of the cycles depends on biological and geological factors, but their existence is deeply embedded in the physical chemical properties of closed systems subject to energy flux. A consideration of chemical thermodynamics makes possible one further conclusion: one component of the chemical cycle will be the molecular form of the element with the largest enthalpy of formation, given the other atoms present and other boundary conditions such as temperature and pressure. The second law tells us that the system is constantly drawing toward a chemical equilibrium in which all elements are combined in their lowest energy states, such as carbon dioxide, phosphate, sulfate, and so forth. The most efficient cycles will be able to operate with these chemical forms.

The realization of the critical role of living systems in all of the Earth's geochemical cycles is a relatively recent discovery. The recognition of biotic factors as potential homeostatic controls of biogeochemical cycles has allowed for significant advances in our understanding of the natural metabolism responsible for the compositions of the atmosphere, oceans and sediments on the surface of our planet. Since such a planetary metabolism is now, and has been for some time in the past, interactive, wherein physical, chemical and biological processes are inextricably linked, quantification of the contribution of the biota is essential for a better understanding of global processes. The recognition of living organisms as a global homeostatic control factor can be attributed to the fact that even though biological reactions allow for extremely high chemical fluxes globally, such fluxes are characterized by high turnover rates and in some instances, are thus underestimated because of what appears to be a very modest net synthesis on a global scale. Due to the restricted elemental makeup of biological systems, the possible chemical transformations that are directly mediated by the biota are limited in number and are dominated by the elements carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur. As a first approximation, the following class of reactions dominates the natural global biological cycles:

\[
\begin{align*}
(i) \quad & \quad \text{H}_2\text{O} \\
& \quad \text{CO}_2 + \text{H}_2\text{S} \\
& \quad \text{H}_2\text{A} \\
\quad \arrow{\text{(CH}}_2\text{O) + S'}} \\
& \quad \text{A}_2 \\
(ii) \quad & \quad \text{CH}_2\text{O) + O}_2 \\
& \quad \arrow{\text{CO}_2 + \text{H}_2\text{O}} \\
& \quad \text{(Carbon fixation)} \\
& \quad \text{(Respiration)}
\end{align*}
\]
(iii) \[ \text{COO}^- + H_2 \rightarrow CH_4 + H_2O \] (Methanogenesis)

(iv) \[ N_2 + H_2 \rightarrow NH_3 \] (Nitrogen fixation)

(v) \[ NH_3 + O_2 \rightarrow NO_2, NO_3 \] (Nitrification)

(vi) \[ NO_2, NO_3 \rightarrow N_2O, N_2 \] (Denitrification)

(vii) \[ S \rightarrow S' \rightarrow S_2O_3 \rightarrow SO_3^- \rightarrow SO_4^- \] (Sulfur Oxidations)

(viii) \[ SO_4^- \rightarrow S' \rightarrow S^- \] (Sulfur Reduction)

(ix) \[ \text{PO}_4^- \] Assimilation and excretion by the Biota

(x) Biotransformation of Minerals

(xi) Cycling of halocarbons

Although elements have "natural cycles," human activity has significantly altered several of them. Certain indicators of the state of particular cycles, for example the level of atmospheric CO_2, have moved well outside their recent historical distributions. Some of these changes are well documented on the global scale. For example, we now have good data about the production of CO_2 from fossil fuel combustion as well as tentative estimates of the changes in global stocks of carbon in terrestrial ecosystems over the past century as humans convert some forests to agriculture and harvest others for fuelwood. The consequences of these and other changes, however, for the cycle of N, P, and S are just now being evaluated. In the forefront of these studies is the Scientific Committee on Problems of the Environment (SCOPE) which has begun to model not only the individual cycles but their interactions as well. This report of the NASA workshop "Interactions of Global Biogeochemical Cycles" hopefully will lend support to this important activity.

Despite the fact that knowledge of the carbon cycle is a key to comprehending the biosphere, that cycle is not well understood globally. Uncertainty centers on the role of terrestrial ecosystems, in which at least two factors govern the level of carbon storage. First and most obvious is the alteration of the earth's surface, such as the conversion of forest to agriculture which results in a net release of CO_2 to the atmosphere. Second and more subtle is the possible change in net ecosystem production resulting from changes of global cycles. Measuring such changes will require a much clearer understanding of the nitrogen and phosphorus cycles, since they (not carbon) are the limiting nutrients in most terrestrial ecosystems.
Unfortunately, our knowledge of the way these biogeochemical cycles relate to each other compares poorly even with our general understanding of the individual cycles themselves.

When humans burn fossil fuels, they not only release large amounts of carbon to the atmosphere, but they may also increase the input of nitrogen to the atmosphere. Some of this nitrogen may enter terrestrial ecosystems in bulk precipitation. This rise in available nitrogen may stimulate both carbon fixation and storage in, for instance, forest ecosystems. Conversely, wood harvests can reduce not only the carbon stock for forest ecosystems, but the nitrogen stock as well. First, nitrogen exits the forest in harvested material. Second, erosion, accelerated by the harvest, carries off nitrogen-bearing soil. Third, forest cutting can dramatically raise losses of inorganic nitrogen, principally nitrate removed in solution by streams that drain cutover areas. A fourth pathway may also exist: wood harvests may stimulate denitrification. Further understanding of these cycles will require a clearer picture of the coupling between the two elements.

Like carbon, phosphorus is essential to plant growth and yet unlike carbon it is frequently in short supply. Its relative insolubility limits its availability to organisms in soils, rivers, and oceans, and sedimentary deposits provide its major reservoir. Phosphorus is nonvolatile, a quality that restricts its role in atmospheric chemistry. In the absence of human activity, these characteristics limit this element's role in global biogeochemical cycling. Human activity, however, has altered the availability of phosphorus in direct and indirect ways. The application of phosphorus fertilizer in a direct perturbation, but subtler alterations of the phosphorus cycle may influence the dynamics of other cycles. Fire, either natural or as a management technique, may increase the available stocks of phosphorus, since oxidation of plant litter transforms organically bound phosphorus into "more available" forms. Increased levels of available phosphorus can, in turn, raise the rate of nitrogen mineralization in soils. In addition, there is another possible coupling between C and N through fire. Rapid oxidation of carbon in litter with a high C:N ratio reduces the amount of nitrogen that can be immobilized by microorganisms during decay, thereby increasing the amount of N available to plants.

Sulfur plays an equally important role in maintaining biological systems, since it is an essential nutrient for all plants, bacteria, and animals. In fact, sulfur is a limiting nutrient in parts of Canada's grain belt, and because it is so widely available in seawater (as sulfate), it has great impact on the cycles of carbon and energy in marine ecosystems.

On a global scale, the sulfur cycle is assuming increasing importance as the effects of acid rain and atmospheric sulfur pollution become known. Indirect calculations suggest that emissions of gaseous sulfur to the atmosphere from fossil fuel combustion are already on the same order of magnitude as discharges from natural systems. In comparison, man's contributions to the global cycles of carbon, nitrogen, and phosphorus represent relatively minor components of their respective natural fluxes, although, as noted earlier, human activity is altering these cycles in potentially important ways.
At the present time, major questions need to be answered regarding not only the details of global budgeting of individual cycles but more importantly the interactions of such cycles with each other for which very little, if any, experimental data exists. Hence, whereas it is clear that carbon (in the form of CO$_2$) has been accumulating in the atmosphere for at least the last 20 years at the rate of 1 ppm yr$^{-1}$, attempts to balance the sources and sinks of atmospheric CO$_2$ remain elusive.

One difficulty lies in the higher C/N, and C/P ratio in fossil fuels as compared to organic carbon, thereby limiting even the potential for lower carbon (fossil fuel derived) assimilation by biota due to limiting nitrogen loading from fossil fuels. In addition, major uncertainties remain in our estimates (due to the paucity of data) of net CO$_2$ release due to biota and CO$_2$ uptake by the oceans.

With respect to the nitrogen cycle important issues remain unresolved with respect to nitrogen cycling on land as well as the oceans. For terrestrial ecosystems, a major dilemma exists as to why even though nitrogen is abundant in the atmosphere and soils, fixed nitrogen is generally the element that limits the growth of plants in both natural and agricultural ecosystems. Once again, some insights with respect to the recalcitrant nature of the nitrogen bound to organic carbon in the soil are gained by achieving an understanding of the relationships and linkages between carbon and nitrogen cycling: Considerable microbial immobilization of soil nitrogen could occur due to the much lower C:N ratios (6 to 12:1) of microbial decomposers as compared to their substrates whose ratios are as high as 120:1 (for fresh litter) and 500:1 (for wood). In addition, the coupling of nitrogen fixation to carbon fixation is reciprocal due to its biochemistry; i.e., nitrogen fixation is biochemically a very expensive process (to fix 1 mole of N$_2$ requires anywhere from 25-50 moles of ATP) and generally occurs at the expense of oxidation of fixed carbon.

With respect to the cycling of nitrogen in the oceans the notion of a steady-state concentration for oceanic nitrogen (on time scales of 10$^4$ yrs) appears to be difficult to support due to the apparent imbalance between the sources of oceanic nitrogen (transport from land, input from the atmosphere, and in situ fixation) and oceanic losses (due to denitrification and removal to sediments). It has been proposed that if the present source and sink terms are to be relied upon, oceanic nitrogen would undergo a gradual depletion on a time scale of 10$^5$ years followed perhaps by a major deposition of nitrogen into the oceans during the onset of ice ages. This problem, however, is of profound importance, especially from a climatic point of view, since it is believed that both N and P could limit the fixation of carbon in the oceans which in turn can profoundly affect atmospheric carbon dioxide. However, the nonsteady-state condition of oceanic nitrogen rests on existing global data for sources and sinks that are meager at best and better global data have to be acquired to validate any such hypothesis.

Our understanding of the global sulfur cycles is at an even more primitive state of understanding than that of carbon, nitrogen, or phosphorus. It is generally accepted that most of the reduced sulfur gases [(CH$_3$)$_2$S, CS$_2$, H$_2$S, etc.] are biogenic in origin but no data exists regarding the nature of the sources or source strengths and their spatial and
temporal distributions. Furthermore, such reduced gases are oxidized to SO₂ whose mechanisms and rates of reaction remain poorly understood. As much as half of the oxidized sulfur gases could be accounted for by such oxidation reactions, the other half being acquired by combustion of fossil fuels.

Since the surface of our planet is dominated by water and is subject to energy flow, the existence of water cycles also follows in a very natural way. Meteorology, hydrology, and biogeochemistry all present examples of the cycling of the ubiquitous water substance. Water cycles involve all the possible energy storage modes. At the macroscopic (meteorological) level, we have the primary evaporation-precipitation cycle in which energy goes from electromagnetic to thermal to gravitational potential to thermal. At the molecular level we can describe the flow from H₂O to O₂ and biological reducing power, then back to H₂O. Here the energy goes from electromagnetic to chemical to thermal.

It is hard to resist discussing water without reminding ourselves of the obvious; ordinary water is a compound of the most extraordinary macroscopic and molecular properties. We have come to understand most of these in terms of hydrogen bonds, electric asymmetry and proton mobility. It is nonetheless remarkable that these molecular features render water such a fit substance for all its varied roles in the cycles we are about to discuss.

The following papers deal with critical aspects in the global cycles of carbon, nitrogen, phosphorus and sulfur in detail as well as the cycle of water and the flow of energy in the earth's environment. The objective of the report is to set partly the foundation for the development of mathematical models that allow exploration of the coupled dynamics of the global cycles of carbon, nitrogen, phosphorus, sulfur, as well as energy and water flux. We state this objective with the recognition that a scientifically rigorous model—one that captures the details of the interactions and resulting dynamics in a way faithful to the heterogeneity of these cycles—is beyond our current ability. Yet, we believe that it is not too early to begin developing a framework designed to help us consider the behavior of these interactions and their implications for global biogeochemical cycles.
GLOBAL BIOGEOCHEMICAL CYCLES:
STUDIES OF INTERACTION AND CHANGE -
SOME VIEWS ON THE STRATEGY OF APPROACH

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I. INTRODUCTION

The biosphere comprises most of the atmosphere, the oceans, the top layers of the soil, lakes and rivers. Climatologists call this part of the earth the climatic system. Their attempts to describe, understand, and model the climate of the earth may thus be considered as attempts to develop a consistent theory for the physical state of the biosphere. Still its structure and way of functioning is only known in broad outline. The role of air and water as transport agents of the basic elements of life, carbon, oxygen, hydrogen, nitrogen, phosphorus and sulfur has been described qualitatively and we have a general idea of the biochemical interactions.

It is easy to talk in general terms about the global features of the biosphere and possible changes, whether natural or induced by man. Satellites have given us detailed pictures of forests, farm land, savannas and deserts on land. We can measure key parameters that describe the behavior of the atmosphere and the sea. Some such data series are becoming long enough to reveal changes, and careful surveys in the future will undoubtedly further enhance these extensive data bases.

It is also easy to talk about possible processes and interactions within the global biosphere that might "explain" its present structure and observed changes. As a matter of fact there are many such hypotheses but rather few quantitative theories that have been reasonably well established. It therefore seems important to develop programs that will yield dynamic diagnosis that gradually will improve our understanding of the global biosphere. Only then will we be able to foresee with some certainty future changes due to natural variations or man's ever increasing interventions.

A systematic approach is needed and there is much in this regard we can learn from the development of dynamical climatology. A brief outline of some key elements in climatic modeling will be given, followed by what they imply with regard to the development of more precise models for terrestrial and marine ecosystems. In this way we will also approach the problem of biogeochemical cycles interaction.
II. CLIMATE MODELING

A. The Development of Climate Models

Dynamic climatology has grown out of dynamic meteorology and the development of models for numerical weather forecasting. The first trials of applying numerical methods to weather forecasting began a little more than thirty years ago. As computers became more powerful the area covered by the computations and the forecasting period were extended. In the early 1960's hemispheric forecasts were attempted, but showed limited success because of lack of data over large areas of the globe. The first meteorological satellites promised, however, major improvements for the future. The idea of measuring vertical temperature profiles through the atmosphere from a platform in space had already been proposed. The idea of launching a Global Atmospheric Research Programme (GARP) with the aim of improving weather forecasting and advancing dynamic climatology was born at about that same time. It took a few years until GARP was organized and about another decade until a truly global experiment was launched. Of course much was learned from the series of meteorological satellites that were put into orbit during the 1960's and 1970's but a well-planned global experiment was not realized until 1979. During that year, all together eight satellites were in operation in a coordinated manner and the data collected during the eighteen months of the experiment has proved to be of great value.

In retrospect the most important aspect of the planning of GARP was the major theoretical efforts that were pursued continuously in an internationally coordinated manner. A standing working group had the responsibility to carry out this work and the OSSE experiment, i.e., Observational Systems Simulation Experiment; making use of the best numerical models available at the time was of great importance, in this context. The questions were asked: Which mix of data (temperature, wind, upper atmosphere data, surface data, clouds, etc.) will provide the best definition of the atmospheric state at any one time? What is the time-space resolution that should be aimed for? How could data redundancy best be used to increase our understanding of time and space inter-correlations in atmospheric structures?

There exist today several global models for studying the General Circulation of the Atmosphere (GCM's). In attempts to extend the forecasting range and to apply them to climatological problems, considerable efforts have been made to couple the atmospheric models to models that describe oceanic processes and land surface processes. A GCM for climatic studies includes in addition to the detailed treatment of atmospheric motions:

1. Visible and IR radiative transfer through the atmosphere with due regard to the presence of clouds
2. Cloud formation and dissipation
3. Precipitation formation
4. Evaporation from sea and land
5. Water infiltration into soil and run-off
(6) Energy and momentum transfer between the atmosphere and the underlying surface

(7) Ocean circulation induced by wind action and the creation of density inhomogeneities in ocean surface water

One becomes easily impressed by the complexity of General Circulation Models. How do we know, however, that they describe relevant processes adequately? There are several ways to ascertain this:

(1) The models deal explicitly with the weather by integrating with 15 min to 1 hour time steps. We may thus study how useful these models are for forecasting the weather.

(2) We may ask the model to develop its own climatology by merely prescribing external conditions (e.g., distribution of land and sea, atmospheric composition, solar radiation), assuming that the atmosphere initially is isothermal and at rest, and compare it with reality.

(3) We may attempt to reproduce the climate 20,000 years ago by prescribing another distribution of incoming solar radiation (computed astronomically) and with due consideration of the different orography caused by the presence of the Laurentide and Scandinavian ice sheets. A comparison with paleoclimatic data can be made for validation.

(4) By varying the solar radiation as a function of the year we may explore how well seasonal variations are reproduced.

Studies of these kinds give us some confidence in the results obtained from GCM's. The characteristic time response to changes on time scales longer than a year have, however, not been tested in this way. It cannot be excluded, therefore, that important feed-back mechanisms have been omitted. The problem is crucial, since this time scale is most important to man and concerns for example the questions if and how the climate on earth may change due to an increase of atmospheric carbon dioxide or other atmospheric constituents. We note that the characteristic time scale of the surface mixed layer and the thermocline region in the sea is of the order of decades. Similarly many important features of the terrestrial ecosystems also may change over such periods of time. We may very legitimately ask the question whether these components of the climatic system, i.e., the biosphere, are dealt with adequately in this context.

B. Soil Moisture, Vegetation and the Hydrological Cycle

Present climate models include the moisture budget of the soil, i.e., precipitation, evaporation and run-off, in a very simplified manner. Soil moisture capacity is defined as a reservoir, which can be filled by precipitation up to a given maximum value. When this maximum is exceeded, the excess is classified as run-off. The amount of soil moisture decreases because of
evaporation, temperature, relative humidity, and is dependent on winds in the atmospheric surface layer. They in turn are determined by air motions in the atmosphere, radiation and a condition of energy balance at the earth's surface.

To a first approximation this simple formulation is adequate. Daily and seasonal variations of the water budget are handled reasonably well. It is obvious, however, that important spatial variations depending on different characteristics of different biomes are disregarded. The distribution of biomes on earth depends on climate and distribution changes as climate changes. Soil moisture capacity and moisture availability for evaporation are important climatic variables, if we are concerned with climatic changes over time periods of decades to centuries. The comparison of the water budget of a grass field and a forest as shown in Figure 1 is very revealing in this context. Obviously the depth of the roots, i.e. the root zone, is a crucial parameter since only the water reached by the roots is available for evaporation. Because grass biomes usually have shallow root zones, evaporation is less, while the direct heating of the atmosphere becomes more significant. The opposite is true for a forest.

We need global maps of the thickness of the root-zone to determine its dependance on type of vegetation and climate. It is further important to deduce how it responds to climatic change. Does this represent a positive or negative feed-back between the plant cover and climate? No scenarios of future climate have been produced so far with a consideration of such interactions. Obviously ecosystem modeling is required to produce the tools that the dynamic climatologist needs.

C. Surface Albedo

It is well known that the albedo of the land surface varies considerably in space and time. The obvious variations depending on snow-cover are accounted for in most climate models. Differences that are due to different kinds of vegetation cover, on the other hand, have usually not been considered and certainly not in terms of a dynamic interplay between climate and vegetation.

The albedo values shown in Table 1 have been arranged in order to bring out three characteristic features that are of interest in the present context.

(1) The albedo of vegetation is less at high than at low latitudes. This may be due to adaptation. At high latitudes it is important for plants to be able to use efficiently the sparse solar radiation during a short growing season, while at low latitudes it is important to strike a balance between their need for solar radiation in the process of photosynthesis and minimization of evapotranspiration, which increases with temperature.

(2) Both vegetation and bare soil have larger albedos during dry conditions than when wet.
In winter the albedo of a forest is much less than that of an open field. The former also differs markedly depending on whether snow is covering the branches or the trees have lost their snow cover during thawing.

Analyses of the large data source from satellites certainly would bring out such or other systematic differences more accurately.

There obviously exist feedback mechanisms between vegetation and climate. We note, for example, that the duration of periods with dry or wet vegetation depends much on temperature. At low temperature, but above freezing, modest amounts of precipitation may keep the ground constantly wet, while at high temperatures even abundant rains may be quickly evaporated (or absorbed into the ground) whereby periods of wet ground are reduced to short spells. The advancement of the boreal forest into regions at present covered by tundra in the Northern Hemisphere may markedly decrease the mean winter albedo. We may also ask what a change from larch as the dominating species in the Siberian taiga to pine or spruce with a smaller albedo in winter might imply for the regional climate in Asia, or even possibly for the global climate.

D. Climate-Terrestrial Vegetation Interaction

It is easy to propose feedback mechanisms of the kind outlined above. Their significance can, however, not be analyzed without the use of climate models. Few experiments have been done that shed light on this problem. There are few quantitative, dynamical models of how the terrestrial plant cover and climate interact, which could be used as schemes for parameterization of this interaction in the GCM’s. Shukla and Mintz (1982) have, however, tried to determine the difference in climate that would result from drastic changes of the land surface characteristics. Figure 2 shows an example that clearly reveals the potential importance of terrestrial vegetation in climate studies. We need, however, to know in which way and particularly how rapidly vegetation responds to climatic change and not the least which climatic variables are most important in this regard.

III. MODELING TERRESTRIAL ECOSYSTEMS

A. Scale and Resolution

It is clear from the discussion above that good spatial resolution of land surface characteristics is essential for the further development of climate models. Similarly the analysis of the global biogeochemical cycles and their interaction and more detailed models are required to describe the most essential dynamical features.

Global models of the fundamental cycles of carbon, nitrogen, sulfur and phosphorus have so far essentially been budget consideration as, for example, in the case of carbon shown in Figure 3. They are useful to obtain first order approximations of turn-over times for the different elements in the
major reservoirs. Thus the turn-over time for carbon in the atmosphere relative to terrestrial plants is about 15 years and relative to the sea about 7 years. These numbers are meaningful since the internal mixing time of the atmosphere (troposphere) is merely about one year and therefore the atmospheric carbon dioxide is rather well mixed. Only close to the earth's surface does the daily cycle of photosynthesis and respiration bring about marked variations. The turn-over times of sulfur and nitrogen in the atmosphere, on the other hand, are merely a few days. Global mean concentrations of the various nitrogen oxides are meaningless information in studying the nitrogen cycle. We need to resolve the distributions into scales appropriate to deal with the photochemical transformations in the atmosphere, i.e. scales of 100-1000 km. Rodhe, Crutzen and Vande-jp.j (1981) have shown how the relative concentrations of SO₂ and NOx determine the way the OH-radical is used for the further oxidation of these species. This implies that the patterns of wet-deposition of sulfate and nitrate ions are dependent on the interacting processes of air transport, chemical oxidation and precipitation formation. Processes of this kind need to be considered, at least in some statistical sense, when we proceed from global bulk models of the nitrogen and sulfur cycles to models that provide for regional inhomogeneities and chemical interaction in the atmosphere.

The same is obviously true for the terrestrial biota. The circulation of carbon between the atmosphere, living matter on land and dead organic matter in the soil, 50-60 pg yr⁻¹, corresponds to an average turn-over time for carbon in the atmosphere and terrestrial biota of about 15 years and in the soils of about 30 years. These figures are, however, not very useful. As a matter of fact, the turn-over time in short lived biota is merely 1-2 years. On the other hand, about 30% of the organic matter formed by plants becomes structural matter, primarily cellulose in wood. The forests contain about 90% of the carbon in living matter and the average turn-over time is rather 40 years. This, however, also varies from one forest biome to another. In the northern boreal forest (taiga) the turn-over time is 100 years or more, in the tropical rainforest merely 20-30 years. The heterogeneity of soils is even greater and global averages are not meaningful.

It is essential to consider spatial resolution in global models for biogeochemical cycles to permit the development of dynamical models for these cycles and their interaction. The problem is, however, a rather formidable one. Most ecological models developed so far consider plant communities and animal associations over land areas up to perhaps a hectare. The main reason for this limitation is, of course, that field measurements can be made with reasonable efforts to test such models. Still, our aim must be to try to generalize results from such studies to much larger areas. We shall return to this problem after having reviewed briefly some aspects of present modeling efforts in the field of plant ecology.

B. Models for Terrestrial Ecosystems

Early modeling attempts were often characterized by the formulation of detailed models of the physiological processes of the plants being considered, particularly when concerned with homogeneous ecosystems, such as a grassland
or a pine forest. Most success was achieved if key parameters could be identified in the process of model testing and validation, whereby considerable simplifications could be achieved.

Most such ecosystem models are aimed at determining the interplay between key parameters at quasi-steady state and the simulation of the daily or yearly variations. The problem becomes quite different, and more difficult, if we rather are concerned with the dynamics of slow change. We need to determine which environmental (abiotic) variables are most important in this context. The answer to such a question may well be most dependent on the rate of change. Also, few observations are available that can be used in such studies. Two approaches are of interest.

We may assume that the present unmanaged terrestrial ecosystems are in approximate balance with prevailing climate. The distribution observed today can then be used to determine relations between climate and ecosystem properties (Holdridge, 1967). On this basis we may deduce an approximate distribution of vegetation associated with other climatic conditions on earth. As a matter of fact, the reverse of this method has been used to give a picture of climate in the past using palynological data. Figure 4 shows the shift of the southern border of spruce forest during the period 12,000 to 8,000 years B.P., which can be translated into an approximate pattern of climatic change in the area. There are, however, complicating factors that need to be considered carefully in analyses of this kind.

(1) We implicitly assume that species do not adapt to changing climate. This may be a reasonable assumption when analyzing recent climatic variations, but does not necessarily hold for geological time scales.

(2) There is considerable inertia in an established ecosystem. At least a tree-generation, i.e. decades to a century, is required for the establishment of a new forest type, in many cases considerably more. Further, soil characteristics change when the plant cover changes. The characteristic time scale for such changes is from a century to many millennia when the existing soil is poor. In the very long time perspective we need also to consider the gradual immobilization of phosphorus and the aging of soil.

(3) A changing distribution of biomes may well influence climate. We therefore need models that can describe the mutual interaction between climate and the plant cover on earth.

We may also consider the response of individual species to climatic change and develop a statistical model of ecosystem change analyzing the interaction of as many as 50-100 species (Botkin, et al., 1972; Shugart and West, 1977; Solomon et al., 1980). A more detailed account of this work will be presented later during this conference, but some comments are most relevant here. Their model approach is based on the determination of how individual species respond to environmental parameters such as temperature, precipitation, light, space (surrounding vegetation density, above and below ground), etc. The species composition on a site may then be simulated statistically by also including the aging process of tree species and the opportunities offered.
for new seedlings to compete in openings when dead trees fall and depending on
the characteristic litter conditions available on the ground. Figures 5 and 6
show a comparison between pollen records collected and analyzed from Anderson
Pond in Tennessee and a simulation in which climate has gradually been chang-
ing in accordance with best available paleoclimatological information. In
spite of the fact that these pollen data partly have been used to define the
climatological forcing of the system, the experiment is of great interest.
Quite a rapid change of the ecosystem composition may occur for quite small
changes of the external climatic parameters. The rapid switch-over from
spruce to oak about 13,000 years ago as simulated in the model and also
observed in the pollen record is most interesting.

Some questions arise. Is it possible to generalize this statistical
approach to become applicable to land areas of a size of 10,000 km² or more,
within which quite variable soil conditions may exist and accordingly differ-
ent ecosystem types? Such a development would be necessary to use this meth-
odology for treating land surface processes dynamically in climate models.
Further, how can such ecosystem models be further developed to account for
changes in the nutrient availability, i.e. changes of the circulation of the
basic elements nitrogen, phosphorus, sulfur (and also minor constituents)?

Sophisticated climatic models exist which resolve atmospheric motions
down to a scale of a few hundred kilometers. More adequate treatment of land
surface processes are needed to account for possible feedback processes
between terrestrial biota and climate. The terrestrial ecosystems are primar-
ily spatially inter-connected by the patterns of climate and the air-transport
of water and essential nutrients. Obviously climatic models, i.e. both gen-
eral circulation models (GCM's) and simplified climatic models should be
employed for more detailed studies of the global features of biogeochemical
cycles.

A model reconstruction of the likely regional characteristics of the pre-
industrial nutrient cycles would be of immediate interest and would provide
the background distribution of these elements to be compared with those
observed today which have been modified due to increasing atmospheric pollu-
tion. Admittedly the first such attempts would be crude, since our knowledge
about exchange processes between land and the atmosphere is still poor. We
would, however, undoubtedly be learning by doing. Experimentation with rather
extreme assumptions such as previously mentioned for the role of soil moisture
for the hydrological cycle may be very useful in this context (Shukla and
Mintz, 1982). An integration of climate models and models for the study of
biogeochemical cycles requires, however, the development of good parameteriza-
tion of sub-grid scale processes.

C. Sub-grid Scale Parameterization of Terrestrial Processes and the Need for
a World Data Bank

In view of the very complex features of the land surface it is a major
task to find methods of how to represent the key processes in global models
for climate studies as well as studies of biogeochemical cycles. The problem
has several aspects that are closely interwoven. We need to describe the essential features of a land area of the size of a grid in a global model. The basic set of observations required for this purpose most certainly is large, but the principal problem is to reduce this data set in an optimum manner for our present aims. We need a statistical representation which also should permit a dynamical description of the processes that maintain the prevailing quasi-steady state and those of prime concern in dealing with change. As a starting point we may well consider the fundamental processes in a manner similar to what is given for water as shown in Figure 7. The generalization of these simple features to consider also the heterogeneity of the terrestrial biomes is essential. The statistical distribution of vegetation types and what this implies for the area as a whole should be assessed with regard to these variables. In a similar manner we need to describe statistically the parameters that determine net primary production and bacterial decomposition (i.e. exchange of carbon), nitrogen fixation and release of nitrogen from the soil into the air or run-off water, etc.

Any major observational program (using satellites or observations at ground level) should be preceded by a thorough analysis of what would be needed for the present purpose, techniques available to obtain the data, and the data analysis schemes to be employed to transform the basic observations into a data set that could be used in combined climate-biogeochemical models.

Human activities on earth today have reached a level which is significant at a global level, both with regard to climate and biogeochemical cycles. It is therefore also important to record human activities in a manner similar to what has been sketched above for natural processes. It is not merely enough to consider the primary impact caused by man, but also secondary changes as for example in the case of deforestation as shown in Figure 8. Present rather approximate quantitative estimates need to be transformed into more rigorous models with due regard taken to their dependence on climate and other abiotic factors.

Present GCM's have a resolution of about 300 km, i.e. about 1600 unit areas in a global grid are needed to cover the land surface on earth. This resolution or preferably somewhat better is probably what to aim for in a global data bank for climate and biogeochemical modeling. J. Olson of Oak Ridge National Laboratory has produced a global map for vegetation on land with 1/2° longitudinal resolution, which could serve as an excellent starting point for building such a data bank. It seems necessary, however, to provide more quantitative information. A few workshops should be arranged, in which climatologists, hydrologists, ecologists and soil scientists would be given the task of defining reasonably objectives for how to develop models for synthesizing data to the characteristic scale of the grid used in global climate and biogeochemical models and appropriate techniques to get the necessary data.
IV. MODELING MARINE ECOSYSTEMS

A. The Importance of the Oceans

Even though the terrestrial ecosystems play an important role in the global carbon cycle, a major part of the emissions of $CO_2$ into the atmosphere by burning fossil fuels is absorbed by the oceans. The greater homogeneity of the oceans as compared to land provides a better opportunity to determine quantitatively their role in the carbon cycle. The broad scale features of biological activity in the sea is largely determined by the general circulation of the oceans. Particularly important are the areas of upwelling or deep convection, since the nutrient flux from deeper layers of the ocean is maintained in this way. This circulation in turn is determined by the prevailing climate.

The following simple considerations illustrate present uncertainties with regard to the response of the carbon cycle to the emissions of carbon dioxide to the atmosphere by fossil fuel combustion and changing land use. A better knowledge of the role of the oceans in this regard is crucial.

Carbon dioxide emissions to the atmosphere due to fossil fuel burning during the period 1860-1980 have been $(163 \pm 10) \cdot 10^{15}$ gC (Rotty, 1981). Deforestation, afforestation and expansion of agricultural land have caused an additional flux of carbon to the atmosphere of $(150 \pm 50) \cdot 10^{15}$ gC during this same period (Moore et al., 1981). The total emissions thus have been $(310 \pm 60) \cdot 10^{15}$ gC.

Unmanaged forests may have increased their carbon-storage because of increased photosynthesis as a result of the increasing $CO_2$ concentration in the atmosphere. This view is, however, not shared by all ecologists studying the problem and in any case no quantitative assessments of the possible magnitude of this transfer have been made. The most reliable measurements of atmospheric $CO_2$ concentrations during the latter part of last century (Bray, 1959) give a value of 290 ppm, but the scatter of the observations is large and the uncertainty of this figure considerable. Recent measurements of $CO_2$ concentrations in Antarctic glacier ice formed during the last 1000 years on the other hand yield an average $CO_2$ concentration of 265 ppm, with an estimated uncertainty of 10 ppm. The atmospheric $CO_2$ concentration in 1980 was $338 \pm 1$ ppm, which implies an increase of 45-80 ppm, or $(95-170) \cdot 10^{15}$ gC, i.e. an increase between 15 and 30%. The percentage of the total emissions that has been retained in the atmosphere thus has been 30-76%. A much more accurate value is necessary for making reasonably reliable projections of $CO_2$ concentrations in the atmosphere associated with different scenarios of future energy use. A closer analysis of the role of the oceans as a sink for $CO_2$ would obviously be valuable.

B. A Diagnostic Model for the Interplay between Ocean Circulation and the Ecosystems

Life in the sea is essentially limited to the photic zone, i.e. the upper part of the mixed layer above the thermocline which is about 75 m deep except
in polar regions. Here photosynthesis takes place at a rate of about $40 \times 10^{15}$ gC yr$^{-1}$ for the oceans as a whole. More than 90% of the organisms die, decay and dissolve within the mixed layer, and at any one time only about $3 \times 10^{13}$ gC is present in the form of living organic matter (de Vooy, 1979). The turnover time of carbon within the surface layer is thus merely about one month.

The limiting factor for phytoplankton growth is lack of nutrients, particularly phosphorus and nitrogen, even though nitrogen compounds may become available by nitrogen fixation. When organisms die they settle out of the photic zone before much bacterial decomposition and dissolution occurs. For this reason the uppermost part of the mixed layer usually has low nutrient concentrations. Vertical mixing and upwelling within the mixed layer are necessary processes to maintain phytoplankton growth in the photic zone. It follows that on the average the nutrient content of this uppermost layer is renewed once a month.

About 10% of the inorganic particulate matter (carbonate and silicon shells) and dead organic matter settle out of the mixed layer into the intermediate and deep waters of the sea, in the case of carbon, 3 to 5 $\times 10^{15}$ gC yr$^{-1}$. Most of these particles dissolve before reaching the bottom of the sea. Direct measurements of this particle flux are difficult (Fiadeiro, 1983), but possibly 10%, i.e. $0.5 \times 10^{15}$ gC reaches the bottom, where it serves as an energy source for the sparse bottom fauna. Only a small fraction is incorporated into the bottom sediment.

The particle flux into the thermocline region and the deep sea also brings with it nutrients. Carbon, phosphorus, nitrogen, silicon and many other elements are therefore enhanced in these deeper layers. The decomposition of organic matter further requires oxygen whereby its concentration is diminished. The quasi-steady distributions of all these elements as observed below the thermocline represent a balance of the particulate flux and the decomposition processes on one hand and the transfer of the dissolved compounds by water motions on the other (Bolin, 1983; Bolin et al., 1983). The rate of this slow turnover of the oceans, which depends on climate, determines the vertical gradients of all chemical elements involved in the life processes. Figure 9 shows the distribution of total dissolved inorganic carbon (DIC) in the oceans. We note that 15% difference between surface concentrations and those of the deep sea. If the vertical turnover of the sea were slower, the rate of nutrient supply by upwelling would be reduced and thus also the rate of photosynthesis. The vertical carbon profile (Figure 9) would probably not change much (cf. Keeling, 1973). If on the other hand more nutrients were supplied to the sea without any change of vertical turnover, the rate of photosynthesis would increase and the quasi-steady state now maintained would be disturbed. We then recall that the percentage increase of the CO$_2$ partial pressure in sea water increases by a factor of 10 to 15 more quickly than the amount of DIC, because of the chemical characteristics of the carbon system of the sea (cf. Keeling, 1973). Thus the prevailing concentration of atmospheric CO$_2$ is fundamentally dependent on this dynamic balance. An understanding of these interconnections is also important when interpreting climatic records in marine sediments, e.g., those of $^{14}$C (cf. Broecker and Takahashi, 1977; Bolin, 1981).
The circulation of the deep sea is not well known. Direct measurements are difficult because of the slow and sluggish motions, even though neutrally buoyant floats have been used successfully in recent years (Rossby, 1983). Data are, however, inadequate to verify prevailing theories for deep ocean circulation (Veronis, 1978) in more than their broad outline. We may, however, ask ourselves in which way the quasi-steady distributions of a large number of tracers can be used to gain information about the circulation and turbulent processes that establish them. Such attempts are of course not new, but have long been employed in regional studies of water transfer and exchange.

There are basically two approaches that can be used. Most directly the general circulation models of the oceans as developed by Bryan (1975) and others, in which the biogeochemical processes appear as sources and sinks, can be supplemented by a series of continuity equations for the chemical compounds concerned. These latter equations are integrated in parallel with those that account for changes of momentum, heat, water and salt until a steady state is reached. Assuming that a quasi-steady state prevails in reality, we may compare the computed distributions with those observed. A principle difficulty is of course that the biogeochemical processes are not well known and therefore difficult to incorporate properly into such computations. It should be noted, however, that a detailed understanding may not always be needed. In a first attempt one might use the hypothesis advanced by Redfield (1958) that the approximate proportions in which basic elements are incorporated into organic tissue and also released in the decomposition process can be specified as constants, "Redfield ratios." Fractionation processes, that certainly occur, may in a first approximation be neglected. A series of computations can be made with different assumptions about the biochemical processes and their spatial distribution to achieve optimum agreement with the observed distribution of the trace elements. There is of course, no standard method for how to proceed. Attempts of this kind do not necessarily converge and may in any case be very time consuming.

As an alternative method we may address this inverse problem more directly, i.e., attempt to solve for the distribution of water circulation, rate of turbulent water exchange and biological transfer that is consistent with the steady state spatial distributions of a set of tracer elements (cf. Bolin et al., 1983; Wunsch and Minster, 1982). To illustrate the method we consider a finite difference formulation of the continuity equations for k tracers. Let us divide the ocean into a set of m reservoirs in exchange with each other across altogether internal surfaces between these reservoirs. We further define a mean advective and a turbulent flux of water across each such surface which become our 2n unknown variables, that we wish to determine. In addition we introduce the rates of net production or decomposition of organic tissue, and carbonate in each one of the reservoirs as 2m more unknown variables. We assume that the sources and sinks of other tracer elements can be related to the processes of primary production and decay as expressed by sources and sinks of organic tissue and carbonate by using Redfield ratios. With the aid of the k tracer distributions we can formulate k • m equations based on the condition that the amount of tracer material for each tracer and for each reservoir is conserved. These equations can be used to determine the 2n + 2m unknowns that describe the water motions and the biochemical processes. If k • m < 2n + 2m, constraints may have to be introduced to
derive a solution. We can also apply a principle of minimization, e.g., as for the minimum vector with the \(2n + 2m\) unknowns as components that satisfies our set of equations. In the case \(k \cdot m > 2n + 2m\), we may instead ask for the solution that minimizes the errors in satisfying the \(k \cdot m\) conservation equations. Methods of matrix inversion are available to solve large sets of equations, but practical difficulties arise when \(k \cdot m\) becomes large.

The method has been preliminarily tested by using a 12-box model of the ocean as shown in Figure 10. In addition to water continuity five tracers were used: total dissolved inorganic carbon, alkalinity, \(^{14}\text{C}\), oxygen and phosphorus (see Bolin et al., 1983). Water motions between reservoirs were described by 21 advective velocities and turbulent exchanges by 21 exchange rates. Considering also the particulate transfer of organic and carbonate carbon there were altogether \(2n + 2m = 66\) unknowns. In addition to the \(6m - 72\) conservation equations, we demanded that the detritus formation in each surface reservoir was balanced by decomposition (of organic matter) or dissolution (of carbonate) in the reservoirs below. This yielded an additional eight equations. Even though the spatial resolution is crude and the errors in the finite difference formulation thus considerable, we obtain spatial patterns of advective and turbulent motions and detritus flux that in general agree with what has been deduced by other methods (Figure 10).

We have a diagnostic tool which can be further developed. Thus the incorporation of some dynamic constraints and the inclusion of heat and salt transfer obviously is desirable.

Even though the results described briefly above are tentative, some further considerations are of interest. Having derived a set of advective and turbulent transfer rates for an ocean model, which in their gross features reasonably well depict the real ocean, we may ask the question: How effective is this model of the oceans as a sink for the \(\text{CO}_2\) emissions that have been occurring during the last 100 years? The transient response of the model to such an emission has been analyzed (Bolin et al., 1983). We find that the part of the total emissions that remains in the atmosphere, i.e. the airborne fraction, using the present model, is about 73%. It is clear, however, that the resolution as adopted is not sufficient to determine this value accurately. A more detailed consideration of the thermocline region would most likely reduce this figure. It is of interest in this context to compare this result with a similar analysis by Siegenthaler (1983). He has used an ocean model in which he considers both vertical diffusion from the ocean surface through the mixed layer into deeper layers and turbulent transfer along isopycnic surfaces from the Arctic and Antarctic surface waters. If assuming that the latter process is infinitely rapid the rate of transfer of \(\text{CO}_2\) into the ocean primarily is dependent on the size of the part of surface ocean water that communicates directly and rapidly with deep ocean waters and the rate of air sea exchange in this area. On the basis of his model Siegenthaler determines the minimum value for the airborne fraction to be 62%. Also this value is quite inaccurate since a rather schematic model of the oceans is used and detailed data on ocean circulation and tracer distributions are not used for its validation. By applying the methodology as described above (see Bolin et al., 1983) to each ocean separately, and with considerably better resolution it should be possible to determine more accurately the role of the oceans in the carbon cycle. Work using such an approach is in progress.
V. CONCLUDING REMARKS

The global biosphere is an exceedingly complex system. To gain an understanding of its structure and dynamic features, it is necessary to increase our knowledge about the detailed processes, but also to develop models of how global interactions take place. Our attempts to analyze the detailed physical, chemical and biological processes need, in this context, to be guided by an advancement of our understanding of the latter. It is necessary to develop a strategy of data gathering that serves both these purposes simultaneously. Climate research during the last decade may serve as a useful example of how to approach this difficult problem in a systematic way. Large programs for data collection may easily become rigid and costly. While realizing the necessity of a systematic and long lasting effort of observing the atmosphere, the oceans, land and life on earth, such a program must remain flexible enough to permit the modifications and even sometimes improvisations that are necessary to maintain a viable program.

REFERENCES


Fig. 1. Water and energy balance of grass-covered and forest-covered catchments in central Wales, U. K. (from Calder and Newson, 1979, Shuttleworth and Calder, 1979 as summarized by Mintz et al., 1983).
Table 1. Albedo (%) for bare soil and different vegetation types (from Kondratiev, 1969)

<table>
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<tr>
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<tr>
<td>Deciduous forest</td>
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<tr>
<td>Tops of oak</td>
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<td>Coniferous forest</td>
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<td>Tops of fir</td>
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<td>6</td>
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<tr>
<td>Grey earth</td>
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<td>10-12</td>
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<table>
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<td>Forest, unstable snow cover, spring</td>
<td>25</td>
</tr>
<tr>
<td>Forest, coniferous, without snow</td>
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Fig. 2. Simulated July precipitation (millimeters per day) in: (a) the wet soil; and (b) the dry soil case (from Shukla and Mintz, 1982).
Fig. 3. Global carbon cycle model. Reservoir sizes are in units of $10^{15}$ g and fluxes in units of $10^{15}$ g yr$^{-1}$. 
Fig. 4. The shift northward of the southern border of spruce forests during the time of withdrawal of the Laurentide ice sheet 12,000 to 8,000 years (expressed in thousands of years) before present (from Bernabo and Webb, 1977).
Fig. 5. Pollen diagram from Anderson Pond White County, Tenn., for the past 16,000 years. Derived values for growing degree-days and precipitation are shown at the right (from Solomon et al., 1980).
Fig. 6. Simulated taxa and biomass using the climatic variables shown at right in Figure 5 (from Solomon et al., 1980).
Fig. 7. Water transfers and water storages in vegetation soil system (after Rutter, 1975).
Fig. 8. The changes of carbon content of living vegetation and soil in an ecosystem following conversion of forest into agriculture (after Moore et al., 1981).
Fig. 9. The mean vertical distribution of total dissolved carbon in seven regions of the world oceans: NA = North Atlantic, SA = South Atlantic, NP = North Pacific, SP = South Pacific, NI = North Indian Ocean, SI = South Indian Ocean and AA = Antarctic region (from Takahashi et al., 1981)
Fig. 10. 12-reservoir model of the world oceans. Deduced fluxes: Adveotive (→) and turbulent (↔) fluxes of water (10^{15} m^3 yr^{-1}). In boxes: Upper figure, net organic detritus formation and loss of carbon (−) or decomposition and gain of carbon (+) in 10^{15} mol C yr^{-1}. Lower figure: Net carbonate formation and loss of carbon (−) or dissolution and gain of carbon in 10^{15} mol C yr^{-1}. Bottom figure is turn-over time for water in box (see further Bolin et al., 1983).
SOME ASPECTS OF UNDERSTANDING CHANGES IN THE
GLOBAL CARBON CYCLE

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I. INTRODUCTION

Carbon is fundamental to life, and studies of the global biosphere and element cycles tend to include intensive treatment of the carbon cycle. The pathways of carbon cycling include assimilation by primary producers, utilization by consumer organisms, and loss from the biotic pool by decomposition and fire. The transfers of other elements between abiotic and biotic components of the biosphere interact closely with these carbon pathways, and in this sense, the carbon cycle dictates many aspects of the structure and function of other element cycles. At the same time, the availability of nutrients, as prescribed by their element cycles, controls carbon cycling.

At time scales ranging from decades to centuries, the major carbon reservoirs subject to change are the atmosphere, the inorganic pool of carbon in the world oceans, and carbon stored in plants and soil in the world's terrestrial ecosystems. Marine organisms which assimilate dissolved CO$_2$ in the surface waters also play an important role in determining the distribution of carbon in the oceans, and at longer time scales, other pools and processes associated with geologic phenomena must be considered.

Perturbations to the carbon cycle by human activities are evident in measurement records. Accurate measurements of the concentration of carbon dioxide in the atmosphere at Mauna Loa Observatory, Hawaii (Keeling et al. 1976a) and at the South Pole (Keeling et al. 1976b) indicate a systematically increasing trend in the abundance of this trace gas. The trend is also evident in shorter records at a number of additional stations (e.g., Machta 1979). These rather remarkable records seem to confirm conjectures of the turn of the century (e.g., Arrhenius 1903) that CO$_2$ released to the atmosphere by fossil fuel combustion might accumulate there and serve to increase the average atmospheric concentration.
Carbon dioxide in the earth’s atmosphere is relatively transparent to incoming solar radiation but absorbs energy in the infrared portion of the spectrum radiated back to space by the earth. This so-called “greenhouse effect” may lead to significant changes in the earth’s climate if a substantial increase in CO₂ concentration occurs (e.g., Manabe and Stouffer 1980). This potential for climate change forces a more quantitative study of the global carbon cycle and its response to the fossil fuel perturbation than has been undertaken for other element cycles.

From 1959 to 1980, the annual average concentration of CO₂ at Mauna Loa Observatory has increased from approximately 315.68 ppmv to 338.36 ppmv, corresponding to an increase of 48.34 x 10¹⁵ g of carbon in the atmosphere. Utilizing data compiled by the United Nations, Marland and Rotty (1983) estimate the release of CO₂ to the atmosphere from the combustion of fossil fuels and the manufacturing of cement to have been approximately 84.4 x 10¹⁵ g of carbon in this time period.

The observed increase in the carbon content of the atmosphere is less than the estimated release of carbon from fossil fuels and other sources because of interactions between the atmosphere and other reservoirs which collectively serve as a sink for the excess carbon from the atmosphere. Changes in CO₂ concentration in response to the fossil fuel input are controlled by these interaction fluxes so that projecting future changes in CO₂ concentration as further fossil fuel combustion occurs requires an understanding of carbon exchanges with the atmosphere and their dependence on physical and chemical factors. Mathematical models of the global carbon cycle are used to synthesize this information in a quantitative framework and then to project CO₂ concentrations due to further fossil fuel use (e.g., Bolin 1981).

In this paper, we review several aspects of our understanding of the carbon cycle from the standpoint of its response to perturbations such as fossil fuel combustion and disturbance to terrestrial ecosystems. The status of efforts to reconcile model calculations, observations, and estimates of the magnitude of historical perturbations to the cycle is described. Some refinements in our view of the carbon cycle are suggested.

II. MAJOR ELEMENTS OF THE CARBON CYCLE

The reservoir of CO₂ in the atmosphere serves to link the oceanic and terrestrial carbon pools to form the global cycle of carbon which responds on time periods from decades to centuries (Fig. 1). Ultimately, the oceans are the primary sink for excess carbon from the atmosphere (e.g., Broecker et al. 1979). Carbon as CO₂ dissolved is surface waters incorporated in other compounds, primarily carbonates or bicarbonates, and by mixing, the circulation is transported to deeper layers where it may be sequestered for substantial periods of time. Carbon is also assimilated by marine organisms, and some fraction of this organic carbon is deposited in sediments.

Carbon storage in terrestrial ecosystems has decreased over the past several centuries as a result of human disturbance, particularly forest clearing and other land-use change (e.g., Bolin 1977, Woodwell et al. 1978,
Houghton et al. 1983). This decrease in terrestrial carbon storage implies a release of carbon to the atmosphere in addition to that due to fossil fuel combustion; however, the timing, magnitude, and degree to which this release has been balanced by terrestrial sinks remain uncertain.

A. The Atmosphere

The record of atmospheric CO₂ concentration obtained by Keeling and co-workers at the Mauna Loa Observatory is plotted in Fig. 2 (Keeling et al. 1982). The increasing trend in these data is clearly evident; average concentration increased from approximately 315.66 ppmv in 1959 to 338.36 ppmv in 1980. In addition to this secular trend, which has a rate of exponential increase of approximately 0.04 yr⁻¹, the time series contains at least two significant cyclic components, the first with a period of 1 year and the second with an irregular period of approximately 3.74 years which is irregular in period and amplitude (e.g., Rust et al. 1979).

The annual cycle is generally attributed to seasonality in the exchange of carbon between the atmosphere and terrestrial ecosystems (e.g., Hall et al. 1975) while the 3.5 to 4 year cycle corresponds to the southern oscillation (e.g., Bacastow 1977, 1979). The southern oscillation, a large-scale meteorological and hydrological variation, is reflected as a cycle in the barometric pressure difference between Easter Island and Darwin, Australia with a variable period of approximately four years. The cycle influences pressure, wind strengths, ocean current flow rates, sea surface temperatures, sea surface levels, and rainfall. Changes in sea surface temperatures are a likely explanation for the influence of the southern oscillation of atmospheric CO₂ concentration.

The presence of cyclic variations in atmospheric CO₂ records complicates the analysis of the secular trend due to fossil fuel combustion and other perturbations to the carbon cycle. However, analysis of these cycles in the data can provide insight into the interactions between the atmosphere and other reservoirs in the carbon cycle.

The amplitude of the annual cycle in the Mauna Loa record appears to be increasing (Keeling 1983). This increase may imply a corresponding increase in the extent of terrestrial ecosystems which have a pronounced seasonality in atmospheric exchanges; however, an increase in the amplitude of the annual cycle in CO₂ records does not necessarily imply an increase in longer term terrestrial carbon storage.

The amplitude and phase of the annual CO₂ cycle depend on latitude. The largest amplitude has been observed at stations located at northern latitudes such as Pt. Barrow, Alaska; the smallest at the South Pole station (e.g., Machta 1979). Using models of the general circulation of the atmosphere to simulate the influence of circulation in conjunction with representations of atmospheric exchanges with terrestrial ecosystems and the oceans, the latitudinal dependence of the annual CO₂ cycle can be simulated as a further test of our understanding of the carbon cycle (e.g., Fung et al. 1983). By assuming the observed pattern in the annual CO₂ cycle, it may be
possible to infer the exchanges of carbon between the atmosphere and the world's terrestrial ecosystems in this modeling framework (e.g., Machta et al. 1977, Pearman and Hyson 1980).

Observed changes in the relative abundance of carbon isotopes ($^{14}$C and $^{13}$C) in the atmosphere also demonstrate the influence of man's activities on the carbon cycle. Combustion of fossil fuels releases CO$_2$ essentially free of $^{14}$C to the atmosphere, thereby lowering the specific activity of this reservoir. This dilution of $^{14}$C in the atmosphere, and in turn in other carbon cycle pools, is referred to as the Suess effect and has been estimated from tree-ring data for the atmosphere and biogenic carbonates for the surface ocean. Estimates summarized by Keeling (1979) indicate that the degree of decrease in atmospheric $^{14}$C specific activity from the middle of the 19th century to the early 1950's is approximately 1.7%. In a recent paper, Stuiver and Quay (1981) indicate a somewhat larger decrease, 2.4%.

Atmospheric testing of nuclear weapons has released large quantities of $^{14}$C to the atmosphere. Since the test ban treaty in 1967, the magnitude of these releases has been substantially lower than peak values in 1961 and 1962. The specific activity of $^{14}$C in the atmosphere has decreased exponentially as this excess $^{14}$C is taken up by other reservoirs (Nydal et al. 1979). The time constant for this exponential decrease is approximately 15 years.

Time series of $^{13}$C/$^{12}$C ratios in tree rings collected by a number of investigators (e.g., Wilson 1978, Stuiver 1978, Freyer 1979, Tans and Mook 1980) potentially can serve as a surrogate for the history of atmospheric CO$_2$ concentration. Time series of $^{13}$C/$^{12}$C show a decreasing trend in the relative abundance of $^{13}$C which in general cannot be accounted for by the release of carbon from fossil fuel that is depleted in $^{13}$C relative to the atmosphere. Release of carbon by forest clearing activities is conjectured to have been an additional source of $^{13}$C depleted CO$_2$ (e.g., Peng et al. 1983, Emanuel et al. 1984). Direct measurements of $^{13}$C/$^{12}$C ratio in the atmosphere in 1958 and regularly since 1978 indicate the expected decrease and further show a dependence of this change on latitude.

B. The Oceans

The oceans are the largest active reservoir of carbon. Recent estimates of the total amount of dissolved inorganic carbon range between 35,000 and 38,000 x 10$^{15}$ gC. Only a small fraction is CO$_2$ (0.5% mole fraction); whereas, HCO$_3$ comprises 90% and CO$_3$ slightly less than 10%. As CO$_2$ is taken up by seawater, the buffering reaction

$$ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} + \text{CO}_3^- \rightleftharpoons 2\text{HCO}_3^- \quad (1) $$

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is driven to the right, consuming surface stocks of CO₃. This large pool of inorganic carbon in the world oceans appears to be the primary sink for excess CO₂ from the atmosphere (e.g., Baes et al. 1977).

As Broecker et al. (1979) detail, three primary factors determine the net uptake of carbon from the atmosphere by the oceans: (1) the capacity of seawater in equilibrium with the atmosphere to incorporate excess CO₂, (2) the rate of CO₂ invasion into the surface ocean, and (3) the rate of carbon transport into deeper layers by mixing and circulation.

The invasion of CO₂ at the atmosphere-ocean interface is primarily through diffusion; therefore, the exchange is governed by the difference in the CO₂ partial pressure in the atmosphere as compared with the sea surface. The flux from the atmosphere to the ocean is proportional to the atmospheric CO₂ partial pressure, which in turn is proportional to the ratio of the masses of CO₂ and dry air in the atmosphere. The atmosphere-surface ocean flux can therefore be expressed:

\[
F_{AS} = k_{AS} \frac{c_A}{c_S} \tag{2}
\]

where the transfer coefficient \( k_{AS} \) is a constant which is interpreted as an average over the global ocean surfaces and time.

The flux of carbon from the surface ocean to the atmosphere depends on the shifting chemical equilibria among carbon bearing species as CO₂ is added to the surface waters. A thermodynamic calculation relates the partial pressure of dissolved CO₂ and the total mass of inorganic carbon. The flux of carbon from the surface ocean to the atmosphere is expressed

\[
F_{21}(c_2) = k_{SA} \frac{P_S(c_2)}{P_S^0} \tag{3}
\]

where \( P_S(c_2) \) is the initial, steady-state partial pressure of dissolved CO₂ in the surface ocean. The partial pressure of dissolved CO₂, \( P_S(c_2) \), is affected by the incorporation of carbon in species other than CO₂. The reactions of primary concern are

\[
\begin{align*}
\text{CO}_2(g) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3(aq) \\
\text{H}_2\text{CO}_3(aq) & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}
\end{align*}
\tag{4}
\]
From the equilibrium constants,

$$K_0 = \frac{[CO_2]/P_s}{H^+}$$

$$K_2 = \frac{[H^+]\left[CO_3^-\right]}{[HCO_3^-]}$$

$$K_w = [H^+]\left[OH^-\right]$$  \hspace{1cm} (5)

$$K_1 = \frac{[H^+]\left[HCO_3^-\right]}{[CO_2]}$$

$$K_B = \frac{[H^+]\left[B(OH)_4^-\right]}{[B(OH)_3]}$$

and the equations for total boron, $EB$ (mol/l), and titration alkalinity, $A_l$ (aq/l):

$$EB = [B(OH)_3] + [B(OH)_4^-]$$  \hspace{1cm} (6)

$$A = [HCO_3^-] + 2\left[CO_3^{2-}\right] + [B(OH)_4^-] + [OH^-] - [H^+]$$
the partial pressure of dissolved CO₂ and total mass of carbon can be related to the hydrogen ion concentration H and hence, implicitly, to each other:

\[
P_S = \frac{C}{[H^+]^2 + k_1[H^+] + k_1 k_2} \left( [H^+] + A_1 - k_w[H^+] \right)
\]

Mixing and circulation serve to remove carbon from the surface layers of the ocean into deeper layers where it may be sequestered for some time, making the ocean a more effective sink for carbon from the atmosphere than is suggested by the thermodynamic considerations outlined above. In polar regions, exceptionally dense water is formed at the surface by ice formation and this water, by penetrative convection, sinks into the thermocline region and, more importantly, beyond. These cold surface waters are the primary vehicle for transporting carbon into the thermocline and deep ocean. As such, they offer the potential for forming, in effect, a pipeline for transferring atmospheric CO₂ to the large reservoir of abyssal waters.

The penetrative convection of Antarctic waters has been estimated to be between 1.9 and 2.4 x 10¹⁵ m³ y⁻¹ (Munk 1966, Gordon 1971), divided approximately evenly between the Indian-Pacific intermediate waters and intermediate Atlantic waters. There appears to be greater uncertainty about the North Atlantic bottom water formation where recent estimates vary between 0.32 and 0.95 x 10¹⁵ m³ y⁻¹ (Broecker 1979).

The polar advective fluxes and corresponding turbulent exchanges imply a deep equatorial flow of 4.0 to 6.0 m yr⁻¹ and a deep sea turnover time of 600 to 1000 years (Bolin 1981). Stuiver et al. (1983) conclude that ¹⁴C distributions for abyssal waters of the oceans indicate somewhat shorter replacement times. For waters below 1500 m in the Pacific, Indian, and Atlantic oceans the turnover times are approximately 560, 230, and 175 years respectively. Broecker (1979) concludes that the average residence time of water in the deep sea is 450 to 550 years. Sorting out the various advective and turbulent exchanges and the associated residence times of carbon in different regions of the oceans is crucial to understanding the role of the oceans in the carbon cycle.

Assimilation of CO₂ by marine organisms and subsequent deposition also serve to remove carbon from the surface waters (e.g., Mopper and Degens 1979). In most instances however, carbon fluxes associated with marine organisms are not limited by availability of CO₂ and as a result are likely
independent of rising atmospheric CO₂ concentrations. Peterson (1981) discusses the possibility of increased nutrient availability in coastal areas from agricultural runoff and releases of sewage (see also Peterson and Melillo in this volume).

C. Terrestrial Carbon Storage

The balance between assimilation by photosynthesis and releases of carbon from both living and dead material dictates the magnitude of the net exchange of carbon between the atmosphere and the world's terrestrial ecosystems. For reasonably undisturbed ecosystems, uptake and loss fluxes frequently are assumed to balance over sufficiently long time periods, with the average standing crop of carbon accepted as a steady-state level (e.g., Olson 1963). At shorter time scales, the balance certainly shifts with changes in nutrient availability, climate, and sporadic disturbances (e.g., Bormann and Likens 1979). During the period of substantial CO₂ releases from fossil fuels, disturbances by human activities, particularly forest clearing and other land-use changes, have been the dominant influence in determining the net transfer of carbon between terrestrial ecosystems and the atmosphere (e.g., Bolin 1977, Woodwell et al. 1978).

With land-use change such as forest clearing, carbon is immediately released to the atmosphere by burning, or with a delay of decomposition. In many instances, ground vegetation rather than trees is established after clearing, and by management this conversion may continue indefinitely with a longer carbon storage than in the original ecosystems. Following clearing or a similar disturbance, net productivity generally exceeds losses, and disturbed ecosystems may act as sinks for carbon from the atmosphere for some time.

The magnitude and timing of historical releases of carbon to the atmosphere as a result of disturbance to the world's terrestrial ecosystems by human activities remain uncertain. To estimate the magnitude of these historical releases, the areal extent of land-use change or other disturbances and the effects of disturbance on carbon storage in terrestrial ecosystems must be assessed. To determine the net flux of carbon from terrestrial pools to the atmosphere, any net ecosystem production must also be considered.

A number of investigators have estimated a contemporary flux of carbon to the atmosphere as a result of forest clearing, for example: 3 x 10^{15} \text{ gC/yr} (Seiler and Crutzen 1980), 6 x 10^{13} \text{ gC/yr} (Woodwell et al. 1978), 1.5 x 10^{15} \text{ gC/yr} (Bolin 1977), and 2.8 x 10^{15} \text{ gC/yr} (Moore et al. 1981; Houghton et al., 1983). The stated uncertainty in these estimates is large, and in some instances it is difficult to determine whether a particular value should be interpreted as a net transfer of carbon to the atmosphere or as a gross decrease in terrestrial carbon storage.
III. RECONCILING HISTORICAL CHANGES IN THE CARBON CYCLE

To project changes in atmospheric CO₂ concentration as fossil fuel use continues, the interactions between the atmosphere and other carbon reservoirs must be quantified. Observed changes in the carbon cycle must be reconciled with estimates of the historical releases of carbon by fossil fuel combustion, land-use change, or other perturbations to the cycle. This analysis of historical changes is a prerequisite verification of our understanding of the carbon cycle. Mathematical models of the global carbon cycle are used extensively in this analysis (e.g., Bolin 1981).

It is classical in oceanography to use the inhomogeneous distributions of chemical elements in the oceans to deduce features of ocean circulation. For example, the tongue of low salinity water in the thermocline region extending northward from the Antarctic circumpolar convergence zone has been interpreted as northward flowing water, in which the relative magnitude of the advective flow to that of the turbulent flux can be determined from the salinity profile.

In recent years the use of radioactive tracers, particularly \(^{14}\text{C}\) and \(^{3}\text{H}\), has provided important information on water exchange between the surface layers, the intermediate waters, and the deep sea (e.g., Broecker et al. 1979, Broecker and Peng 1982). However, steady-state tracers are also useful. Keeling and Bolin (1967, 1968) studied the problem of using simultaneously six tracers (salinity, oxygen, dissolved inorganic carbon, \(^{14}\text{C}\), alkalinity, and phosphorus), for developing a three box model of the oceans.

Models of carbon turnover in the atmosphere and oceans based on two or three reservoirs and used first to study the distribution of \(^{14}\text{C}\) and the Suess effect (e.g., Craig 1957, Revelle and Suess 1957), continue to be useful in analyzing the fate of fossil fuel CO₂. Keeling (1973) analyzed a two-box ocean representation with several alternative configurations of one or two boxes to include carbon in the world's terrestrial ecosystems. Bacastow and Keeling (1973) suggested parameterizations of a similar model to project CO₂ concentrations under alternative scenarios for future fossil fuel use. The primary difficulty in calibrating a two compartment ocean model lies in achieving consistency between model results and the observed distribution of radiocarbon (Bacastow and Keeling 1977). If the surface ocean compartment corresponds to waters above 260 m, the model calculated Suess effect agrees reasonably well with estimates from tree-ring \(^{14}\text{C}\) series.

To provide more resolution in representing the vertical distribution of \(^{14}\text{C}\) in the oceans, Oeschger et al. (1975) introduced a box-diffusion model. In this model, the turnover of carbon below 75 m is represented by diffusion equations. A constant coefficient of diffusivity is estimated by associating an idealized profile with measurements of the distribution of natural \(^{14}\text{C}\). To solve the diffusion equations governing the dynamics of carbon and \(^{14}\text{C}\), the model is distinguished into approximately 40 layers resulting in a system of ordinary linear differential equations with rate coefficients associated with each layer.

Broecker et al. (1980) analyzed the box-diffusion model with parameter values estimated from several alternative data sets including GEOSECS results. These investigators concluded that the box-diffusion model verified
reasonably well against measured distributions of $^{14}$C and tritium, and indicated that this model provides a good representation on time scales up to several centuries.

The sinking of cold water at high latitudes is an important mechanism for transporting carbon from surface waters to deeper layers. The box-diffusion model does not explicitly incorporate these advective aspects of mixing. Several models have been introduced that include fluxes associated with advective flow (e.g., Björkström 1979). Intuitively, a model such as Björkström's with direct fluxes from surface to deeper layers might be expected to have a higher propensity for taking up carbon from the atmosphere than a box-diffusion style representation.

Three models—(1) the two compartment model of Bacastow and Keeling (1973), (2) the box-diffusion model (Oeschger et al. 1975), and (3) models that include advective fluxes (e.g., Björkström 1979)—typify the designs of globally averaged representations of carbon turnover in the oceans. Several studies comparing these models have been reported. Bacastow and Björkström (1981) adjusted the computer implementations of these three models to be as consistent as possible and compared the response of the models in terms of several indicators such as airborne fraction. Killough and Emanuel (1981) considered five consistently calibrated prototypes, three of which correspond structurally to the three models listed above. In both of these comparisons, the models based on diffusive mixing displayed intermediate response in the variables considered.

Carbon cycle models which emphasize CO$_2$ exchange between the atmosphere and oceans generally incorporate terrestrial carbon storage by including one or two compartments designated "live" and "dead" or "fast" and "slow." In studies of the distribution of $^{14}$C, even these simple representations provide some indication of the influence of terrestrial pools on transit time and age distributions; however, in analyzing changes in atmospheric CO$_2$ levels, perturbations which alter the total storage of carbon in terrestrial ecosystems must be considered.

Bacastow and Keeling (1973) utilized "fast" and "slow" compartments to include terrestrial carbon storage in their model. The fluxes of carbon from the atmosphere to these pools were allowed to increase logarithmically with increasing atmospheric CO$_2$ concentration. This dependence improves the agreement between model response and CO$_2$ measurement records. Oeschger et al. (1975) incorporated a similar "CO$_2$ fertilization effect."

Although changes in terrestrial carbon fluxes due to rising CO$_2$ levels eventually may be demonstrated to be significant, over the past several centuries, terrestrial ecosystems have been a net source of CO$_2$ to the atmosphere. To simulate the historical interaction between atmospheric CO$_2$ and terrestrial ecosystems, models must include provision for changing terrestrial carbon fluxes and storage as a result of disturbance.

Emanuel et al. (1984a) describe a five-compartment model for carbon storage in terrestrial ecosystems. Carbon in plants is divided between "ground vegetation" and "trees"; while, carbon in dead organic matter is designated as either "detritus/decomposers" or "active soil carbon." In this
model, the relative magnitude of fluxes corresponding to plant productivity
are changed when disturbances such as forest clearing occur in model simula-
tions. Provision is made for specifying the fate of carbon removed from plant
compartments (i.e., direct transfer to the atmosphere or transfer to a
"detritus/decomposer" compartment) and whether a particular disturbance
results in land-use change.

Houghton et al. (1983) use a set of response functions to simulate the
effects of forest clearing and other land-use change on the storage of carbon
in various kinds of ecosystems. These response functions are combined with
tables of changing areal extents of the major biomes to yield reconstructions
of the net historical flux of carbon between the atmosphere and terrestrial
ecosystems. The response of the global carbon cycle to these reconstructed
historical fluxes can be simulated by treating the net terrestrial flux as an
exogenous input to the atmosphere.

The release of fossil fuel CO₂, forest clearing, and other disturbances
are viewed in the context of models of the global carbon cycle as perturba-
tions to an initial steady-state condition in which the decay of ¹³C is
assumed to be exactly balanced by natural production in the upper atmosphere,
and all other inputs to the system are assumed to be zero (e.g., Emanuel et
al. 1984b). The preindustrial concentration of CO₂ in the atmosphere,
appropriate as an initial condition in such model calculations, remains
uncertain.

If the trend in the Mauna Loa CO₂ record is extrapolated backward in
time to 1860, a point when substantial fossil fuel use began, an initial con-
centration of 297 ppmv is indicated (e.g., Rust et al. 1979). If fossil fuel
CO₂ is the only input of carbon to the atmosphere considered in a diffusive
ocean representation similar to that of Oeschger et al. (1975), best agreement
with the Mauna Loa record is achieved if an initial concentration of approxi-
mately 292 ppmv is assumed (Emanuel et al. 1984b). If net sources of CO₂ to
the atmosphere in addition to the release by fossil fuel combustion are
included, a lower initial atmospheric CO₂ concentration must be used in
order to admit agreement with even the average level of the Mauna Loa record.

The situation is further illustrated in Figs. 3 and 4. The response of a
globally averaged diffusive ocean model (Killough 1980, Killough and Emanuel
1981) is graphed in Fig. 4 for each of the reconstructions of the historical
net flux of carbon to the atmosphere from the world's terrestrial ecosystems
graphed in Fig. 3, as well as for the case in which fossil fuel CO₂ is the
only input of carbon to the atmosphere. In Fig. 3, curve (a) is the reference
case reconstruction of the terrestrial flux from land-use and demographic data
developed by Houghton et al. (1983). Curve (b) is derived from ¹³C tree-
ring data (Peng et al. 1983).

For each case that includes a significant source from the terrestrial
component of the cycle, the initial concentration of CO₂ is assumed to have
been 245 ppmv, in contrast to 292 ppmv for the case with fossil fuel CO₂ as
the only source. Even at this lower initial concentration, the trend in the
Mauna Loa record is not satisfactorily simulated when terrestrial CO₂
releases continue to within a decade of the CO₂ record (case c).
The difficulty of reconciling the observed change in atmospheric CO₂ concentration with estimates of carbon inputs to the atmosphere and models is illustrated by these few examples. The focus of the problem is the absence of reliable CO₂ records prior to the Mauna Loa and South Pole records of Keeling and co-workers, and proxy data which indicate changes in atmospheric CO₂ levels are of considerable importance. Ice cores, isotope abundance in tree-rings and corals, and historical measurements of atmospheric absorption of incoming infrared radiation are being analyzed. At the same time, models of each aspect of the cycle are being refined to improve confidence in inferential estimates and interpretation of measurement records.

IV. REFINEMENTS IN CARBON CYCLE STUDIES

An understanding of the global carbon cycle that permits satisfactory interpretation of observed changes requires refinement in the treatment of the heterogeneity of various aspects of the cycle. Globally averaged descriptions of the cycle make inadequate use of available data and do not incorporate principles governing various exchanges.

A. Spatially Detailed Terrestrial Studies

Houghton et al. (1983) consider major geographical areas in developing reconstructions of terrestrial fluxes associated with land-use change; however, data and model assumptions in this study are not considered in a cartographic system. As a result, difficulties arise in assigning tabulations of land-use change to particular areas of the landscape, and questions posed in terms of particular locations can not be addressed. Problems in adopting a uniform classification for major complexes of terrestrial ecosystems continue to impose further inconsistencies on efforts to synthesize terrestrial carbon data.

Climate based classifications offer an objective nomenclature and provide some insight as to the distribution of terrestrial ecosystems before human disturbance. A number of climate classification systems have been proposed (e.g., Köppen 1931, Thornthwaite 1947, Holdridge 1947). Among these, the Holdridge Life-Zone Classification is ecologically oriented in that the nomenclature for climate implies ecosystem associations expected in each climatic zone. A world map based on a life-zone classification such as Holdridge's provides insight as to the natural distribution of vegetation, terrestrial ecosystems, and their associated character. Furthermore, since the classification is climatically based, the effects of climate change whether natural or induced by human activities can be considered.

Holdridge life-zone maps have been developed for a number of regions (e.g., Sawyer and Lindsey 1963, Steila 1966, Ewel and Whitmore 1973). A recently developed Holdridge Life-Zone map of the world derived solely from meteorological data indicates applicability of this climate based approach to organizing terrestrial carbon studies (Emanuel et al. 1980). This map delineates the broad scale climatic boundaries defined by Holdridge's system and indicates the general distribution of terrestrial ecosystems expected under natural conditions.
The Holdridge Life-Zone Classification System (1947, 1964) is a three-level, hierarchical classification based on climate, edaphic, and atmospheric variables. The first level is defined by the climatic factors heat, precipitation, and moisture. It is this level which establishes a quantitative relationship between the principle climatic variables and the broad scale distribution of vegetation and is of interest in world scale mapping.

The elements of the life-zone classification are prescribed in a diagram (Fig. 5) in which equally weighted ecological divisions of the world's climate appear as a series of hexagons. The hexagons are set off by logarithmically scaled guide lines for ranges of long-term average annual biotemperature, precipitation, and effective humidity.

The second hierarchical level of the Holdridge system identifies distinctive ecosystem types or associations within each life zone. Associations within a life zone share a similar overall climate and are naturally grouped in an ecological context. Two forest ecosystems, classified as warm temperate forest by the life-zone scheme, may differ in species composition; however, the overall structural and functional characteristics of these ecosystems are expected to be similar.

Associations or ecosystems within a life zone are distinguished on the basis of edaphic, atmospheric, and local climatic factors. The number and landscape arrangement of the associations within any area for a particular life zone depend on the array of geological substrates, hydrology, soils, and special atmospheric conditions including exposure, fog, etc. The ecosystem is conceptually a relatively basic unit of study, but local variability in biomass and productivity may occur due to natural or human disturbances. Each association has a distinctive recovery process from disturbance. Therefore, the third and most detailed level of the Holdridge Life-Zone System involves identification of the successional stages of disturbed associations.

Mapping at the life-zone level of Holdridge's classification requires two climatic variables, biotemperature and annual precipitation, which can be determined as long-term averages from meteorological records. Biotemperature is a mean temperature which discounts air temperatures below 0°C in the sum of all unit-period temperatures used to calculate the mean for a day, week, month, or year. For purposes of world scale life-zone mapping, biotemperature can be calculated by dividing the sum of monthly mean air temperatures by twelve.

Although biotemperature and annual precipitation are sufficient to determine life-zone classification, a second triangular axis, potential evapotranspiration ratio, provides additional insight to the organization of the Holdridge system. Potential evapotranspiration (PET) is defined as the amount of water which will be evaporated at a given biotemperature under optimum soil moisture and vegetation conditions. PET is closely correlated with biotemperature and for natural conditions can be estimated in the context of Holdridge's classification system by multiplying biotemperature by 58.93. The potential evapotranspiration ratio is the ratio of PET to annual precipitation. A ratio of one indicates that potential evapotranspiration is balanced by annual precipitation.
To develop a world life-zone map, biotemperature and annual precipitation values calculated from data at approximately 9500 meteorological stations were interpolated to a uniform 0.5° latitude x 0.5° longitude grid. The Holdridge classification was applied to these interpolated values to generate the map. The areal extent of life zones, associated density of carbon storage in vegetation and soils, and the carbon content of these pools are tabulated in Table 1.

Maps of the distribution of terrestrial ecosystems derived from climate provide a basis for characterizing the terrestrial component of the carbon cycle under natural conditions. Satellite imagery and improved vegetation and soils maps are improving the reliability of estimates of contemporary terrestrial carbon storage and exchanges. The history of change from natural to present day conditions as a result of human activities remains insufficiently clear to reconstruct the historical role of terrestrial ecosystems in the carbon cycle.

Two kinds of direct data bear on the task of documenting the history of land-use change from the standpoint of terrestrial carbon storage: (1) maps or tabulations of the extent of major terrestrial ecosystem associations at particular points in time, (2) tabulations of the intensity of land-use change either directly or through related variables such as propulsion change. Methods must be developed to transform land-use change and demographic information into a sequence of maps of ecosystem distribution beginning with the climatically based natural conditions discussed above and running to the present.

B. Refinements to Ocean Models

One-dimensional or globally averaged models of carbon turnover in the oceans are limited in several respects:

(1) Substantial adjustments must be made to depth profiles of tracers such as $^{14}$C to accommodate variation with latitude and between oceans.

(2) Model testing is difficult when it is based on comparison of simulated profiles with measurements.

(3) Nonuniformity in the uptake of carbon by the oceans at different latitudes is particularly important in analyzing the weapons-produced $^{14}$C as a tracer, which in the early 1960's had its maximum atmospheric concentrations in high northern latitudes.

(4) Spatial detail in ocean models permits a more satisfactory treatment of the role of the marine biota in the redistribution of carbon.

In an effort to clarify the importance of particular aspects of circulation and chemistry, several investigators have suggested refinements to spatially homogeneous ocean models. The Bjørkstrøm (1979) advective-turbulent model, discussed in a previous section, provides for carbon transfers directly from a cold surface water box to deeper layers. Crane (1982) considers a
four-reservoir model which treats separately the turnover of carbon in polar regions and splits diffusive formulations for the Atlantic and for the Indian and Pacific Oceans. Enting and Pearman (1982) separate warm and cold waters and provide for transfers of carbon from surface to deep water in a cold ocean reservoir. Siegenthaler (1983) analyzes the implications of including transfers of carbon between each layer in the box-diffusion model and the atmosphere.

The explicit representation of aspects of carbon turnover in the oceans, such as deep water formation or organic matter production and decomposition, introduces additional parameters and complicates calibration procedures. Although selected model formulations may permit unambiguous calculation of parameter values from tracer data (e.g., Killough and Emanuel 1981), more realistic models often require application of fitting procedures to determine some parameter values, and in many instances, several sets of parameter values yield equally satisfactory agreement with available data.

Spatially detailed ocean models that treat each major region of the oceans with two or three-dimensional formulations support a large number of parameters, and calibration procedures become quite complex. Ultimately, one would like to deduce the appropriate structure of ocean models from tracer data as well as estimate parameter values. Major oceanographic programs such as GEOSECS and TTO (Transient Tracers in the Oceans) have provided sufficient data to support such a general approach, and the development of calibration procedures that can accommodate large numbers of parameters in fitting these data is now of major importance.

Bolin (1981) and Wunsch and Minster (1982) consider general approaches to using ocean circulation tracers in model calibration. These investigators cast the calibration as a linear algebra problem in which model parameter values are calculated to support observed distributions of steady-state tracers. In this general framework, three cases arise:

1. The exactly determined case in which selected tracer data exactly conforms to the number of free parameters.
2. The overdetermined case where there are too few adjustable parameters to support the observed tracer distributions selected for calculation.
3. The underdetermined case in which there are more adjustable parameters than can be uniquely determined from the selected calibration data.

As indicated above, the exactly determined case rarely occurs. The overdetermined case suggests that the formulation of the model is inadequate to support the data being considered and must be modified. This case has been given the least attention in work thus far. In the underdetermined case, alternative model structures and parameter values arise; only some of which are physically realistic. To force realistic solutions, constraints may be added to the problem; however, multiple solutions may still arise.
Bolin (1981) applies an algebraic approach to calibrate a twelve reservoir model. These reservoirs correspond to the major components of the oceans, and the model emphasizes the large scale features of ocean circulation. The exchanges derived from multiple tracers match the actual circulation reasonably well. In preliminary tests, the response of this model to historical fossil fuel CO2 releases is not substantially different than that of the box-diffusion model. Higher resolution models of mixing within these major reservoirs appear to be needed.

V. SUMMARY AND CONCLUSIONS

The collective character of carbon exchanges between the atmosphere and other pools is partially revealed by comparing the record of CO2 concentration beginning in 1958 with estimates of the releases from fossil fuels during this period. An airborne fraction (a ratio of the change in carbon content of the atmosphere to the input of carbon from fossil fuels) is frequently evaluated as a simple measure of this interaction (e.g., Bacastow and Keeling, 1981). This approach is limited because the magnitudes of the individual fluxes that maintain airborne fraction cannot be resolved. Furthermore, the character of these interactions has changed in the past and will likely do so in the future.

In analyzing the secular increase in CO2 concentration induced by fossil fuel use, the atmosphere can generally be treated as a single well-mixed reservoir; however, to study finer structure in the CO2 records, such as patterns in the seasonal cycle or the Southern Oscillation, the influence of atmospheric circulation must be more carefully considered. As atmospheric circulation models and spatially detailed models of other reservoirs are coupled, the capability for testing assumptions about the role of these reservoirs in the carbon cycle is substantially enhanced. Because of the pronounced influence of terrestrial ecosystems on the annual CO2 cycle, this improved analysis capability may be particularly important in resolving uncertainty as to the influence of changes in the terrestrial pools (e.g., Fung et al., 1983; Pearman and Hyson, 1980).

The rate of carbon uptake by the oceans, the primary sink for fossil fuel CO2, can be assessed more reliably than influences on the atmosphere due to interactions with other pools (e.g., Broecker et al., 1979). Analysis of tracer distributions is particularly important in this analysis. Most ocean models resolve changes only with depth and suggest that oceanic carbon uptake is too low to accommodate substantial releases of carbon to the atmosphere from vegetation and soils in addition to the fossil fuel input. However, data indicate that these globally averaged or one-dimensional models may be unsatisfactory. The distribution with depth of tracers used to analyze the turnover of carbon is quite variable with location in the oceans, and certain aspects of mixing and circulation that are not explicitly treated in models, such as advective fluxes at high latitudes, may be especially important (e.g., Broecker et al., 1980). Two-dimensional models that resolve both depth and latitude are being developed to confront these limitations of earlier formulations and may indicate larger rates of oceanic carbon uptake (e.g., Bolin et al., 1983).
The greatest improvement in the reliability of reconstructions of the history of changes in carbon storage in vegetation and soils is likely to result from the incorporation of geography in the analysis of land-use data. Mapping and distribution of land use assumed to result from tabular data will force consistency at a reasonably fine spatial resolution between the areas assumed to be altered and the area available for the specified change and will permit direct comparison of the land cover at any stage of development implied by land-use data and maps of land cover including those generated by remote sensing.

If the complete history of land-use change is eventually to be considered, the distribution of major terrestrial ecosystem complexes prior to changes in land cover by man's activities must be mapped. Climate-based classifications such as the Holdridge Life-Zone System may be the best means of generating such maps. An approach based on a climate classification has the additional benefit of providing a basis for assessing the sensitivity of the major zones of terrestrial ecosystem complexes to climate change as a preliminary assessment of the importance of this aspect of the feedback of CO$_2$-induced climate change on the carbon cycle.

Models of the global carbon cycle are being substantially refined while data that reflect the response of the cycle to fossil fuel use and other perturbations are being extended. This series such as $^{13}$C/$^{12}$C ratios in tree rings may permit indirect evaluation of the historical influence of terrestrial ecosystems on atmospheric CO$_2$ levels. The development of proxy data on CO$_2$ concentration in the atmosphere, such as CO$_2$ levels in ice cores, may eventually provide a useful atmospheric CO$_2$ record across the entire period of anthropogenic perturbation and form the data base required for reconciling improved models and the estimated production CO$_2$ in the atmosphere by fossil fuel use -- a prerequisite for reliably projecting future CO$_2$ levels.

REFERENCES


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<th>Life Zone</th>
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Table 1. Carbon Storage in Vegetation and Soil (Continued)

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| **Total**        | 129.294           | 923.115               | 1305.90                |                       |                        |
Fig. 1 Schematic of the global carbon cycle
Fig. 2 Concentration of atmospheric CO₂ at Mauna Loa Observatory, Hawaii. Dots indicate monthly averages. (Keeling et al. 1982).
Fig. 3. Historical releases of carbon from the terrestrial component of the model to the atmosphere as a result of disturbance: (A) Reference case generated by Houghton et al. (1983) from land-use and demographic data; (B) reconstruction based on $^{13}$C tree-ring data by Peng et al. (1983).
Fig. 5. Diagram depicting the Holdridge Life-Zone Classification System
Fig. 4. Simulated histories of atmospheric CO₂ concentration: (A) Fossil fuel release is the only input to the atmosphere; (B) Terrestrial source is the Houghton et al. (1983) reference case; (C) Terrestrial source is the reconstruction by Peng et al. (1983). Annual average values at Mauna Loa Observatory are indicated.
CARBON CYCLE: TERRESTRIAL INTERACTIONS

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Duke University
Durham, North Carolina

I. THE TERRESTRIAL CARBON CYCLE

A. Pools (Figure 1)

1. Living biota

The current estimate (Olson, 1982) suggests that the widely quoted storage of 800 x 10^{15} gC of Whittaker and Likens (1973) is too high. It may represent prehistoric storage in biota but the present pool is estimated at 560 x 10^{15} gC.

2. Soil Organic Matter

Estimates by Schlesinger (1977) using vegetation zones, and Post et al. (1982) using life zones show a storage of 1500 x 10^{15} gC. Most other estimates range from 1200 to 2000. Apparently the large estimates by Bohn (1976, 1982) are too high, but the uncertainty may result from the peatland areas (Armentano, 1979).

3. Arid A+Zone Soil Carbonates

Widespread deposits known as caliche or calcrite are estimated to contain a carbon pool of 800 x 10^{15} g (Schlesinger, 1982). Some uncertainty is involved in the definition of this pool separate from geologic carbonate deposits.

B. Natural or Steady-State Exchange (Figure 2)

Cross Primary Production minus Plant Respiration equals Net Primary Production. Net Primary Production, easily measured as new biomass, is estimated at 70 x 10^{15} gC/y (Olson, 1982) or 50 x 10^{15} gC/y (Whittaker and Likens, 1973).

Gross Primary Production is estimated as 2 x NPP, since laboratory photosynthesis studies suggest that night-time respiration is about half of daytime carbon uptake. Gross primary production may be underestimated to the extent that photorespiration occurs. If terrestrial pools are in steady-state, then all NPP is decomposed by microbial activity, herbivores and fire; i.e., there is no net storage if organic matter on land equals net ecosystem production. Thus soil respiration is 70 x 10^{15} gC/yr.
The steady-state assumption is questionable, since organic matter has accumulated in soils, especially peatlands. For example, the humus content of glaciated soils, ca. 10 kgC/m², has accumulated in 10,000 years or 1 gC/m²/yr.

Arid Zone Carbonates: Estimates of rate of natural formation suggest a flux in the $10^{13}$ gC/yr magnitude (Schlesinger, 1982 and unpublished) based on isotope dating.

Rivers: A variety of flux estimates are available. Some appear much too high in an attempt by some workers to balance the carbon cycle by transport of resistant carbon to the deep ocean. Current estimates converge on $0.4 \times 10^{15}$ gC/yr (Schlesinger and Melack, 1981; Meybeck, 1982). These do not include enhanced continental shelf production due to nutrient transport (Walsh et al., 1981). Presumably, some of the organic carbon flux in rivers is derived from weathering of organic carbon (kerogen) from rocks. Are rivers in steady-state? Residence times for terrestrial pools vary over 4 orders of magnitude (Table 1), based on natural flux and pools.

C. Anthropogenic Perturbations (Figure 3)

Fossil fuels: There is fairly widespread agreement on a flux of $5 \times 6 \times 10^{15}$ gC/yr. Can this be regarded as an increased rate of weathering of kerogen?

The alteration of Net Primary Production is due to the disturbance of natural ecosystems and reductions in leaf area, coupled with the alteration of decomposition (due to increases in soil aeration and fertilizers etc.). The alteration of Net Primary Production suggests a net release of carbon from terrestrial organic pools to the atmosphere. Houghton et al. (1983) assign $2 \times 10^{15}$ gC/yr as a probable value. Some regions are sinks (Delcourt and Harris, 1980). The main source area is probably the tropics. The alteration of carbon storage is reservoirs and lakes (Mulholland and Elwood, 1982) up to $0.2 \times 10^{15}$ gC/yr net storage. Altered carbonate formation has not been studied.

II. INTERACTIONS

If terrestrial primary production is limited by nutrients in many areas, it can increase in nutrient mobilization from the burning of fossil fuels, and the mining of fertilizers acts to increase NPP in many areas and "soak up" CO₂ release. However, the ratios of C:N:P:S in fossil fuel release and terrestrial carbon storage suggest not (Table 2, from Likens et al., 1981).

III. MODELS

Terrestrial accounting models (see Houghton et al., 1983, Moore et al., 1981) attempt to account for carbon storage and changes in storage in land ecosystems. These models use initial values for pool sizes and changes in
pools following theoretical response functions. Response curves are reasonably formulated on empirical data; errors are largely due to differences in land use conversion estimates.

Other models are based on interpretations of the atmospheric record (See Keeling, 1983; Hall et al., 1975; Pearman and Hyson, 1981). Does the increasing amplitude of the Mauna Loa record suggest increasing biotic activity in seasonal ecosystems (temperate region)? Could it suggest increasing storage? (Figure 4).

IV. DATA GAPS

A. Natural Pools

Better aerial estimates for land ecosystems are essential and could be the most important addition from NASA. Some problems arise because different workers use vegetation, soil or life zone (climate) classification schemes. However, when models show convergence despite the above, the conclusions appear more substantial.

Limited field work in Boreal forest, tropical forest and tropical savannah might be helpful.

B. Natural Flux

Evaluation of the steady-state assumption is needed. The question is, Have terrestrial ecosystems been in steady-state for any part of the Holocene period? The following suggest not: peatland accumulations, soil organic matter in glaciated soils, and soil respiration vs. climate changes (Schleser, 1982). Is river flux a steady-state value? We should use the interpretation of C\(^{13}/C\(^{12}\) in accumulated storage.

C. Perturbed Flux

Better estimates of land use conversion will be essential and will be an important goal for NASA. Field studies of the effects of \(\text{CO}_2\) enrichment on NPP, respiration and total carbon storage will be important to these estimates.

D. Models

Models need to begin incorporating climatic changes, both past (through Holocene and beyond) and future (in response to global warming?).
REFERENCES


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Fig. 1. Terrestrial Carbon Pools
Fig. 2. Terrestrial Carbon Exchange
Table 1. Mean Residence Times for Terrestrial Pools

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Fig. 3. Perturbations of the Terrestrial Carbon Cycle
Table 2. Elemental Ratios (by weight) for Major Nutrients (from Likens et al., 1981)

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Fig. 4. Mauna Loa Record of Carbon Storage
GLOBAL CARBON - NITROGEN - PHOSPHORUS CYCLE INTERACTIONS:
A KEY TO SOLVING THE ATMOSPHERIC CO₂ BALANCE PROBLEM?

B. J. Peterson and J. M. Mellillo
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I. INTRODUCTION

Dramatic changes in the carbon cycle over recent decades have been paralleled by equally large changes in some segments of the cycles of nitrogen, phosphorus and sulfur (Delwiche and Likens 1977). These elements together with oxygen are, not by chance, also the major elements in the biota of the earth. Redfield (1958, 1963) has noted that the "interactions of organisms and environment are reciprocal" and "the influence of organisms on the composition of their environment is determined by physiological influences and consequently exhibits the regularity inherent in organic processes." Recently Lovelock (1979) has taken these considerations even further to suggest that the composition of the atmosphere-ocean system is controlled by organisms in a homeostatic manner to maintain environmental conditions within the range favorable to life processes. The theses of Redfield and Lovelock have great appeal for biologists because we see so many of the life processes we study in terrestrial and aquatic ecosystems reflected in the chemical composition of the water and air flowing through these systems. However, since our understanding of the range, capacity, and time frame of global biotic responses to changes in the circulation of essential elements is so limited, one must question the wisdom of causing large perturbations such as the current atmospheric CO₂ increase in an uncontrolled manner.

The general purpose of this paper is to outline a framework for considering the biota-mediated linkages in the global cycles of C, N, P, and S. The specific purpose is to examine the hypothesis that the rate of atmospheric CO₂ increase has been limited by a stimulation of net storage of carbon in forests, coastal oceans, and the open sea caused by the man-induced acceleration of nitrogen and phosphorus cycling.

We reach the conclusion that the biota undoubtedly does respond rapidly and on a large scale to changes in the supply of nitrogen, phosphorus, and sometimes sulfur to both terrestrial and aquatic ecosystems. However, a consideration of the elemental ratios of the organic matter held in the major reservoirs involved in the current short-term perturbation of the C, N, P, and S cycles suggests that it is unlikely that a large fraction of the total CO₂ released to the atmosphere will be stored in biotic reservoirs as organic carbon in trees, soils, and aquatic sediments. The reason for this is that both the C:N and the C:P ratios in the CO₂ sources (fossil fuels and primary forests) are much greater than the ratios in the sinks (successional forests and aquatic sediments). It appears that a rapid stabilization of the atmospheric CO₂ levels will not be achieved unless both the rate of fossil fuel
combustion is regulated and the exploitation of forests is reduced or reversed. In the longer-term, atmospheric CO₂ is undoubtedly controlled by a series of mechanisms such as the level of productivity of plankton in the surface ocean, sediment carbonate dissolution, and rock weathering and formation. However, the time required for these controls to operate is longer than the decade to 100 year time frame considered here.

II. DIMENSIONS OF THE PROBLEM

The atmospheric CO₂ concentration has been shown to be increasing exponentially in the period from 1958 to the present (Bacastow and Keeling 1981). While it is clear that one cause of this CO₂ increase is fossil fuel burning, a second large source from forest harvest and clearing is also contributing to the increase. Over the period from 1860 to the present, it appears likely that the net CO₂ release from land use changes causing organic matter oxidation equals or exceeds the total fossil fuel CO₂ release (Houghton et al. 1983). The measured atmospheric increases and the estimated net fluxes to and from the atmosphere in 1980 are shown in Table 1. The table demonstrates that the sum of the measured atmospheric increases and model-calculated ocean uptake is less than the fossil fuel plus harvest and clearing CO₂ inputs to the atmosphere by 2.7 Gt C yr⁻¹. This residual changes from year to year; its range is 1.3 to 4.1 for the period 1959 to 1980. Actually, Table 1 may exaggerate somewhat the difficulty of balancing the atmospheric CO₂ budget because the carbon uptake calculated by ocean models is a function of the preindustrial CO₂ level assumed for the atmosphere - ocean CO₂ pools. If one accepts the possibility that the total CO₂ release is double the fossil fuel CO₂, then the preindustrial CO₂ level was probably lower than the roughly 290 ppm often assumed in the ocean modeling runs. Under these conditions of lower initial CO₂ and larger atmospheric loading, the ocean models take up more CO₂, perhaps up to about 3 Gt C yr⁻¹ in 1980. Still the atmospheric CO₂ balance is off by about 2 Gt C yr⁻¹ and one is forced to consider the possibility that other sinks may be involved. In this paper, we examine three organic carbon sinks that seem potentially important: forests and their soils, continental shelf sediments, and the sedimentation of organic carbon in the open ocean.

III. ELEMENTAL RATIOS IN THE SOURCES AND SINKS OF ORGANIC CARBON

Table 2 summarizes much of the data needed to test the idea that increased carbon storage in forests and oceans is occurring as a result of eutrophication. Several points should be noted: (1) The total of terrestrial net primary production (NPP) and aquatic NPP is still large relative to the rate of fossil fuel CO₂ release and thus the capacity to alter the atmospheric CO₂ balance exists. We also know that productivity of both forests (Miller and Miller, 1976) and aquatic ecosystems (Ryther and Dunstan 1971) can be stimulated by added nutrients; however, the stimulation of production by added CO₂ alone is questionable for forests (Kramer 1981) and probably out of the question for most fresh water aquatic ecosystems and oceans (Schindler 1971, Broecker 1974). Here we assume that added nutrients are required to stimulate additional carbon storage. (2) The combustion of fossil fuels
releases about half as much nitrate ($20 \times 10^{12}$ g N) into the atmosphere as the nitrogen fertilizer industry produces in a year. (3) The C:P and the C:N ratios in fossil fuel and to a lesser extent in forest biomass are very high relative to the ratios in the terrestrial soils, plankton, and marine sediment pools.

The conceptual model of the carbon and nutrient flows to be considered here is illustrated in Figure 1. We are particularly concerned with the influences of fossil fuel use, land use, sewage, and fertilizer production on the major segments of the biota as illustrated here by terrestrial ecosystems, coastal ocean areas and open ocean regions. We seek to answer the question "How large is the increment of net ecosystem production (NEP) in units of carbon that may be accumulating due to eutrophication of forests and oceans?" We emphasize the word increment because while any one segment of the linked system may show a net storage of organic carbon in the unperturbed state, such storage would not provide a sink for the additional CO$_2$ recently added to the atmosphere by man.

IV. FORESTS

We have calculated the possible increase in carbon storage in forested ecosystems as shown in Table 3. The forests have been divided by region and by vegetation - litter - soil compartments since both the stature of the forests and the division by compartments are different in the different regions. We have assumed that $6 \times 10^{12}$ g N ($10^{12}$ g - Tg) or about 30% of the fixed nitrogen release via fossil fuel combustion actually reaches forests via atmospheric transport and precipitation and we have assigned 4 Tg to temperate forests, 1 Tg to boreal forests, 0.5 Tg to tropical forests, and 0.5 Tg to woodlands and shrublands, reflecting the non-uniform distribution of sources. We further assume that the forest retains 60% of the added nitrogen and that this is invested in growth of the vegetation, litter, and soil compartments in proportion to the initial carbon distribution in these compartments and that the C:N ratio of the compartments does not change. The results demonstrate that if storage is occurring, most of it is in temperate forest vegetation since vegetation has the widest C:N ratio of all compartments and since the temperate zone presumably receives anat of the inputs. The total potential storage is not a trivial amount, about 0.3 Gt C yr$^{-1}$. Since this is an annual increment of roughly 0.06%, or one part in about 1600, even in the most heavily fertilized region including temperate forests, detecting such a change by empirical measurement of forest carbon stocks would be quite impossible in the short term. Studies of forest tree growth have shown both positive and negative trends in industrialized regions in recent decades (Whittaker et al. 1974). Our calculations reflect a maximum potential. There are several reasons that such a potential might not be realized: 1) some of the excess nitrogen may undergo active denitrification; 2) some of these ecosystems are probably not nitrogen limited; 3) added nitrogen may be used with less efficiency and hence produce less carbon mass storage as the system is enriched in nutrient; and 4) added nitrogen may even stimulate decomposition which outweighs carbon storage. This summary treatment of forest responses is pursued in greater detail by Melillo and Gosz (1983).
V. THE COASTAL ZONE

The distribution of human activity and therefore, human pollution and waste, is strongly concentrated in the coastal zone, and hence, a large impact on coastal oceanic production and possibly carbon storage might be anticipated. In addition to fertilizers lost from agricultural lands, sewage, and combustion products of fossil fuels, there is the possibility that the extensive oxidation of natural organic matter from forest clearing and harvest and from soils under agriculture will generate additional flows of nitrogen and phosphorus in waters draining the continents. For example, in 1980 the net oxidation of 2.6 Gt C from forest clearing and agricultural conversions (Table 1) would presumably mobilize about 70 Tg N and 9 Tg P which rivals global fertilizer production for both N and P (Table 3). Obviously, care must be taken not to overestimate the amounts reaching the coastal oceans and to avoid double accounting. For example, nutrients in sewage may originally come largely from fertilizer production and nitrogen in rivers may be derived partly from fossil fuel nitrogen pollution from the atmosphere.

We have used Meybeck’s recent comprehensive summary of the fluxes of C, N, and P to the ocean based on measurements from a large sample of rivers in both heavily polluted and more pristine areas (Table 4). One advantage of Meybeck’s approach for our purpose is that he calculated both the natural N and P load and the increment in N and P loading due to human perturbation. Increased carbon buried in the coastal zone sediments could be occurring through two mechanisms: (1) the burial of excess organic carbon carried by rivers to the oceans and (2) the burial of some fraction of the enhanced primary production due to eutrophication (Fig. 2). Because of a paucity of good information on change in organic carbon load in rivers, Meybeck chose not to advance a figure for man-derived C. We give an estimate of 0.1 Gt C yr⁻¹ for illustrative purposes as this seems to be a plausible amount based on the potential limits of error (~30%) and the more thoroughly documented increases in N and P. Therefore, the potential increment to burial from continental erosion and export to the coastal ocean is 0.1 Gt C yr⁻¹.

The increased nitrogen load to coastal oceans of 7.0 Tg N yr⁻¹ is 7 times greater than the increased P load. Since this is close to the weight ratio of N:P in plankton (Table 2) the question of whether N or P is limiting coastal productivity is avoided as the calculation of potential C storage will be similar in either case. The total primary production in the coastal zone of about 4 Gt C yr⁻¹ is supported, as is most productivity in aquatic systems, by recycled nutrient. Burial of carbon requires addition of nutrients from outside the system, such as from rivers, lest the system run down. An increment to carbon burial requires increased loading, and using Meybeck’s man-derived nutrient the potential carbon burial is 0.04 to 0.08 Gt C yr⁻¹.

The range given allows for the fact that early diagenesis regenerates N and P preferentially relative to organic carbon over a period of years such that the nutrients may reenter the water column (or be lost) and possibly deliver more C to the sediments. Thus for the permanently buried material the C:N and C:P ratios may be twice the Redfield ratios of 6:1 or 40:1 by weight (Rosenfeld 1981, Froelich et al. 1982).

A recent review by Berner (1982) shows that only a small fraction of this potentially large (up to 0.2 Gt C yr⁻¹) burial of organic carbon in coastal oceans is likely to be realized (Table 5). Berner has summarized data on the
rate of accumulation of sediments in four sediment types of the coastal and open ocean along with their weighted mean C content. Most of the carbon burial in the modern ocean occurs in shelf sediments. Berner calculates the burial rate by multiplying the global flux of continent-derived sediments, most of which are deposited on the continental shelves, by their mean % C content of 0.75% for a burial of 0.13 Gt C yr⁻¹. This will be reduced by some 20% due largely to sulfate reduction in these anoxic sediments to about 0.1 Gt C yr⁻¹. The recent increment to burial due to human activity must be, of course, a fraction of this; probably an upper limit of 0.05 could be readily defended as a maximum allowable increment.

A comparison between the potential for burial and the actual burial calculated by Berner reveals two interesting points. Most of the carbon coming down rivers must either be metabolized to CO₂ or exported probably as DOC from the shelf. Coastal zone productivity may be stimulated considerably by added nutrients, especially considering the 5-10 times of N and P both in the plankton and between the plankton and benthos. However, only a very small fraction of total primary production is buried and of this the man-caused increase probably is 50% or less on a global scale. Details of the argument for the coastal zone were presented previously (Peterson 1981) but at that time less documentation of nutrient fluxes and sedimentation was available.

VI. THE OPEN SEA

As already shown in Table 5, the total sediment accumulation of organic carbon in pelagic (open ocean) sediments is so low that any increment due to recent human nutrient cycle perturbation certainly falls below the noise level in this analysis. However, as illustrated in Figure 3 it is not necessary to actually sequester carbon in bottom sediments to achieve the objective of finding a short-term (decades to several hundred years) biotically-mediated sink for CO₂. Increased sedimentation of organic carbon well into or through the permanent thermocline zone would provide a temporary sink and might be invoked to aid the CO₂ balance problem (Peterson 1981, Eppley and Peterson 1979). The increased deposition of nitrogen (NO₃ and NH₄) on the oceans due to fossil fuel combustion would be a mechanism for stimulating open ocean primary production and for allowing an increased flux of organic carbon from the surface to intermediate and deep layers. We have assumed that 6 Tg N (about 30% of the fossil fuel N release) is delivered via the atmosphere to the open ocean. The resultant increased sinking carbon flux is about 0.04 Gt C yr⁻¹ assuming a planktonic C:N ratio of six (Table 2). Again this is an upper estimate since probably less than 30% of the fossil fuel released N actually reaches the open ocean and this "sink" may be only a temporary one at best. Also, if the total supply of N and P were in balance relative to the needs of the plankton, the rate of aeolian P delivery might serve to limit this excess nutrient-matching flux. It is interesting to note that the forests have the potential to store, with the same nutrient load, about six times more carbon than does the plankton system because of the wider C:N ratio in the forest ecosystems.
VII. SUMMARY AND CONCLUSIONS

If we add all biotic sinks of atmospheric CO₂ reported herein (Table 6), we arrive at a value of about 0.4 Gt C yr⁻¹. For each category, we feel we have used a very high (non-conservative) estimate. This still does not provide a sufficient basis for achieving a balance between the sources and sinks of atmospheric CO₂ illustrated in Table 1. We feel that probably the bulk of the discrepancy lies in a combination of errors in the major terms, the greatest being in the net biotic release and ocean uptake segments, but smaller errors or biases may exist in calculations of the rate of atmospheric CO₂ increase and total fossil fuel use as well. The reason why biotic sinks are not capable of balancing the CO₂ increase via nutrient-matching in the short-term is apparent from a comparison of the stoichiometry of the sources and sinks. The burning of fossil fuels and forest biomass releases much more CO₂-carbon relative to N and P than can be sequestered as organic carbon with this same amount of nutrient in the biotic sinks that appear to be most important in the short-term.

Several questions remain to be answered that were not addressed in our analysis:

1. Is there the possibility that CO₂ alone will stimulate carbon storage especially in terrestrial ecosystems? If this occurs, it implies a widening of the C:N ratio in the organic matter pools or an increase in nitrogen fixation or retention in terrestrial ecosystems. The impact of CO₂ appears to be moving terrestrial systems in the other direction since early successional forests have lower C:N and C:P ratios than mature forests. It is the rapidly disappearing old growth forests that are most efficient in carbon storage.

2. Are there other sinks that may remove excess atmospheric CO₂ not considered here? There are some possibilities:
   a. Mulholland (1980) estimates that carbon accumulation rates in river delta regions may have averaged 0.6 Gt C yr⁻¹ over the last 12,000 years. Again, here one would want to know if there has been a recent increase. Also, movement of carbon from uplands to lowlands by erosive processes does not necessarily result in net carbon storage.
   b. Marine macrophytes fix annually about 1 Gt C but there is no evidence that macrophyte biomass or carbon storage due to macrophyte activity has been altered in recent decades (Smith 1981).
   c. The formation of caliche (carbonates) in soils of arid regions may serve to sequester CO₂, but the gross rate of fixation is only about 0.02 Gt C yr⁻¹ globally (Schlesinger 1982) and thus perturbations in this flux would have little impact.
d. The net accumulation of carbon in tundra and boreal regions that were glaciated about 10,000 years ago would be only 0.05 Gt C yr⁻¹ if a linear increase to the total current stock is assumed.

e. The idea that the formation of charcoal during forest clearing and burning has sequestered significant amounts of carbon (Seiler and Crutzen 1980) has been examined by Houghton et al. (1983) and found to change the amount of CO₂ released by only about 3% over the period 1860 to 1980.

f. MacKenzie (1980) argues that the increasing CO₂ level in the surface oceans will dissolve shallow water magnesian calcites but that the additional uptake allowable via this mechanism is only about 1% of the fossil fuel CO₂ release (MacKenzie et al. MS).

None of these possibilities appears to us to alter our general conclusion that an atmospheric CO₂ balance can not be achieved currently by invoking biotic sinks. Neither does it appear likely that an appreciable change in this situation will occur soon unless the pressure from exploitation of forests globally can be reduced or reversed by a massive program of afforestation. Prospects for this appear at present uncertain at best.

This is not to suggest that Gaea is not alive and well, or that the homeostatic mechanisms which regulate atmospheric CO₂ are not at work. As we see the situation, it is a problem of time, not ultimate potential. We are burning fossil fuels much more rapidly than they are formed. We are also depleting what are potentially renewable resources -- stocks of organic matter and nutrients held in forests and soils -- at rates which exceed the regrowth of these reservoirs.

Thus the possibilities for short-term storage increases in forests are being forgone. However, a continuation of these trends of depletion of the nutrient stores on land along with other human activity will probably lead to what may be termed the ultimate eutrophication problem; that is, a widespread increase in oceanic productivity. Over a period of the order of $10^3$ to $10^5$ years man could conceivably double the levels of NO₃ and PO₄ in the deep ocean waters that supply nutrients to the surfician plankton communities whose activity controls the levels of dissolved CO₂ at the ocean surface. More nutrients mean lower partial pressure of CO₂ and a more effective oceanic sink. Similar arguments are presented by Broecker (1982) for interpreting the linkages between plankton activity, atmospheric CO₂, and glaciations. The opposing scenario of a reduction in surface ocean productivity as might be caused by toxic substances could occur more rapidly and would lead to an increase of surface ocean pCO₂ levels and a positive feedback or further increase in atmospheric CO₂ levels.
ACKNOWLEDGEMENTS

The author thanks Jennifer Dungan, John Hobbie, and Bo Bergquist for assistance and review of this manuscript.

REFERENCES


## Table 1. Atmospheric Carbon Dioxide Balance in 1980 (units are Gt per year)

<table>
<thead>
<tr>
<th>Change in CO$_2$</th>
<th>Forest Fuel Use</th>
<th>Clearing</th>
<th>Harvest &amp; CO$_2$ Uptake</th>
<th>Ocean Storage</th>
<th>Atmospheric CO$_2$ Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in Forest</td>
<td>+5.2</td>
<td></td>
<td>+2.6</td>
<td>-2.0</td>
<td>+5.2</td>
</tr>
<tr>
<td>Change in Ocean</td>
<td></td>
<td></td>
<td></td>
<td>-3.1</td>
<td>+2.6</td>
</tr>
<tr>
<td>Change in Carbon Storage</td>
<td></td>
<td></td>
<td></td>
<td>-2.0</td>
<td>+2.7</td>
</tr>
</tbody>
</table>

or rearranging to isolate sources and sinks

### Sources:
- **Atmosphere:** derived by smoothing Mauna Loa record (Bacastow and Keeling 1981)
- **Fossil Fuel:** Rotty (1981)
- **Ocean Uptake:** Broecker et al. (1979)
- **Harvest and Clearance:** Houghton et al. (1983)
- **Carbon Storage:** by difference
Table 2. Selected Annual Fluxes and elemental Ratios in the Global Circulation of Carbon and Nutrients (for 1980).

<table>
<thead>
<tr>
<th>Category</th>
<th>Flux ($10^{15}$ g yr$^{-1}$)</th>
<th>Elemental Ratios by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C : N : S : P : C:N</td>
</tr>
</tbody>
</table>

1. Terrestrial NPP
   - Litter: 500 : 10 : 1 : 1 : 50
   - Soils: 120 : 10 : 1 : 1 : 12
   - Forests Only: [40C]
     - Biomass: 1500 : 10 : 1 : 1 : 130
     - Litter: 500 : 10 : 1 : 1 : 50

2. Aquatic NPP
   - Sediments: 12

3. Fossil Fuel
   - 5.2C: 9000 : 36 : 130 : 1 : 250

4. Nitrogen Fertilizer Production: .050N

5. Phosphate Fertilizer Production: .012P

Sources: Whittaker and Likens (1973)
         Platt and Subba Rao (1975)
         Rotty (1981)
         UN Yearbook (1977)
         Melillo and Gosz (1983)
         Redfield (1958)
         Delwiche and Likens (1977)
Table 3. Potential Carbon Storage in Forests Due to Nitrogen Loading from Fossil Fuel (adapted from Melillo & Goss 1983).

<table>
<thead>
<tr>
<th>Region</th>
<th>Area ($10^6$ ha)</th>
<th>Carbon Mass (kg C m$^{-2}$)</th>
<th>Compartments (% of C)</th>
<th>N load (Tg yr$^{-1}$)</th>
<th>C Storage (Tg yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tropics</td>
<td>24.5</td>
<td>31.5</td>
<td>0.5</td>
<td>Vegetation (66.5)</td>
<td>29.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Litter (0.5)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Soil (33.0)</td>
<td>1.3</td>
</tr>
<tr>
<td>Temperate</td>
<td>12</td>
<td>29.1</td>
<td>4.0</td>
<td>Vegetation (55.2)</td>
<td>198.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Litter (4.2)</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Soil (40.6)</td>
<td>12.6</td>
</tr>
<tr>
<td>Boreal</td>
<td>12</td>
<td>26.5</td>
<td>1</td>
<td>Vegetation (37.2)</td>
<td>33.5</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Litter (7.4)</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Soil (55.4)</td>
<td>4.3</td>
</tr>
<tr>
<td>Woodland and</td>
<td>8.5</td>
<td>13.2</td>
<td>0.5</td>
<td>Vegetation (45.5)</td>
<td>20.5</td>
</tr>
<tr>
<td>Shrubland</td>
<td></td>
<td></td>
<td></td>
<td>Litter (2.1)</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Soil (52.3)</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td></td>
<td></td>
<td>6 Tg N</td>
<td>306 Tg C</td>
</tr>
</tbody>
</table>
Table 4. Global Fluxes of Carbon, Nitrogen & Phosphorus by World Rivers to the Ocean (Adapted from Meybeck (1982)).

<table>
<thead>
<tr>
<th>Category</th>
<th>Natural Flux</th>
<th>Man Derived</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Units $10^{12}$ g yr$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>Particulate Organic Carbon</td>
<td>180</td>
<td>100**</td>
</tr>
<tr>
<td>Total</td>
<td>395</td>
<td></td>
</tr>
<tr>
<td><strong>Nutrients</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Dissolved Organic</td>
<td>11.00</td>
<td>7.0 TDN***</td>
</tr>
<tr>
<td>Particulate Organic</td>
<td>21.00</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>36.25</td>
<td></td>
</tr>
<tr>
<td>Phosphorus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Dissolved Organic</td>
<td>0.55</td>
<td>1.0 TDP</td>
</tr>
<tr>
<td>Particulate Organic</td>
<td>8.00</td>
<td></td>
</tr>
<tr>
<td>Particulate Inorganic</td>
<td>12.00</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>21.00</td>
<td></td>
</tr>
</tbody>
</table>

*corresponds to drainage of $100 \times 10^6$ km$^2$ out of total land surface of $149 \times 10^6$ km$^2$ (omits interior drainages and glaciated areas).

**a rough estimate based on discussion in Meybeck (1982) and on data from highly impacted Asian drainages reported by Milliman and Meade (1983) and by Milliman (personal communication).

***TDN refers to total dissolved nitrogen, TDP refers to total dissolved phosphorus.
Table 5. Organic Carbon Burial in Marine Sediments (Adapted from Berner 1982)

<table>
<thead>
<tr>
<th>Sediment Type</th>
<th>Accumulation (10^9 tons yr^-1)</th>
<th>Mean % C</th>
<th>Carbon Burial (10^12g C yr^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deltaic-Shelf Sediments</td>
<td>17.3*</td>
<td>0.75</td>
<td>130</td>
</tr>
<tr>
<td>Shallow Water Carbonate Sediments</td>
<td>0.7</td>
<td>1.00</td>
<td>7</td>
</tr>
<tr>
<td>Pelagic Sediments (upwelling)</td>
<td>1.0</td>
<td>1.40</td>
<td>14</td>
</tr>
<tr>
<td>Pelagic Sediments (low productivity)</td>
<td>1.7</td>
<td>0.33</td>
<td>6</td>
</tr>
</tbody>
</table>

World Total Supplied to Sediment Surface 157
Subtract 20% Carbon Loss in Early Diagenesis -31
126

*Milliman and Meade (1983) estimate 13.5 x 10^9 tons for total river discharge of sediments.
Table 6. Potential Carbon Sinks in Forests and Sediments via Nutrient Matching

<table>
<thead>
<tr>
<th>Category</th>
<th>Gt C yr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Vegetation and Soils&lt;br&gt;due to N fertilization</td>
<td>0.30</td>
</tr>
<tr>
<td>Coastal Sediments&lt;br&gt;due to erosion and eutrophication</td>
<td>0.05</td>
</tr>
<tr>
<td>Open Ocean&lt;br&gt;due to N fertilization</td>
<td>0.05 0.40</td>
</tr>
</tbody>
</table>

Comparison with C Budget Imbalance = 2.7

Contribution to Balance 15% for 1980 Rates.
Figure 1. Diagram of the Short-Term (Decades) Perturbation of the Global Carbon Cycle (units are Gt C yr\(^{-1}\) for NPP)
RIVER INPUTS

TOTAL ORGANIC CARBON 0.4
"EXCESS" ERODED C ~ 0.1?

COASTAL WATERS

NET PRIMARY PRODUCTION
~ 4 Gt

BURIAL OF BOTH IMPORTED AND AUTOCHTHONOUS CARBON

TOTAL ANNUAL BURIAL IN MODERN SEDIMENTS ~ 0.10 IS LESS THAN THE POTENTIAL MAXIMUM INCREMENTS TO BURIAL DUE TO:

1) EXCESS NUTRIENT LOAD STIMULATING PRODUCTION 0.04 - 0.08 (C/N = 6) (C/N = 12)

2) EXCESS EROSION OF CARBON DUE TO LAND-USE CHANGE 0.10 (BUT LITTLE OF THIS CAN BE BURIED)

Fig. 2. Carbon Cycling in the Coastal Ocean (units are 10^15 gC yr^-1)
Fig. 3. Oceanic Carbon Cycle Stimulation by Excess Nitrogen in Precipitation (Gt C)

EXCESS NITROGEN IN PRECIPITATION

\[ 6 \times 10^{12} \text{ gN yr}^{-1} \]

\[ \text{NPP} \sim 26 \]

SURFACE OCEAN

NATURAL FLUX

EXCESS IN MATCHING FLUX

\[
\begin{align*}
4.7 & \text{ DUE TO UPWELLING NO}_3 \\
0.04 & \text{ DUE TO N IN PRECIPITATION}
\end{align*}
\]

DEEP SEA

\[ 0.02 \text{ Gt C yr}^{-1} \]

CALCULATION: \[ 6 \times 10^{12} \text{ gN yr}^{-1} \times 6 \text{ C/N} = 0.04 \text{ Gt C} \]
THREE DIMENSIONAL GLOBAL MODELING OF ATMOSPHERIC CO₂

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I. INTRODUCTION

It seems likely that a great amount of information on the sources and sinks of atmospheric CO₂ is contained in the geographical, seasonal and interannual variations of the global atmospheric CO₂ distribution. The measured variations of CO₂ at several locations (Figure 1) illustrate large variations in the amplitude and phase of seasonal change, as well as interannual variations, superimposed in an increasing secular trend. Recent analysis of the CO₂ records by Keeling and his collaborators (1982) reveal that the amplitude of the seasonal cycle has detectable interannual variations and may be increasing in time (Figure 2). Keeling (1982) has also found that the meridional gradient of CO₂ in the atmosphere is also changing in time (Figure 3).

We have initiated a modeling effort to study the prospects of extracting some of the potential information on CO₂ sources and sinks from observed CO₂ variations. The approach is to use a three-dimensional (3-D) global transport model, based on winds from a 3-D general circulation model (GCM), to make the advection of CO₂ noninteractive, i.e. as a tracer, with specified sources and sinks of CO₂ at the surface. If the model can reproduce the general character of observed CO₂ variations on the basis of physically justified sources and sinks, it may then be used for experiments to determine the sensitivity of the global CO₂ distribution to various assumptions about CO₂ sources and sinks. It is anticipated that this approach may lead to useful quantitative limits on some CO₂ sources and sinks.

In the following we first identify the 3-D model employed in this study and then discuss biosphere, ocean and fossil fuel sources and sinks, including discussion of some preliminary tracer model results.

II. TRACER MODEL

The tracer model uses winds generated from the GISS General Circulation Model (Hansen et al., 1983) to advect CO₂ as an inert trace constituent. While the GCM model II is able to reproduce the main features of the atmospheric circulation, the model deficiencies must be kept in mind in interpreting tracer experiments. The model resolution usually employed (8° latitude x 10° longitude), illustrated in Figure 4, is sufficient to produce fairly realistic atmospheric long waves and large scale eddies as occur at middle and high latitudes; it cannot, however, resolve the smaller scale tropical disturbances and this may affect transports at low latitudes. Also our understanding and modeling ability for many physical processes (Figure 5) is
rudimentary; accurate parameterization of moist convection may be especially important for simulating transports, but this process is presently treated in very simple ways in GCM's.

It is important to understand the limitations of the present 3-D modeling, discussed for example, by Hansen et al. (1983), as these affect the ability to interpret observed characteristics of the global CO₂ distribution. However, we believe that it is appropriate to begin to do tracer experiments with existing 3-D modeling capability, because these experiments will be useful for helping to define model capabilities and deficiencies, thus aiding the process of 3-D model development.

Fung et al. (1983) have used a global vegetation map (Matthews, 1983) and simple ad-hoc definitions of CO₂ exchange between the biosphere and the atmosphere as input to the tracer model to study the geographical variation of the seasonal cycle of CO₂ in the atmosphere. The study demonstrates that large longitudinal variations exist in the atmospheric CO₂ distribution and that a 3-D approach is necessary for accurate analysis of the global carbon cycle.

We present here the results of three experiments with different biospheric CO₂ exchange functions. These functions are based on (1) Machta (1972), (2) Pearman and Hyson (1980), and (3) a global net primary productivity (NPP) map based on vegetation type to which Azevedo's (1982) seasonal CO₂ uptake and release curves were applied.

Experiment 1. Machta (1972) constructed a table of carbon exchange by month and 20° latitude belts based on information from Lieth (1965) and assumptions about seasons of growth and decay. For each month, we perform an area-weighted interpolation from Machta's 20° latitude zone to our model's 18° latitude zone. The monthly carbon flux within each model belt is then uniformly distributed over the land areas in the zone.

Experiment 2. The Pearman and Hyson (PH) model consists of 20 equal-area zones for the surface of the globe. By requiring their model simulated CO₂ distributions to match those observed, PH obtained values of CO₂ flux for each month and each of their model zones. We assume that PH's monthly fluxes are evenly distributed over land within their zones. In order to equivalence PH's equal-area zones to the tracer model's latitude belts, we use a weighting by continental area and interpolate their fluxes to the model's latitude belts. The monthly carbon flux within each belt of the tracer model is again uniformly distributed over land area in the belt.

Experiment 3. Using about 90 sources, Matthews (1983) constructed a global, 1° x 1° resolution vegetation file containing about 200 vegetation types. Annual NPP values are assigned to each vegetation type in each 1° x 1° cell and the resultant NPP map at the model resolution is shown in Figure 6. The global NPP value is 45 x 10¹² kg C/yr.

Azevedo (1982) constructed simple curves of CO₂ uptake and release by the biosphere. These curves are based loosely on the assumption that uptake and release are governed by air and soil temperatures and that these processes are turned off when temperatures fall below some critical value. They are
illustrated in Figure 7. From 40°N to 70°N, biospheric uptake of CO₂ is concentrated in the months of May to August, while release occurs throughout the year but with maxima in the same months. From 10°N to 40°N, release occurs uniformly throughout the year while maximum uptake occurs from May to August. Like Machta (1972), Azevedo assumes that from 10°N to 10°S, uptake and release overlap throughout the year, resulting in zero net seasonal exchange. Azevedo shifts the curves by 6 months for the southern hemisphere.

In this experiment we combined the NPP map with Azevedo’s carbon uptake and release curves to form the monthly flux of carbon to the atmosphere:

\[
\text{SOURCE}(λ, e, t) = \text{NPP}(λ, e) \times (\text{RELEASE}(e, t) - \text{UPTAKE}(e, t))
\]

The UPTAKE and RELEASE curves are normalized so that

\[
\text{year} \quad \sum \text{RELEASE}(e, t) = \sum \text{UPTAKE}(e, t) = 1
\]

or that no net annual exchange of carbon occurs. Note that this exchange, like the NPP, possesses both latitudinal and longitudinal variations even with these extremely simple seasonal distributions.

The tracer model with these biospheric sources/sinks was run for 25 months until the annual cycles repeated themselves. The CO₂ concentrations are defined relative to a globally uniform (and arbitrary) background concentration, so that a positive (or negative) \( R \) (CO₂ mole fraction) means that the simulated concentration is greater (or less) than the background.

The seasonal oscillations of CO₂ concentrations simulated at grid boxes corresponding to five observation sites are shown in Figure 8 together with the observed annual cycles as cited by PH and Bolin and Bischof (1970). As one would expect from the magnitudes of the source functions in the three experiments, the peak-to-peak amplitudes of the CO₂ oscillations at these locations increase from experiments 1 to 3. Machta’s biospheric exchange function underestimates the amplitudes, as has been noted by other investigators (Pearman and Hyson, 1980; Azevedo, 1982). In experiment 1, the underestimation is about 50% at Mauna Loa and 63% at Point Barrow. PH’s source functions, constructed to duplicate the observations with their model, produce a peak-to-peak amplitude of 6.0 ppm at Mauna Loa, close to that observed. However, the amplitudes at Papa and Barrow are underestimated by about 45%. In experiment 3, the amplitudes simulated at the grid boxes of Point Barrow and at Mauna Loa are within 10% of those observed. The amplitude at OWS Papa is underestimated in all three experiments even though the amplitudes at the land stations are reasonably simulated in experiment 3.

The phase of the CO₂ annual cycles at station locations can be seen in Figure 8. In all three experiments the months of predicted maxima and minima at the station locations are within 2 months of those observed. However, the simulated annual cycles at the northern stations, especially at Point Barrow, lack the asymmetry seen in the observed cycles. This is probably because we have assumed, even at 70°N, that the growing season starts in May instead of in early June, when the snow melts at this latitude.
The azonal nature of the CO₂ distributions is apparent in Figure 9, which shows the seasonal amplitudes at the surface as simulated in experiment 3.Except in the northern hemisphere tropics which is relatively well-mixed zonally, the isopleths of amplitude closely parallel the coastlines. The highly productive and seasonal land vegetation and, in this experiment, the absence of oceanic source/sinks create large contrasts in CO₂ concentration between land and sea. These contrasts are not smoothed effectively by the wind. The amplitudes simulated over ocean are only half the maximum amplitudes simulated over land at similar latitudes. The isopleths tighten and wrap the coastlines more closely at higher latitudes as land biomes become more strongly seasonal. Amplitudes greater than 0 ppm are seen in the boreal forests of North America and Siberia. In South America, Azevedo's seasonality applied to the rain forests south of 10°S results in an amplitude of 10 ppm. Validation of model results in these regions is presently impossible because of the limited observations of CO₂ in the atmosphere.

Figure 10 shows the surface concentrations of CO₂ simulated in experiment 3 for the month of August, the end of the growing season at mid-latitudes in the northern hemisphere. The diversity of vegetation types over land and the lack of CO₂ exchange over the oceans produce longitudinal gradients as large as 4 ppm over 20° longitude at ~50°N. In general, isopleths of CO₂ concentration at the surface closely follow the trajectories of the surface wind (cf. Figure 10, lower part). This can be easily seen in the southern hemisphere tropics. The southeasterly trades sweep CO₂ off the continents, creating tongues of CO₂ downwind. In the northern hemisphere tropics, in the rising branch of the Hadley circulation, the relatively small amplitude of CO₂ exchange with the terrestrial biosphere and very effective vertical mixing by convection create a small contrast in CO₂ concentration between land and sea. This contrast is further reduced by the steady easterly winds, resulting in small longitudinal gradients. The dynamics are reversed at mid-latitudes in the northern hemisphere. The net biospheric flux of CO₂ is large over a percentage of the surface area in a latitude belt, and vertical mixing is weak except under storm systems. The persistent cyclonic and anticyclonic wind systems transport CO₂ along a meandering path around the latitude circle. The zonal wind speed simulated by the GCM is ~5 m/s at these latitudes. This implies that the time scale for zonal mixing, about 2-3 months at 45°N, is longer than the time scale for the source/sink (about a month) and zonal homogeneity is never achieved.

Of the three biospheric exchange functions investigated, that of experiment 3, constructed from a global NPP map and Azevedo's (1982) seasonal exchange curves, produces CO₂ annual cycles at locations of monitoring stations most similar to those observed. In this exchange function, the net flux of carbon to the biosphere during the growing season (i.e., the GSNF) is 10.7 x 10¹² kg C in the northern hemisphere and 2.3 x 10¹² kg C in the southern hemisphere. The GSNF estimate for ~45°N to 90°N is 7.7 x 10¹² kg C, which is larger than PH's estimate of 2.5 x 10¹² kg C and Bolin and Keeling's (1963) estimate of 4.1 x 10¹² kg C for the same region. These biospheric exchange functions, when input to the respective models, all reproduce reasonably well the amplitudes of the observed CO₂ cycles. However, only one tracer transport model and one biospheric exchange function can be correct.
The differences in GSNF thus underlie the need for an ecological model of CO2 exchange rather than one based on model requirements.

Analysis of the zonal mean balance in the lower troposphere confirms the dominant role played by the total meridional transport in the redistribution of CO2 within each hemisphere. Eddy transport is diffusive, while mean meridional transport is in the direction of the mean meridional winds and may therefore be countergradient. At mid-latitudes, convergence of total meridional transport alters by 50% or more the signal from local biospheric exchange. In April, in particular, the transport processes at mid-latitudes nearly cancel the local biospheric input, resulting in a near-zero concentration tendency. This suggests that year-to-year variations of the CO2 concentration at the monitoring stations may result from internal variability of the atmospheric circulation. Information about changes in the biosphere can be deduced only from concurrent changes in CO2 concentration at several stations whose natural variability is understood.

It may be fortuitous that a simple biospheric exchange function such as used in experiment 3 closely reproduces the annual cycles at several coastal monitoring stations. However, the experiment underestimates the amplitude at OWS Papa and predicts amplitudes as large as 25 ppm in the northern hemisphere boreal forests. The mid-latitudes in the northern hemisphere are shown to be a region with large biospheric source/sink, incomplete zonal mixing, and possibly the greatest sensitivity to changes in atmospheric circulation and/or sources/sinks. Annual oscillations of sea surface temperatures at these latitudes have peak-to-peak amplitudes of ~10°C. Indeed GEOSECS measurements have revealed amplitudes of ~50 ppm in oscillations of oceanic pCO2 in the Sargasso Sea (Takahashi et al., 1980). These seasonal changes in the upper ocean may thus have a significant, albeit small, effect on the annual cycles of atmospheric CO2. The sparsity of CO2 monitoring sites at present places a great reliance on model calculations to deduce information about the sources and sinks of CO2. While an ecological model of the terrestrial biosphere is imperative for understanding the role of the biosphere in the atmospheric CO2 cycle, the influence of the oceans on the annual cycle of CO2 must not be overlooked.

For instance, the observed seasonal cycles of sea surface temperature give rise to large seasonal oscillations in oceanic pCO2 (Weiss et al., 1982). The atmospheric response to such oscillations in oceanic pCO2 has been investigated with the tracer model coupled to the upper ocean. Temperature dependent carbon chemistry (Takahashi et al., 1980) is included in the mixed layer. Figure 11 shows the amplitude of the seasonal cycle of atmospheric CO2 thus induced. As is expected, this cycle is small compared to that induced by exchange with the terrestrial biosphere. Nonetheless, the amplitudes at the observing sites are about 10% or more of those observed; the phasing is opposite that resulting from biospheric exchange. Hence, in order to infer information about the activities of the terrestrial biosphere and about changes in these activities, the oceanic contribution to the seasonal cycle should not be neglected.
Finally, the temporal and spatial distribution of anthropogenic CO₂ release is fairly well known (Rotty, 1983). It is not likely that study of atmospheric CO₂ will improve quantification of the anthropogenic source. However, in order to interpret observed atmospheric CO₂ changes, it is necessary to include the fossil fuel source in the model, or at least to subtract the secular trend from the observations.

III. DISCUSSION

The initial attempts to model the atmospheric CO₂ distribution, including couplings to the ocean and biosphere as sources and sinks of atmospheric CO₂, encourage the notion that this approach will lead to useful quantitative constraints on CO₂ fluxes. Realization of this objective will require:

1. Continued improvement in the realism of the global transport modeling. Model development should proceed in concert with tracer studies, including CO₂ and other constituents, because such studies can contribute substantially to the understanding of key model deficiencies and thus to the improvement of the models.

2. Extended timeline of atmospheric CO₂ monitoring, with improved precision and improved definition of the uncertainties in the measured CO₂ amounts. Many of the potential applications depend upon measurement of perturbations of the CO₂ distribution, changes in time or in geographic distribution, and hence accurate calibration and intercalibration among different observing stations are important.

3. Given an accurate knowledge of model capabilities and limitations and given a good understanding of CO₂ observations and their limitation, there is a need for good ideas concerning what quantitative information on the carbon cycle can be inferred from global modeling. Potential examples:

   A. It may be possible to determine information on the global distribution of NPP, if the seasonality of CO₂ uptake and release can be well defined on the basis of vegetation type and climate. Figure 12 suggests the plausibility of relationships between climate parameters and CO₂ uptake and release by vegetation.

   B. Detectable interannual variations of photosynthetic uptake, illustrated at a specific location in Figure 13, may exist on a larger scale. If relationships between droughts and the atmospheric CO₂ distribution can be determined, it would provide valuable information on the terrestrial biospheric source of CO₂.
C. Can El Nino and other sea surface temperature anomalies (Figure 14) be related to observed changes in atmospheric CO$_2$? This could provide a useful check on our understanding of the ocean chemistry portion of the carbon cycle. If this is well in hand, it may be possible to relate deviations between modeled and observed ocean CO$_2$ to ocean plant productivity.

REFERENCES


Fig. 1. CO$_2$ trends observed at several stations, based on data of Keeling et al., 1982.
RELATIVE AMPLITUDE OF THE SEASONAL CYCLE

STN 'P' 50°N

SLOPE = 0.77% /YR

MAUNA LOA (19° N)

SLOPE = 0.66% /YR

Fig. 2. Interannual variation of the seasonal amplitude of atmospheric CO₂ concentration at a) Papa and at b) Mauna Loa (from Keeling, 1982). The mean seasonal amplitude is ~12 ppm at Papa and ~6 ppm at Mauna Loa.
Fig. 3. North–South variation in the mean annual concentration of atmospheric CO₂ for 1962, 1968 and 1980 (from Keeling, 1982).
Fig. 4. Grid spacing for 8° x 10° model.
Fig. 5. Schematic illustration of model processes at a single gridbox.
Fig. 7. Seasonality of biospheric uptake and release of CO₂ (after Azevedo, 1982) employed in experiment 3.
Fig. 8. Simulated and observed annual cycles of CO$_2$ at five locations. Observations are from Pearman and Hyson (1980), except those for Scandinavia which are from Bolin and Bischof (1970).
Fig. 9. Peak-to-valley amplitude (ppm) of seasonal surface CO₂ variation, as simulated in experiment 3.
Fig. 10. August surface winds in model II (upper) and August surface CO$_2$ perturbation (ppm) as simulated in experiment 3 (lower).
Fig. 12. Some field measurements showing the covariation of biospheric carbon uptake and release with ambient temperature and precipitation. (a) shows the photosynthetic capacity of sun shoots of a mature spruce and the surface air temperature in Innsbruck, Austria (from Tranquilini, 1979 and Larcher, 1980). (b) shows the net photosynthesis of *Opuntia basilaris* in Palm Desert, California and the precipitation events at the site (from Szarek and Ting, 1974). *Opuntia basilaris* is a CAM plant adapted to dry arid environments. An enhanced level of CO$_2$ assimilation persists during periods of rainfall. (c) shows the CO$_2$ evolution rates from the soil and the soil temperature measured in an oak forest in Anoka, Minnesota (from Reiners, 1968).
Fig. 13. Net photosynthetic uptake of CO₂ by an evergreen shrub in the Mojave Desert for 1972 and 1973 (after Bamberg et al., 1976).
Fig. 14.  

b) CO₂ anomalies at Station P and SST anomalies at 45°N, 180°W (from Hanson et al., 1981).
THE PHOSPHORUS CYCLE
ABSTRACT

The pre-man reactive phosphorus flux to the oceans is dominated by the fluvial contribution. About one-third of the input is in particles that release their P within estuaries. Virtually all the fluvial reactive flux reaches the oceans after being extensively recycled in estuaries. The input to the oceans is estimated to be about $5.0 \times 10^{10}$ moles-P yr$^{-1}$ ($\{P\}_{\text{rivers}} \sim 1.4 \ \mu$M yr$^{-1}$).

Phosphorus cycling within the ocean is dominated by upwelling, uptake into organic matter and calcium carbonate in the surface ocean, and the vertical particulate flux of biogenic debris. The small fraction of biogenic particles that survive regeneration and dissolution is buried both in the deep sea (organic matter: P/C $\sim 4 \times 10^{-3}$; calcite: P/C $\sim 1 \times 10^{-3}$), and on productive shelves in the surface ocean (phosphorites: P/C $\sim 30 \times 10^{-3}$). The three sinks are of comparable magnitude (each about $1.6 \times 10^{10}$ moles-P yr$^{-1}$).

Feedback mechanisms controlling the steady-state nutrient and carbon cycles, upon which the CO$_2$-content of the atmosphere is dependent, are related to factors affecting the P/C burial ratios in the three sinks and to shifts in oceanic ecology affecting the P/C extraction ratio from the surface ocean, which are presently poorly understood. Nevertheless, shifts in ocean nutrient chemistry at the close of the last glacial are inferred from dramatic changes in atmospheric pCO$_2$ recorded in ice cores, 13C of deep ocean water recorded in benthic forams, and perhaps in the level of the calcite and aragonite saturation horizon on the deep-sea floor. The ocean today may still be recovering from glacial times, resulting in transient N-limitation of...
oceanic primary production and an apparent lack of sufficient N-fixation to balance the oceanic N-cycle.

I. INTRODUCTION

Unlike carbon, nitrogen, oxygen or sulfur, phosphorus has no significant volatile phases, nor any important atmospheric transport pathways, nor does it exhibit more than one oxidation state in solution or in minerals. Thus in attempting to identify the major pathways and rates of passage through the ocean, we may concentrate our efforts on continental weathering, river transport, estuarine processes, and the recycling and burial of biogenic phases in the sea. In a sense, this should make our job easier. The major stumbling block lies in phosphorus' widely-disseminated distribution. It displays concentrations in a variety of igneous and sedimentary rocks of about 0.1 to 0.2%. This is a direct result of the unreactive nature of most of the phosphorus weathered from rocks. In fact, the vast majority of the P eroded from continents passes inertly through the oceans in unreactive detrital phases that are buried in marine clays without ever having entered the biological cycles. Thus in trying to identify the "reactive" fluxes (i.e., those that are biogeochemically active), we must be constantly aware of this enormous inert background, and worry whether in fact some fraction of it is more reactive in the oceans than we presently believe. In addition, estimation of the "reactive" burial sites in the ocean requires that we be able to separate it from the much larger sedimentation of detrital-P, since analytically we often cannot distinguish between the "reactive" or "detrital" origins of inorganic phases if they exist together in the same sample.

Thus the major purpose of this paper is to update our understanding of the marine biogeochemistry of phosphorus and its interactions with the carbon cycle. Much of what I will say here is a review, but there are two pieces of new information. The first has to do with nutrient recycling in natural, unperturbed estuaries, and the effect these potential nutrient modifiers have on the transfer of reactive-P from continents to oceans. The second is a new estimate of the contemporaneous rate of phosphorite formation on the Peru shelf, which turns out to be quite large.
The approach I will take here is to review briefly the evidence for making quantitative estimates of the input and removal fluxes of P to and from the ocean, and of the extent of internal recycling of P with C within the sea. Toward the end I will speculate on whether this model might be useful in understanding the glacial to interglacial shift in atmospheric CO₂ observed in ice cores, and the Redfield paradox of N:P ratios and nutrient limitation of oceanic production.

II. INPUT FLUXES

Previous work has demonstrated that the major flux of reactive-P to the oceans derives from continental weathering (Froelich et al., 1982b). Thus we will ignore high-temperature submarine hydrothermal weathering, low-temperature seawater-basalt exchange, and the aerosol flux (Edmond et al., 1982; Hart, 1970; Graham and Duce, 1979; Von Damm, 1983). The major uncertainty here is whether or not high-temperature seawater circulating through mid-ocean ridge basalts at active spreading-centers extracts P from the rocks and expels it to seawater via submarine vents.

Attempts to estimate the fluvial flux of "reactive" phosphorus encounter at least four problems: (1) it is unknown what fraction of the total phosphorus eroded from the continents is solubilized, that is, we do not know what controls the dissolved phosphorus concentrations of rivers; (2) we do not know the extent (or even the direction!) to which the riverine P-flux is modified in estuaries; (3) some of the riverine particulate phosphorus flux (including an anthropogenic component) may dissolve (or desorb) and become geochemically reactive once in the oceans; and (4) man's tremendous influence on the present phosphorus flux through deforestation and use of fertilizer precludes estimating the "pre-agricultural" dissolved phosphorus flux directly from most of the contemporary river data.

Table 1 presents a summary of fluxes of P to the oceans based on various estimates of the rates of pre-man continental erosion and contemporary suspended and dissolved loads in rivers. The pre-man total fluvial P-flux was about 30 X 10¹⁰ mole yr⁻¹. Man's acceleration of the denudation process (through deforestation, cultivation and urbanization) may have more than
doubled this flux. In addition, man mines P from phosphorite deposits at a rate comparable to the erosion rates, about $45 \times 10^{10}$ mole yr$^{-1}$. Almost all of this mined-P goes into fertilizers that are applied to agricultural soils. Some of this ends up fixed in soils, some goes directly into streams and rivers, but a lot goes into the food we eat and transfers to coastal rivers and estuaries. The relative importance of each fraction is in dispute, but the point is that the effect is potentially large, especially on the large, urban river/estuary systems.

The pre-man reactive flux is more difficult to estimate, since it includes not only dissolved reactive phosphate but also dissolved organic phosphorus plus any potentially dissolvable forms, such as phosphate adsorbed to clays and iron oxides, iron and aluminum phosphates, and any particulate organic phosphorus, some portion of which may be released in estuaries and enter the oceans in a reactive state. I have tried to estimate the fluvial dissolved-P flux by simply averaging all the various measurements of dissolved phosphate in more or less "unperturbed" rivers ($\sim 1 \mu M \text{ m}^{-1}$). This results in a "pre-man" dissolved flux of about $36 \times 10^{9}$ mole yr$^{-1}$. Note that this is only about 5-10% of the estimated total flux. Thus about 90% of the phosphorus eroded from the continents is transported to estuaries in particles, and only 10% or so is in the dissolved-reactive form. Maybeck (1982) has arrived at a similar estimate.

The fluvial flux of phosphorus is delivered to the ocean via estuaries and coastal waters. The fluvial reactive flux can be modified here in three ways: (1) adsorption/desorption of reactive-P onto/off of surfaces of river-borne suspended clays (i.e., the phosphate "buffering mechanism"), (2) biological uptake by estuarine organisms or release of reactive-P from dissolved or particulate organic matter produced upstream, and (3) the slow transformation to reactive-P via dissolution, desorption and regeneration of the fluvial particulate unreactive-P in estuarine and shelf sediments. Attempts to separate, identify and quantify these processes are spectacular failures!

What we really want to know is the net result of these processes: whether the dissolved-reactive fluvial flux is enhanced or reduced in estuaries. It seemed to me that one way to get the answer is to completely mass-
balance an entire estuary over a sufficiently long period of time, sort of the geochemical equivalent to Odum's famous ecological studies.

One of my students spent two years doing this in one of Florida's small, simple, pristine river/estuary systems, the Ochlockonee (Kaul and Froelich, 1984). She collected thirteen estuarine profiles of NO₃', PO₄, and Si, and chlorophyll and diatom data, plus the necessary river flux data, and solved the equations for closing the mass balance. She also applied the appropriate equations to correct the fluxes for variations in the riverine end-member concentrations. I have selected a few of her estuarine snapshots to show you (Fig. 1). By deconvolving each profile into its component functions describing linear mixing, first-order removal (biological productivity) and parabolic input (regeneration) it is possible to construct a long-term mass balance for the fluxes of phosphate, nitrate and silica through the estuary, and also to predict net productivity and regeneration rates. The model adequately explains productivity, the "low" estuarine N/P uptake ratio, denitrification, and the fact that 100% of the fluvial silica flux enters the ocean, in spite of biogenic removal of ~ 20%. The success of the model thus encourages me that the results for phosphorus are meaningful.

For example, about one-third of the reactive dissolved P-flux that leaves the estuary to the ocean derives from fluvial particulates whose phosphate is released somewhere within the estuary. We suspect the release occurs from sediments. In addition, although 80% of the fluvial dissolved reactive-P flux is removed by biological productivity in the bay, it is all returned via regeneration. The net result of this is that the reactive P-flux to the ocean is 50% higher than the dissolved P-flux in rivers, and net removal of reactive-P within the estuary is nil. In other words, the dissolved plus particulate reactive-P in the river all escapes the estuary in the dissolved reactive form. In addition, the flux weighted dissolved phosphate concentration in the Ochlockonee River averages ~ 0.9 μM 1⁻¹, very near our estimate in Table 1 of the "global mean". The dissolved plus particulate reactive concentration averaged ~ 1.4 μM/1. This is the effective concentration reaching the ocean.
For lack of better evidence, we will then take the continentally-derived, natural reactive P-flux to the oceans as $\sim 5 \times 10^{10}$ mole yr$^{-1}$, equivalent to a total (dissolved plus particulate) reactive phosphate concentration in rivers of $\sim 1.4 \ \mu$M l$^{-1}$ (Table 1). This value has a large uncertainty (+50%).

III. PHOSPHORUS SINKS

Phosphorus brought to the oceans by rivers must be removed to sinks within the sea. In the following sections, I provide estimates of the magnitudes of the three most significant removal mechanisms: (1) organic-P ($P_{\text{org}}$) associated with organic-carbon in rapidly-accumulating hemipelagic sediments, (2) carbonate-P ($P_{\text{CaCO}_3}$) associated with biogenic calcite deposited above the calcite compensation depth, and (3) authigenic phosphorites formed on continental margins associated with intense coastal upwelling. Removal of P by burial of fish debris (Froelich et al., 1982) and by sorption into metalliferous sediments (Froelich et al., 1977) are of minor importance and will be ignored here.

A. Organic Phosphorus Burial in the Deep-Sea

Almost all the phosphorus brought to the surface ocean by upwelling and rivers is fixed by primary producers into organic matter with a $P/C_{\text{org}}$ mole ratio of $\sim 10 \times 10^{-3}$ (Redfield, 1958). The resulting particulate flux of organic carbon and phosphorus into the deep-sea is the primary transport path of phosphorus out of the surface ocean. A small fraction of the vertical particulate flux escapes destruction in the deep-sea and is buried in sediments. During diagenesis of organic matter in the water column and in marine sediments, the $P/C$ ratio is fractionated to lower values because $P$ is regenerated more efficiently than $C$. The final burial ratio is dependent upon the extent of diagenesis, which is controlled by organic carbon content and sediment accumulation rates (Suess and Mueller, 1981; Heath et al., 1977). These vary greatly from place to place on the ocean floor. Areas of extreme diagenesis display ($P/C_{\text{org}}$) ratios as low as $1-2 \times 10^{-3}$, while areas of low organic carbon accumulation display ($P/C_{\text{org}}$ ratios of $10-20 \times 10^{3}$, occasionally higher than the Redfield ratio.
A knowledge of the average $(P/C)_{org}$ ratio buried in marine sediments would permit us to calculate $P_{org}$-burial from knowledge of the carbon cycle. I have plotted the available $\%C_{org}$ and $(P/C)_{org}$ ratio for sedimentary organic matter (Fig. 2). Sediments with $C_{org} > 2\%$ and $(P/C)_{org}$ ratios $\sim 0.2 \times 10^{-2}$ reflect rare shelf accumulations under upwelling zones thought to represent insignificant $C_{org}$-burial from today's ocean. Likewise, sediments with $C_{org} < 0.5\%$ and $P/C > 6 \times 10^{-3}$ reflect slowly accumulating pelagic sediments with trivial $C_{org}$ burial. The primary $C_{org}$-burial site is the enormous wedge of hemipelagic sediments accumulating in continental rises with average $C_{org} \sim 1\%$ (Walker, 1974). Thus we take the average burial $(P/C)_{org}$ value from Fig. 2 as $\sim 4 + 2 \times 10^{-3}$.

The long-term pre-man burial rate of organic carbon can be calculated from the average river water bicarbonate concentration (0.55 mM, Wedepohl, 1971: corrected for atmospheric cycling) and the world river flow (3.6 X $10^{16}$ 1 yr$^{-1}$). Assuming that 80% of the carbon entering the oceans is buried as CaCO$_3$ and 20% as organic carbon (Li, 1972; Broecker and Peng, 1982; Garrels and Perry, 1974), then the organic carbon burial rate is about 4 X $10^{12}$ mol-C yr$^{-1}$. Taking the $(P/C)_{org}$ value as 4 X $10^{-3}$ and organic carbon burial as 4 X $10^{12}$ mol yr$^{-1}$, I estimate a $P_{org}$ burial rate of about 1.6 X $10^{10}$ mole-P yr$^{-1}$, about one-third of our estimated input flux ($\sim 5 \times 10^{10}$ mole-P yr$^{-1}$). This value has an uncertainty of at least $\pm 30\%$.

B. Phosphorus Burial with Biogenic Carbonates

Analyses of calcareous ooze deposits above the calcite compensation depth on the sea-floor suggest that carbonate fossils contain on average about 300 ppm-P (Table 2). For simplicity I will assume that the phosphorus is incorporated into the tests of calcareous organisms during shell formation in the surface ocean, and bypass the questions of whether the shells gain or lose P after the organisms die and sink into the deep sea (Morse, 1974; deKanel and Morse, 1978), or whether P is completely released to seawater upon calcite dissolution below the calcite compensation depth (Morse and Cook, 1978; Correns, 1937; Arrhenius, 1937). Separation and analysis of P in the vertical particulate flux of $C_{org}$ and $C_{CaCO3}$ at various depths in the oceans would answer
these questions, but to date the manner in which sediment trap material is collected has prevented this assessment.

Most of the calcite accumulating on the sea floor is composed of the tests of foraminifers (a protozoan) and coccolithophorids (an algae). The P-content of coccolith fossils greatly exceeds that of forams (400 ppm-P in coccoliths, vs. 50 ppm-P in forams: Froelich et al., 1982b). Thus the variability of P-contents of calcareous oozes probably reflects varying fractions of forams and coccolith calcite in the vertical particulate flux depending upon the ecological mix in the overlying surface water. The "average" calcite, with 300 ppm-P, contains about 70% coccoliths and 30% forams, in rough agreement with other estimates of these fractions found in the vertical particulate flux (Bishop et al., 1977; Honjo, 1978), and in sediments (Broecker, 1973).

To calculate the burial flux of P in calcite, I take the average calcite-P as 300 ppm, corresponding to a P/C mole ratio of 1 X 10^{-3}. Assuming that phosphorus is completely released to seawater upon calcite dissolution below the calcite compensation depth, and that 80% of the total carbon burial is removed as CaCO_3 (~ 16 X 10^{12} mole-C yr^{-1}), then burial of phosphorus in calcite is about 1.6 X 10^{10} moles-P yr^{-1}, about one-third of our estimated P-influx, and essentially the same as our estimate of P_org-burial.

The major uncertainties in this flux are the origin of the P (whether via occlusion during shell formation in the surface ocean, in the deep-sea by sorption, or in marine sediments by diagenesis), whether any residual calcium phosphate is left behind when carbonate dissolves up below the calcite compensation depth, and whether the aragonite flux carries a significant contribution. The burial flux estimate is probably good to about ± 20% unless calcite does not give up its P congruently upon dissolving. The importance of whether calcite picks up its P from the surface or deep ocean is related to whether this P-sink is a surface or deep-sea removal mechanism.
C. Phosphorite on Shelves

The organic phosphorus that escapes regeneration in the water column is incorporated with refractory organic material into the accumulating sediment column. Here, regeneration continues, releasing dissolved phosphate into the interstitial water where it is available for inorganic precipitation reactions. Thus organic phosphorus buried below the sediment surface faces three possible fates (Fig. 3): (1) ultimate survival of regeneration with consequent burial as $P_{\text{org}}$, (2) regeneration to dissolved phosphate followed by release to the pore water with subsequent diffusion into the overlying water column, and (3) regeneration to dissolved phosphate followed by precipitation as an authigenic phosphate salt to be buried ultimately as an inorganic stand-in for $P_{\text{org}}$. The fraction remaining in the pore water is quantitatively unimportant to the burial flux.

The common phosphate salt formed in marine sediments is carbonate fluorapatite [CARFAP = $Ca_{10}(PO_4, CO_3)_6F_2$; McConnell, 1965], generically termed phosphorite. Ultimate burial of phosphorite is then a surrogate for $P_{\text{org}}$-removal.

I have previously shown that deep-sea burial of phosphorite is very small (Froelich et al., 1982). Almost all organic carbon and phosphorus burial and subsurface regeneration occurs in continental rise hemipelagic sediments. An evaluation of $P_{\text{org}}$-burial, phosphate regeneration and upward diffusive fluxes in Hartmann et al.'s (1973) cores from the northwest African continental margin demonstrated that almost all the regenerated-P escapes - none is buried as phosphorite. Thus phosphorite formation in deep water blue muds is not a significant sink.

It is well known, however, that several giant shelf-type phosphorite deposits exist in the geological column (for example, the Permian Phosphoria Formation), each containing a mass of P larger than that dissolved in the present ocean ($\sim 3 \times 10^{15}$ moles, Cook and McElhinny, 1979). Thus each could have been formed by becoming the primary sink for the fluvial input to the oceans during several residence times of P in the oceans ($\sim 6 \times 10^4$ yrs.) The Phosphoria Formation ($> 20 \times 10^{15}$ moles-P) is thought to have been
deposited over about 4 million years, requiring about 10% of the present yearly fluvial P-flux (Arthur and Jenkyns, 1981). Thus shelf deposits probably provided geochemically significant sinks for phosphorus from past oceans.

The best-studied modern sedimentary analog of the ancient phosphorite deposits is the Peru Shelf, where phosphatic muds and nodules are known to be presently forming (Veeh, Burnett and Soutar, 1973; Burnett, 1977). The environment of deposition here is one of locally patchy but rapidly accumulating C<sub>org</sub>-rich (up to 20% C<sub>org</sub>), extremely anoxic sediments associated with an intense, but climatically-fickle, coastal-upwelling zone (Krissek et al., 1980). Sediments are extensively reworked, resuspended and transported by a complex set of currents so that long hiatuses are punctuated by intervening periods of essentially instantaneous deposition (Reimers and Seuss, 1983). Individual beds are the result of a complex history of initial deposition, diagenesis, transport and mixing with new biogenic debris and with old products of diagenesis, redeposition, additional diagenesis, etc. Most of the original C<sub>org</sub> gets regenerated during the process, and much of the phosphate released gets trapped and beneficiated into phosphorite-rich beds. Some of the more intensely reworked strata contain up to several percent inorganic phosphorus.

The average P/C<sub>org</sub> ratio in these Holocene phosphatic muds is P-enriched three times the Redfield ratio (~30 X 10<sup>-3</sup>; Suess, 1981) (Table 3). Over 90% of the P is in phosphorite. The average (P/C)org ratio is only about one-fifth the Redfield ratio (~2 X 10<sup>-3</sup>). The "ultimate" burial P/C<sub>org</sub> ratio may well be higher than 30 X 10<sup>-3</sup>, since the "average" value is weighted with recent sediments that have not yet undergone the full gamut of repetitive diagenesis, transport and reworking, which drives the P/C<sub>org</sub> ratio up by destroying C<sub>org</sub> and entrapping and beneficiating phosphorite. Assuming that the planktonic (P/C)<sub>org</sub> ratio is initially deposited i.e. the Redfield ratio (~10 X 10<sup>-3</sup>), phosphorus has about three times the probability of surviving in phosphorite as does C<sub>org</sub>. In addition, since the average (P/C)<sub>org</sub> burial ratio we found in hemipelagic muds is about 4 X 10<sup>-3</sup>, phosphatization on shelves is at least ten times more
efficient at entrapping P than C Prosecutor burial in the deep-sea. Unfortunately, because of the complex details of how the phosphorites form and accumulate in a jumbled stratigraphy, there is no easy way to convert our P/C ratio to a removal flux.

There is, however, one geochemical tracer of phosphorite precipitation that turns out to be simple - fluoride. Fluoride is a major anion in seawater; it is conservative, which simply means that it is well mixed in seawater -- its concentration in seawater is determined only by salinity. It is also unreactive in calcite oozes, siliceous oozes and red clays, as demonstrated by pore water fluoride profiles in these sediments which display no gradients and essentially seawater values. However, during the process of carbonate fluorapatite precipitation, the fluoride is extracted from seawater (Froelich et al., 1982b). It turns out that the process leaves its mark as downward decreasing fluoride pore water gradients in the phosphatic muds (Fig. 4). These four F-profiles obtained from different sites on the Peruvian continental margin all display the characteristic signature of a flux from seawater into the sediment, with first order removal rate constants of about 3 yr⁻¹. We've caught the reaction's signature! The estimated fluxes of F into the sediment column are large, about 3 μmol-F cm⁻² yr⁻¹ (Table 4). These fluxes may be representative of the entire area of the Peru margin and also Walvis Bay off Namibia. DeMaster (1979) estimated the combined size of these mud lenses to be about 2.2 X 10¹⁵ cm² (mostly off Peru), which is equivalent to less than 1% of the present global continental shelf area shallower than 200 m. Thus the global F-flux into phosphorites is about 0.6 X 10¹⁰ mole-F yr⁻¹. Analyses of phosphorites from Peru confirm that the P/F mole ratio locked into CARFAP is very close to the theoretical stoichiometric ratio: 3/1. Thus the phosphorus flux being buried in shelf apatites is about 1.8 X 10¹⁰ mole-P yr⁻¹. This is about one-third of the estimated input flux! Since our average (P/C) phosphorite ratio is about 30 X 10⁻³, the carbon flux buried with phosphorites is about 0.6 X 10¹² mole-C yr⁻¹, only about 3% of our estimated deep-sea carbon burial in calcite and organic carbon (∼20 X 10¹² mole-C yr⁻¹), so carbon burial on production shelves is trivial.
Even though these estimated fluxes should be regarded with caution because of the limited data coverage, there is a good chance that this method gives an accurate estimate of the phosphorite formation flux for several reasons. First of all, fluoride, once incorporated into fluorapatite, apparently locks the mineral into an insoluble state. We never observed F-pore water profiles that could be interpreted as F-release via dissolution, even in long piston cores. In contrast, the phosphate pore water profiles display complex signatures of the myriad reactions involved, including regeneration of $P_{\text{org}}$, dissolution of fish debris (hydroxysapatite), and precipitation of fluorapatite (Fig. 4). The fluoride signal records only the last. The relative importance of each varies from core to core, but one characteristic of the phosphate pore water profiles is that the upper few centimeters always display strong downward phosphorus fluxes driven by very high concentrations at the sediment-water interface.

Secondly, the fluoride gradient at the sediment-water interface reflects the integrated sum of both dissolution and precipitation processes below the interface (Berner, 1980). Thus our estimated fluxes reflect net sediment column accumulation. And the last reason is that it is unlikely that the four cores represented here are rare. They were collected from three different mud lenses between 10°S and 15°S on the inner Peru shelf.

My guess is that whenever anoxic diagenesis becomes sufficiently intense in a shallow water environment of deposition with an ample supply of fish debris, the process goes. Its rate-limiting step may be simply the diffusion-limited flux of fluoride into the sediment from the overlying seawater. If so, then the phosphorite burial flux for any period of geologic time can be estimated from the seawater fluoride concentration and the area of the reaction zone.

D. The Marine Phosphorus Cycle

Taking the information we've developed for river input and the various burial fluxes for P and combining it with knowledge of the internal cycling of P and C in the oceans allow us to put together a rough schematic of the marine phosphorus and carbon cycles. Most of the basics are modified from various
treatments of the nutrient cycles in the sea by Broecker (Fig. 5). Thus we'll use the two-box model of surface to deep oceanic mixing and particle fluxes to represent the ocean. Keep in mind during the following discussion that some of the estimated fluxes are poorly known (+30%) or based on evidence gleaned from tracers with different time scales. However, what we hope to characterize here is a picture of a more-or-less steady-rate interglacial ocean resembling the one we live with today.

The internal P and C cycle can be quantified from knowledge of the present average surface to deep ocean concentration differences for TCO$_2$, alkalinity and P (Broecker and Peng, 1982), and the average P/C ratios falling in calcite ($\text{P/C}_{\text{CaCO}_3}$) and organic matter ($\text{P/C}_{\text{org}}$). This yields a particulate $\text{C}_{\text{org}}$ flux about four times the particulate $\text{CaCO}_3$ flux. Since $\text{P/C}_{\text{org}} \approx 10 \times 10^{-3}$ (the Redfield ratio) and $\text{P/C}_{\text{CaCO}_3} \approx 1 \times 10^{-3}$, the $\text{P}_{\text{org}}$ transport to the deep sea is about 40 times greater than that carried by CaCO$_3$.

The fraction of the particulates buried is based on the relative amounts of $\text{C}_{\text{org}}$ and $\text{CaCO}_3$ buried in the geologic column on a much longer time scale, and on requirements that the fractions buried reflect the oceanic $\delta^{13}$C-balance. These restrictions require that about four times more carbon is buried with carbonates than with organics. (On short time scales, this requirement may be relaxed a bit.) Since the buried $\text{P/C}_{\text{org}} \approx 4 \times 10^{-3}$ and $\text{P/C}_{\text{CaCO}_3} \approx 1 \times 10^{-3}$, then about equal amounts of P are buried with carbonates as with organics.

A further restriction on the burial fluxes is the fact that only about 20% of the calcite falling from the surface ocean comes to rest on the sea floor above the CCD. The other 80% falling below the CCD dissolves in the corrosive waters of the deeper ocean. Thus, of the vertical particulate calcite flux into the deep-sea, about 20% is buried and 80% is dissolved up.

The three additional constraints needed to fix the carbon model are to set the surface and deep TCO$_2$ concentrations, the vertical exchange rate of water (upwelling and downwelling) and the further caveat that carbon-burial sites on today's continental shelves are insignificant. I have followed Broecker in setting the TCO$_2$ of nutrient-free surface water at 1.96 mM l$^{-1}$
and of average nutrient-rich deep water at 2.24 mM l⁻¹, and an upwelling and downwelling water exchange of 1.35 X 10¹⁸ l yr⁻¹ (residence time of deep-sea ~ 900 years).

The additional constraint of the P-cycle is our new phosphorite sink in the surface ocean. This burial flux was estimated independently of the carbon cycle, so the carbon burial is derived from the average Pₚ/Cₜtaş in Peru shelf sediments (30 X 10⁻³; Suess, 1981). The carbon burial flux (~0.6 X 10¹² mole-C yr⁻¹) turns out to be less than 4% of that buried in the deep sea with calcite and organic matter, so we will ignore it. All the other fluxes are fixed by mass balance and the river influxes.

Almost all the phosphorus transported into the surface ocean via upwelling of nutrient-rich deep-sea water is quickly extracted and converted into either soft tissue (Cₜtaş) or calcium carbonate (CCₐ₄₃₃) by productivity. Most of the production is recycled extensively in the surface ocean, but some fraction gets packaged into fecal pellets that escape by falling into the deep-sea. Most of this vertical particulate flux of the soft and hard parts of organisms dissolves or regenerates in the deep-sea, enhancing the TCO₂ and nutrient contents there. A small fraction escapes destruction and is buried, helping to balance the river input. Nutrient enriched deep water upwells and completes the internal cycle. Thus the internal cycle of P is dominated by biological extraction from the surface ocean, vertical particulate flux into the deep-sea, regeneration, and upwelling.

Some of the vertical particulate flux falls onto shelves in localized upwelling zones where the phosphatization process sequesters phosphorite.

The resulting picture has some interesting implications. First of all, P-removal is about equally partitioned between deep-sea burial of calcite and organic plus burial of phosphorites from the surface ocean, while C-burial is dominated by calcite. In addition, the P/C ratio leaving the surface ocean in the vertical particulate flux (P/C ~ 8 X 10⁻³) carries about four times the carbon per phosphorus atom as the surface ocean phosphorite removal (P/C ~ 30 X 10⁻²), even though 99.5% of the P-flux from the surface layer is in biogenic debris that rains into the deep-sea. The regenerated P-flux into the
deep-sea is dominated by organic-carbon destruction, so that, of the total biogenic-P transport, about 99% is destroyed and only 1% is buried. Since on every passage through the surface ocean, a P-atom has about a 99.5% chance of being sequestered into biogenic particles destined for the deep-sea, it spends most of its life in the thousand-year surface to deep-sea shuttle. On every 60 passes through the internal cycle, it gets trapped either in the surface ocean (phosphorite) or the deep-sea (calcite and organics).

The significance of the phosphorite sink is two-fold: (1) it's a surface ocean mechanism, and (2) it removes very little carbon in a P/C ratio that is more P-rich than average plankton. Apparently, the processes promoting phosphorite formation trap P more efficiently than \( C_{\text{org}} \), the reverse of the situation during ordinary diagenesis. The wide range of \( P/C_{\text{org}} \) ratios observed in Peru shelf cores (500 to 10 \( \times 10^{-3} \): Suess, 1981) are all much more P-rich than the average carbon being buried in the deep-sea \( (P_{\text{org}} + P_{\text{CaCO}_3})/(C_{\text{org}} + C_{\text{CaCO}_3}) \sim 1.6 \times 10^{-3} \), reflecting the result of repetitive regeneration, reworking and beneficiation of P in phosphorite strata of varying ages and histories.

E. Controls of Oceanic Nutrients, TCO\(_2\), and Atmospheric CO\(_2\)

In Broecker's model, the primary control on the nutrient cycle is via burial of phosphorus with biogenic debris in the deep ocean: The phosphorus concentration of the deep-sea adjusts to that level necessary to provide a sufficient flux of biogenic debris to the deep-sea so that the fraction of the particles escaping destruction and being buried just balances the river flux. Thus there must be negative feedbacks driving the P-concentration of the deep-sea toward a steady-state value that matches inputs and outputs. An increase in \( [P]_{\text{rivers}} \), for example, would enhance productivity, providing a slight excess of particles falling into the deep-sea that are destroyed, thus increasing the \( [P]_{\text{Deep-Sea}} \) until enhanced productivity assured that a sufficient fraction of the excess is buried to balance the river input. Likewise, if the turnover time of the deep-sea were to halve, the particulate flux into the deep-sea would drop, diminishing burial, and raising the deep-sea nutrient concentrations until productivity in the surface ocean again provided the necessary biogenic flux to bury the correct amount of P.
In our model, the feedbacks have several loops. For example, doubling the upwelling rate must double the rain of calcite and organic matter into the deep-sea, and probably also about double phosphorite formation. Overburial of calcite would cause the calcite compensation depth to shoal until enough of the calcite flux was dissolved that the initial burial flux is re-established. Overburial of calcite and C\textsubscript{org} and phosphorite overburies P, drawing down the [P]\textsubscript{Deep-Sea}, so that the upwelled nutrient fluxes and subsequent biogenic fluxes revert toward the original values, allowing the calcite compensation depth to eventually fall back to its original level. The end result is a deep-sea with about half its original phosphate.

If the phosphorite sink were suddenly cut off, for example by a drop in sea-level or by a shift in the location of coastal upwelling near suitable continental shelves, then the enhanced productivity in the surface ocean would provide an increased flux to the deep-sea. If the fractions of this vertical particulate flux destroyed and preserved are initially the same as before the cut-off, then the [P]\textsubscript{Deep-Sea} must increase until it provides the requisite biogenic P-flux to bury the river input. This scenario is identical to increasing the [P]\textsubscript{rivers}.

In order to do so and balance the oceanic carbon and alkalinity budgets, however, one of two things must happen to assure that the P/C burial ratio matches the input ratio. Either the average P/C ratio in the accumulating biogenic material in the deep-sea must increase, or the fraction of carbon buried with organic matter must increase (or some combination of both). If the P/C ratio in accumulating calcite and organics remained the same, then to balance input, about half the carbon will be buried with calcite and half as C\textsubscript{org}. It is improbable that such an oceanic steady-state was ever achieved, since the oceanic $\delta^{13}$C balance for this scenario would require a sea-water $\delta^{13}$C of about +9%, far heavier than any known values for the planktonic forams that record this value. How, then, would the oceans adjust the P/C ratio? Perhaps the simplest answer is to remove calcite with a higher P/C ratio, although the potential mechanism by which the oceans might accomplish this end is not at all clear.
In Broecker's model, the pCO$_2$ of the atmosphere is fixed by the pCO$_2$ of the surface ocean, since the 100-year exchangeable volume of the surface ocean has about four to five times more CO$_2$ than the atmosphere. Surface ocean pCO$_2$ is regulated by the concentration of preformed TCO$_2$ and alkalinity left after biological productivity extracts all the limiting nutrients from upwelled deep water. To a first approximation, this is simply dependent upon the P/TCO$_2$ ratio in the deep sea and the P/C ratio extracted from the surface in biogenic particulates. In today's ocean, about 85% of the upwelled TCO$_2$ and 96% of the upwelled alkalinity remain after complete P-utilization has extracted the maximum biogenic CaCO$_3$ and C$_{org}$. The extraction ratio, $\Delta$CaCO$_3$/ $\Delta$C$_{org}$, is about 1:4 today, presumably determined by average oceanic ecology. In principle one could write an equation for pCO$_2$$_{surface}$ as a function of the phosphate/TCO$_2$ and phosphate/alkalinity flux ratios entering and leaving the surface ocean. In practice, however, we still don't understand the oceanic alkalinity balance well enough to do this. However pCO$_2$ is very sensitive to slight changes in either the surface ocean P/C input or removal fluxes or the calcite to organic rain. For example, were life in the oceans suddenly to cease, TCO$_2$ would no longer be extracted into CaCO$_3$ and C$_{org}$ and alkalinity would no longer be extracted into CaCO$_3$. The surface ocean would be quickly displaced by upwelled water (within 100 years), and pCO$_2$ would rise to ~600 ppm! If the calcite to organic rain ratio were to change, pCO$_2$ of the surface ocean must adjust to reflect different alkalinity and TCO$_2$ residuals left over in nutrient-free surface water. In the short term (several hundred years), the most sensitive control on pCO$_2$ is the balance between P/TCO$_2$/TA inputs and outputs to the surface ocean.

F. Recorders of Oceanic Nutrient Cycles

Understanding past changes in nutrient and CO$_2$ cycles is critically important to verifying models that would predict future changes in the global biogeochemical cycles induced by man. Broecker (1982) has proposed that there are a number of indicators that may reflect past changes in the way the ocean balances its nutrient cycles, including $^\delta$C of surface and deep dwelling foraminifera, the paleodepth of the calcite compensation depth, and pCO$_2$ of
the atmosphere as recorded in ice cores. Each of these indicators responds to changes in oceanic TCO₂, alkalinity and nutrient economics on different time scales. However, at the close of glacial time about 11-13 Kyr b.p., all three indicators showed a dramatic shift coincident with sea-level rise and flooding of the continental shelves. At that time, the δ¹³C of the deep-sea rose ~1% (Shackleton, 1977) while the δ¹³C of the surface ocean remained about constant. The saturation horizon apparently deepened (Berger, 1977) and (pCO₂)ₜₐₜ₉ₙ rose from its glacial value of ~ 200 ppm to about 290 ppmv (Neftel et al., 1982) (Fig. 6). All of these shifts were accomplished within several thousand years, requiring some rapid readjustment of the nutrient and CO₂ economics of the ocean uncoupled from the longer-term response times of P, TCO₂, and TA in the whole system (T ~ 10⁵ yr).

To explain these post-glacial changes, Broecker (1982) has called upon shifting a portion of the organic carbon and phosphorus burial from the deep-sea to shelves at the close of glacial time, coupled with either a decrease in the P/TCO₂ ratio upwelled or an increase in the P/C ratio raining into the deep-sea in biogenic particles.

Recognition of significant phosphorite burial on shelves allows us to alter this picture somewhat. Assume that during low-stands of sea-level, the phosphatization process stopped. P not being buried in carbon-poor phosphorite was available to transport additional carbon-rich calcite and Corg into the deep-sea. Forget for the moment that we don't know how the deep-sea adjusts to this change because over the last hundred thousand years, sea-level was low only half the time. So the deep-sea may never have approached steady-state. Over a hundred-thousand year full glacial to interglacial cycle, phosphorus was sporadically robbed from the phosphorite sink, and TCO₂ and alkalinity from the surface ocean, and carried to the deep-sea. [P]_{Deep-Sea} and [TCO₂]_{Deep-Sea} must have slowly increased, since absence of the surface ocean phosphorite sink is equivalent to addition of a source of P to the surface ocean. The ratio of the deep-sea AΦ/ATCO₂ increase is dependent upon the feedbacks controlling the P/C burial ratios in calcite and organic matter, which we don't understand. However, it is likely that the (P/TCO₂)_{Deep-Sea} ratio by the time of the last drop in sea-level was

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higher than today by about 30%, producing a lower glacial \((p_{CO_2})_{atmos}\) ~200 ppmv.

At the close of glacial time, sea-level rose, \(p_{CO_2}\) fell from 300 to 200 ppmv, \((^{13}C)_{Deep-Sea}\) rose 0.7%, and the aragonite lysocline deepened, all within about 5000 years. One scenario that might account for these rapid shifts is as follows. In order to account for the \(^{13}C\) shift, it is necessary to remove about 3% of the oceanic \(TCO_2\) (~9 X 10\(^{16}\) mole-CO\(_2\)).

Rebirth of temperate forests can account for about two-thirds of this (~6 X 10\(^{16}\) mole-CO\(_2\); Table 5). The oceans must account for the other one-third (~3 X 10\(^{16}\) mole-CO\(_2\)). If the carbon is removed by re-initiation of the phosphorite sink by burying \((P/C)_{Phos}\) in our 30 X 10\(^{-3}\) ratio, then the matching phosphorus burial is about 9 X 10\(^{14}\) mole-P, about one-third of the oceanic P-reservoir. To do this within 5000 years, as suggested by the sediment record, requires shelf burial fluxes of about 6 X 10\(^{12}\) mole-C yr\(^{-1}\) and 18 X 10\(^{10}\) mole-P yr\(^{-1}\), or about 1.5% and 5.5% of the present-day oceanic biogenic fluxes of C and P (respectively) to the deep-sea. This burial flux over the area of the Peru mud lenses would require a Holocene sediment thickness of over 20 m (assuming average \(C_{org}\) in phosphatic muds of about 3-4%). The actual thickness of this section is only about 10-20% of what is required! So the missing phosphorite must have slumped into the deep-sea. This fits with our notion of the hiatuses and sediment dispersal on the Peru shelf and slope (Reimers and Suess, 1983; DeMaster, 1979), and with Burnett and Veeh's (1977) finding that dates of phosphorite nodules on the Peru shelf coincide with high stands of sea-level.

The removal of \(C_{org}\) to shelves and forests caused \((\Delta p_{CO_2}/\Delta TA)_{Deep-Sea}\) to decrease, making deep ocean water less corrosive to CaCO\(_3\) dissolution by shoaling of the calcite and aragonite lysoclines. This event is recorded as an aragonite preservation spike in sediments presently lying above the present calcite compensation depth but below the aragonite lysocline (Berger, 1977).

How do the oceans adjust so rapidly? The easiest way to understand this is to consider the response times of P and C in the various reservoirs. In our model (Fig. 5), the residence times of P and C in the ocean with respect to sources and sinks are about 60 kyr and 160 kyr, respectively. The response

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times of the deep-sea, however are much shorter with respect to biogenic fluxes (Table 5). The response time calculated on this basis of deep-sea TCO$_2$ is about $5 \times 10^3$ yr, and that of deep-sea phosphate, about 600 yr. Thus deep-sea chemistry could have adjusted to the rapid transients occurring in the surface ocean.

In the longer term, C and P must balance sinks and sources over $\sim 10^5$ yrs, so the ocean is probably today still recovering from the post-glacial event. One consequence of this scenario is an explanation for apparent N-limitation in today's ocean, and the existence of preformed P in the deep ocean in excess of the N:P Redfield ratio required by oceanic plankton. If the N:P ratio being removed on productive interglacial shelves is greater than 16:1 (dentrification/phosphorites), then as the deep-sea NO$_3$ and PO$_4$ concentrations continue decreasing toward their steady-state values, PO$_4$ decrease will lag the NO$_3$ decrease. My suspicion is that evidence for this will come from the N-cycle, perhaps from analyses of N$_2$O in the ice cores.

IV. SUMMARY

In conclusion, then, I've tried to incorporate a few bits of new information into our previous understanding of the P-cycle. About 30-50% of the fluvial P-input to the oceans derives from release of reactive-P from particles during their passage through estuaries. Our estimate of the continental P-flux is about $5 \times 10^{-10}$ mole-P yr$^{-1}$, equivalent to [P]$_{rivers}$ $\sim 1.4$ $\mu$M l$^{-1}$. No other inputs are thought to be significant.

The input is matched by P-removal into three approximately equivalent sinks: (1) burial in phosphorites on productive shelves ($\sim 1.8 \times 10^{10}$ mole-P yr$^{-1}$); (2) burial with C$_{org}$ in the deep-sea ($\sim 1.6 \times 10^{10}$ mole-P yr$^{-1}$); and (3) burial with biogenic calcite in the deep-sea ($\sim 1.6 \times 10^{10}$ mole-P yr$^{-1}$). The P/C burial ratio in these three phases is very different: (P/C)$_{org}$ $\sim 4 \times 10^{-3}$; (P/C)$_{CaCO_3}$ $\sim 1 \times 10^{-3}$; (P/C)$_{Phos}$ $\sim 30 \times 10^{-3}$.

The removal mechanisms are all coupled to primary production in the surface ocean, but the details of the feedback mechanisms controlling the steady-state nutrient and carbon budgets in the sea are obscured by lack of
knowledge of how the P/C ratios in the sinks adjust, and how shifts in oceanic nutrients affect oceanic ecology and the relative fraction of biogenic CaCO$_3$ and C$_{org}$ production.

REFERENCES


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Table 1. Phosphorus Fluxes From Continents To Oceans

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. TOTAL PRE-MAN FLUVIAL P-FLUX</td>
<td>$30 \times 10^{10}$ mole yr$^{-1}$</td>
</tr>
<tr>
<td>2. TOTAL CONTEMPORARY FLUVIAL P-FLUX</td>
<td>$80 \times 10^{10}$ mole yr$^{-1}$</td>
</tr>
<tr>
<td>3. TOTAL MINED BY MAN (~1980) (MOSTLY FERTILIZER)</td>
<td>$40 \times 10^{10}$ mole yr$^{-1}$</td>
</tr>
<tr>
<td>4. FLUVIAL DISSOLVED P-FLUX</td>
<td>$(3.6 \pm 2.2) \times 10^{10}$ mole yr$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$[P] \sim 1.0$ µM l$^{-1}$</td>
</tr>
<tr>
<td>5. FLUVIAL REACTIVE P-FLUX</td>
<td>$5.0 \times 10^{10}$ mole yr$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$[P]_R \sim 1.4$ µM l$^{-1}$</td>
</tr>
</tbody>
</table>
Table 2. Phosphorus In Sedimentary Biogenic Carbonates

<table>
<thead>
<tr>
<th>NO. SAMPLES</th>
<th>%CaCO₃</th>
<th>PPM-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PETTERSSON (1952)</td>
<td>9</td>
<td>95±3</td>
</tr>
<tr>
<td>(SWEDISH DEEP-SEA EXPEDITION)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. EL WAKEEL AND RILEY (1961)</td>
<td>1</td>
<td>91</td>
</tr>
<tr>
<td>(DISCOVERY &quot;D&quot;)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. MARCHIG (1972)</td>
<td>10</td>
<td>93±2</td>
</tr>
<tr>
<td>4. COOK (1977)</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>5. CORRENS (1937)*</td>
<td>SEVERAL*</td>
<td>100*</td>
</tr>
<tr>
<td></td>
<td>HUNDRED</td>
<td></td>
</tr>
<tr>
<td>6. FROELICH ET AL., (1982)</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

*CALCULATED ON THE BASIS OF THE P-INTERCEPT AT 100% CaCO₃ ON A %CaCO₃ VS. %P₂O₅ REGRESSION FROM THE EQUATORIAL ATLANTIC METEOR EXPEDITION (1925-27).
Table 3. Average P/C Ratios in Holocene Phosphatic Muds Off Peru (Seuss, 1981)

\[
\frac{(P_{\text{ORG}} + P_{\text{INORG}})}{C_{\text{ORG}}} \sim 30 \times 10^{-3}
\]

\[
P_{\text{ORG}}/C_{\text{ORG}} \sim 2 \times 10^{-3}
\]

[REDFIELD RATIO (AVERAGE PLANKTON) (P/C)_{\text{ORG}} \sim 10 \times 10^{-3}]

[AVERAGE DEEP-SEA ORGANIC MATTER P/C)_{\text{ORG}} \sim 4 \times 10^{-3}]

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Table 4. Phosphorite Burial A La Fluoride

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride Flux to Peru Shelf Muds</td>
<td>( \mu \text{mol-F cm}^{-2} \text{yr}^{-1} )</td>
<td>( \sim 3 )</td>
</tr>
<tr>
<td>Area of Peru and Walvis Bay Muds</td>
<td>( \text{cm}^2 )</td>
<td>( \sim 2.2 \times 10^{15} )</td>
</tr>
<tr>
<td>Global F-Flux into CARFAP</td>
<td>( \text{mole-F yr}^{-1} )</td>
<td>( \sim 0.6 \times 10^{10} )</td>
</tr>
<tr>
<td>Composition of Average CARFAP</td>
<td></td>
<td>( \text{P:F} \sim 3/1 )</td>
</tr>
<tr>
<td>Global P-Flux into CARFAP</td>
<td>( \text{mole-P yr}^{-1} )</td>
<td>( \sim 1.8 \times 10^{10} )</td>
</tr>
<tr>
<td>((\text{P/}C_{\text{org}})) in Phosphatic Muds</td>
<td></td>
<td>( \sim 30 \times 10^{-3} )</td>
</tr>
<tr>
<td>Global C(_{\text{org}})-Flux in Phosphatic Muds</td>
<td>( \text{mole-C yr}^{-1} )</td>
<td>( \sim 0.6 \times 10^{12} )</td>
</tr>
</tbody>
</table>
Table 5. Carbon and Phosphorus Reservoirs

<table>
<thead>
<tr>
<th>Reservoir Description</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPERATE FOREST</td>
<td>~6 x 10^16 moles</td>
</tr>
<tr>
<td>ATMOSPHERIC CO₂</td>
<td>5.4 x 10^16 moles</td>
</tr>
<tr>
<td>SURFACE OCEAN TCO₂</td>
<td>26.5 x 10^16 moles</td>
</tr>
<tr>
<td>DEEP-SEA TCO₂</td>
<td>275 x 10^16 moles</td>
</tr>
<tr>
<td>TCO₂ (Atmos. and Surface Ocean)</td>
<td>~10^2 yr</td>
</tr>
<tr>
<td>TCO₂ (Deep-Sea)</td>
<td>~7 x 10^3 yr</td>
</tr>
<tr>
<td>TCO₂ (E)</td>
<td>~160 x 10^3 yr</td>
</tr>
<tr>
<td>SURFACE OCEAN PO₄⁻</td>
<td>~0</td>
</tr>
<tr>
<td>DEEP-SEA PO₄⁻</td>
<td>2.9 x 10^15 moles</td>
</tr>
<tr>
<td>TPO₄ (Surface Ocean)</td>
<td>&lt;10^2 yr</td>
</tr>
<tr>
<td>TPO₄ (Deep-Sea)</td>
<td>~10^3 yr</td>
</tr>
<tr>
<td>TPO₄ (E)</td>
<td>~60 x 10^3 yr</td>
</tr>
</tbody>
</table>
Fig. 1. Estuarine nutrient profiles in Ochlockonee Bay, FL. Four of the thirteen nutrient vs. chloride profiles generated during a fourteen-month study of estuarine nutrient dynamics. Each profile shows curvature characteristic of removal (productivity: bowed down), input (regeneration: bowed up) and simple mixing (linear). Curves through the data points are best-fits to a modification of the one-dimensional reaction-mixing model for estuaries.
Fig. 2. $\%C_{org}$ vs. $(P/C)_{org}$ for marine sediments. About all marine sediments which accumulate significant amounts of organic carbon display $(P/C)_{org}$ ratios lower than the Redfield ratio. The "average" carbon atom buried in marine sediments carries a $(P/C)_{org}$ ratio of about $4 \times 10^{-3}$. This value is very uncertain, but almost surely lies in the range $2-6 \times 10^{-3}$. 
FATE OF $P_{\text{org}}$ BURIED BELOW SEDIMENT-WATER INTERFACE

Fig. 3. Phosphorite burial as a Surrogate for $P_{\text{org}}$-burial in marine sediments
Fig. 4. Fluoride and phosphate pore water profiles in four cores from the phosphatic mud lenses of the Peru continental margin. The F-profiles can be modeled as a first order reaction removing F into solid phases in the upper 20-30 cm. The model provides an estimate of the diffusive flux of F from seawater into the sediment column, which ranges from 2.5 to 3.2 nmol-F cm$^{-2}$ yr$^{-1}$ for these four cores. The phosphate profiles are more complex, displaying both uptake of P into carbonate fluorapatite near the interface, and the cumulative increase in P deep in the cores due to organic diagenesis and perhaps dissolution of fish debris. Unlike the situation for F, the source of P at the interface must be either dissolution of fish debris (hydroxyapatite) or regeneration of the organic fluff at the interface. The arrows above each horizontal axis give the bottom water concentrations.
Fig. 5. Two-box model of carbon and phosphorus cycle in present ocean.
Fig. 6. Atmospheric CO$_2$ concentration for the last 40,000 years derived from ice cores (Neftel et al., 1982).
THE NITROGEN CYCLE
Atmospheric interactions involving the nitrogen species are varied and complex. These interactions include photochemical reactions, initiated by the absorption of solar photons and chemical kinetic reactions, which involve both homogeneous (gas-to-gas reactions) and heterogeneous (gas-to-particle) reactions. Examples of heterogeneous reactions include the absorption of soluble gases by cloud and rain droplets and the chemical formulation of atmospheric aerosols. Another important atmospheric interaction is the production of nitrogen oxides by atmospheric lightning. The nitrogen cycle strongly couples the biosphere and atmosphere. Many nitrogen species (i.e., molecular nitrogen, nitrous oxide, nitric oxide and ammonia) are produced by biogenic processes (i.e., nitrification, denitrification, etc.). Once in the atmosphere nitrogen oxides are photochemically and chemically transformed to nitrates, which are returned to the biosphere via precipitation, dry deposition and aerosols to close the biosphere-atmosphere nitrogen cycle.

The sources, sinks and photochemistry/chemistry of the nitrogen species are summarized in the following set of figures. The original source from which the figure is based is indicated on the figure. Information on the rates for the photochemical and chemical processes given on the figures can be found in the cited references, as well as in the review papers listed at the end of the cited references.

The atmospheric nitrogen species are summarized in Figure 1. The species name, chemical symbol and surface concentration or concentration range are given. Note that all of the species in the table are gaseous, except for the last two entries, which are solid aerosols.

Surface and atmospheric sources of the nitrogen species are schematically represented in Figure 2. Surface sources include biogenic production in soil and anthropogenic activities, i.e., coal burning, internal combustion engines, etc. Atmospheric sources include photochemical/chemical processes and lightning.

The sources and sinks of nitrous oxide are summarized in Figure 3. Biogenic production is the overwhelming source of nitrous oxide. Nitrous oxide is chemically inert within the troposphere. Once it diffuses up to the stratosphere it is destroyed by photolysis and by reaction with excited oxygen atoms (O(1D)) (reactions (1) to (3)). Reaction (3) is an important source of nitric oxide in the stratosphere which leads to the catalytic destruction of stratospheric ozone (see Figure 24).

Recently, it has been shown that lightning is also a source of nitrous oxide. Figure 4 shows a scan of nitrous oxide before and after a laboratory
discharge using a gas chromatograph with an electron capture detector. After a single laboratory discharge, the concentration of nitrous oxide doubled. Actual nitrous oxide levels measured within electrically-active thunderstorms are summarized in Figure 5.

The sources, sinks and photochemistry/chemistry of ammonia are summarized in Figure 6.

The seasonal variation of the vertical distribution of ammonia in the troposphere is shown in Figure 7. These measurements were obtained with the Infrared Heterodyne Radiometer, a remote sensing instrument that utilizes the Sun as a radiation source. The maximum levels of ammonia measured in March are believed to have resulted from the rapid volatilization of nitrogen fertilizer applied to agricultural fields in the vicinity of Hampton, Virginia.

The seasonal variation of ground level ammonia from August, 1979, through April, 1980, is shown in Figure 8. The daily variation of ground level ammonia in August and September, 1979 and 1980 is shown in Figure 9. Note that the 1979 measurements are significantly higher than the 1980 measurements. The higher ammonia measurements in 1979 may be related to enhanced levels of rainfall in 1979, as shown in Figure 10.

The sources and sinks of the "active" nitrogen species, defined as the nitrogen oxides (nitric oxide + nitrogen dioxide) and nitric acid are summarized in Figure 11. Note that there are large uncertainties in our understanding of the source strengths of nitrogen oxides production due to biogenic activity, the oxidation of biogenically-produced ammonia and biomass burning. In the atmosphere, the oxides of nitrogen are photochemically/chemically transformed to nitric acid. The loss of nitric acid via rainout, dry deposition and aerosol formation are the overwhelming sinks of the active nitrogen species and constitute a source of nitrates to the biosphere.

Measurements and theoretical calculations of the vertical distribution of the nitrogen oxides in the troposphere are summarized in Figures 12 and 13. Measurements and theoretical calculations of the vertical distribution of nitric acid in the troposphere are summarized in Figure 14.

Lightning is an important source of nitrogen oxides. Figure 15 shows the production of nitric oxide after a laboratory discharge.

The oxidation of ammonia, initiated by the reaction with the hydroxyl radical (OH) leads to the photochemical production of the nitrogen oxides when background levels of the nitrogen oxides are below about 70 parts per trillion by volume. The reactions involved in the ammonia oxidation scheme are summarized in Figure 16. Upper limit estimates for the global annual production of the nitrogen oxides from the oxidation of ammonia are given in Figure 17. Note that most of the ammonia in the troposphere is lost due to rainout. Very little tropospheric ammonia reaches the stratosphere.

The latitudinal distribution of the production of the nitrogen oxides is given on the left side of Figure 18. Note that all of the sources exhibit a strong latitudinal dependence. The total production of the nitrogen oxides
(the summation of the individual sources shown on the left side of the figure), as well as the total deposition of the nitrogen oxides, measured as nitrates in rain, both as a function of latitude, are given on the right side of the figure.

The key photochemical and chemical processes involving the major and minor "active" nitrogen species in the troposphere are summarized in Figure 19. Note that there is very strong photochemical coupling between the "active" species in the troposphere. The only nitrogen species that undergoes photolysis in the troposphere is nitrogen dioxide. The photolysis threshold for nitrogen dioxide is at about 400 nm, just about the shortest wavelength of solar radiation that can penetrate to the surface of the Earth. The reactions given in Figure 19 are schematically shown in Figure 20 for both daytime and nighttime conditions.

The hydroxyl radical \(^{(OH)}\) which is produced by the reaction of excited oxygen atoms \((O(\text{I}D))\) with water vapor \((H_2O)\) is a key species in the chemistry of the nitrogen species in the troposphere. The hydroxyl radical is involved in the photochemical production of nitric acid and in the oxidation of ammonia. Measurements and theoretical calculations of the vertical distribution of the hydroxyl radical in the troposphere are summarized in Figure 21.

Due to their photochemical coupling, most of the "active" nitrogen species in the troposphere exhibit strong diurnal variability. The theoretically calculated diurnal variation of the "active" nitrogen species and oxides of hydrogen are summarized in Figure 22.

The dependence of the vertical distribution of the nitrogen oxides and nitric acid on the assumed vertical distribution of the atmospheric nitrogen oxide source term (i.e., lightning and the oxidation of ammonia) is shown in Figure 23 based on theoretical photochemical calculations. The assumed nitrogen oxide atmospheric source term ranging from no atmospheric source term (i.e., neglecting lightning and the oxidation of ammonia) to an integrated column production of 27 \(\text{Mt(N)/yr}\) through the troposphere is shown on the left side of the figure. The resulting nitrogen oxide and nitric acid profiles are given on the right side of the figure. All other boundary conditions were kept constant in these calculations to highlight the importance of the atmospheric nitrogen oxide source term.

The photochemical and chemical reactions involving the "active" nitrogen species in the stratosphere are summarized in Figure 24. Note that every "active" nitrogen species undergoes photolysis in the stratosphere, compared to the troposphere, where only nitrogen dioxide can be photolyzed. With the exception of nitrogen dioxide, the photolysis of the "active" nitrogen species require energetic solar ultraviolet radiation, which does not penetrate into the troposphere, due primarily to its absorption by stratospheric ozone. Reactions (24) and (31) form a catalytic cycle, which is the main photochemical destruction mechanism for ozone in the stratosphere.
REFERENCES


Other References (Review Papers)


SPECIES
MOLECULAR NITROGEN (N₂)
NITROUS OXIDE (N₂O)
AMMONIA (NH₃)
NITRIC ACID (HNO₃)
HYDROGEN CYANIDE (HCN)
NITROGEN DIOXIDE (NO₂)
NITRIC OXIDE (NO)
NITROGEN TRIOXIDE (NO₃)
PAN (CH₃CO₃NO₂)
DINITROGEN PENTOXIDE (N₂O₅)
PERNITRIC ACID (HNO₃O₂)
NITROUS ACID (HNO₂)
NITROGEN AEROSOLS:
  AMMONIUM NITRATE (NH₄NO₃)
  AMMONIUM CHLORIDE (NH₄Cl)

SURFACE CONCENTRATION OR RANGE
(BY VOLUME)¹

78.08%  330 ppbv
0.1 - 1.0 ppbv  50 - 100 pptv
~ 200 pptv  10 - 300 pptv
5 - 100 pptv²  100 pptv³
50 pptv  0.5 pptv²
1 pptv³  0.1 pptv

¹ ppbv = PART PER BILLION BY VOLUME = 10⁻⁹; pptv = PART PER TRILLION BY VOLUME = 10⁻¹²; THE TOTAL ATMOSPHERIC NUMBER DENSITY AT THE SURFACE = 2.55 × 10¹⁹ MOLECULES cm⁻³.
² EXHIBITS STRONG DIURNAL VARIATION WITH MAXIMUM CONCENTRATION DURING THE DAY.
³ EXHIBITS STRONG DIURNAL VARIATION WITH MAXIMUM CONCENTRATION DURING THE NIGHT.

Fig. 1. Atmospheric Nitrogen Species.
Fig. 2. The Nitrogen Budget of the Troposphere.
### SOURCES (SURFACE)

<table>
<thead>
<tr>
<th>Source Description</th>
<th>Source Strength (Mt(N)/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogenic production in soil + waters</td>
<td>~ 10</td>
</tr>
<tr>
<td>Fossil fuel burning</td>
<td>~ 2</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>~ 1 - 2</td>
</tr>
</tbody>
</table>

### SINKS (STRATOSPHERE)

1. \( \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O} \)
2. \( \text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{N}_2 + \text{O}_2 \)
3. \( \text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{NO} \)

\(\text{TOTAL DESTRUCTION OF N}_2\text{O} = 9.4\ \text{Mt(N)/yr}\)

\(\text{GLOBAL PRODUCTION OF NO} = 1\ \text{Mt(N)/yr}\)

### Global Atmospheric Inventory of \(\text{N}_2\text{O}\)

\(\text{GLOBAL ATMOSPHERIC INVENTORY OF N}_2\text{O} = 1620\ \text{Mt(N)}\)

### \(\text{N}_2\text{O}\) Residence Time with Respect to Photochemical Destruction

\(\frac{1620\ \text{Mt(N)}}{9.4\ \text{Mt(N)/yr}} = 175\ \text{yrs}\)

---

Fig. 3. Nitrous Oxide (\(\text{N}_2\text{O}\)).
Air sample prior to discharge.

Air sample after discharge (Levine et al., 1979).

Fig. 4. Production of N₂O in laboratory discharge (Levine et al., 1979).
Fig. 5. N$_2$O Levels in Electrically Active Thunderstorms (Levine and Shaw, 1983).
SOURCES

BIOMASS BURNING
NATURAL FIELDS
DOMESTIC ANIMALS
COAL BURNING
WILD ANIMALS
FERTILIZED FIELDS

SINKS

RAINOUT
REACTION WITH OH
FORMATION OF AMMONIUM AEROSOLS

SOURCE STRENGTH (Mt(N)/yr)

<60
<30
10 - 20
4 - 12
2 - 6
<3

NH\textsubscript{3} RESIDENCE TIME WITH RESPECT TO:

~10 DAYS
~40 DAYS
?

PHOTOCHEMISTRY

- AMMONIA OXIDATION CHAIN:
  (4) \( \text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O} \)
  (5) \( \text{NH}_2 + \text{O}_3 \rightarrow \text{NO}_x + \text{PRODUCTS} \)
  (6) \( \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \)
  (7) \( \text{NH}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \)

- AEROSOL FORMATION
  (8) \( \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3(s) \)
  (9) \( \text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4(s) \)

Fig. 6. Ammonia (NH\textsubscript{3}).
Fig. 9. Surface Measurements of Ammonia: Daily Variation in August and September, 1979 and 1980 (Hoell et al., 1982).
Fig. 10. Average Monthly Precipitation for Hampton, Virginia Area (Hoell et al., 1982).
<table>
<thead>
<tr>
<th>Sources of ( \text{NO}_x )</th>
<th>Source Strength (Mt(N)/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic (High Temp. Combustion):</td>
<td>20</td>
</tr>
<tr>
<td>Biogenic Production:</td>
<td>0 - 15</td>
</tr>
<tr>
<td>Oxidation of Ammonia:</td>
<td>0 - 10</td>
</tr>
<tr>
<td>Biomass Burning:</td>
<td>10 - 40</td>
</tr>
<tr>
<td>Lightning:</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Transport from Stratosphere:</td>
<td>0.5 - 1.0</td>
</tr>
</tbody>
</table>

**Source of \( \text{HNO}_3 \)**

Photochemistry: \( \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \): 22 - 77

**Sinks of \( \text{HNO}_3 \)**

Rain and Aerosol Formation

Fig. 11 "Active" Nitrogen Species: \( \text{NO}_x(\text{NO} + \text{NO}_2) + \text{HNO}_3 \).
Fig. 12. NO, NO\textsubscript{2} and NO\textsubscript{x} (NO + NO\textsubscript{2}): Measurements and Calculations (Callis et al., 1983).
Fig. 13. Vertical Distribution of NO\textsubscript{x} (Ehhalt and Drummond, 1982).
Fig. 16. Nitric Acid (HNO₃) Mixing Ratio: Maritime and Continental Measurements (Huebert and Lavers, 1980) and Calculations (Callis et al., 1983).
Fig. 15. Production of NO\textsubscript{x} in Laboratory Discharge (Levine et al., 1981).
Fig. 16. The Oxidation of NH₃: Source or Sink of NOₓ?

\[
\begin{align*}
\text{NH}_3 + \text{OH} & \rightarrow \text{NH}_2 + \text{H}_2\text{O} \quad (1) \\
\text{NH}_2 + \text{O}_2 & \rightarrow \text{NO}_X + \text{PRODUCTS} \quad (2) \\
\text{NH}_2 + \text{O}_3 & \rightarrow \text{NO}_X + \text{PRODUCTS} \quad (3) \\
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (4) \\
\text{NH}_2 + \text{NO}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad (5)
\end{align*}
\]

NH₃ IS SOURCE OF NOₓ WHEN NOₓ ≤ 70 ppt

NH₃ IS SINK OF NOₓ WHEN NOₓ > 70 ppt
• FOR UPPER LIMIT ESTIMATE, ASSUME THAT EVERY NH₃ MOLECULE THAT REACTS WITH OH LEADS TO PRODUCTION OF NOₓ. WHAT PERCENTAGE OF NH₃ REACTS WITH OH?

• FROM PHOTOCHEMICAL MODEL INTERPRETATION OF IHR NH₃ PROFILES:
  • LIFETIME OF NH₃ AGAINST REACTION WITH OH: 40 DAYS
  • LIFETIME OF NH₃ AGAINST RAINOUT: 10 DAYS
  •:. ABOUT 20% OF ALL NH₃ FORMS NOₓ

• FOR A GLOBAL NH₃ FLUX OF 50 MTON (N)/YR * THIS CORRESPONDS TO ABOUT 10 MTON (N)/YR OF NOₓ

*THIS VALUE DOES NOT INCLUDE ANTHROPOGENIC SOURCES OF NH₃, e.g., COAL BURNING, VOLATILIZATION OF NITROGEN FERTILIZER

Fig. 17. Upper Limit Estimate of NH₃ as a Source of NOₓ.
Fig. 18. Production and Deposition of NO: Latitudinal Distribution (Enhalt and Drummond, 1982).
\[ \text{\textbullet{} HNO}_3, \text{ NO}_x(\text{NO} + \text{NO}_2) \]

\begin{align*}
(10) \quad \text{NO} + O_3 & \rightarrow \text{NO}_2 + O_2 \\
(11) \quad \text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \\
(12) \quad \text{NO}_2 + h\nu & \rightarrow \text{NO} + O \\
(13) \quad \text{NO}_2 + \text{OH} + M & \rightarrow \text{HNO}_3 + M \\
(14) \quad \text{HNO}_3 & \rightarrow \text{HETERGENEOUS LOSS, I.E.,} \\
& \text{RAINOUT, DRY DEPOSITION} \\
& \text{AND AEROSOL FORMATION} \\
(15) \quad \text{NO}_2 + O_3 & \rightarrow \text{NO}_3 + O_2 \\
(16) \quad \text{HNO}_3 + \text{OH} & \rightarrow \text{NO}_3 + \text{H}_2\text{O} \\
(17) \quad \text{CH}_3\text{CO}_3 + \text{NO}_2 & \rightarrow \text{PAN} \\
(18) \quad \text{NO}_2 + \text{NO}_3 & \rightarrow \text{N}_2\text{O}_5 \\
(19) \quad \text{NO} + \text{NO}_3 & \rightarrow 2\text{NO}_2 \\
(20) \quad \text{NO}_2\text{HO}_2 + M & \rightarrow \text{HO}_2\text{NO}_2 + M \\
(21) \quad \text{NO}_2\text{HO}_2 + \text{OH} & \rightarrow \text{NO}_2 + \text{H}_2\text{O} + O_2 \\
(22) \quad \text{NO}_2 + \text{HO}_2 & \rightarrow \text{HNO}_2 + O_2 \\
(23) \quad \text{NO} + \text{OH} & \rightarrow \text{HNO}_2 + M
\end{align*}

**Fig. 19.** Photochemistry of "Active" Nitrogen Species in the Troposphere.
Fig. 20. Photochemistry of NO$_x$: Daytime and Nighttime (Enhalt and Drummond, 1982).
Fig. 21. The Hydroxyl Radical (OH): Measurements and Calculations (Callis et al., 1983).
Fig. 22. Calculated Diurnal Variations of Hydrogen and Nitrogen Oxides (Logan et al., 1981).
Vertical distribution of $\text{NO}_x$ and $\text{HNO}_3$

**U.B.C.**

$\phi (\text{NO}_x) \downarrow = 0.2 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$

$\phi (\text{HNO}_3) \downarrow = 1.2 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$

**L.B.C.**

$f (\text{NO}_x) = 100 \text{ ppt}$

$\phi (\text{HNO}_3) \downarrow = 1 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$

Fig. 23. Calculated Vertical Profiles of $\text{NO}_x$ and $\text{HNO}_3$ in the Troposphere for Different $\text{NO}_x$ Source Production Profiles.
(24) \( \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \)
(25) \( \text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \)
(26) \( \text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2 \)
(27) \( \text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3 \)
(28) \( \text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH} \)
(29) \( \text{HNO}_2 + h\nu \rightarrow \text{NO} + \text{OH} \)
(30) \( \text{HO}_2\text{NO}_2 + h\nu \rightarrow \text{NO}_3 + \text{OH} \)
(31) \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)

(32) \( \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \)
(33) \( \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \)
(34) \( \text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl} \)
(35) \( \text{NO}_2 + \text{O} + \text{M} \rightarrow \text{NO}_3 + \text{M} \)
(36) \( \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \)
(37) \( \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \)
(38) \( \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \)
(39) \( \text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \)

Fig. 24. Photochemistry of "Active" Nitrogen Species in the Stratosphere.
TERRESTRIAL NITROGEN CYCLES:
SOME UNANSWERED QUESTIONS

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Nitrogen is generally considered to be the element which most often limits the growth of plants in both natural and agricultural ecosystems. It can regulate plant growth because photosynthetic rates are strongly dependent on the concentration of nitrogen in leaves (Mooney and Gulmon 1982), and because relatively large amounts of protein are required for cell division and growth. Yet nitrogen is abundant in the biosphere - the well-mixed pool in the atmosphere can be considered inexhaustible compared to biotic demand, and the amount of already fixed organic nitrogen in soils far exceeds annual plant uptake in terrestrial ecosystems.

This seeming limitation in the midst of plenty leads many to question whether nitrogen is as limiting as assumed (cf. Gutschick 1981). There is direct evidence (from fertilization studies) and indirect evidence (from plant nitrogen use efficiencies) that nitrogen limits tree growth in most intact coniferous and many deciduous forests (Keeney 1980, Cole and Rapp 1980, Miller 1981, Vitousek 1982). Nitrogen deficiency is secondary to water deficits (but the most important of the elements) in many prairie and desert sites (cf. Reynolds and Cunningham 1981). In contrast, most lowland tropical forests do not appear to be nitrogen limited, although many montane tropical forests may be nitrogen deficient (Vitousek 1983). Temperate communities in regions receiving substantial anthropogenic nitrogen deposition are not generally nitrogen deficient (Ulrich et al. 1980).

Even in regions where intact natural vegetation is not nitrogen limited, continuous cultivation can induce nitrogen deficiency. Nitrogen losses from cultivated lands are much more rapid than those of other elements (Switzer et al. 1978, Sanchez et al. 1982), and nitrogen fertilization of some kind is generally required to maintain crop yields under any continuous cropping system.

The pervasiveness of nitrogen deficiency in many natural and most managed sites leads terrestrial ecologists to ask several questions. Why is soil nitrogen turnover slow (compared to that of other nutrients)? Why is nitrogen lost more rapidly from disturbed sites than other nutrients? And why are rates of biological nitrogen fixation so low even in nitrogen-deficient sites? Those concerned with the interactions of global element cycles would add related questions. To what extent is carbon, phosphorus, and sulfur accumulation in terrestrial ecosystems limited by nitrogen? What is the fate of the nitrogen lost from disturbed and cultivated sites? What controls these fluxes?
The answers to these questions are not all in hand, but the dimensions of several of them can be derived. The International Nitrogen Unit of the Royal Swedish Academy of Sciences has systematically collected and synthesized the information available; this effort has yielded several iterations of a global nitrogen budget (most recently Rosswall 1983), book-length collections of nitrogen cycling research in tropical West Africa (Rosswall 1980, Robertson and Rosswall 1983), Southeast Asia (Wetselaar et al. 1981), and Latin America (Robertson et al. 1982), a synthesis of terrestrial nitrogen cycling models and processes (Clark and Rosswall 1981), and related summaries of the interactions of the nitrogen cycle with those of other elements (Likens 1981, Bolin and Cook 1983). This massive body of information can be summarized in many ways (cf. Clark 1981); one level of resolution is presented in Fig. 1, a simple flow diagram of the nitrogen cycle within a site. It leaves out fluxes such as NO\(_2\) production during nitrification (Bremner and Blackmer 1978), which can be important globally but are a small part of a within-system cycle. At the opposite extreme, a global-scale budget of nitrogen in terrestrial ecosystems is summarized in Table 1 (Soderlund and Rosswall 1982). It gives a useful idea of the magnitude of the various pools and fluxes, although it cannot be applied to any particular region. (In this case, it also suggests a soil organic nitrogen pool size that is probably too high by a factor of 2; the soil organic carbon pool is about 1500 Pg [cf. Schlesinger, this volume]; the carbon:nitrogen ratio in most soils is at least 10; and the value for C has been subjected to much more thorough scrutiny and revision than that for N.)

Why then is nitrogen so often limiting? First, why does it turn over relatively slowly in soil? The most important reason is that the turnovers of carbon and nitrogen are closely linked; most soil nitrogen is held in organic matter by C-N bonds, and release of nitrogen requires that the organic compound containing it be broken down. Much of the organic matter in soils is highly recalcitrant, either because it is chemically difficult to break down (cf. lignin) or because it is adsorbed on soil particles. In contrast, large pools of cations are held in available form on soil cation exchange sites, and most organic phosphorus (and much organic sulfur) is ester-bonded (C-O-P or C-O-S) rather than carbon-bonded (McGill and Cole 1981, Hunt et al. 1983). Ester bonds can be cleaved by extracellular enzymes without breakdown of the nutrient-containing compound.

In addition, microbial (decomposer) demand for soil nitrogen is substantial. The C:N ratio of microbes ranges from 6 to 12:1 (McGill et al. 1981), but the ratio for their substrates can be as high as 120:1 (for fresh litter) or even 500:1 (wood). Microbes decomposing such material hold nitrogen within their own biomass while they release carbon as CO\(_2\); they even withdraw available nitrogen from the soil solution (Bosatta and Staaf 1982, Berg and Ekbohm 1983). This microbial immobilization can restrict nitrogen availability to plants, especially in sites that are already nitrogen deficient (Gosz 1981, Vitousek et al. 1982). A number of models have been developed to deal with microbial mineralization/immobilization dynamics (cf. McGill et al. 1981, Aber et al. 1982).

A second major question is "why is nitrogen lost from disturbed or cultivated sites more readily than other elements?" The supply of mobile anions is limiting to the leaching of cations through soils to streams and
ground water (Johnson and Cole 1980); without anions, cations are retained on cation exchange sites. Phosphorus forms relatively insoluble complexes with aluminum, iron, and calcium, and hence is nearly immobile in soil (Nye and Tinker 1977). Sulfur is often (not always) present in excess and in addition can be adsorbed by soil sesquioxides (Johnson et al. 1980). Most nitrogen is held in organic matter. When released as ammonium, nitrogen can be held on cation exchange sites, but once oxidized to nitrate it is highly mobile in solution. Following disturbance, net nitrate production in soils is often delayed by microbial immobilization or by lags in nitrification (Vitousek et al. 1982). Given enough time (or a severe enough disturbance such as cultivation), nitrate production and leaching generally occur.

In addition, nitrate can serve as a terminal electron acceptor in respiration (in place of oxygen), and in consequence it can be reduced to N₂O and N₂ and lost to terrestrial ecosystems. The technology to measure such fluxes became available relatively recently (cf. Tiedje 1983), but balance-sheet calculations and initial measurements show this to be a substantial flux of nitrogen (cf. Rosswall 1983). Other pathways for gaseous losses of nitrogen occur: a small proportion is lost as N₂O during the autotrophic oxidation of ammonium to nitrate (but this can add up to a large total flux in fertilized sites), chemical denitrification of nitrite can occur in acid soils, and ammonia can be volatilized from basic soils or animal excreta (Woodmansee 1978).

Nitrogen loss from agricultural systems by all of these pathways can add up to 60% or more of the total nitrogen pool prior to disturbance. Such losses occur rapidly in wet tropical areas where decomposition is fast (1500 kg N/ha can be lost in 2-3 years; Nye and Greenland 1964), or more slowly in cool temperate regions (60-80 years for similar losses in the Great Plains; Haas et al. 1957). The pattern of loss is similar to either case - and the pattern is not substantially altered by nitrogen fertilizer as long as cropping is continuous. Sulfate losses are usually slower, while phosphorus losses are generally slight (unless erosion occurs) (Haas et al. 1961).

The third question—why is nitrogen fixation low in many nitrogen-deficient sites—is more difficult to address. Nitrogen fixation is an energy and phosphorus demanding process which is only carried out by a restricted set of organisms (Gutschick 1981, Rosswall 1981). Still, symbiotic associations between plants and microorganisms which are capable of fixing atmospheric nitrogen have arisen several times, and given the widespread importance of nitrogen deficiency it is surprising that nitrogen fixers don't have a greater competitive advantage in many circumstances.

Perhaps part of the reason for the relatively restricted occurrence of nitrogen fixers can be found in the amount of energy and phosphorus required. Gutschick (1981) calculated that about 16 moles of glucose are required to fix one mole of atmospheric nitrogen (including the cost of building the structures involved)—this energy would then not be available for growth and reproduction in a competitive community. Potentially nitrogen-fixing plants are most abundant in the tropics, where energy input is greatest. Walker and Syers (1976) examined phosphorus pools in soil development—they showed that available phosphorus peaks relatively early in a range of substrates. They further suggested that nitrogen is deficient early in soil development, and
that the combination of high phosphorus and low nitrogen causes a peak in nitrogen fixation relatively early in soil development in most sites (Walker and Syers 1976). After that time, phosphorus availability declines and high rates of nitrogen fixation can no longer be supported (Cole and Heil 1981). Similar peaks in nitrogen fixation early in succession could also occur in regions where communities turn over in fires (Gorham et al. 1979).

What are the implications of these patterns for global biogeochemistry? The most important (and perhaps the least understood) is the need to know what forms of nitrogen are lost from disturbed sites in different regions and under different conditions, and what controls the distribution of forms lost. Up to several thousand kg/ha (and as much as 15 Pg globally) of native soil N has been lost from agricultural land, and much of the nitrogen added in fertilizer annually (.04 Pg/yr) is similarly lost. The amount lost per year is likely to increase as deforestation in the tropics (where soil changes are most rapid) continues (Lanly and Clement 1979). Some of this N is lost as dissolved nitrate, which can decrease water quality (Magee 1977) and accelerate the eutrophication of coastal waters. Most of the rest is lost through denitrification to $N_2$ and $N_2O$. The $N_2$ produced is relatively benign, but the $N_2O$ produced plays a fundamental (and complex) role in atmospheric chemistry (Crutzen 1983).

Denitrification is an extremely heterogeneous process both spatially and temporally; and the fraction of nitrogen released as $N_2O$ can be similarly variable (Firestone et al. 1980). The overall process is dependent on a supply of nitrate and anaerobic conditions in the soil, but anaerobic microsites can occur on the scale of a single soil aggregate to otherwise well-aerated soils. Rates of denitrification are likely to be greatest, though, where soil is water-saturated (slowing oxygen diffusion) and decomposition is rapid. Measuring the rate of the process (and the fraction released as $N_2O$) will require high-quality measurements of fluxes in a few points coupled with a simultaneous assessment of soil conditions over a larger area.

Another concern is the area over which nitrogen is lost following forest clearing. Reasonable estimates of how much nitrogen is lost upon cultivation exist, and there are some estimates of how fast it is lost in different regions, but our estimates of the rates of deforestation (especially in the tropics) are questionable. An estimate of rates of land conversion based on ecologically meaningful land units (such as the Holdridge life zones – Holdridge et al. 1971) would be most helpful.

A related concern is the effect of intensity of disturbance on nitrogen balances. The range of practices now in use in agriculture (cf. conventional tillage, minimum tillage, no-till) and forestry (cf. whole-tree vs. stem-only harvest, burning, site preparation) can substantially alter the retention and/or loss of nitrogen and the pathways by which it is lost. These were legitimately considered second-order variations in the past but they must be incorporated in the more realistic global models now under development.

Another important implication of this picture of terrestrial nitrogen cycling is that the nitrogen added to intact forests as a result of anthropogenic emissions is causing some increase in carbon fixation and
storage (cf. Melillo and Gosz 1983). The limits of this storage have probably been exceeded in the most heavily impacted areas, where in addition this "fertilization" is confounded by sulfuric acid and oxidant air pollution (Ulrich et al. 1980). The magnitude of this carbon storage is not known, although it is certainly far from sufficient to balance the global carbon budget (especially since lowland tropical forests are likely to prove largely unaffected by added nitrogen).

A final area of interest is of course nitrogen fixation. Here a relatively simple technique has allowed many measurements of potential nitrogen fixation to be made, but our understanding of the ecological regulation of the process is insufficient to yield generally applicable models.

REFERENCES


Vitousek, P.M. 1983. Litterfall, nutrient cycling, and nutrient limitation in tropical forests. Ecology 64, in press.


Table 1. A global inventory and budget for nitrogen in terrestrial ecosystems. All pools and fluxes in Pg (10^15 g). Drawn from the summary in Söderlund and Rosswall (1982).

<table>
<thead>
<tr>
<th>Pools</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant biomass</td>
<td>12.0</td>
</tr>
<tr>
<td>Animal biomass</td>
<td>0.2</td>
</tr>
<tr>
<td>Microorganism biomass</td>
<td>0.5</td>
</tr>
<tr>
<td>Litter</td>
<td>2.5</td>
</tr>
<tr>
<td>Soil organic N</td>
<td>300.0</td>
</tr>
<tr>
<td>Soil inorganic N</td>
<td>16.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluxes</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Through plants</td>
<td>2.0</td>
</tr>
<tr>
<td>Through microorganisms</td>
<td>2.5</td>
</tr>
<tr>
<td>Biological nitrogen fixation</td>
<td>0.14</td>
</tr>
<tr>
<td>Industrial nitrogen fixation</td>
<td>0.04</td>
</tr>
<tr>
<td>Deposition</td>
<td>0.08-0.24</td>
</tr>
<tr>
<td>Denitrification</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Ammonia volatilization</td>
<td>0.04-0.09</td>
</tr>
<tr>
<td>River runoff</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Fig. 1. The Major Pathways of Nitrogen Cycling Within Natural Ecosystems.
RECENT STUDIES OF THE OCEAN NITROGEN CYCLE

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These remarks will be very brief as the subject was reviewed recently (Hattori, 1982) and a major new work is in progress (Carpenter and Capone, in press). The nitrogen cycle in the ocean is dominated by the activities of organisms. External nitrogen inputs from land and from the atmosphere are small compared with rates of consumption and production by organisms and with rates of internal rearrangements of nitrogen pools within the ocean (Hattori, 1982).

I. DESCRIPTION OF THE OCEANIC NITROGEN CYCLE

The chief reservoirs of nitrogen are, in decreasing order of size: nitrogen in sediments, dissolved N\(_2\), nitrate, dissolved organic nitrogen (DON), particulate organic nitrogen (PON) (mostly organisms and their by-products). The quantities of nitrogen in these pools are shown in Table 1. The DON and PON estimates of Table 1 are very approximate; only a few deep profiles of PON are available and not all ocean regions are represented in the PON calculations, for example.

The biogenic fluxes of nitrogen were also reviewed recently by Hattori (1982). He suggested the photosynthetic formation of PON represents a consumption of ammonium of about 6.5 \( \times 10^{15} \) gN y\(^{-1}\) and of nitrate about 1.5 \( \times 10^{15} \) gN y\(^{-1}\). Corresponding estimates from Eppley and Peterson (1979) were 3-5 \( \times 10^{15} \) g ammonium N y\(^{-1}\) and 0.3-0.5 \( \times 10^{15} \) g nitrate-N per year (Table 2). The larger estimates are probably the more consistent with the 500 year mean replacement time of the abyssal waters of the world ocean of Stuiver, Quay and Ostlund (1983). But the present uncertainty in these biogenic fluxes is at least a factor of three. Nevertheless, the rate of PON decomposition in the surface layer must be comparable to the rate of ammonium consumption, and at the same time the nitrate consumption rate will be similar to the rates of a) sinking of PON out of the surface layer and its decomposition at depth, b) the rate of nitrification at depth, and c) the rate of nitrate return to the surface layer by upwelling (Eppley, Renger and Betzer, 1983).

I think it is fair to say that the biologists have been disappointed that nitrogen fixation in the ocean, much studied in the 1970's, contributes so little to PON formation. Hattori (1982) suggests a flux only 1.1 \( \times 10^{13} \) gN y\(^{-1}\).

McElroy (1983), Walsh et al. (1981) and Hattori (1982) recently considered sources and sinks of N in the ocean (Table 3). The values are similar to those of Simpson et al. (1977) even though new data and concepts have been used in the latest revisions.
II. INTERACTIONS WITH OTHER BIOGEOCHEMICAL CYCLES AND MODELING APPROACHES

One of the most interesting generalizations in oceanography is the Redfield ratio: that the proportions of dissolved N and P are similar to their proportions in organisms, about 15 or 16 to 1 by atoms. Similarly, oxygen and carbon are consumed to form organisms and released on the decomposition of the organisms in fairly uniform proportions relative to N and P, i.e., ~270 O: 106C: 16N: 1P (Redfield, Ketchum and Richards, 1963). The uniformity of these ratios insures fairly close coupling in the processing of these elements in the oceans by organisms. This stoichiometry has provided the basis for a variety of models of biogenic production and consumption relative to ocean circulation.

It should be noted that nitrogen inputs to the surface layer of the subtropical ocean, including the vast central gyres, drive the biogenic production. Baes (1982) and McElroy (1983) suggested that this interaction between the nitrogen and carbon cycles may be significant relative to the ocean as a sink for atmospheric CO2. Walsh et al. (1981) postulated a sink for carbon via sediment burial of biogenic carbon, produced by plankton, on the upper portions of the continental shelf, as off New York. Eppley and Peterson (1979) argued that nitrate inputs to the surface layer of the central ocean would not provide such a sink since each nitrogen atom transported upward from depth would be accompanied by carbon atoms in the Redfield ratio.

Biogenic production/consumption fluxes in the ocean seem to be very responsive to interannual changes in ocean climate (cf. Chelton et al., 1982). The present warm water conditions in the eastern Pacific underscore the importance of such relationships. Climate-related changes in biological production in the ocean are no doubt brought about by changes in stratification and mixed layer depth, ice-edge phenomena, and other features as well as changes in the rate of nutrient input to the surface layer. Reconstruction of the history of such changes over geologic time presents a fascinating challenge, as does prediction of future changes associated with increasing atmospheric CO2. McElroy (1983) suggested that "variations in productivity associated with changes in nitrogen are expected to influence the distribution of carbon between the atmosphere-biosphere-upper ocean and lower ocean" on a time scale of $10^3$-$10^4$ years based on denitrification in upwelling regions.

III. NEEDS FOR INFORMATION

We have before us hypotheses to the effect that climate-related changes in the ocean nitrogen cycle influence the global carbon cycle. Oceanographers have described variability in primary production related to changes in nitrate input to the surface layer on time scales varying from days to 1-2 years. Interannual changes in upwelling regions could lead to marked differences in POC and PON burial at shelf-slope depocenters as visualized by Walsh et al. (1981) on time scales as short as 1-2 years. McElroy (1983) suggested that changes in N supply to the ocean on $10^3$-$10^4$ year time scales, related to ice sheets, sea level changes, and the alternate exposure and flooding of continental shelves, may be important for ocean production and the atmospheric CO2 content. One can imagine intermediate time scales of interest to ocean
productivity due to climate-related changes in bottom water formation, leading to changes in the stratification and nutrient input rates to the surface waters of the great subtropical gyres. Likewise there is evidence for smaller temperature gradients between the deep ocean and its surface layers in past geological epochs (Schopf, 1980, Figure 4-11). A smaller temperature gradient implies greater mixing and increased rates of nitrate input to the surface layer in pre-glacial times. It is easy to imagine that nutrient input rate to the central subtropical oceans could have been high enough in the past such that stratification and illumination could regulate production rather than nutrient input rates as we now think. Oceanic primary production could have been much greater than at present, or not, depending upon mixing depths and the mean irradiance experienced by the phytoplankton. One wonders if increases in atmospheric CO₂ and climate warming will lead to change in the regulation of productivity in the central oceans. Models exist to estimate local changes in carbon and nitrogen in the surface ocean, but probably not for assessing global changes in the carbon and nitrogen cycles such as a change in the regulatory control of oceanic productivity might bring about.

To a first approximation ocean productivity is proportional to the surface concentrations of plankton measured as chlorophyll (Smith and Baker, 1978) and synoptic measurements of surface chlorophyll are now possible with the Coastal Zone Color Scanner aboard the NIMBUS 7 satellite and the error of estimate is only about 30-40% or less (Gordon et al., 1983). This technology appears to provide a means of monitoring synoptically the plankton content of the surface ocean. If this monitoring could be carried out for several years or decades, concomitant with continuing advances in conventional research in oceanography, it may be possible to evaluate less ambiguously the relations discussed above and to comprehend better both the past and the future relations between climate, ocean productivity and the related biogeochemical cycles.

REFERENCES


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Table 1. Ocean Nitrogen Cycle. Sizes of N-reservoirs

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Size in grams N</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediments</td>
<td>$4 \times 7.8 \times 10^{20}$</td>
<td>Simpson, et al. (1977)</td>
</tr>
<tr>
<td>$N_2$</td>
<td>$2.0-2.2 \times 10^{19}$</td>
<td>Simpson, et al. (1977)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>$5.8 \times 10^{17}$</td>
<td>*</td>
</tr>
<tr>
<td>Dissolved organic nitrogen</td>
<td>$3.8 \times 10^{16}$</td>
<td>**</td>
</tr>
<tr>
<td>Particulate organic nitrogen</td>
<td>$5 \times 10^{14}$</td>
<td>†</td>
</tr>
</tbody>
</table>

*Assume ocean volume contains an average nitrate concentration of 30 µM.

**Assume ocean volume contains an average DON content of 2 µM (G. A. Jackson and P. M. Williams, 1983. Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. Manuscript.)

†Assume average PON concentration is 3 µg l⁻¹ in the upper 100 m of the ocean and 0.25 µg l⁻¹ below this depth (see Williams, Carlucci and Olson, 1980).
Table 2. Biological Fluxes of Nitrogen in the Ocean

<table>
<thead>
<tr>
<th>Process</th>
<th>Flux gN y(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoplankton consumption of nitrate*</td>
<td>1.5 x 10(^{15})</td>
<td>Hattori (1982)</td>
</tr>
<tr>
<td></td>
<td>0.5-1 x 10(^{15})</td>
<td>Eppley and Peterson (1979)</td>
</tr>
<tr>
<td>Phytoplankton consumption of ammonium</td>
<td>6.5 x 10(^{15})</td>
<td>Hattori (1982)</td>
</tr>
<tr>
<td></td>
<td>3-5 x 10(^{15})</td>
<td>Eppley and Peterson (1979)</td>
</tr>
</tbody>
</table>

*The rate at which phytoplankton consume nitrate will be approximately equal to the sinking flux of PON out of the surface layer, the rate of PON decomposition and nitrate formation (nitrification) at depth, and the rate of nitrate return to the surface layer by upwelling (Dugdale and Goering, 1967; Eppley and Peterson, 1979; Eppley, Renger, and Betzer, 1983).
<table>
<thead>
<tr>
<th>Sources</th>
<th>Flux in gN y(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>River input</td>
<td>(2 \times 10^{13})</td>
<td>McElroy (1983),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hattori (1982),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Walsh et al. (1981)</td>
</tr>
<tr>
<td>Atmospheric input</td>
<td>(2 \times 10^{13})</td>
<td>Hattori (1982),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>McElroy (1983)</td>
</tr>
<tr>
<td>Sewage</td>
<td>(1 \times 10^{13})</td>
<td>Walsh et al. (1981)</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burial</td>
<td>(3 \times 10^{13})</td>
<td>Walsh et al. (1981)</td>
</tr>
<tr>
<td>Denitrification</td>
<td>(3 \times 10^{13}) in water</td>
<td>Hattori (1982)</td>
</tr>
<tr>
<td></td>
<td>(2 \times 10^{13}) in sediment</td>
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ENERGY AND WATER CYCLES
MODELING LONG-TERM CHANGES IN FORESTED LANDSCAPES AND THEIR RELATION TO THE EARTH'S ENERGY BALANCE

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I. INTRODUCTION

Despite the relatively small portion of total incoming solar radiation that ultimately maintains the earth's vegetation, the energy balance of the earth and the associated hydrologic cycle are strongly influenced by the earth's land cover (e.g. Gates 1971, Woodwell 1970). Any changes in the land cover as a result of either natural or human disturbance and the succession that follows such disturbance can be expected to induce shifts in the energy balance and water cycles (Sagan et al. 1979). If the perturbations are sufficiently large, the climate will be altered with a subsequent influence on the dynamics of terrestrial plant communities. This coupling between the physical aspects of the energy balance (and water cycles) and the world's vegetation has been recognized for some time. The mechanisms of the coupling of energy, water and vegetation have also been studied at a number of field sites where intensive measurements are available (e.g. Gates 1980, Miller 1981). These investigations involved observations of phenomena occurring at time scales of less than one year and under essentially steady state conditions (e.g. micrometeorology of forest stands).

In addition to the direct influence of terrestrial vegetation on the earth's energy balance, there is an indirect effect from changes in the composition of gasses in the atmosphere induced by alterations and changes on the vegetative landscape (e.g., Crutzen et al. 1979). The contribution to increasing atmospheric CO₂ concentration attributed to decreases in terrestrial carbon storage as a result of forest clearing may be the principal example of such an indirect influence. Changes in the atmospheric CO₂ alter the earth's energy balance. The resultant climate change in turn influences the land cover and also alters the dynamics of terrestrial ecosystems in response to disturbance. For forest ecosystems, the characteristics which determine these interactions with the earth's energy balance are on time scales from decades to centuries.

In this paper, we discuss the dynamics of the forested parts of the earth's surface on time scales from decades to centuries. A set of computer models developed at Oak Ridge National Laboratory and elsewhere are applied as tools for this investigation. These models simulate a landscape by duplicating the dynamics of growth, death and birth of each tree living on a 0.10 ha element of the landscape. This spatial unit is generally referred to as a gap in the case of the forest models. The models have been tested against and applied to a diverse array of forests (Table 1) and appear to provide a
reasonable representation for investigating forest-cover dynamics (Shugart and West 1981). Because of the climate linkage, one important test is the reconstruction of paleo-landscapes (Solomon et al. 1979, 1983). Detailed reconstructions of changes in vegetation in response to changes in climate are crucial to understanding the association of the earth's vegetation and climate and the response of the vegetation to climate change.

The tabulation of the model characteristics in Table 1 indicates the time scales of abiotic variables that might drive an ecosystem displaying responses like those of a gap model. One important abiotic driving variable that is important in the domain of applicability of gap models is listed by Delcourt et al. (1982) under the category of climatic fluctuations. Mitchell (1976) has discussed the overall pattern of variation in the earth's climate and has synthesized this discussion as a general diagram of climate variation in the frequency domain. Using Mitchell's display of the pattern of climate variation (Fig. 1a) that spans 14 orders of magnitude, one can inspect the range of climate periodicities that are within the temporal range of gap models. The upper temporal scale of gap model applications is on the order of 10^4 years for some of the paleo-landscape reconstructions (Table 1). The lower limit is the annual computation step used in the model to grow trees. By transforming the spectral analysis of Emanuel et al. (1978a) for an east Tennessee mixed deciduous forest (the FORET model) to the scales used by Mitchell (1976), one can also determine the expected performance of a gap model in the range of gap model applications (Fig. 1a). The part of Mitchell's diagram in the temporal range of the gap model is reasonably uniform with respect to major large periodic components in the climate. This part of Mitchell's diagram was designed to be consistent with Quaternary climate history published in Fig. A.2 of the U.S. Committee for the Global Atmospheric Research Program (1975).

The range of gap model tests and applications is slightly longer than the major astronomically dictated climate variations (1 year and 1 day with harmonically related peaks at 6 and 3 months and at 12 and 6 hours). The range does overlap with the longer, 2500-year periodicities that Mitchell associates with the "Neo-glacial (Little Ice-Age) cycle of the Holocene." There is also some overlap with the "Quaternary ice-volume shifts" of periods near 20000 years. Behavior of forests in response to these longer periodicities is the focus of attempts to reconstruct pollen chronologies. Even though the periodicities in climate are not as pronounced over the range of the gap models, the spectral content of the responses of the models is quite rich in this range (Fig. 1b). The models display a strong 500-year periodicity that is associated with changes in composition of the canopy trees. There is a 200-year canopy replacement cycle that is the subject of the discussions of the forest regeneration cycle (e.g. Watt 1947). There is also a 100- to 50-year periodicity that appears to be related to mortality events in subcanopy trees. Gap models have not been inspected for periodic components longer than 500 years (see Emanuel et al. 1978a).

The fluctuations in one of the more important driving variables in the models (climate) are essentially random on the time periods to which gap models have been applied (1 to 10^4 years), but the responses of the models are comprised of a fairly rich set of cyclic fluctuations in this range.
These important periodicities in the model performance are associated with canopy replacement processes. Given a notion of the range of application of theories derived from gap models and a general inspection of the dynamics of both the models and one of the important driving variables in this range, it is appropriate to inspect some of the theoretical implications of these models with respect to the earth's global energy budget at longer than annual time scales.

II. THE EXPECTED BIOMASS DYNAMIC OF FORESTED LANDSCAPES

A small patch of forested landscape has a longer term dynamic pattern that is characterized by a cycle (Watt 1947, Bormann and Likens 1979, Shugart and West 1981, Fig. 1b). Following the death of a large tree, a size cohort of small trees in the break in the forest canopy begins to grow. Some of the trees in the cohort may have been in the vegetative layers below the dead canopy tree and some of the trees may germinate after the dominant tree dies. The trees grow and compete with one another. According to the sizes and species attributes of the particular assemblage of trees at the site (and with a degree of randomness), some of the trees die as others grow toward the canopy. Eventually a few and ultimately one tree comes to dominate the forest canopy in the small area. When this canopy-dominant tree eventually dies a new cohort begins to grow and the cycle is closed. Whitmore (1982) has asserted that this underlying pattern is the unifying aspect in the dynamics of the forests of the world.

If the mass of material on a small (ca 0.10 ha) part of a forested landscape were plotted over time, the resultant graph of this biomass (Fig. 2) would be a cyclical saw-toothed curve. One can think of the total landscape as a mosaic of such small patches and use a gap model to predict the fate of each of these patches. By tabulating the fate of hundreds of such patches one can obtain the expected response of the mosaic landscape over time (Fig. 3).

Gap models incorporate explicitly the regeneration delays, age-structure effects and mortality responses that are often implicit in delay functions incorporated in alternate formulations. The response of interest is the successional change of a landscape composed of many patches when all the patches are altered by a single disturbance event and the patches each begin a synchronized regrowth. If there are no strong interactions among the patches that make up the forest mosaic, this case can be simulated by summing the responses of several gap model runs with each run initiated on a bare plot. Such a Monte Carlo simulation of a landscape is based on the assumption that each patch is independent of the others.

The mosaic nature of forested landscapes is an old and well-established paradigm in ecology (e.g. Aubreville 1933, 1938; Watt 1925, 1947). Gap models have been used to construct the landscape dynamics of several forests (Bormann and Likens 1979, Shugart and West 1977, 1981). Some forested landscapes are dominated by a single species of tree and the total landscape response is a consequence of the species' particular ecological attributes. The pattern of biomass change over time following a single synchronous event that removes the biomass from several of the mosaic patches that make up the landscape can be 231
taken as the intrinsic pattern of dynamics expected from forests in general. The expected response in a monospecies landscape is for the landscape biomass to increase as the trees on each of the stands grow and compete. Eventually a single large tree comes to dominate the others at each of the patches. When the trees in this cohort reach their maximum size, the biomass of the landscape is at a maximum. The even-aged initial cohort begins to die more or less synchronously and the forest cover on the landscape becomes a mixed age forest with enhanced regeneration and survival in canopy gaps. If the mortality is synchronized across all patches making up the landscape, then the regeneration of the second cohort is also synchronized. A high degree of such synchrony produces an oscillatory return of the landscape biomass dynamics to an equilibrium; a lesser degree produces a less oscillatory return.

For example, the response expected at landscape scale in Arkansas for stands dominated by loblolly pine (Pinus taeda) under the influence of fire (Fig. 3) features (as one would expect for a monospecies dominated landscape) a biomass overshoot response and a return to stochastic equilibrium. A slighter overshoot is in evidence for simulations of alpine ash (Eucalyptus delegatensis) in the Australian Alps and without wildfire (Fig. 3). In forests of low diversity and in which there is a composition shift of the dominant species following the breakup of the even-aged initial canopy (Fig. 3), the overshoot can be amplified if the initially dominant species are larger than the species that come to dominate the mixed-size forest that develops over long periods of time. The case shown in Figure 3 is for Arkansas forests without wildfire and in which oak (mostly Quercus falcata) replaces pine (mostly Pinus taeda) as the dominant species. Even more dramatic cases of such a landscape biomass dynamic are found in the successional sequences involving Douglas fir (Pseudotsuga menziesii) in the North American Pacific Northwest (Fugimori et al. 1976) and involving Eucalyptus regans and E. obliqua in Tasmania (Gilbert 1958, Jackson 1968).

In other systems of low diversity, a compositional shift at the time of first canopy break-up does not amplify the biomass overshoot response but the overshoot behavior is still quite discernable. This case has been discussed in detail by Bormann and Likens (1979) for the northern hardwood forest. The persistence of such dynamics in the presence of moderate diversity is a consequence of the similar size and longevity among the dominant species causing the biomass dynamics of the landscape elements to have the synchrony needed to produce the landscape overshoot response. Some low diversity forests (Fig. 3, Australian alpine ash forest with fire) show a loss of the landscape biomass response.

Generally in diverse forests that have a mixture of growth rates, tree species sizes and mortality rates, the synchrony across the patches that make up the landscape is lost due to the differences in the attributes of the species that are locally abundant at a given patch (Fig. 3). Similarly, some monospecies forests may feature irregular regeneration and can thus be desynchronized across the patches of the landscape mosaic (with a loss of landscape biomass overshoot).
An important implication of these studies is that the dynamics of the earth's two large living carbon reservoirs, the low diversity Boreal Forest and the high diversity Tropical Rain Forest, probably have very different patterns in their biomass dynamics following a large scale change.

III. ASSESSING THE POTENTIAL EFFECTS OF CARBON DIOXIDE FERTILIZATION

Accurate measurements of the concentration of CO$_2$ in the atmosphere since 1958 at Mauna Loa Observatory, Hawaii (Fig. 4) and at the South Pole indicate an increasing trend attributed in large part to the release of CO$_2$ to the atmosphere by fossil fuel combustion (see Baes et al. 1977). The change in atmospheric CO$_2$ levels that result from perturbations such as fossil fuel combustion depends on the interactions among the atmosphere and the other carbon reservoirs, particularly the inorganic pool of carbon in the world oceans and the carbon in the terrestrial biosphere. On the long term, the oceans are thought to be the primary sink for excess carbon from the atmosphere (Broecker et al. 1979). Over the period of substantial fuel combustion, the total storage of carbon in terrestrial ecosystems has probably decreased with forest clearing and other land use changes (Bolin 1977, Woodwell et al. 1978). However, particular regions have acted as net sinks for carbon for significant periods of time.

Calculations aimed at reconciling the observed change in atmospheric CO$_2$ concentration and estimates of the uptake of carbon by the oceans indicate the existence of a net sink for carbon over the period of the atmospheric CO$_2$ measurement records. This sink is in addition to that provided by the oceans (Killough and Emanuel 1981, Keeling 1982, Broecker et al. 1979). An increase in terrestrial carbon storage stimulated by increasing atmospheric CO$_2$ levels has been suggested in several studies as a means by which the terrestrial component of the carbon cycle could have acted as a net carbon sink with respect to the atmosphere (Oeschger et al. 1975).

Increases in plant productivity under elevated CO$_2$ concentrations have been observed in numerous greenhouse experiments and a similar CO$_2$ fertilization might also be expected under field conditions in the absence of other growth limiting factors (e.g. intensively managed agriculture or forestry). Kramer (1981) discusses this problem with a view to the plant physiological aspects of the problem and notes that it is often assumed that the increasing carbon dioxide concentration of the atmosphere will automatically bring about an increase in global photosynthesis and dry matter (biomass) production. These assertions are based on the assumptions that the rate of photosynthesis is limited chiefly by CO$_2$ concentration and further that the rate of productivity is limited chiefly by a low potential rate of photosynthesis. Kramer (1981) in his review points out that there are potential difficulties with both of these assumptions and that, “we cannot make reliable predictions ... until we have information based on long-term measurements.” One question that can be approached using models is to determine the maximum effects if both of the assumptions that Kramer identifies were met and the response of each tree in the stand was similar. The question is, “What is the biomass response expected of a forest if the growth rates of all trees are uniformly increased in a systematic fashion?”
The models used in this investigation are the FORET, FORAR, FORICO, KIAMBRAM and BRIND models. A brief description of the models and a tabulation of the tests (see also Table 1) that have been used to inspect their reliability are:

1. **FORET** - A model simulating the dynamics of forests in the Southern Appalachians. The model has successfully been tested in its ability to simulate pre- and post-chestnut blight forests in Anderson Co., Tennessee; to reconstruct a 16,000 year fossil pollen chronology from a site in the Cumberland Plateau, Tennessee stand structure and measured tree ring increments in Anderson Co., Tennessee; to duplicate patterns of vegetation along altitudinal gradients in the Great Smoky Mountains National Park.

2. **FORAR** - A model of 33 tree species in mixed oak-pine forests in southern Arkansas including the effects of wildfire. The model has been tested on its ability to predict forest composition in the region based on a 1859 reconnaissance of the region; to reproduce yield tables for loblolly pine (Pinus taeda); to predict structure and composition of upland forests on southern Arkansas. The model has also been applied to design management schemes to preserve habitat for the rare and endangered Red-cockaded Woodpecker (Dendrocopus borealis).

3. **BRIND** - A model of 18 arborescent species found on southeast-facing slopes between elevations of 900 and 2400 m in the Brindabella Range, Australian Capital Territory. The model is able to predict the qualitative pattern of tree replacement at the 1600 m elevation; to predict the response to wildfire of communities at different altitudes in the Brindabella Range; to predict the altitudinal zonation of forests between 900 and 2400 m; to predict field data on means diameter, basal area and stocking density of alpine ash (Eucalyptus delegatensis) stands of different ages.

4. **KIAMBRAM** - A model of the subtropical rain forest in the vicinity of the New South Wales/Queensland border. Including 125 species, the model is able to compare favorably with stands of known age in Lamington National Park, Queensland and to predict the abundances and basal areas in mature forests at Wiangaree State Forest, N.S.W. The model has also been used to evaluate timber harvest schemes for Australian subtropical rain forest.

5. **FORICO** - a model of the tabonuco (Dacryodes excelsa) forests of the Luquillo Experimental forest in northeastern Puerto Rico. The model simulates the dynamics of some 36 common species in subtropical montane rain forest. The model includes the effects of hurricanes and has been tested on its ability to duplicate diameter frequency curves for forests of different known ages and on its ability to reproduce dominance/diversity curves. All these models successfully simulate a considerable variety of the longer-term responses of forested landscapes and are reasonable tools to assess the potential
consequences of perturbations on forests. The models are particularly useful to inspect the potential consequences of carbon dioxide fertilization since the fundamental equation (see Botkin et al. 1972, Shugart and West 1977) used in the models to calculate the annual increase in the diameter of a tree in the simulated stand is derived from a simple growth model that balances photosynthate production against the respiratory cost of maintaining living tissue. A change in the rate of photosynthate production can be simulated by adjusting the "G" growth parameter directly.

To inspect the potential magnitude of a fertilization of the photosynthate production, the intrinsic growth rate (G) of each simulated tree was systematically increased by 100%, by 50%, by 15%, by 12.5%, by 6.25% and by 3.125% (six levels of photosynthate change) for 50 replicate computer runs of a duration of 500 simulated years each for 7 different gap model cases (Fig. 5). The percentage change in the amount of organic matter in living plants (phytomass) was determined by averaging the phytomass on each of 50 simulated plots over the time period of 300 to 500 years and comparing these results to a control with no fertilization of the photosynthesis production process. This comparison amounts to judging the magnitude of the gain of total carbon on a forested landscape that is represented by a set of samples (each sample being one 0.10 ha simulation run of the gap model). These responses are complex at low levels of growth enhancement but are generally linear at higher levels of fertilization. One case (the FORET model; Fig. 5g) actually demonstrates a diminution of phytomass at low fertilization levels. Inspection reveals this is caused by the uniform increase in growth rate allowing an increased survival of suppressed understory trees. These trees are of species that tend to grow more slowly and attain a smaller mature size, hence the competition-induced change in total phytomass.

The increase in phytomass of all forests examined ranges from 20% to 60%. The increase is not due to an elevated maximum phytomass at any point in the landscape. It is caused by an increased rate of filling of gaps made in the canopy. For this reason forests with a high rate of disturbance and more growth associated with gap filling (Fig. 5a, b) produce a larger landscape-scale fertilization response. In the present simulations, the amount of phytomass on a single simulated plot is limited by shading (for the smaller trees) or by the maximum size (for the largest trees). In actual forest systems, other limiting factors such as nutrients could likely reduce any carbon dioxide induced growth enhancement.

These results should be regarded as the maximum expected for a uniform increase in growth rate across natural forested landscapes. If the changes in growth rates were not uniform across all the species involved, then the potential expression of carbon dioxide induced fertilization effects could involve changes in the community composition and could be very complex.

IV. RECONSTRUCTING PREHISTORIC VEGETATION

Pollen analysis techniques are often used to reconstruct the composition of prehistoric plant communities. Reconstruction of the changes in forest communities over the past 16000 years at Anderson Pond in Tennessee has
already been mentioned as a test on the FORET model (see Table 1). The principal advantages of the use of pollen grains for paleological reconstruction are:

1. Pollen grains are ubiquitous, being produced in about the same amounts every year.

2. Species composition of the pollen grains is related to the species composition of the surrounding forests.

3. Most pollen grains can be identified at the genus level and some can be identified to the species level.

4. Pollen deposited in anaerobic conditions of lakes and bogs is preserved almost indefinitely in the contemporaneous sediments.

For all these positive aspects, it is fair to say that the reconstruction of prehistoric forest patterns from fossil pollen data is an art as well as a science. In Europe these reconstructions have been accomplished by relating fossil pollen percentages (proportions) to tree frequencies (e.g. Anderson 1970, 1973, Faegri and Iverson 1975) and then sorting out separate influences from the pollen diagrams. Using this sort of approach, Iverson (1949) was able to detect prehistoric land use patterns in Denmark. Iverson (1964) was also able to detect the influence of soil development over time in other pollen reconstructions as Tauber (1965) has been able to do for climate change.

Due at least in part to the increased complexity of the North American forest flora, the reconstruction of forest communities by applying a pollen/tree-taxon representation value that has been so successful in Europe has not worked nearly so well in North America (Davis and Goodlett 1960, Davis 1963, Janssen 1967) although there is promise in recent work in this area (Webb et al. 1981, Heide and Bradshaw 1982). The more successful approach has been to match the multiple proportions of fossil pollen to a modern pollen pattern collected from the surface samples of a lake or bog (McAndrews 1973, Davis 1969). If the fossil pollen is sufficiently similar (Ogden 1969, 1977) to the modern pollen then one assumes that they were derived from similar forests. The validity of this assumption is improved when lake basing used to build the modern "reference" data base are of similar size and morphometry to the lake containing the fossil pollen.

In the same way, one can use the weather station data from near the sites involved in calibrating the modern pollen analog to provide a tool for paleoclimatic reconstruction (e.g. Delcourt 1979). The more direct method to accomplish this is to relate modern climate to pollen without reconstructing the forests as an intermediate step. This approach uses multivariate statistics ("transfer functions") and was initially used by Cole (1969) and Webb and Bryson (1972).

Bryson and Wendland (1967) suggested that in North America but not in Europe the colder summers during full-glacial time may have been accompanied by winters with temperatures that were little different from those of today. This concept was based on relating features of the Laurentide ice sheet to
biotic anomalies, in particular, to explain the presence of thermophilous deciduous trees growing within boreal conifer forests over large geographical areas (Wright 1968, Birks 1976), King 1981, Delcourt 1979, Ogden 1966, Watts 1975). Such mixtures have little areal extent at present. Traditional approaches to analysis of prehistoric plant communities (Davis 1969, Webb and Bryson 1972, Webb et al. 1981) are precluded when no modern analogs exist. Since the occurrence of this vegetation has been thought of as a response to climate, the problem is to determine if any of several plausible hypotheses on the climate during full-glaciation are simultaneously consistent with fossil pollen data and with simulated response from the FORET Model to these climates.

As an application of the FORET model to explore this problem, Solomon et al. (submitted) developed a series of model simulations that explored the vegetation pattern expected for four different scenarios of the climate at a point during the last full-glacial. The forest reconstructed (Delcourt 1979) at Anderson Pond, White County, Tennessee about 16000 years ago has the mixed boreal and deciduous forest character and was used as the test data to judge the four simulations. The four cases were:

1. The Periglacial Climate Scenario. July temperatures were lower by 11.7°C and January temperatures were higher by 1.4°C. This case is developed from Moran's reconstruction of full-glacial climatic conditions based on periglacial indicators.

2. The Climate Model Scenario. This case is based on Adem's (1981) reconstruction of a full glacial climate using an energy balance climate model with enhanced albedo to map January, April, July and October temperatures. This case featured a late cold summer (12°C colder than present) and a less strongly altered winter temperature regime (4.6°C less than present).

3. The Traditional Pollen Analog Scenario. This climate was produced by matching the pollen pattern for Anderson Pond in 16000 BP with the most similar present day analog (Davis and Webb 1975, Webb and McAndrews 1976). Because of the mixed nature of the prehistoric forest there are no suitable modern analogs and the best of the imperfect matches was used. The matching to a traditional pollen analog indicates that the climate at Anderson Pond 16000 years ago was most like that of Kenora, Ontario, today.

4. The Composite Pollen Analog Scenario. Following the logic of Bryson and Wendland (1974) and Bryson and Kutzbach (1974) a composite was developed by using only the boreal taxa to calibrate the summer climate and using the deciduous taxa to determine the winter climate. Under this reconstruction the climate at Anderson Pond (16000 BP) had summers like those of Kenora, Ontario but winters like Duluth, Minnesota.

For each of the four climate scenarios, forest succession was simulated under three different soil and slope conditions: (1) rolling uplands adjacent to Anderson Pond (and the likely source of much of the pollen in the pond)
with well-drained loams; (2) steep south-facing slopes (temperatures 2°C warmer) with a thin loamy surface mantle and a plastic clayey subsoil; (3) steep north-facing slopes (temperatures 2°C cooler) also with a thin loamy surface mantle and a plastic clayey subsoil.

Results of the simulation are shown in Fig. 6. The pollen spectrum for 16500 to 15500 14C-years ago from Delcourt (1979) appears along the left margin. During that time, spruce pollen ranged from 15-25%, pine averaged from 50-80% and deciduous trees varied from 10-20% of the total pollen. A summary of the response of the simulated forest under the different scenarios is:

1. The Traditional Pollen Analog Scenario. The simulated winter conditions were too cold to allow oak and other thermophilous trees to grow and survive in any of the simulation cases except for a small proportion of the south-facing slopes. The model produced a boreal forest that is much like that found growing near Kenora, Ontario at the present time but it is not particularly like that found 16000 BP at Anderson Pond.

2. The Climate Model Scenario. Under the climate model scenario, the growth of thermophilous trees was also greatly reduced but in this case by the coldness of the summers. This is logical since the growing conditions simulated by the Adem (1981) climate model correspond to what is now the northern limit of the closed boreal forest rather than the southern limit (Hare and Thomas 1979, Rowe 1977). This scenario provides the forest simulation model with little power to reproduce the Anderson Pond 16000 BP conditions.

3. The Periglacial Climate and The Composite Pollen Analog Scenarios. Both these scenarios produced responses from the forest simulation model that are consistent with pollen spectra from Anderson Pond. The two scenarios produced forest responses that were similar except for the conditions on the north-facing slopes. These differences are due to the differences in moisture conditions in the summer in the two scenarios.

The overall indication from these results is that a decrease in seasonality associated with the full-glacial climate could indeed produce the stable mixed boreal and deciduous forest ecosystems not presently extant in North America but recorded in the fossil pollen at Anderson Pond, Tennessee 16000 years ago.

V. CONCLUSIONS

In this paper, we have attempted to explore the longer term dynamics of the vegetative cover of the earth's landscape as a consequence of a set of forest dynamics models. The important implications of this work in terms of the earth's energy balance are a consequence of the secondary effects (on albedo and on the \( \text{CO}_2 \) dynamics of the earth's atmosphere in particular) of
changing the earth's terrestrial surface and not a consequence of the relatively small amount of energy actually stored in or released from the vegetation. The information that is most important to the understanding of the longer than annual energy budget of the earth is:

1. There are general patterns of biomass dynamics expected from forests in different places in the world but these patterns can be generalized to a degree. The most important consideration is that the transient response expected from a diverse forest following a disturbance is a more or less monotonic rise to an equilibrium while the equivalent response from a less diverse forest should feature an overshoot response under the same condition. Since the two major living carbon reservoirs are the low-diversity boreal forest of the northern hemisphere and the high-diversity tropical rain forest of the equatorial zone, the implication is that the feedbacks between vegetation and climate via atmospheric CO₂ dynamics contain a mixture of two sorts of transients depending on the vegetation zone affected by the changes.

2. The effect of a CO₂ increase in the atmosphere, even under extremely optimal conditions for plant growth, should not increase the standing inventory of carbon by a great percentage.

3. It is possible using forest succession models coupled with the analysis of fossil pollen in lake sediments to test our understanding of vegetation dynamics under altered climatic conditions. Such tests are necessary to determine our ability to predict future changes in the world's vegetation in response to climate change that could be induced by alteration of the global cycles of several elements, particularly carbon.

REFERENCES


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Table 1. Tests of Gap Models\(^a\) Showing Structural and Functional Responses\(^b\)
(From Shugart and West 1981)

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<th>Type of Test</th>
<th>Structural Response</th>
<th>Functional Response</th>
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<td>Verification</td>
<td>is consistent with structure and composition of forests in New Hampshire (JABOWA), Tennessee (FORET), and Puerto Rico (FORICO), and floodplain of the Mississippi River (FORMIS)</td>
<td>Predicts forestry yield tables for loblolly pine in Arkansas (FORAR)</td>
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<td>Predicts Arkansas upland forest based on 1859 reconnaissance (FORAR)</td>
<td>Predicts relations of forest types in succession in middle altitudinal zone in Australian Alps (BRIND)</td>
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<td>Predicts frequency of trees of various diameters in rain forests in Puerto Rico (FORICO) and uplands in Arkansas (FORAR)</td>
<td>Predicts response to clear cutting in Arkansas wetlands (SWAMP)</td>
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<td>Predicts vegetation change in response to elevation in New Hampshire (JABOWA) and Australian Alps (BRIND)</td>
<td>Predicts change in forest types as a function of flood frequency in Arkansas wetlands (SWAMP) and the Mississippi floodplain (FORMS)</td>
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<td>Determines effects of hurricanes on diversity of the Puerto Rican rain forest (FORICO)</td>
<td>Predicts response of Eucalyptus forests to fire (BRIND)</td>
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<td>Assesses effects of the chestnut blight on forest dynamics in southern Appalachian forests (FORET)</td>
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<td>Predicts forestry yield tables for alpine ash in New South Wales (BRIND)</td>
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\(^a\)BRIND is a model of Australian Eucalyptus forests (Shugart and Noble 1981); FORAR of Arkansas mixed pine-oak forests (Mielke et al. 1978); FORET of Tennessee Appalachian hardwood forest (Shugart and West 1977); FORICO of Puerto Rican Tabonuco montane rain forest (Doyle 1981); FORMIS of Mississippi River floodplain deciduous forest (Tharp 1978); JABOWA of northern hardwood forest (Botkin et al. 1972); KIAMBRAM of Australian subtropical rain forest (Shugart et al. 1981); SWAMP of Arkansas wetlands forest (Phipps 1979).

\(^b\)Structural responses describe a forest at one time, or on the broad level of species composition only. Functional responses allow for more quantitative detail, examining a forest over a period of time.
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<td>Australian Alps (BRIND)</td>
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<td>Compares to subtropical rain forest of known age (KIAMB RAM)</td>
<td>Predicts response to clear cutting in Arkansas wetlands (SWAMP)</td>
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<td>Predicts forestry yield tables for alpine ash in New South Wales (BRIND)</td>
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<tr>
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<td>Determines effects of hurricanes on diversity of the Puerto Rican rain forest</td>
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<td></td>
<td>(FORICO)</td>
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BRIND is a model of Australian Eucalyptus forests (Shugart and Noble 1981); FORAR of Arkansas mixed pine-oak forests (Mielke et al. 1978); FORET of Tennessee Appalachian hardwood forest (Shugart and West 1977); FORICO of Puerto Rican Tabonuco montane rain forest (Doyle 1981); FORMIS of Mississippi River floodplain deciduous forest (Tharp 1978); JABOWA of northern hardwood forest (Botkin et al. 1972); KIAMB RAM of Australian subtropical rain forest (Shugart et al. 1981); SWAMP of Arkansas wetlands forest (Phipps 1979).

Structural responses describe a forest at one time, or on the broad level of species composition only. Functional responses allow for more quantitative detail, examining a forest over a period of time.
Fig. 1. Climate variance: (a) Estimate of relative variance of climate over all periods of variation, from those comparable to the age of the Earth to about one hour. Strictly periodic components of variation are represented by spikes of arbitrary width. Solid triangles indicate the scaling relationship between the spikes and the amplitude of other features of the spectrum if these latter (somewhat less strictly periodic) features were represented as spikes (from Mitchell 1976); (b) Equivalent graph for periodic features of the FORET Model. Graph transformed from spectral analysis of FORET Model in Emanuel et al. (1978b).
Fig. 2. The biomass in a typical small patch of forest, a 1/12 ha plot simulated here by the FORET Model, fluctuates in response to the death of canopy trees and growth of their successors (From Shugart and West, 1981).
Fig. 3. Biomass dynamics of several forest landscapes as simulated by gap models. Each simulation is the sum of 50 plots with open plots in year 0 simulated for 600 years. For aid in comparison each graph is scaled so that the biomass at year 600 is given a value of 1.0.
Fig. 4. Atmospheric concentrations (in ppm) of carbon dioxide at Mauna Loa Observatory, Hawaii (data from Keeling, 1980).
Fig. 5. Response of seven different simulated cases of increased growth rate mimicking a maximum, non-species specific response to carbon dioxide fertilization. Lines are percentage of standing crop over years 300 to 500 of a 500 year simulation for systematic increases in all growth rates of 3.125%, 6.25%, 12.5%, 25%, 50% and 100% relative to a control case with no alteration in growth rate. The cases are: A. FORAR Model with wildfire, B. BRIND Model with wildfire, C. FORAR Model without wildfire, D. FORICO Model, E. KIAMBRAM model, F. BRIND model without wildfire, G. FORET Model.
Fig. 6. Measured and simulated full-glacial vegetation at Anderson Pond, White County, Tennessee. Full glacial pollen spectra at the left consist of the maximum and minimum pollen percentages from 16500 to 15500 14C-years ago (Delcourt 1979) and are repeated in each row for ease of comparison. Each row is a simulation under 4 different climate scenarios for three different types of sites.
AIR-SEA HEAT EXCHANGE, AN ELEMENT OF THE WATER CYCLE

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I. INTRODUCTION

A basic objective in the study of the atmospheric water cycle is to understand the distribution and variation of water vapor, clouds and precipitation. Principal driving forces for these distributions are energy exchange and evaporation at the air-sea interface, which are also important elements of air-sea interaction studies. The overall aim of air-sea interaction studies is to quantitatively determine mass, momentum and energy fluxes, with the goal of understanding the mechanisms controlling them.

The sensitivity of weather and climate processes involving air-sea interaction is probably greatest in the tropics where the thermal variations in the ocean mixed layer and the atmosphere boundary layer are comparable. In mid-latitudes the variability of the atmospheric boundary layer is much stronger than its oceanic counterpart. The results of general circulation simulations indicate that the atmosphere in mid-latitudes responds to changes in the oceanic surface conditions in the tropics. This correlation reflects the strong interaction between tropical and mid-latitude conditions caused by the transport of heat and momentum from the tropics.

Studies of air-sea exchanges involve a large number of physical, chemical and dynamical processes including heat flux, radiation, sea-surface temperature, precipitation, winds and ocean currents. In this presentation we will focus on the fluxes of latent heat and evaluate the potential use of satellite data in determining them. Alternative ways of inferring heat fluxes will be considered.

II. LATENT HEAT EXCHANGE

Quantitative determination of the exchange of latent heat between the ocean and the atmosphere has been difficult over large areas of ocean because of the lack of necessary surface and atmospheric data such as atmospheric water vapor, sea-surface temperature, and wind speed.

The dominant sea-to-air heat transfer over the oceans occurs where dry air blows over water; the water is cooled by evaporation. A good estimate of evaporative cooling rate of the ocean is obtained from the bulk formula

$$Q_E = C_E \omega u_{10} [q_s - q_{10}]$$

Where

$$C_E = 1.25 \times 10^{-3}$$ — "drag coefficient" for water vapor,
\[ L \quad \text{latent heat of evaporation (581 cal/gm at 25°C)}, \]
\[ \rho \quad \text{isobaric density of air - (sea level isobar)}, \]
\[ u_{10} \quad \text{wind speed at 10m above the water surface}, \]
\[ q \quad \text{specific humidity near the ocean surface}; \]

\[ \rho \text{ and } C_E \text{ depend weakly on air temperature, } L \text{ depends weakly on sea surface temperature, } T_s, \text{ and } C_E \text{ depends weakly also on air-sea temperature differences. Experimental determination of these functions is continually improving.} \]

The quantities \( u_{10}, T_s \) and \( L \) will be estimated eventually from satellite data. The central problem here is the computation of \( q_{10} \), or a measure which reflects its variability, from satellite observations.

A joint research effort with P. Niiler (Scripps Institution of Oceanography), T. Liu and R. Haskins (JPL) is currently directed towards the use of satellite data to study the latent heat exchange between the ocean and the atmosphere. The aim is to develop and assess a means by which air-sea latent heat exchange can be determined globally with a sufficient degree of accuracy to be useful for understanding climate variability.

### III. REMOTE SENSING DATA

For computation of latent heat exchange, the sea-surface temperature, air humidity and wind speed are needed. Satellite data obtained in the infrared and microwave parts of the spectrum are capable of recovering atmospheric vertical profiles of temperature and humidity with a good degree of vertical resolution. However, this degree of vertical resolution is not yet adequate to determine the atmospheric structure near the surface so that heat fluxes can be computed.

In this presentation we will discuss the present and future capabilities of remote sensing and describe alternative ways of improving its accuracy by combining multispectral satellite data from several sounders such as the High Resolution Infrared Sounder (HRIS), the Microwave Sounding Unit (MSU), and the Scanning Multichannel Microwave Radiometer (SMMR). Weekly or monthly averages will be used on a horizontal grid of 200 x 200 km. Surface observations will be needed to verify and/or to supplement satellite data.

Briefly, the current status of retrieved satellite data is

1. **Sea-surface temperature:** the accuracy on a monthly average over a grid of 200 x 200 km is about 1 K

2. **Humidity near the surface:** This parameter is estimated from knowledge of the total atmospheric precipitable water column (known to an accuracy of ±10%) and the vertical water vapor profile (known to an accuracy of ±30% in the lowest 2-4 km of the atmosphere).
3. **Surface wind speed**: at present we plan to use available in situ wind observation. In the future, wind data would be obtained from a scatterometer instrument capable of determining surface winds to ~2 m/sec.

Three ocean areas will be selected for the JPL/SIO study. These areas are to be selected on the basis of large values of \( (q_s - q_{10}) \), high probability of clear fields of view and adequate HIRS II coverage. Initially this will be done at:

<table>
<thead>
<tr>
<th>Area</th>
<th>Atmospheric Regime</th>
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<tbody>
<tr>
<td>35° - 25°N, 155°E - 180°E</td>
<td>continental westerlies</td>
</tr>
<tr>
<td>25° - 15°N, 160°W - 120°W</td>
<td>northeast trades</td>
</tr>
<tr>
<td>10°N - 10°S, 140°W - 90°W</td>
<td>tropical easterlies</td>
</tr>
</tbody>
</table>

- continental westerlies (heavy ship traffic)
- northeast trades (moderate ship traffic)
- tropical easterlies (light ship traffic)

**IV. ESTIMATING FLUXES FROM THE GROWTH OF THE CONVECTIVE BOUNDARY LAYER**

An alternative way of computing air-sea heat fluxes is through observations of the growth of the boundary layer. The fluxes of moisture and heat from the sea produce effects which can be seen in the growth of the convective boundary layer and clouds. Observation of these effects may provide a basis for estimating the fluxes which have produced them. Measurements of the height and structure of the boundary layer have recently been made by Dr. S. Melfi of the NASA Goddard Space Flight Center. Interpretation of these observations to infer air-sea fluxes is currently underway.