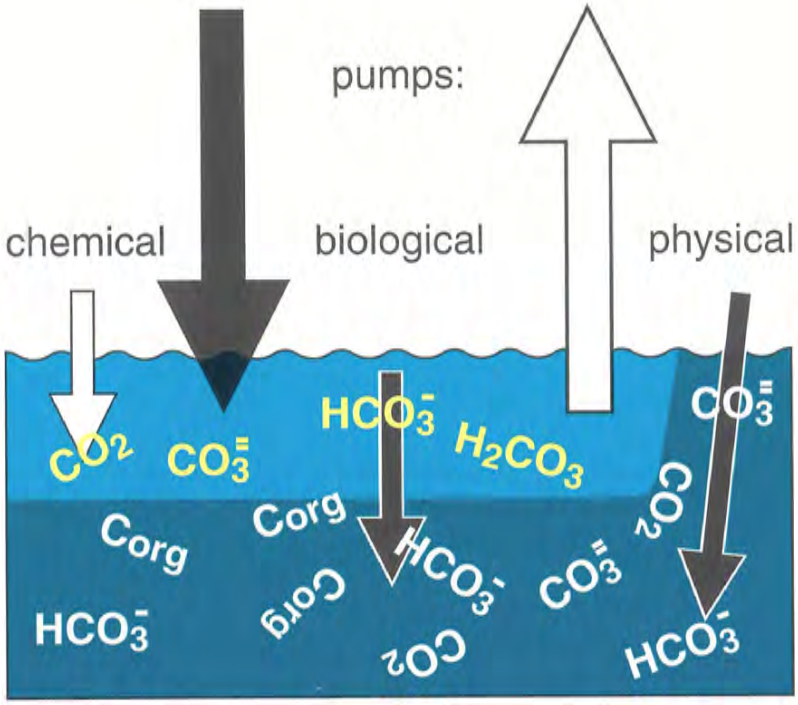
LAND-OCEAN INTERACTIONS IN THE COASTAL ZONE (LOICZ)

Core Project of the
International Geosphere-Biosphere Programme: A Study of Global Change (IGBP)
of the International Council of Scientific Unions (ICSU)



COASTAL SEAS:
A NET SOURCE OR SINK OF ATMOSPHERIC CARBON DIOXIDE ?

S. Kempe

LOICZ REPORTS & STUDIES NO. 1

LOICZ Core Project Office
Netherlands Institute for Sea Research
P.O. Box 59, 1790 AB Den Burg-Texel
The Netherlands
Tel. (31) 222 369404
Fax (31) 222 369430
e-mail loicz@NIOZ.NL

July 1, 1996

Errata for

A NET SOURCE OR SINK OF ATMOSPHERIC CARBON DIOXIDE ?

S. Kempe

LOICZ REPORTS & STUDIES NO. 1

1) Figure 12:
Y-axis of left-hand panel should be labelled "calc. pCO_2 at 25°C (µMol/kg)".
Y-axis of right-hand panel should be labelled "calc. pCO_2 at 25°C (ppmv)".

2) Figure 13:
brackets at the end of the caption should read:
"(data kindly provided by W. Hickel, Hamburg, Germany)".

3) Figure 15:
Y-axis of lower panel should read: "CO_2-Fluxes in 10^6 moles/A/d".

4) Figure 16:
The "Mlo" should read as "Mio" and the "ka" should read as "kg"

5) Missing References:

Degens, E.T. (ed.) 1982. Transport of Carbon and Minerals in Major World Rivers, Pt. 1. Mitt. Geol.-Paläont. Inst. Univ. Hamburg. SCOPE/UNEP Sonderbd. 52, 765 pp.

Bennekom, A.J. van and W. Salomons. 1981. Pathways of nutrient and organic matter from land to ocean through rivers. In *River Inputs to Ocean systems.* Proc. Worksh. Rome. March 1979. UN/UNEP/IOC/SCOR. 33-51 pp.

COASTAL SEAS:

A NET SOURCE OR SINK OF ATMOSPHERIC CARBON DIOXIDE?

S. Kempe
Geologisch-Paläontologisches Institut,
Darmstadt, Germany.

LOICZ REPORTS & STUDIES NO. 1

Published in the Netherlands, 1995 by:
LOICZ Core Project
Netherlands Institute for Sea Research
P.O. Box 59
1790 AB Den Burg - Texel
The Netherlands

The Land-Ocean Interactions in the Coastal Zone project is a Core Project of the "International Geosphere-Biosphere Programme: A study of Global Change", of the International Council of Scientific Unions.

The LOICZ Core Project is financially supported through the Netherlands Organisation for Scientific Research by: the Ministry of Education, Culture and Science, the Ministry of Transport, Public Works and Water Management; the Ministry of Housing, Planning and Environment; and the Ministry of Agriculture, Nature Management and Fisheries of the Netherlands, as well as the Royal Netherlands Academy of Sciences, and the Netherlands Institute for Sea Research.

Copyright © 1995, Land-Ocean Interactions in the Coastal Zone Core Project of the IGBP.

Reproduction of this publication for educational or other, non-commercial purposes is authorised without prior permission from the copyright holder.

Reproduction for resale or other purposes is prohibited without the prior, written permission of the copyright holder.

Citation: Kempe, S. 1995. *Coastal seas: a net source or sink of atmospheric carbon dioxide?* LOICZ/R&S/95-1, vi + 27 pp. LOICZ, Texel, The Netherlands.

ISSN: 1383-4304

Cover: "Schematic representation of the 'pumps' involved in CO_2 uptake by the coastal sea." Kempe, 1993

Disclaimer: *The designations employed and the presentation of the material contained in this report do not imply the expression of any opinion whatsoever on the part of LOICZ or the IGBP concerning the legal status of any state, territory, city or area, or concerning the delimitation's of their frontiers or boundaries. This report contains the views expressed by the author and may not necessarily reflect the views of the IGBP.*

The LOICZ Reports and Studies Series is published and distributed free of charge to scientists involved in global change research in coastal areas.

TABLE OF CONTENTS

	PAGE
Preface	v
Introduction	1
Magnitude and Variability of River Input	3
Organic carbon	3
Nutrients	7
The pCO_2 of Coastal Seas	13
Other Sinks for Respired Terrestrial Organic Carbon	20
Sulphate reduction	20
Calcium carbonate dissolution	23
Summary	23
References	25

Page

Tables

Table 1. Carbon and nutrient loads, concentrations and ratios for the Paraná, Amazon, Rhine and Mississippi. 8

Table 2. Estimates of global carbon and nutrient transport by rivers (Sources: 1 = Degens *et al.*, 1991; 2 = Meybeck, 1982; 3 = Wollast, 1983). 9

Table 3. Dissolved inorganic carbon, total organic carbon and nutrient, transport from Europe for two different total discharge scenarios; Q_1 is derived from the SCOPE river data set (Kempe *et al.*, 1991); Q_2 is the discharge assumed by Baumgartner and Reichel (1975). 10

Figures

Figure 1. Schematic representation of the 'pumps" involved in CO_2 uptake by the coastal sea. 1

Figure 2. A question of scales is involved in deciding whether coastal seas are a net source or sink of atmospheric CO_2. Note that the anthropogenic reduction of a natural source of CO_2 represents a net sink for the disturbed global carbon cycle. 2

Figure 3. Annual river discharge of freshwater and total suspended solids by continental land mass (after, Degens *et al.*, 1991). 3

Figure 4. Annual river discharge of total organic carbon and dissolved inorganic carbon (after, Degens *et al.*, 1991). 4

Figure 5. Effect of the 1982-83 ENSO event on total discharge, and selected dissolved and suspended materials from the Paraná (after, Depetris and Kempe, 1990). 5

Figure 6. Estimates of labile organic carbon in major world rivers as a percentage of their total organic carbon content (data from: Degens and Ittekkot, 1984). 5

Figure 7. Conservative mixing of dissolved organic carbon discharged from the Ems, Elbe and Weser Rivers into the German Bight (data from: Ittekkot *et al.*, 1982). 6

Figure 8. Diagrammatic representation of shelf transport processes. 6

Figure 9. Relationship between nitrogen and phosphorus content of freshwater discharge for a selection of world rivers (data from Degens, 1982; Bennekom and Salomons, 1981; Meybeck, 1982). 11

Figure 10. Increase in nitrate in the Black Sea between 1969 and 1988. The inset illustrates the increase in nutrient discharge from the Danube between the ninteen firties and 1989 (Codispoti *et al.* 1991, Tugrul *et al.* 1992, Brewer 1971). 12

Figure 11. Relationship between pCO_2 and pH in the North Sea during May/June 1986 ($pCO_2 = 158.86 \times 10^9 \times e^{(-2.4420 \times pH)}$: Kempe and Pegler, 1991). 14

Figure 12. Diurnal changes in partial pressure of CO_2 in the Sargasso Sea (upublished data by Pegler *et al.*) 14

Figure 13. Long term records of pH (above) and calculated values of pCO_2 (below) at a station off Helgoland in the German Bight, North Sea. (data provide by W. Hidal, Hamburg, Germany). 15

Figure 14. Surface pCO_2 in the North Sea in May/June 1986 (Kempe and Pegler, 1991). 16

Figure 15. Spatial extent of waters of different pCO_2 distribution (above) and corresponding CO_2 flux values (below) in the North Sea (Kempe and Pegler, 1991). 18

Figure 16. A preliminary carbon cycle budget for the North Sea (Kempe and Pegler, 1991) 19

Figure 17. Diagrammatic representation of the Alkalinity pump (Kempe, 1990). 20

Figure 18. Alkalinity distribution in the North Sea in May/June 1986 (Pegler and Kempe, 1988; Kempe and Pegler, 1991). 21

Figure 19. Relationship between alkalinity and salinity along the discharge paths of the rivers Weser (above) and Elbe (below) in the North Sea (Kempe, 1982a). 22

Figure 20. Non-conservative increase in alkalinity and pH in the estuary of the Elbe caused by the dissolution of marine suspended carbonates and the consumption of free CO_2 from the Elbe water (Kempe 1982b, 1984). 22

Preface

The Land-Ocean Interactions in the Coastal Zone (LOICZ) is one of eight Core Projects that comprise the International Geosphere-Biosphere Programme: A study of Global Change. As its name implies LOICZ is that component of the IGBP which focuses on the area of the earth's surface where land, ocean and atmosphere meet and interact. The overall goal of the project is to determine at regional and global scales: the nature of that dynamic interaction; how changes in various compartments of the Earth system are affecting coastal zones and altering their role in global cycles; to assess how future changes in these areas will affect their use by people; and to provide a sound scientific basis for future integrated management of coastal areas on a sustainable basis.

Land-derived carbon, nutrients, freshwater and sediments all enter the coastal zone at point inputs, the river mouths. Changes in these inputs have major consequences for the entire sediment, nutrient and carbon balance of the coastal sea. Annually around 0.4 gigatons of organic carbon in dissolved and particulate form reach the ocean via river discharge and may be partially or totally respired thus forming a potential natural source of atmospheric carbon dioxide. How much is actually respired is unknown, since apparently much of this carbon is highly inert and mixes with seawater conservatively. Anthropogenic inputs of nutrients, particularly nitrate and phosphate, to the coastal seas may result in increased biomass production and therefore constitute a new additional sink for atmospheric carbon. Many of the uncertainties in global carbon flow models may represent unquantified processes occurring in the coastal zone and the present document provides a review of some of these uncertainties.

The need to understand the role of the coastal ocean in the global carbon cycle is of more than just academic interest since, under the United Nations Framework Convention on Climate Change signatory states are obligated to assess the sources and sinks of greenhouse gases in territories and areas (including the Exclusive Economic Zones) under their jurisdiction. This obligation extends to both natural and anthropogenic sources and sinks of greenhouse gases including carbon dioxide. Our present inability to state definitively whether coastal seas are sources or sinks of carbon dioxide and the conditions under which their status might change, represents a serious impediment not only to states wishing to meet their obligations under the Convention but also, and perhaps more importantly, to our ability to predict the way in which the Earth system is responding to global changes.

The present document represents a revised and expanded version of a presentation originally made by Dr Kempe at the First LOICZ Open Science Meeting held in Raleigh, USA in June 1993. It provides a broad and general overview of the issues and uncertainties surrounding carbon cycling in coastal seas, and serves as a useful introduction to the literature. It has been produced by the LOICZ Core Project Office as a stimulus to the network of coastal scientists participating in the LOICZ project and those interested in global change and the coastal zone.

J.C. Pernetta,
December, 1995,
LOICZ Core Project Office,
Texel, The Netherlands.

COASTAL SEAS:
A NET SOURCE OR SINK OF ATMOSPHERIC CARBON DIOXIDE ?

Introduction

Despite many years of research, it is still not possible to satisfactorily balance the disturbed global carbon cycle. The global ocean is recognised as one of the major sinks for fossil and biogenic carbon released to the atmosphere by human action. Several mechanisms (or pumps) are involved in the uptake of CO_2 by the ocean (Figure 1). One is the net CO_2 uptake in the mixed surface layer by thermodynamic equilibration in response to the rising CO_2 partial pressure (pCO_2) in the atmosphere (the chemical pump). A second mechanism involves the organic fixation of inorganic dissolved carbon by phytoplankton through the process of photosynthesis and the export of new primary production to sediments or abyssal water (the biological pump). This pump may be enhanced by anthropogenic eutrophication of coastal seas. The third mechanism involves the sinking of cold surface waters equilibrated to the recent high pCO_2 in polar regions (the physical pump). Both the chemical and the biological pumps can operate in coastal seas as well as in the open ocean. An important question to address is whether coastal seas, which constitute about 7.6% of the surface area of the world ocean, are a net source or sink of atmospheric CO_2.

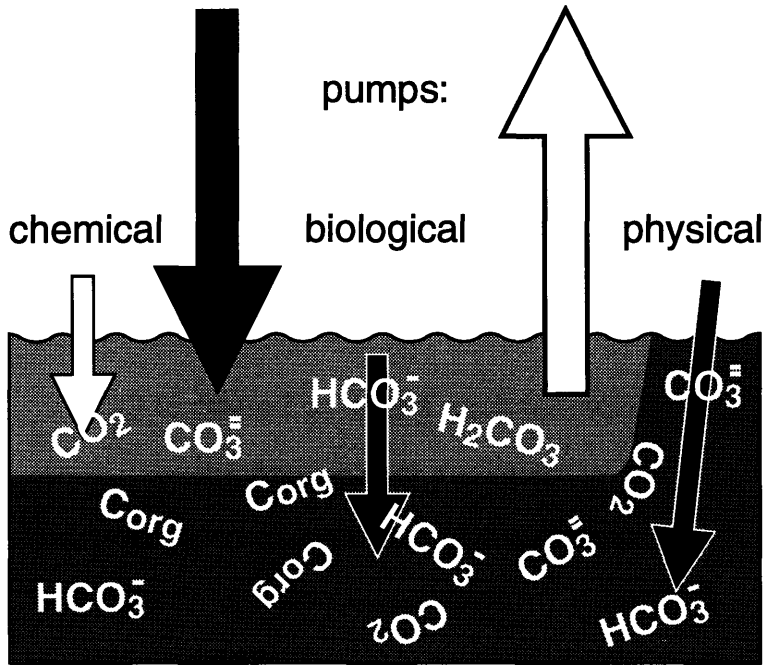


Figure 1. Schematic representation of the 'pumps" involved in CO_2 uptake by the coastal sea.

At present, the question of whether coastal seas are net sinks or sources of atmospheric CO_2 cannot be answered. Like all other natural systems, coastal seas are governed by numerous physical, chemical, biological and geological processes which respond to external change on various spatial and temporal scales. Therefore, a certain region of the coastal sea may be a sink for CO_2 under some conditions (for example during the daytime, summer months, anthropogenic era, etc.) but not under others (for example during the night-time, winter months, undisturbed conditions, etc.). Similarly a particular coastal sea may be subjected to anthropogenic impacts such as enhanced inputs of nutrients, altering its capacity as a source of sink of carbon.

Smith and Mackenzie (1987) and Smith and Hollibaugh (1993) have suggested that the ocean as a whole is net heterotrophic, that is it releases or "exhales" more carbon dioxide to the atmosphere than it takes up or "inhales". If it "inhales" more carbon dioxide from the atmosphere than it "exhales" it would be net autotrophic. The difference between uptake and release, which is thought to be of the order of 0.25 GtC/a, is actually quite small when compared to the total exchange of CO_2 across the sea/air interface of roughly 90-100 GtC/a (gigatons = 10^9t carbon per year) or to the total global primary production of the oceans of 45 GtC/a (Bolin *et al.*, 1979).

How is it possible to measure such a small difference in view of the large fluxes and their equally large uncertainties? Smith and Mackenzie (1987) and Smith and Hollibaugh (1993) have argued that the net flux should be represented by the apparent imbalance between total river input of organic carbon and total organic carbon sedimentation in the ocean. They quote a total river transport of about 0.4 GtC/a (Meybeck, 1981; 1982) and a marine organic carbon burial rate of 0.15 GtC/a (Lerman *et al.*, 1988) or 0.13 GtC/a (Berner, 1982). Over the long-term the difference should be returned to the atmosphere and cannot reside in the ocean. However, long-term in this case means in the order of several ocean turnovers with one turnover taking on the order of 1500 years.

Therefore, if we were merely interested in the geological time scale of the carbon cycle, we would conclude that coastal seas are a net source of carbon dioxide to the atmosphere (Figure 2). However, the figures quoted for river delivery and marine burial can be debated. For example, Smith and Hollibaugh (1993) list carbon burial rates ranging from 0.030 to 1.680 GtC/a. It is also possible that on shorter or regional scales, coastal seas may act as significant net sinks for anthropogenic carbon in the atmosphere. Even if coastal seas are a net overall source of CO_2 to the atmosphere, a reduction in this source would constitute a net sink for anthropogenic carbon in the atmosphere. This seemingly paradoxical statement becomes understandable if we consider that any naturally released CO_2 has also been consumed somewhere in a steady-state world. Once a particular source is anthropogenically reduced, the original sink is free to consume additional anthropogenic CO_2.

It is therefore necessary to investigate the role of the coastal seas in the global carbon cycle more thoroughly if we want to know what happens regionally and on anthropogenically relevant time scales. This is reflected in the research recommended in the LOICZ Implementation Plan (Pernetta and Milliman, 1995).

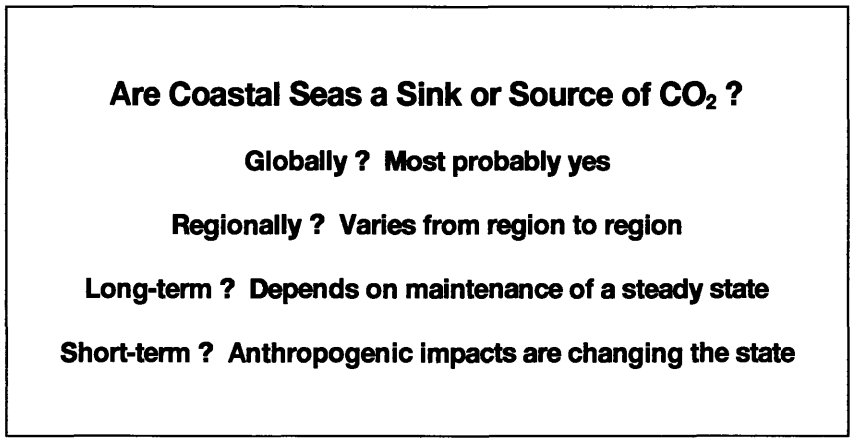


Figure 2. A question of scales is involved in deciding whether coastal seas are a net source or sink of atmospheric CO_2. Note that the anthropogenic reduction of a natural source of CO_2 represents a net sink for the disturbed global carbon cycle

Magnitude and Variability of River Input

Organic Carbon

Coastal seas receive a total of 35,000 km^3/a of fresh river water plus 15 x 10^9 t/a of total suspended solids. Breakdown by continent is shown in Figure 3. Additional detail for individual rivers can be found in Milliman *et al.*, 1995. As a result of these inputs the coastal seas can have salinity and turbidity gradients that are much stronger than those occurring in the open ocean. Only certain phytoplankton species can thrive under such conditions and many highly turbid river plumes cannot sustain substantial photosynthesis until their sediment load settles or becomes dispersed enough to allow minimal penetration of light.

The global organic matter transport by rivers has been quantified with a reasonable degree of certainty (probably within ± 30%). The results of the SCOPE/UNEP project (Degens *et al.*, 1991) suggest a global continental discharge of total organic carbon on the order of 0.33 GtC/a. This estimate is less than those of Meybeck (1981; 1982) and may therefore diminish the necessity to postulate a net coastal sea source of carbon dioxide. However, the SCOPE/UNEP estimate is based primarily on data from large rivers and on longer sample records, some of them multi-annual. The contribution of organic carbon to the total particulate matter in large rivers and its per area removal rate is known to be less than in smaller rivers. Therefore, the SCOPE/UNEP estimate may be biased somewhat to the low side.

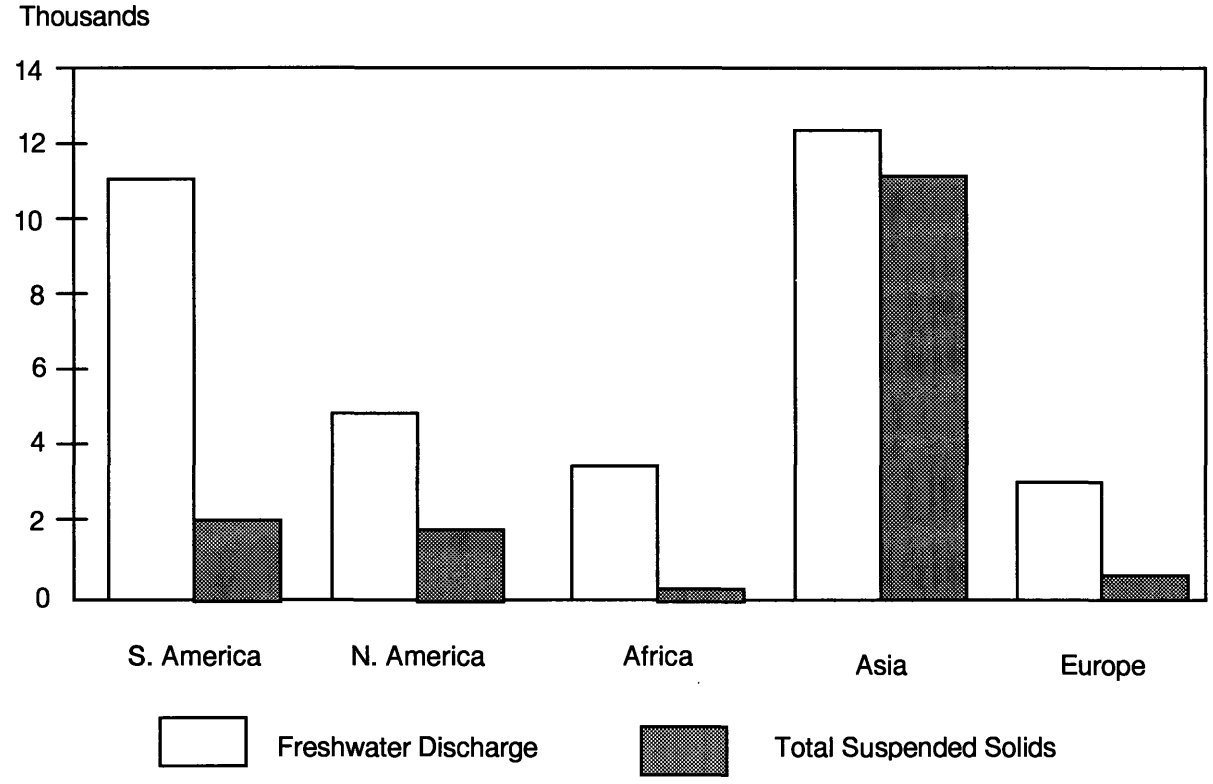


Figure 3. Annual river discharge of freshwater (km^3/a) and total suspended solids (10^6 t/a) by continental land mass (after, Degens *et al.*, 1991).

Asian rivers furnish much higher quantities of organic carbon to the ocean than do the rivers of any other region of the world (Figure 4) (Milliman and Syvitski, 1992). In Asia, organic carbon is largely transported in particulate form (POC) whereas in South America organic carbon is mostly transported in dissolved form (DOC). The total dissolved inorganic carbon flux, of 0.4 GtC/a, is somewhat larger than the total organic carbon flux and it is removed preferentially from the northern temperate humid regions (i.e. Europe and North America) (Figure 4) which have vast areas of carbonate source rocks. In contrast, much less inorganic carbon is mobilised on the deeply weathered continents of Africa and South America.

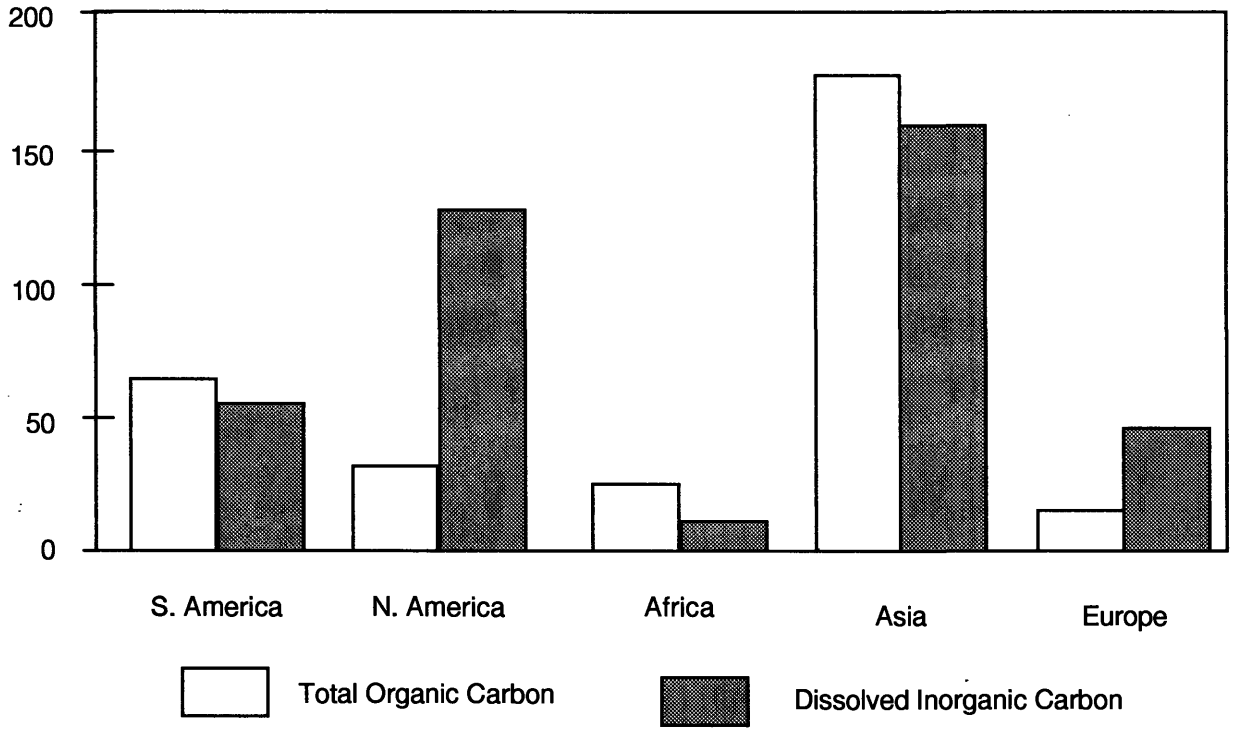


Figure 4. Annual river discharge of total organic carbon (TOC) and dissolved inorganic carbon (DIC) in 10^6t/a (after, Degens *et al.*, 1991).

We will never know the values for total organic carbon or dissolved inorganic carbon flux more precisely than at present, simply because all "measurements" of transport are actually interpolations toward the annual total based on a few samples widely dispersed in space and time. Methods of estimation, sampling frequencies, sampling devices and analytical procedures all differ from river to river and from investigator to investigator. Furthermore, rivers experience large intra- and inter-annual changes in their transport capability.

This is illustrated using the example of the Paraná River in Argentina which was sampled throughout a century-flood triggered by the extraordinary strong ENSO (El Niño/Southern Oscillation) event of 1982-1983 (Figure 5). Water discharge increased by roughly 75% but total dissolved and total suspended solids stayed nearly constant. At first thought, this may seem surprising. However, more water discharge does not necessarily mobilise more sediment and, in case of the Paraná River, increased amounts of the total suspended solids are trapped in the inundated vegetation on the flood plain causing a *de facto* decrease of their transport beyond a certain rise of the water level. As a consequence of this trapping effect, and the increased proportion of inorganic material in the total suspended solids, the POC actually decreased by 43% despite the strong increase in water discharge. In contrast, excess removal of leached organics from the soil and from the flood plain increased the DOC transport by 168%. Therefore, the DOC/POC ratio changed from 1.7 to 8.1 and the total organic carbon transport increased from 4.4 to 8.4 x 10^6 t/a.

In addressing the question of whether coastal seas are a net source or sink of atmospheric CO_2, however, it is not the total organic carbon load that is of primary interest, but that fraction of it, which is easily accessible to heterotrophic degradation (i.e. labile carbon). The majority of eroded terrestrial organic carbon is derived from soil and consists of material which is rather inert or refractory. As a proxy measure of labile organic carbon, we can use the fractions of sugars and amino acids found in the total organic carbon. In the particulate organic carbon component, this fraction is between 10-30 % with an average probably close to 15% (Figure 6). Together with the St. Lawrence and the Orinoco Rivers, the Paraná belongs to the group of rivers having relatively highly labile POC fractions (over 20%). In contrast, the labile fraction in the DOC component appears to be lower in the Paraná. For example, it was found to be less than 6% for samples collected in 1981 and about 20% for samples collected in 1985 (Kempe and Depetris, 1990).

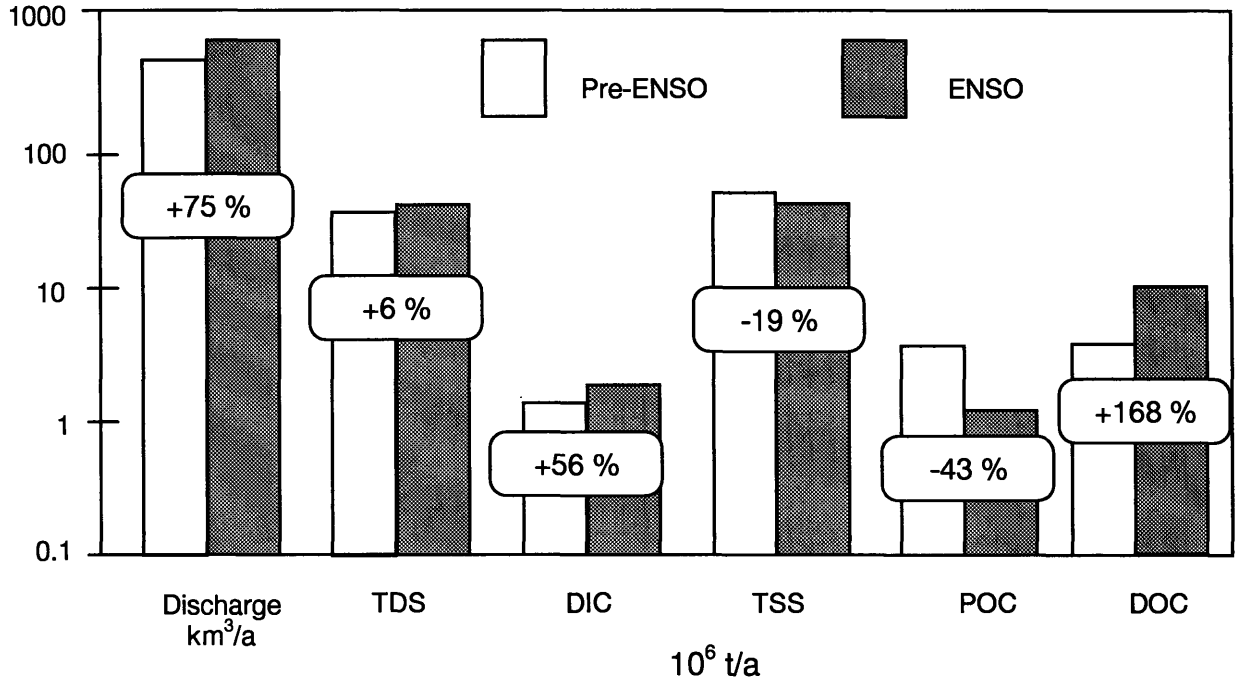


Figure 5. Effect of the 1982-83 ENSO event on total discharge, and selected dissolved and suspended materials from the Paraná (after, Depetris and Kempe, 1990).

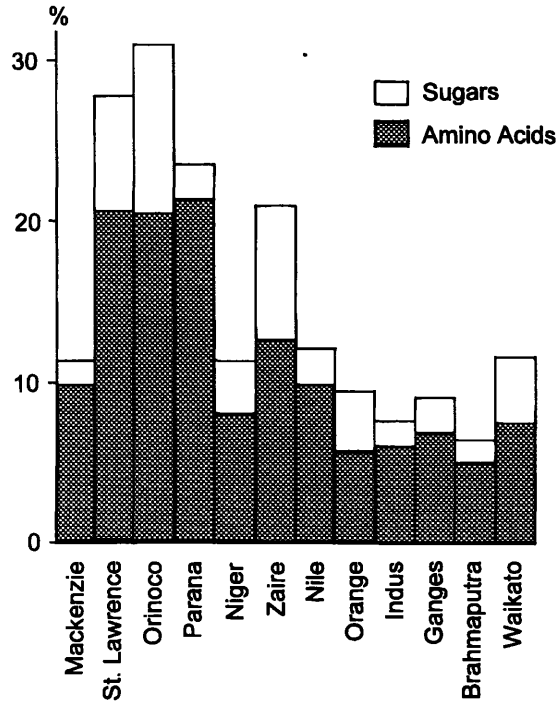


Figure 6. Estimates of labile organic carbon in major world rivers as a percentage of their total organic carbon content (data from: Degens and Ittekkot, 1985)

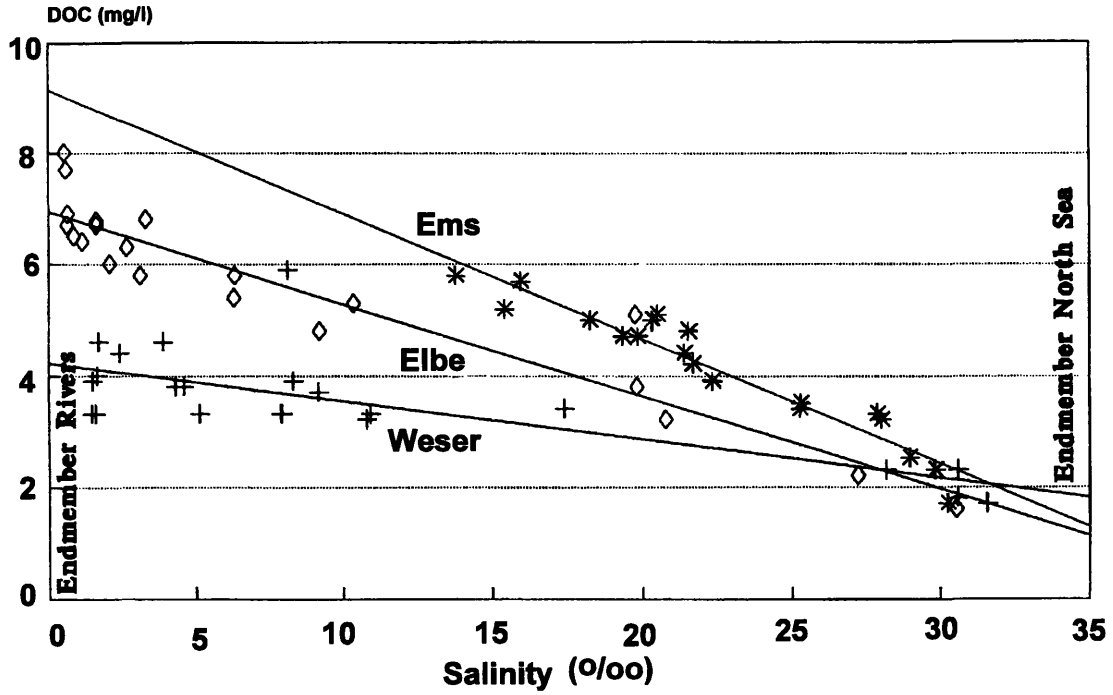


Figure 7. Conservative mixing of dissolved organic carbon discharged from the Ems, Elbe and Weser Rivers into the German Bight (data from: Ittekkot *et al.*, 1982).

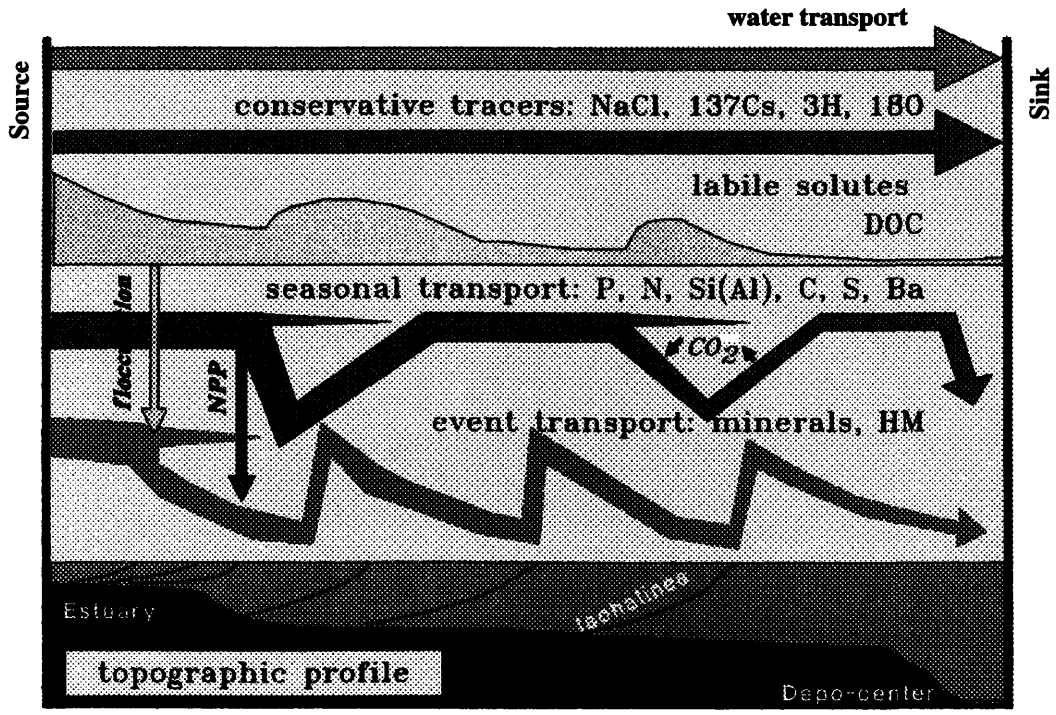


Figure 8. Diagrammatic representation of shelf transport processes.

Thus, it is safe to conclude that roughly 15% of the exported organic carbon in rivers could be readily respired by micro-organisms in coastal seas to yield a potential source to the atmosphere on the order of 0.05 GtC/a. For comparison, Etcheber *et al.* (1993) reported that Wadden Sea sediments contain about 15% degradable organic matter, suggesting that this amount is characteristic of the labile organic carbon in riverine POC.

The remaining refractory organic carbon delivered by the rivers probably reaches the open sea eventually and contributes to the large pool of oceanic DOC (about 1000 GtC) which has a long and unknown residence time and for which the removal mechanisms are unresolved. Conservative behaviour of refractory organic carbon is also suggested by DOC data measured across river plumes which almost all show linear change with salinity (Figure 7). Although flocculation of up to 10% is observed, substantial active consumption by micro-organisms has never been reported (Burton, 1983).

The various processes which can affect the transport of carbon across the continental shelf are illustrated in Figure 8. Conservative tracers are simply dispersed in relation to the increasing salinity. Suspended matter is settled rather quickly by flocculation triggered by organic substances (not by salt as often assumed). Storms can resuspend benthic sedimentary material, release nutrients from sediments and move material both onshore or offshore, until it finally reaches a depositional environment, usually in deeper water, where it will stay on the seafloor. Other processes, specifically the uptake of nutrients and inorganic carbon by phytoplankton, occur seasonally. Most of the organic matter produced by the phytoplankton is consumed in the water column, however, some fraction is deposited on the seafloor and subsequently remineralised by benthos. It can also be recharged to the water column during storms or by bioturbation. The refractory POC delivered by rivers must be quickly deposited near-shore and subsequently be diluted with marine POC. Over several cycles of re-suspension and re-sedimentation, it may eventually be transported to the edge of the continental shelf where it can be carried to deeper marine basins by turbidity currents (Walsh *et al.*, 1985).

Nutrients

The transport and partial consumption of terrestrial organic carbon in river discharge is accompanied by phytoplankton productivity. Smith and Mackenzie (1987) correctly point out that coastal seas can only be net heterotrophic systems if the liberated CO_2 is not subsequently consumed by photosynthesis. Photosynthesis is fuelled by nutrients and therefore the nutrient load of a river is a decisive factor in determining whether its plume will be net heterotrophic or autotrophic. Redfield (1958) has established that marine phytoplankton utilise carbon, nitrogen and phosphorous at an average molar ratio of 106/16/1. This is commonly known as the Redfield ratio and can be used to estimate the amount of potentially sequestered carbon using nutrient transport data for rivers.

This is illustrated using data from four rivers: the Paraná, Amazon, Rhine and Mississippi (Table 1). The Paraná and Amazon serve as examples of pristine rivers with very low nutrient loads while the Rhine and Mississippi serve as examples of rivers which drain industrialised regions and have high nutrient loads.

As may be seen from Table 1, the Paraná and Amazon carry roughly the same amount or more, of inorganic as organic carbon. At first sight, the potentially sequestered carbon in the Paraná appears to be much less than the total organic carbon load. However, if we calculate the potentially labile organic carbon load, then the potentially sequestered carbon is of the same order of magnitude. This makes it doubtful if the Rio de la Plata, the estuary of the Paraná, is a net source of CO_2 to the atmosphere. In the case of the Amazon, clearly not enough phosphate and nitrate are delivered to compensate for the total organic carbon load. If one assumes that 20% of the total organic carbon load is labile, then the potentially sequestered carbon is roughly equivalent, as it also appears to be in the Paraná. Richey *et al.* (1991) measured particulate phosphorus in the Amazon. Surprisingly, they found that ten times more particulate phosphorus is transported than dissolved inorganic phosphorus. If all or part of this particulate phosphorus could be used by phytoplankton, then all of the labile organic carbon plus most of the inorganic carbon delivered could potentially be sequestered by phytoplankton. Under these circumstances, the Amazon plume should be a net sink for CO_2.

Table 1. Carbon and nutrient loads, concentrations and ratios for the Paraná, Amazon, Rhine and Mississippi.

Paraná					
Parameter	**1981 - 1982** (Kempe and Depetris, 1990)			**1978 - 1979** (Kempe, 1982a)	
	Dissolved Inorganic Carbon	**Dissolved Organic Carbon**	**Particulate Organic Carbon**	**NO_3**	**PO_4**
Loads (10^6 t/a)	1.6	2.8	1.63	0.093	0.0099
% labile	-	ca. 6	ca. 25	-	-
labile loads	-	0.17	0.41	-	-
loads (10^9 M)	133	14.2	34.2	6.6	0.32
normalized to P	416	44	106	20.6	1

Amazon (Richey *et al.*, 1991)						
Parameter	**Dissolved Inorganic Carbon**	**Dissolved Organic Carbon**	**Fine Particulate Organic carbon**	**Coarse Particulate Organic carbon**		
mg/l	5.8 - 8.0	1.7 - 4.7	1.2 - 3.3	0.05 - 0.4	-	-
µM/l	485 - 667	225 - 391	100 - 275	4.2 - 33	-	-
ratio to PO_4-P[1]	613 - 844	289 - 494	126 - 348	5.3 - 42	-	-
ratio to PP[2]	62 - 85	28 - 49	13 - 35	0.5 - 4.2	-	-
	Dissolved Organic Nitrogen		**Particulate Organic Nitrogen**		**NO_3**	**PO_4**
µM/l	14.0		23		12.1	0.79
ratio to PO_4-P	17.7		29		15.3	
ratio to PP	1.8		2.9		1.5	
						DOP / **POP**
µM/l						0.50 / 7.85

Rhine Average values at station, Lobith, 1969 - 1976 (Kempe, 1982a)					
Parameter	**Bicarbonate Carbon**	**Dissolved free CO_2 Carbon**	**Total Organic Carbon**	**Dissolved NO_3 Nitrogen**	**Dissolved PO_4 Phosphorus**
	348	31	79	27	1

Mississippi Average values at station, New Orleans, 1967 - 1979 (Kempe, 1982a)					
Parameter	**Bicarbonate Carbon**	**Dissolved free CO_2 Carbon**	**Total Organic Carbon**	**Dissolved NO_3 Nitrogen**	**Dissolved PO_4 Phosphorus**
ratio to N	93.7	13.1	12	1	0.09
ratio to P	1200		134	11.2	1

[1] *PO_4-P = dissolved phosphate phosphorus*
[2] *PP = particulate phosphorus.*

Table 2. Estimates of global carbon and nutrient transport by rivers (Sources: 1 = Degens *et al.*, 1991; 2 = Meybeck, 1982; 3 = Wollast, 1983).

Parameter	Quantity		Ratio of C:N:P for different estimates of river transport				
	t/a 10^6	M/a 10^{12}	natural[2]	anthropogenic[2]	Dissolved Phosphorus[2]	Particulate Phosphorus	anthropogenic[3]
Dissolved Inorganic Carbon[1]	407	34	2635	1054	527	52.7	618
Total Organic Carbon[1]	335	28	2170	868	434	43.4	509
Labile Fraction of Total Organic Carbon[1]	50	4.2	323	131	70	6.46	76
Dissolved Nitrate Nitrogen - natural input[2]	4	0.29	22.5				
Total Inorganic Nitrogen	4.55	0.32	25				
Dissolved Phosphate Phosphorus - natural input[2]	0.4	0.013	1				
Additional anthropogenic loads as of 1970 (Meybeck, 1982)							
Dissolved Nitrate Nitrogen - anthropogenic input	7	0.5		15.5			
Dissolved Phosphate Phosphorus - anthropogenic input	1	0.032		1			
Total Natural & Anthropogenic Dissolved Nitrogen	21.5	1.54			24		
Total Natural & Anthropogenic Dissolved Phosphorus	2	0.06			1		
Particulate Nitrogen	21	1.5				2.3	
Particulate Phosphorus	20	0.65				1	
Additional anthropogenic loads as of 1983 (Wollast, 1983)							
Dissolved Nitrate Nitrogen.	21	1.5					27
Dissolved Phosphate Phosphorus.	1.7	0.055					1

In the case of the two rivers high in nutrients, the potentially sequestered carbon in the Rhine is large enough to compensate for more than all of the transported total organic carbon, or nearly all in the Mississippi (Table 1). If we also consider total organic carbon lability and particulate nutrient loads (for which no data are available), then clearly the plumes of both these nutrient-rich rivers should be net autotrophic.

Obtaining accurate estimates of nutrient discharge in rivers is complicated by the fact that anthropogenic eutrophication has been increasing dramatically over the past few decades. The Danube provides a rather extreme example of this. Between 1948-1959 and 1989, the total transport of dissolved nitrate + nitrite-nitrogen rose from 12,500 to 273,000 t/a, a 22-fold increase. More recent measurements indicate an even larger transport, greater than 300,000 t/a (C. Humborg, personal communication). Over the same time interval, the phosphate-phosphorus increased five times from 5,500 to 29,300 t/a. As a result, the N/P ratio increased from 5 to 21 which shifted the Danube from conditions of nitrogen limitation to phosphorus limitation with respect to the Redfield ratio (N/P = 16). The dynamic situation in riverine nutrient loads makes it difficult to establish reliable estimates of global transport loads. Current estimates are presented in Table 2 along with respective C/N/P ratios.

The overview of current estimates of global riverine transport for numerous important biogeochemical variables in given in Table 2. Potentially sequestered carbon induced by natural nitrate and phosphate fluxes is obviously much lower than total organic carbon loads. However, if anthropogenically increased fluxes, plus particulate phosphorus and the lability of total organic carbon are taken into account, then potentially sequestered carbon surpasses by far the point at which coastal seas would become net sinks of CO_2. Therefore, anthropogenic eutrophication in recent years must be causing a shift from heterotrophy to near equilibrium conditions or even to autotrophy in coastal waters. This trend is especially prominent in Europe where 70% of the total organic carbon transport is already balanced by inorganic N and P inputs, the ratio of total organic carbon to nitrate nitrogen to phosphate phosphorus being 157:21:1 (Table 3).

Table 3. Dissolved inorganic carbon, total organic carbon and nutrient transport from Europe for two different total discharge scenarios; Q_1 is derived from the SCOPE river data set (Kempe *et al.*, 1991); Q_2 is the discharge assumed by Baumgartner and Reichel (1975).

	Discharge				Ratio C:N:P
	Q_1 = 2344 km^3/a		Q_2 = 2800 km^3/a		
	t/a 10^6	M/a 10^{12}	t/a 10^6	M/a 10^{12}	
Dissolved Inorganic Carbon	-	-	60.4	5.03	423
Total Organic Carbon	18.87	1.57	22.54	1.88	157
Dissolved Nitrate Nitrogen	2.89	0.21	3.45	0.25	21
Dissolved Ammonium Nitrogen	1.0	0.07	1.19	0.085	7
Dissolved Phosphate Phosphorus	0.31	0.01	0.37	0.0119	1
Total Phosphorus	0.38	0.123	0.46	0.0148	1.24

What can we expect to happen with river loads in the immediate future due to human activities that might have an impact on the coastal seas? Rivers suffer increasingly not only from pollution and nutrient input but also reservoir building. Reservoirs are very effective traps for particulate matter. For example, the entire Nile sediment load of 125 x 10^6 t/a is trapped today in Lake Nasser instead of moving downstream to rejuvenate Egyptian flood plain soils and stabilise the Nile delta. Therefore, most of the particulate organic carbon previously delivered to the coastal zone is now trapped and buried in the reservoir. Labile organic carbon is also consumed and released as CO_2 which either enters the atmosphere, or is consumed in the dissolution of suspended calcium carbonates. Therefore, the dissolved organic carbon finally discharged from the reservoir is much more stable and has lost most of its seasonal variability in concentration. With regard to nutrients, reservoirs behave in a similar manner to sewage plants in that they extract dissolved inorganic N and P and form particulate organic carbon which settles to the sediments. As a result, the Nile is virtually devoid of nutrients below the Aswan Dam until it becomes gradually polluted by anthropogenic input further downstream.

In summary, we should expect a general decrease in the particulate organic carbon discharge of rivers to the coastal zone as a result of reservoir construction. This in turn will diminish the potential of coastal seas for respiration and shift them more toward net autotrophic conditions. Reservoirs also cut down the nutrient loads of rivers. However, since most nutrients enter the rivers in the heavily populated coastal zones situated mostly below the reservoirs, the nutrient input, specifically of nitrate, will probably continue to increase in the immediate future.

Even though nutrient concentrations in major world rivers can differ by more than two orders of magnitude, the ratio between nitrate and phosphate concentrations lies in a rather narrow field (Figure 9). The ratio is in fact quite close to the Redfield ratio of N/P = 15. Rivers above the regression line have a nitrate surplus and phosphate limitations while those below the line have a phosphate surplus and nitrate is the limiting nutrient. Note that all Chinese rivers lie above the line, reflecting the predominant use in China of manure as a fertiliser which is poor in phosphorus.

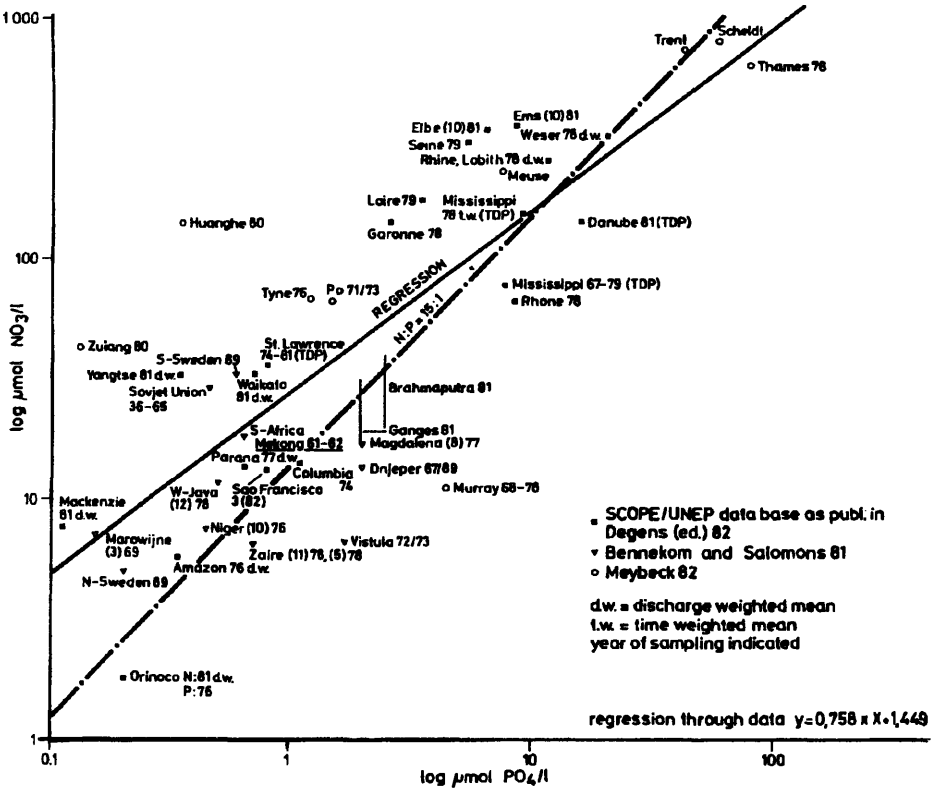


Figure 9. Relationship between nitrogen and phosphorus content of freshwater discharge for a selection of world rivers (data from Degens, 1982; Bennekom and Salomons, 1981; Meybeck, 1982).

The available data indicate that the global average nitrate to phosphate ratio in the coastal zone is most likely greater than 15. Therefore, coastal seas should become increasingly phosphate limited. This has in fact been observed at the long-term monitoring station situated off the island of Helgoland in the German Bight of the North Sea. Over a period of 23 years, the phosphate concentration increased from 0.55 to 0.97 µM/l while NO_3 increased from 5.56 to 16.45 µM/l which has resulted in an increase in the N/P ratio from 10 to 17 (Berg and Radach, 1985).

Another example is the Black Sea where the total amount of nitrate has apparently increased considerably in the past 20 years (Codispoti *et al.*, 1991; Tugrul *et al.*, 1992). The measurements taken during the 1969 Atlantis II cruise (Brewer, 1971) showed that the maximum nitrate concentration was about 2 µM at a density level of about 15.7 sigma theta (Figure 10). During the 1988 Knorr cruise (Friederich *et al.*, 1990), the maximum increased to about 8 µM and had risen to 15.4 sigma theta. In the surface layer (above 14.0 sigma theta), all the nitrate is consumed by phytoplankton. Below 16.2 sigma theta, the nitrate is reduced due to the presence of anaerobic conditions. These limits have not changed in the last 20 years. The

quadrupling of the maximal NO_3 concentration is equivalent to an increase of the NO_3 content on the order of 100-300 mM/m^2. This increase has most probably been caused by the eutrophication of the Black Sea through riverine nutrient inputs. As noted above, the nitrate transport of the Danube River has increased twenty-fold since the 1950's (see inset in Figure 10) and this is equivalent to a cumulative input of roughly 700 mM/m^2. Thus, the Danube alone could be responsible for the observed nitrate increase in the Black Sea. In fact it appears that large quantities of nitrate must have been lost from the system (20-30 mM/m^2/a). This could be happening by sedimentation of organic matter or, more probably, by denitrification at the O_2/H_2S interface in the water column.

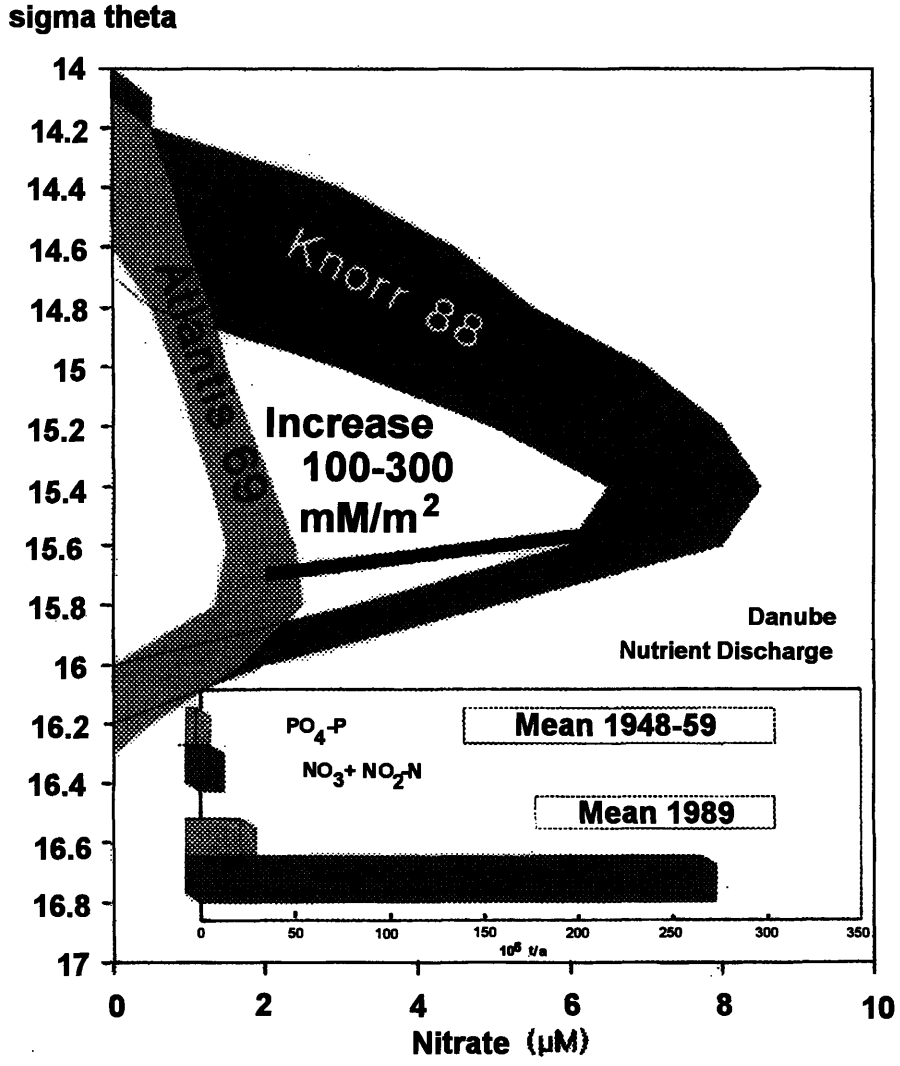


Figure 10. Increase in nitrate in the Black Sea between 1969 and 1988. The inset illustrates the increase in nutrient discharge from the Danube between the ninteen fifties and 1989 (Codispoti *et al.* 1991, Tugrul *et al.* 1992, Brewer 1971).

Denitrification at the interface between the oxygenated surface layer and the anaerobic waters of stagnant basins is also the cause of intensive nitrate loss in the Baltic Sea. As a consequence, this coastal sea has become nitrogen limited giving rise to extensive cyanobacteria blooms in summer which have the ability to conduct nitrification enzymatically. In the Baltic Sea nitrification by cyanobacteria (130,000 t/a) is comparable to the entire discharge of nitrogen from Poland (110,000 t/a) (Rosenberg *et al.*, 1990).

Tugrul *et al.* (1992) also compared the measurements of phosphate and silica made during the 1969 Atlantis II, the 1988 Knorr and the 1991 Bilim cruises. They found only a slight increase in phosphate from about 6 to 8 mM/l. Silica, on the other hand, decreased in concentration in surface waters (above about 15.7 sigma theta) but increased below this density level. As a consequence, less silica is available for spring diatom blooms (diatoms consume silica to build their frustules) today than in the past, and other phytoplankton groups, such as dinoflagellates, are likely to proliferate.

These examples illustrate that the increasing concentrations of nutrients in riverine input can have a pronounced effect on the carbon balance of coastal seas. Changes in the intensity and composition of phytoplankton blooms, and hence in coastal carbon balance, must therefore have occurred in the recent past and are most likely continuing to occur today.

The pCO_2 of Coastal Seas

The above discussion has only dealt with carbon balances and not the actual CO_2 pressure of coastal seas (pCO_2). This has been done deliberately because to date only a few studies have actually measured or calculated pCO_2 in near-shore waters (for example, Kempe and Pegler, 1991).

For surface water to become a source or sink for atmospheric CO_2, its internal CO_2 pressure must be larger or smaller respectively, than the atmospheric pCO_2 (currently 350 ppmv). The internal pressure is determined by the thermodynamics of the carbonate system (Broecker and Peng, 1982) and can be altered by a variety of processes. The most important include the removal of CO_2 by photosynthesis and the release of CO_2 by respiration. Therefore, surface waters will have fluctuating pCO_2 levels related to daily, weekly and seasonally induced changes in the rates of photosynthesis and respiration as well as temperature changes.

There are several ways to obtain accurate figures of pCO_2 in coastal waters. One is to directly measure the CO_2 concentration in a small volume of carrier gas which has been equilibrated with a large volume of seawater. Another method is to measure potentiometrically the alkalinity (sum of the charges of weak ions, mainly carbonate and bicarbonate) and the total dissolved CO_2 (the molar sum of CO_3, HCO_3, CO_2 and H_2CO_3) and to calculate the pCO_2 using standard thermodynamic equations (Pytkowicz, 1983). A third method is to measure the pH, alkalinity and salinity and compute pCO_2 by applying a numeric ionic model of aqueous solutions such as WATMIX or PHREEQE (Wigley and Plummer, 1976; Parkhurst *et al.*, 1980). In seawater, the pH is governed by the acid-base reactions of the carbonate system and is therefore a proxy for the pCO_2.

The relationship between pH and pCO_2 (calculated from pH, alkalinity and salinity) in over 500 surface water samples collected from the North Sea is plotted in Figure 11. In spite of the large range of temperatures, salinities and alkalinities used in the calculations, the pH is apparently, a rather accurate proxy of pCO_2 and therefore should respond to the rather large changes in pCO_2 expected in coastal seas.

No diurnal pCO_2 record is currently available for any coastal site. However, an example from the Sargasso Sea is shown in Figure 12. During the daytime, the pCO_2 and the free CO_2 concentrations decrease slowly due to photosynthesis. During the night, respiration dominates and most of the CO_2 sequestered during the day is slowly returned to the water column until the pCO_2 reaches its diurnal maximum shortly before sunrise. The total diurnal amplitude is 1 µMC/l (or 12 mgC/m^3) and is a measure of the daytime net primary production minus autorespiration and gas invasion from air. The pCO_2 stays below the atmospheric pCO_2 indicating that this region of the ocean is, as is most of the North Atlantic, a net sink for atmospheric CO_2. This particular diurnal cycle was recorded in December illustrating that photosynthesis is important in this subtropical region even under the reduced light conditions of winter.

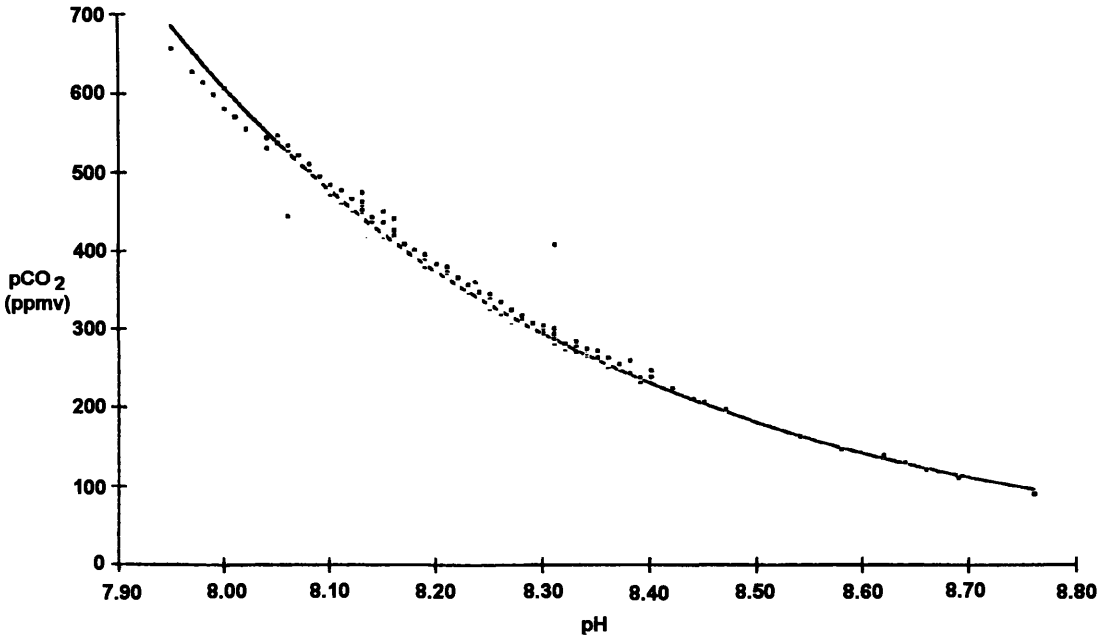


Figure 11. Relationship between pCO_2 and pH in the North Sea during May/June 1986 ($pCO_2 = 158.86 \times 10^9 \times e^{(-2.4420 \times pH)}$: Kempe and Pegler, 1991).

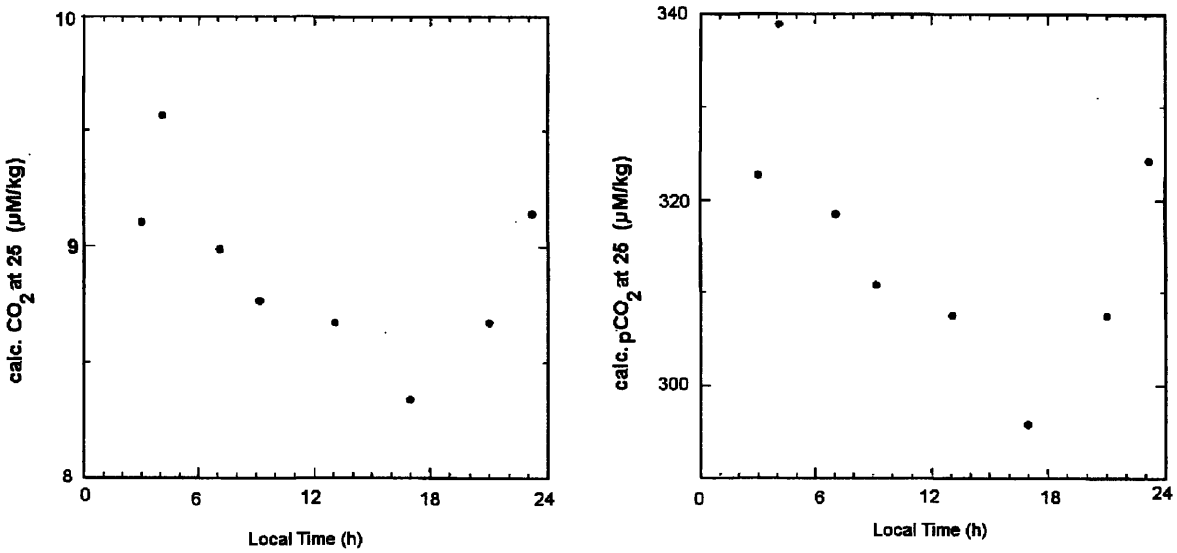


Figure 12. Diurnal changes in partial pressure of CO_2 in the Sargasso Sea (unpublished data Pegler *et al.*)

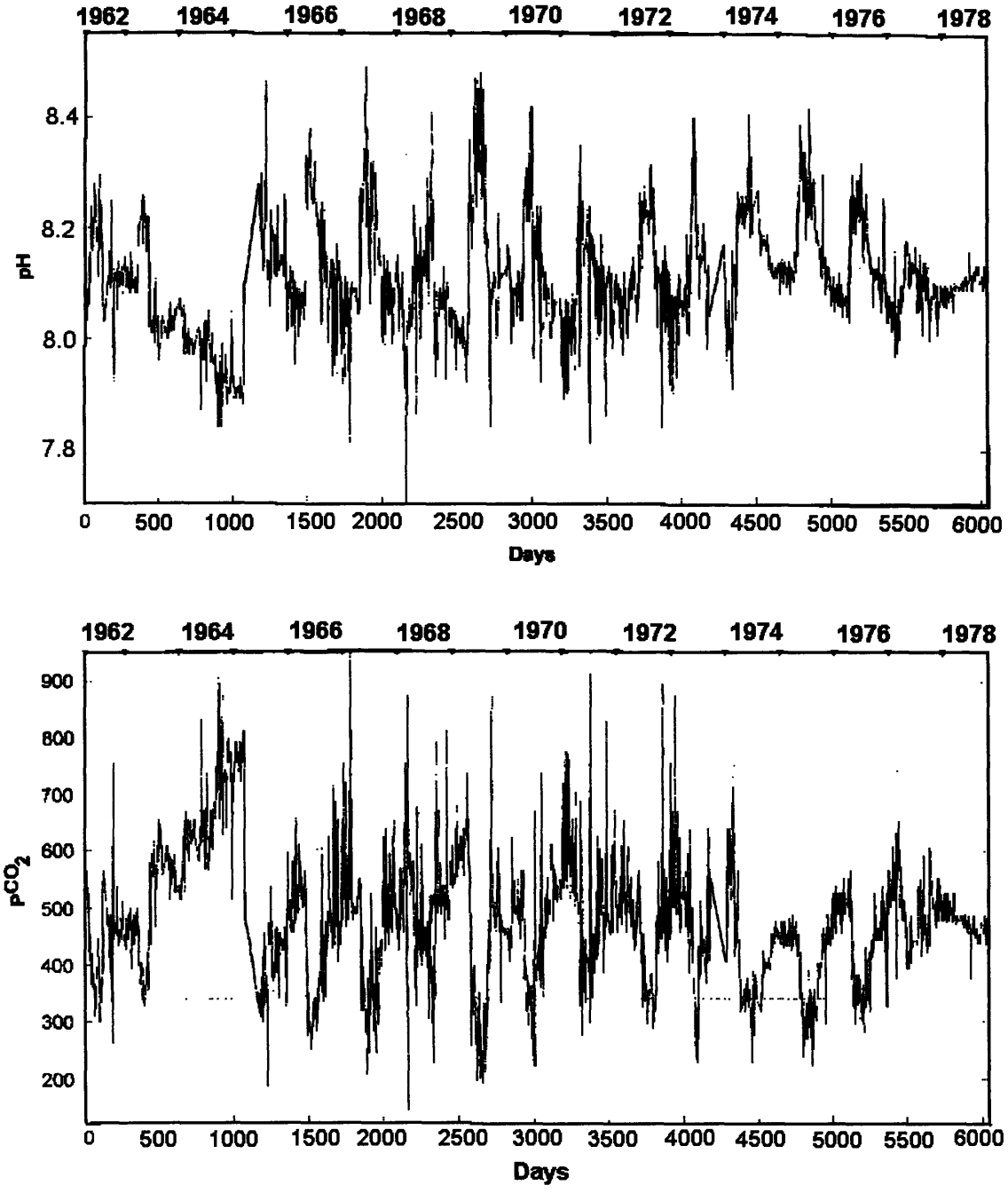


Figure 13. Long term records of pH (above) and calculated values of pCO_2 (below) at a station off Helgoland in the German Bight, North Sea. (data provide by W. Hidal, Hamburg, Germany).

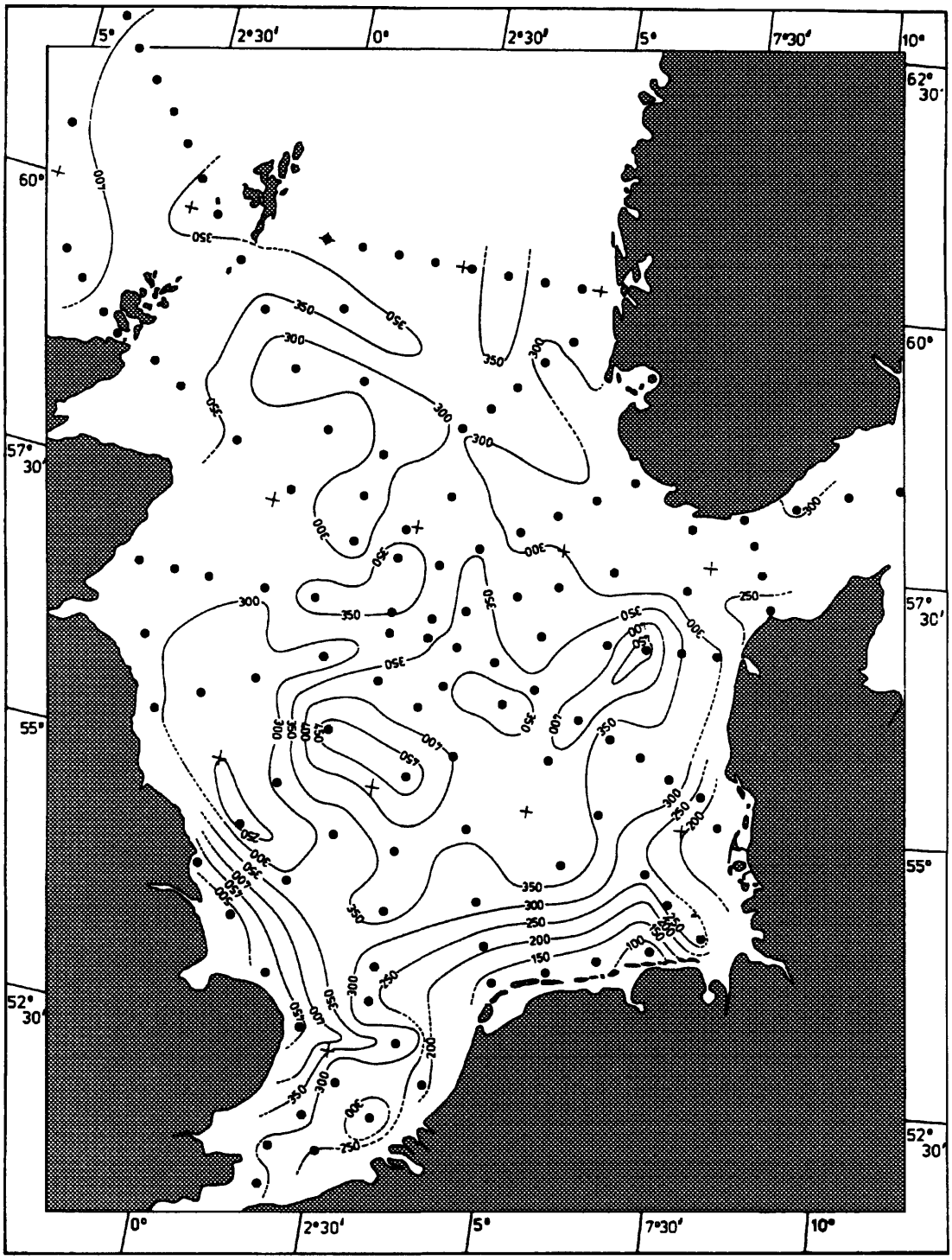


Figure 14. Surface pCO_2 in the North Sea in May/June 1986 (Kempe and Pegler, 1991).

Between 1962 and 1978 the pH was monitored at a station in the German Bight off Helgoland where the plumes of the Weser and Elbe Rivers mix with central North Sea water. This pH record reproduced in the upper half of Figure 13 was converted to pCO_2 using the relationship in Figure 11 and the results are plotted in the lower portion of Figure 13. The data show several distinctive periods with different scattering characteristics. Apparently, the techniques used to measure pH changed several times during the time series and the electrodes used drifted during the first three and the last two years of the record. Despite these problems, a systematic seasonal change in pCO_2 is readily identified. During winter, values are high but they decrease sharply in spring and recover slowly during autumn and winter. This cycle is contrary to what would be expected in an abiotic ocean where the seasonal heating of the water should increase the pCO_2 in summer and lower it in winter. Thus, biological activity not only counterbalances seasonal heating but extracts additional CO_2 from the atmosphere throughout the summer.

The overall average of the record (about 480 ppmv) is much higher than current atmospheric pCO_2 (about 350 ppmv) and suggests that the North Sea is a net CO_2 source to the atmosphere. However, such a conclusion is probably premature because of a poor standardisation of the pH measurement. Furthermore, the large scatter toward positive values suggests that measurements have not been made *in situ* but in samples stored for some time so that respiration could have increased pCO_2. The same conclusion can be drawn from the fact that even in summer the water pCO_2 is only marginally lower than atmospheric pCO_2 in spite of very high nutrient loads and high productivity (Berg and Radach, 1985).

In May-June 1986, a biogeochemical survey of the entire North Sea was conducted as part of the ZISCH program. Alkalinity, total dissolved CO_2, salinity, temperature, pH and nutrients were determined in over 1,000 samples collected from 5m and deeper. Surface pCO_2 for the North Sea was calculated from this data set using the procedures outlined in Pegler and Kempe (1988) and the results are plotted in Figure 14. The central gyre of the North Sea, the inflowing North Atlantic water north of Scotland and a small strip along the British coast showed a pCO_2 value higher than that of the atmospheric (i.e. greater than 350 ppmv) while the rest of the region showed a pCO_2 below that of the atmosphere. Along the Dutch-German-Danish coast a belt of very low pCO_2 was recorded which coincides with the low salinity plumes of the Rhine, Weser and Elbe Rivers. At some places, the pCO_2 dropped below 100 ppmv due to the intense spring plankton bloom.

In order to estimate the net flux of CO_2 from the North Sea, the areas (km^2) of the different pCO_2 concentrations were first determined (Figure 15a). At the time of sampling in 1986, the pCO_2 of the atmosphere was 346 ppmv or 19.9 mM/m^3. Clearly, a greater area of the North Sea has a pCO_2 less than atmospheric pCO_2 than larger. Next, the following CO_2-flux model was applied to the data (Broecker and Peng, 1982; Liss and Merlivat, 1986):

$$CO_2\text{-flux} = D \times ([CO_2]_{air} - [CO_2]_{water}) / Z)$$

where:

- D is the diffusion coefficient (1.32×10^{-5} cm^2/sec or 1.14×10^{-4} m^2/d at the average temperature of 8.6°C during May-June 1986);
- $[CO_2]_{air}$ and $[CO_2]_{water}$ are the respective CO_2 concentrations (not pressures) in air and water; and,
- Z is the thickness of the boundary layer [estimated by Broecker and Peng (1982) to be 40 mm for the ocean).

Decreasing Z by 25% to 30 mm, which happens naturally during storms, increases the flux by 25%. The calculated fluxes for all concentration ranges are plotted in Figure 15b. The largest flux occurs in the 250-300 ppmv range. In total, these data indicate that in 1986 the North Sea released 1.14×10^9 M/d from the areas supersaturated with CO_2 and gained 3.14×10^9 M/d in the areas that were undersaturated. The net gain amounted to 2×10^9 M/d (24×10^3 tC/d). If one assumes that the conditions encountered during this cruise are representative for the warm season of the year, then uptake over a half year is on the order of 4.3×10^6 t C. This figure compares favourably with a potentially sequestered carbon value of 5-6 $\times 10^6$ t C estimated from the average annual anthropogenic nutrient input to the North Sea (120×10^3 t P and 970×10^3 t N) (ICES 1978).

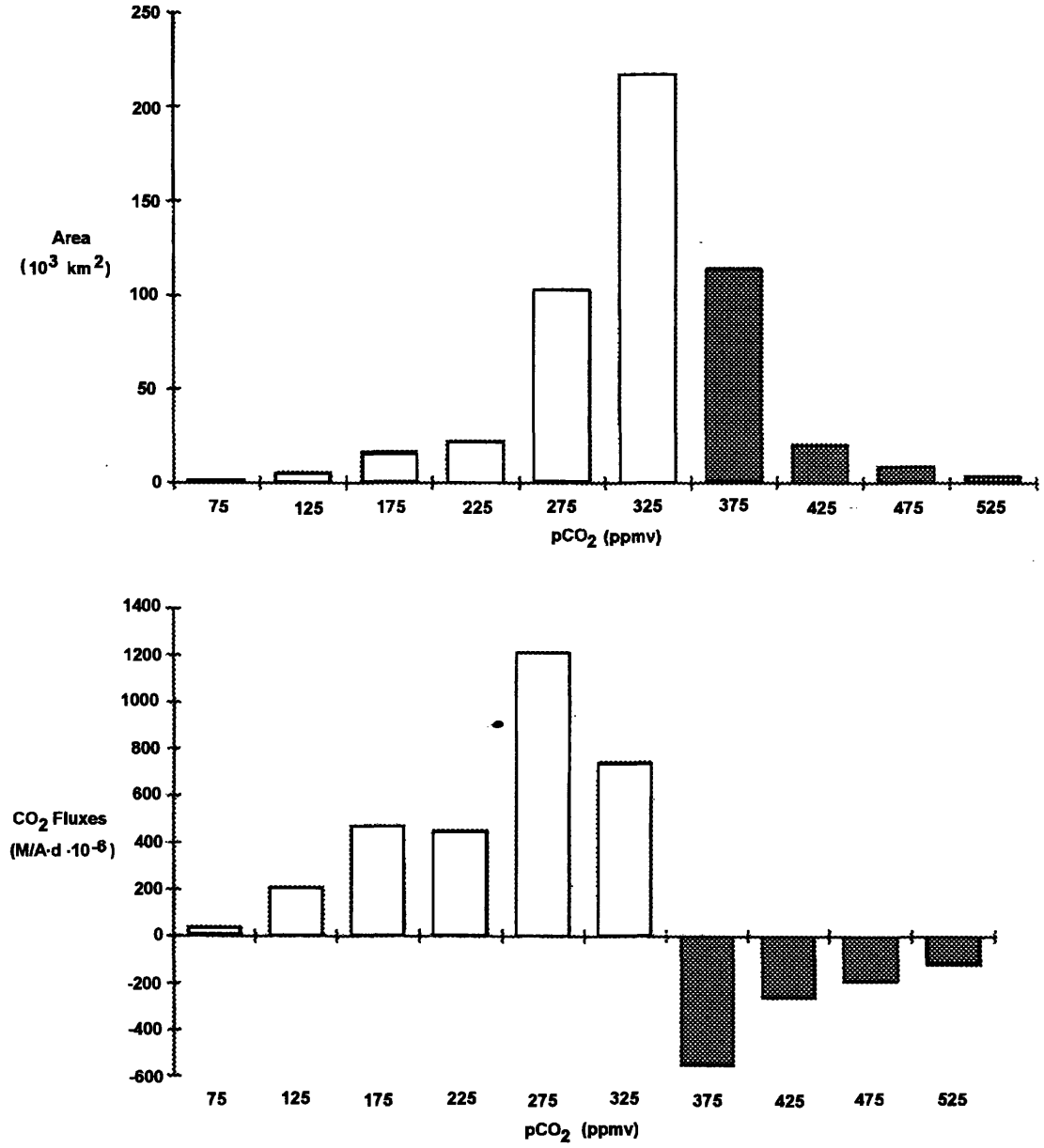


Figure 15. Spatial extent of waters of different pCO_2 distribution (above) and corresponding CO_2 flux values (below) in the North Sea (Kempe and Pegler, 1991).

The net uptake of CO_2 calculated for the North Sea by the above model is very small compared to the estimates of the actual gross primary production. Aletsee and Rick (1988) suggest that gross primary production amounts to 170 x 10^6 t C in summer. Subtracting the autorespiration, which is estimated to be 20 x 10^6 t C, yields a net primary production of 150 x 10^6 t C. This is produced by a standing stock of phytoplankton amounting to only 1.4 x 10^6 t C which means that the carbon must be turned over every 1.3 days on average. If this did not happen, the entire North Sea, which has 270 x 10^6 t C of inorganic carbon in the upper 20 m, would be completely depleted of carbon within 1.6 years. The measurements of the total dissolved CO_2 show only small depletions of inorganic carbon locally (not much more than 100 mM/l). Therefore, remineralisation must quickly return organically fixed carbon to the inorganic carbon pool. Apparently, only small fractions escape heterotrophic consumption. Sediment trap experiments (Kempe and Jennerjahn, 1988) yielded vertical organic carbon fluxes of 8.7-27 mgC/m^2/d and a $CaCO_3$ fluxes of 2.4-8.0 mg C/m^2/d. The average fluxes may therefore reach 1.5 x 10^6 t organic carbon and 0.3 x 10^6 t inorganic carbon over a half year period. This is comparable to only 1% of the net primary production. Sediments in shallower parts of the North Sea may receive larger amounts of net primary production but on the other hand this material could be readily resuspended by storms.

In summary, we are far from being able to construct a fully balanced carbon model for the North Sea (Figure 16). However, one thing is certain. We must look for residual fluxes (net CO_2 uptake or loss through the air-sea interface, net carbon accumulation in the sediments, etc.) which are very small in comparison to the much larger gross fluxes.

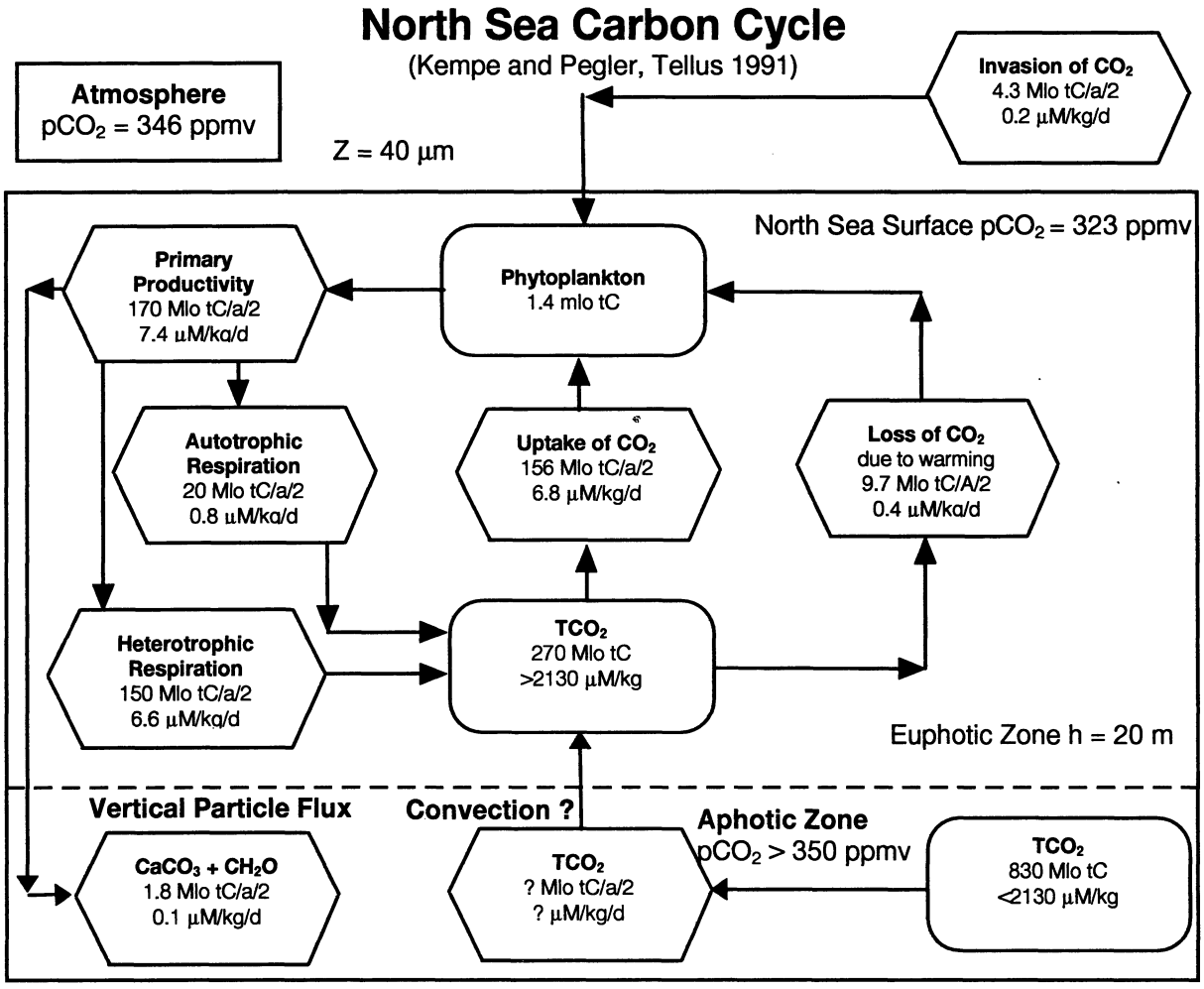


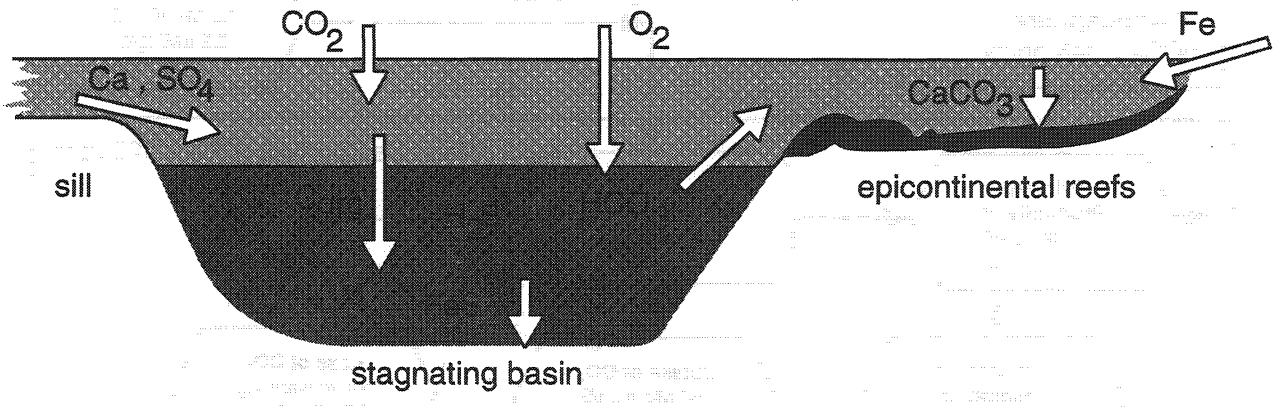
Figure 16. A preliminary carbon cycle budget for the North Sea (Kempe and Pegler, 1991).

Other Sinks for Respired Terrestrial Organic Carbon

The data reviewed above support the hypothesis that large areas of the world coastal zone may have lost their natural heterotrophic status and become autotrophic because of anthropogenic eutrophication. They have become sinks of atmospheric CO_2 instead of sources. However, there may be other processes at work which could have diminished net heterotrophy of coastal seas prior to anthropogenic eutrophication. The most important process is probably sulphate reduction.

Sulphate reduction

The chemistry of bacterial sulphate reduction, during which the charge of the consumed sulphate ion is replaced by alkalinity, is illustrated in Figure 17. Basically, sulphate reduction causes organic carbon to be transformed into alkalinity (HCO_3 ions) thereby preventing its loss to the atmosphere as CO_2 which would occur if the organic carbon was consumed by aerobic respiration. It has been shown that riverine POC delivered to the coastal seas is more labile than riverine DOC. Terrestrial POC, plus a certain portion of marine POC can be deposited at least temporarily near-shore where it can be remineralised in the sediment under reducing conditions to produce alkalinity. This mechanism is at work in stagnant marine basins, such as the Black Sea and the Baltic Sea (Kempe, 1990), and results in the export of excess alkalinity to surface waters. For example, in the Black Sea surface and deep waters have acquired alkalinity's of 3.4 and 4.3 meq/l respectively (compared to the oceanic average of 2.2 meq/l) in spite of the low salinity of this water body (alkalinity is normally a rather conservative property of seawater). Thus, alkalinity increases observed in coastal waters could possibly reveal significant remineralisation of organic carbon by bacterial sulphate reduction.



$$C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1 + 53SO_4^{2-} + 14\ H_2O \Longrightarrow$$
$$53H_2S + 106HCO_3^- + HPO_4^{2-} + 16\ NH_4^+ + 14OH^-$$

Figure 17. Diagrammatic representation of the Alkalinity pump (Kempe, 1990).

Tentative support to this hypothesis is given by the distribution of alkalinity in the North Sea measured in May/June 1986 (Figure 18). A zone of increased alkalinity values is found close to shore. The source of this alkalinity could be sulphate reduction in tidal flat sediments. However, it could also be excess alkalinity derived from freshwater import. The regression of total alkalinity versus salinity suggests a freshwater end-member concentration of 2.61 meq/l (Figure 19). The Elbe had an average alkalinity of 2.2 meq/l in 1975-1977 (Kempe, 1982a) and the Weser had an alkalinity of 2.86 meq/l in 1978 (Kempe, 1982b). Weighting these end-member concentrations according to discharge (24 versus 8.6 km^3/a), the combined riverine end-member would amount to 2.32 meq/l which is still less than the observed end-member composition of 2.61 meq/l. This difference could either arise from the postulated sulphate reduction-generated alkalinity or from interannual changes in the alkalinity of the river inputs. Both these processes will be studied in the North Sea KUSTOS project being conducted by Germany.

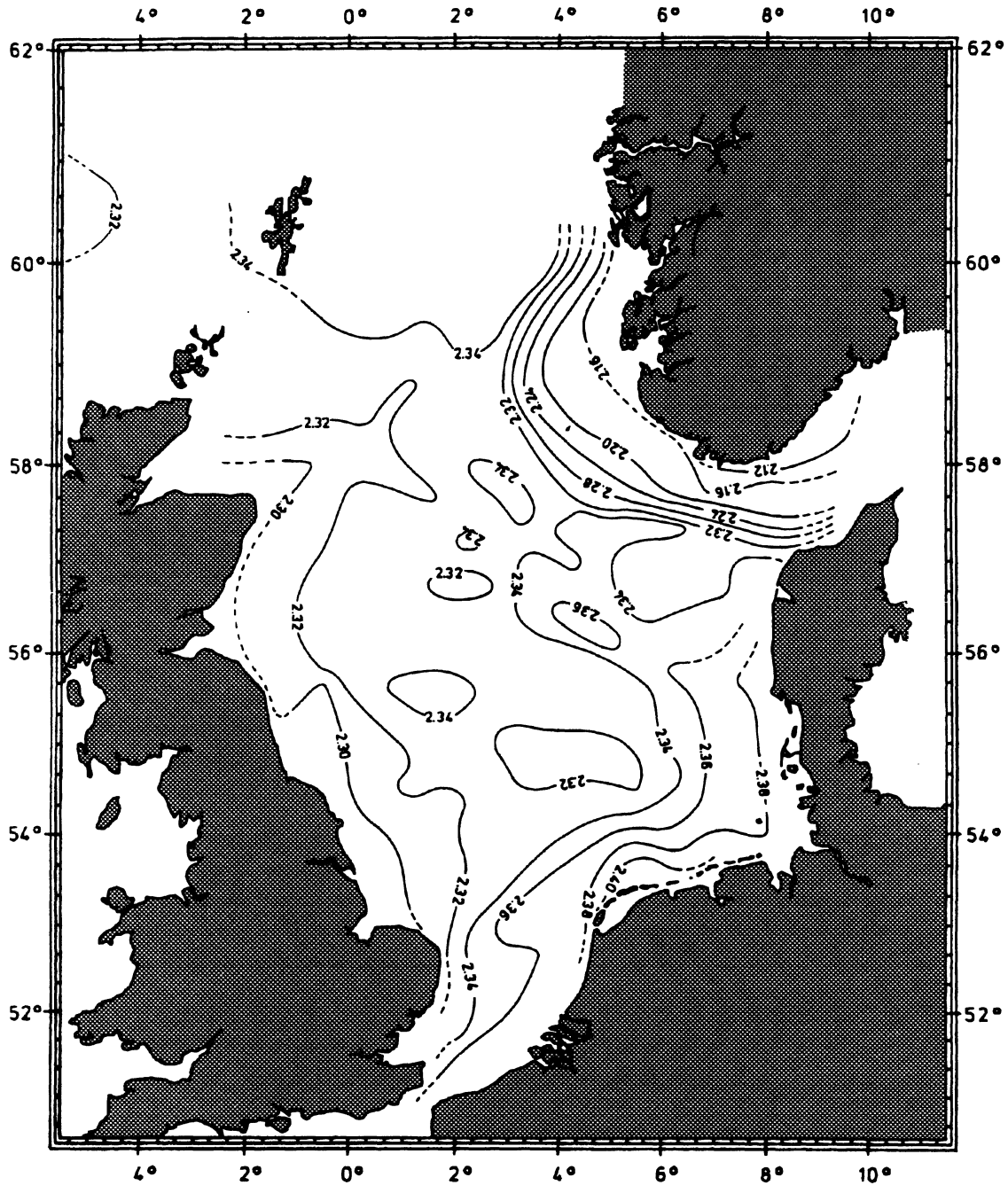


Figure 18. Alkalinity distribution in the North Sea in May/June 1986 (Pegler and Kempe, 1988; Kempe and Pegler, 1991).

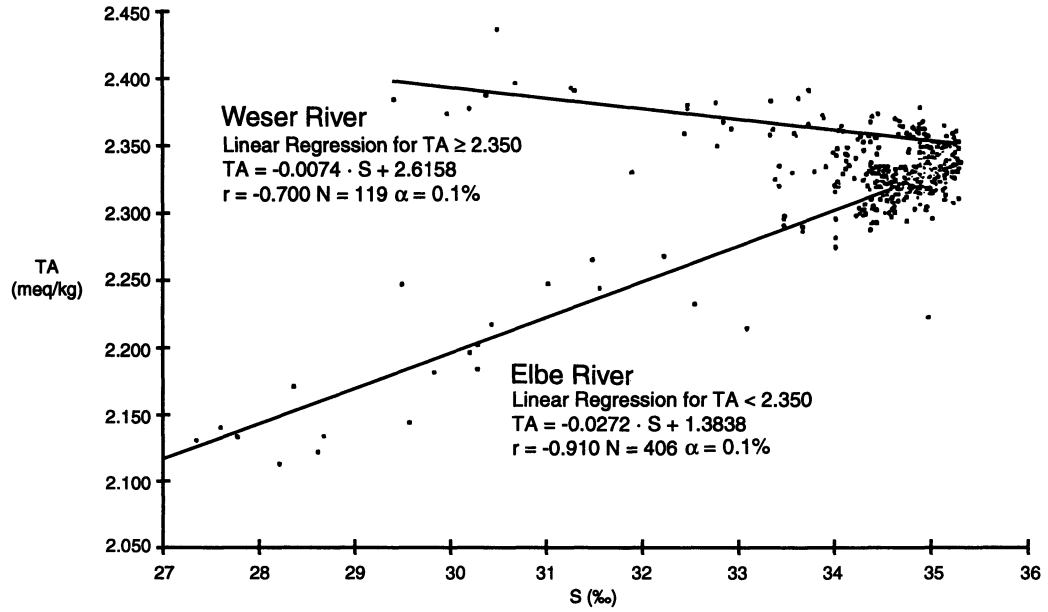


Figure 19. Relationship between alkalinity and salinity along the discharge paths of the rivers Weser (above) and Elbe (below) in the North Sea (Kempe, 1982a).

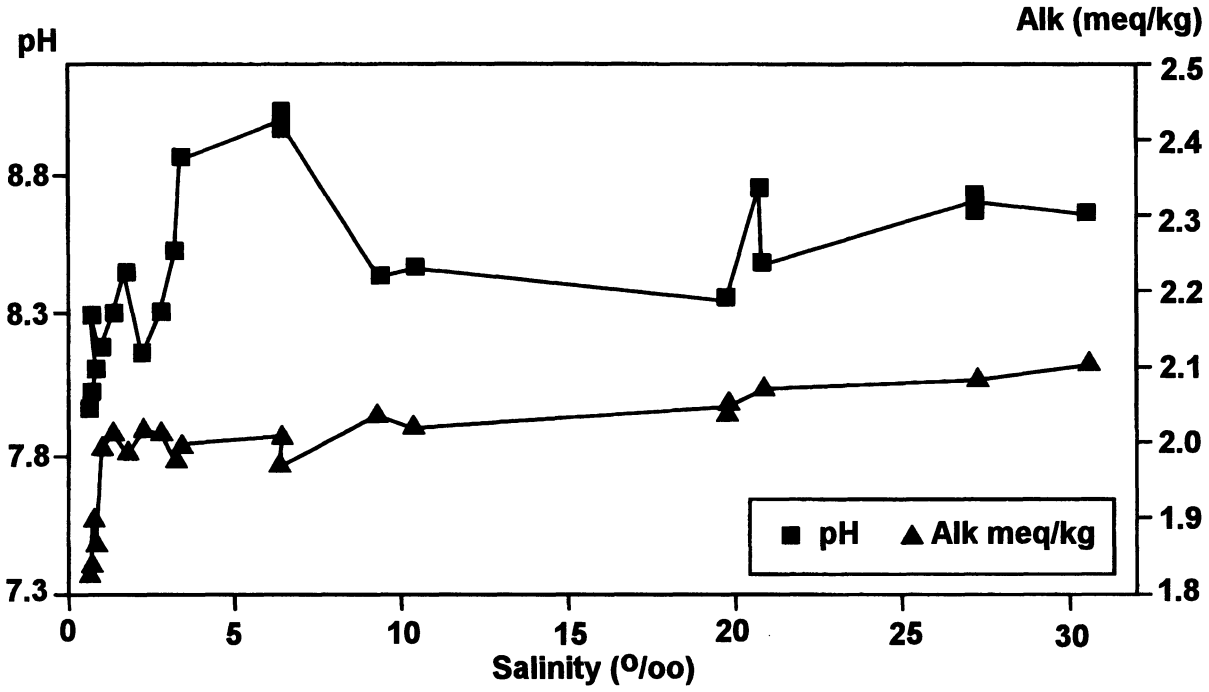


Figure 20. Non-conservative increase in alkalinity and pH in the estuary of the Elbe caused by the dissolution of marine suspended carbonates and the consumption of free CO_2 from the Elbe water (Kempe 1982b, 1984).

The export of excess alkalinity due to bacterial sulphate reduction has been recently reported by Smith *et al.* (1991) in Tomales Bay, California. This result suggests that sulphate reduction may be a universally more important biogeochemical reaction in coastal waters than previously recognised. However, in neither Tomales Bay nor the North Sea was the increased alkalinity balanced by an equivalent increase in total dissolved CO_2 which should have been the case at the original site of sulphate reduction. This equivalent excess total dissolved CO_2 has probably been degassed from Tomales Bay as CO_2 (Smith *et al.*, 1991) or taken up by phytoplankton in the North Sea to form POC. During a vigorous bloom, the extraction of total dissolved CO_2 to form organic matter must cause the formation of carbonate ions in order to keep the charge balance of the increased alkalinity constant:

$$2HCO_3^- = CO_3^{2-} + CH_2O + O_2$$

This in turn will lead to an unusually high pH value for sea water (>8.7 in case of the North Sea). Carbonate ion concentration is, on the other hand, a measure of the buffering capacity of seawater. A high carbonate ion content therefore provides a higher buffering capacity to additional atmospheric or respirational CO_2 uptake that could take place later in the history of the water mass.

Calcium carbonate dissolution

Another possible mechanism that might buffer increased pCO_2 values caused by remineralisation of labile organic carbon is carbonate mineral dissolution which can be represented by the following equation:

$$CO_2 + H_2O + CaCO_3 = Ca^{2+} + 2HCO_3^-$$

The surface waters of the ocean are normally supersaturated with regard to both calcite and aragonite, the two most common phases of calcium carbonate. However, under increased pCO_2, aragonite and even calcite undersaturation may be reached. Such environments are found in estuaries where rivers high in pCO_2 and low in suspended carbonate minerals mix with seawater of low pCO_2 but with carbonate particles in suspension. In general, due to the respiration of labile carbon in transport, rivers have a much higher pCO_2 than the atmosphere, often 20 times higher (Kempe, 1982a; 1984). The non-conservative increase of alkalinity and pH in the Elbe Estuary caused by the dissolution of marine suspended carbonates and the consumption of free CO_2 from the Elbe water is shown in Figure 20. Due to the non-linearity's in the redistribution of the relevant carbonate species (Wigley and Plummer, 1976), the mixing of two water sources with different pCO_2 may cause temporary undersaturation even if both of the end-member solutions are saturated or slightly oversaturated. Therefore, we can suspect that alkalinity is generated from free CO_2 or from *in situ* respired labile organic carbon in many estuaries, thereby diminishing the CO_2 source function of coastal seas (Kempe, 1984, 1988).

It is conceivable that carbonate dissolution induced by increased pCO_2 occurs in porewaters of shallow shelf sediments (prone to re-suspension during storms) and intertidal sediments (prone to discharge at low tide) and can also add alkalinity to seawater. However, there is no quantitative information on the potential significance of this process.

Summary

The question whether coastal seas are a net source or sink of CO_2 to the atmosphere is not easily answered. As a first approach, the difference between riverine discharge of organic carbon and total marine sedimentation, using subjectively "best" estimates, suggests that coastal seas should be net heterotrophic, that is they release more CO_2 to the atmosphere than they take up. However, current "best" estimates on river organic carbon discharge [0.33 GtC/a (Degens *et al.*, 1991) and 0.4 GtC/a (Meybeck, 1981; 1982)] are not more accurate than ± 0.1 GtC/a and estimates of carbon burial differ even more widely. In a recent overview, Smith and Hollibaugh (1993) quote values of carbon burial between 0.030 and 1.680 GtC/a but argue that the "best" estimate is 0.13 GtC/a (Berner, 1982). This leaves a source term between 0.2 and 0.27 GtC/a.

In addition to the question of exact numbers, the question of the lability of riverine total organic carbon is important. Riverine DOC in general is mixed conservatively into ocean waters while POC is much more labile. One measure of lability is to add the concentrations of amino acids and sugars contained in total

organic carbon. Doing this suggests that the lability of riverine total organic carbon is on the order of 15% which substantially reduces the potential for near-shore respiration to 0.05 - 0.06 GtC/a. This amount has to be compared to the potentially sequestered carbon as estimated from the dissolved nutrient input using the Redfield ratio. Again, the available numbers are at best, estimates. Specifically, particulate phosphorus loads could play a much larger role than currently thought in sequestering inorganic carbon released by aerobic respiration. Large differences exist between individual river plumes and those unaffected by pollution are probably close to a balanced CO_2 budget while those from industrialised regions with high nutrient loads probably sequester more inorganic carbon than is released by the remineralisation of their labile carbon. In particular, the coastal seas around Europe have probably changed in recent years from net sources to net sinks for atmospheric CO_2.

On average, the pre-industrial global coastal sea was probably slightly heterotrophic, but in recent decades it has probably become autotrophic thereby causing either an increase in marine organic carbon burial or an increase in the oceanic DOC and dissolved inorganic carbon pools.

Additionally, other natural sinks for CO_2 remineralised from terrestrial carbon must be considered. Sulphate reduction in sediments or calcite dissolution in the estuaries of rivers with high pCO_2 could produce additional alkalinity.

Much needs to be learned about the details of the carbon, nitrogen and phosphorus cycles in the diverse coastal seas around the world before their role in global cycles can be fully understood. Such biogeochemical studies are a major focus of the Land-Ocean Interactions in the Coastal Zone (LOICZ) Core Project of the IGBP described in detail by Pernetta and Milliman (1995). Gordon *et al.* (in press) have produced a guideline document that outlines biogeochemical modelling methodologies that will help promote the collection and analysis of necessary data, and resolve these issues.

References

Aletsee, L. and H. Rick, 1988. *Teilprojekt G5: Phytoplankton. In Zirkulation und Schadstoffumsatz in der Nordsee (ZISCH), Endbericht BMFT Projekt MFU 0545,* pp 236-257. Selbstverl. Inst. für Meeresforschung, Univ. Hamburg.

Baumgartner, A. and E. Reichel, 1975. *The World Water balance.* R. Oldenbourg Verlag, München, Wien, 179 pp.

Berg, J. and G. Radach, 1985. *Trends in the nutrient and phytoplankton concentrations at Helgoland Reede (German Bight) since 1962.* Int. Counc. Expl. Sea, L:2, Sess. R. Biol. Oceanogr. Com. 16 pp.

Berner, R.A., 1982. Burial of organic carbon as pyrite sulfur in the modern ocean: its geochemical significance. *Amer. Journ. Sci.* **282**:451-473.

Bolin, B., E.T. Degens, S. Kempe and P. Ketner, 1979. The global carbon cycle. pp 35-38 In: J. Williams (ed.). *Carbon Dioxide, Climate and Society.* Pergamon Press, Oxford.

Brewer, P.G., 1971. *Hydrographic and Chemical Data from the Black Sea.* Woods Hole Oceanographic Inst. Techn. Rep. 71-65.

Broecker, W.S. and T.-H. Peng, 1982. *Tracers in the Sea.* Lahmont-Doherty Geol. Observ., Columbia Univ., Palisades. 690 pp.

Burton, J.D., 1983. A comment on the behaviour of dissolved organic carbon during estuarine mixing. pp 408-410, In B. Bolin and R.B. Cook (eds.). *The Major Biogeochemical Cycles and Their Interactions.* SCOPE Rep. 21, Wiley, Chichester, New York.

Codispoti, L.A., G.E. Friederich, J.W. Murray and C.M. Sakamoto, 1991. Chemical variability in the Black Sea: implications of continuous vertical profiles that penetrate the oxic/anoxic interface. *Deep-Sea Res.* **38**, Suppl. Issue No 2A S691-S710.

Degens, E. T. and V. Ittekkot, 1985. Particulate organic carbon, an overview. pp 7-27 In E.T. Degens, S. Kempe and R. Herrera (eds.) *Transport of Carbon and Minerals in Major World Rivers, Pt 3* Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 58.

Degens, E.T., S. Kempe and J.E. Richey, 1991. Summary: biogeochemistry of major world rivers. pp 323-347 In E.T. Degens, S. Kempe and J. Richey (eds.). *Biogeochemistry of Major World Rivers.* SCOPE Report 42, J. Wiley & Sons, Chichester, New York.

Depetris, P.J. and S. Kempe, 1990. The Impact of the El Niño 1982 event on the Paraná River, its discharge and carbon transport. *Palaeogeography, Paleoclimatology, Paleoecology (Global and Planetary Change Section)* **89**:239-244.

Etcheber, H., R.W.P.M. Laane, R.G. Lin and R. Kloosterhuis, 1993. Degradability of sedimentary organic matter in estuarine and coastal environment.- In Kempe, S., D. Eisma and E.T. Degens (eds): *Transport of Carbon and Nutrients in Lakes and Estuaries, Pt 6,* Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 74.

Friederich, G.E., L.A. Codispoti and C.M. Sakomoto, 1990. *Bottle and Pumpcast Data from the 1988 Black Sea Expedition.* Monterey Bay Aquarium Research Inst. Techn. Rep. 90-3: 224 pp.

Gordon, D.C, P.R. Boudreau, K.H. Mann, J.-E. Ong, W. Silvert, S.V. Smith, G. Wattayakorn, F. Wulff and T. Yanagi. In press. *LOICZ Biogeochemical Modelling Guidelines.* LOICZ Reports & Studies No. 5.

ICES, 1978. *Input of pollutants to the Oslo condition area.* Comm. Res. Rep. 77.

Ittekkot, V., A. Spitzy and U. Lammerz, 1982. Valdiva Cruise October 1981: Dissolved organic matter in the Elbe, Weser and Ems Rivers and the German Bight. pp. 749-756. In E.T. Degens (ed.) *Transport of Carbon and Minerals in Major World Rivers, Pt 1.* Mitt. Geol.-Palaeontol. Inst. Univ. Hamburg. SCOPE/UNEP Sonderband 52.

Kempe, S., 1982a. Long-term records of CO_2 pressure fluctuations in fresh waters. Habilitationsschrift. pp 91-332 In E.T. Degens (ed.). *Transport of Carbon and Minerals in Major World Rivers, Pt. 1,* Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 52.

Kempe, S., 1982b. VALDIVIA Cruise, October 1981: Carbonate equilibria in the estuaries of Elbe, Weser, Ems and in the Southern German Bight. pp 719-742 In E.T. Degens (ed.). *Transport of Carbon and Minerals in Major World Rivers. Pt 1.* Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 52.

Kempe, S., 1984. Sinks of the anthropogenically enhanced carbon cycle in surface fresh waters. *J. Geophys. Res.* **89**, D3:4657-4676.

Kempe, S., 1990. Alkalinity: The link between anaerobic basins and shallow water carbonates? *Naturwissenschaften* **77**:426-427.

Kempe, S. and P.J. Depetris, 1990. Labile carbon in the Paraná River basin. Mitt. Geol.-Paläontol. Inst. Univ. Hamburg, *Egon T. Degens Memorial Volume*, **69**: 157-165.

Kempe, S. and T. C. Jennerjahn 1988. The vertical particle flux in the northern North Sea, its seasonality and composition. pp 229-267 In S. Kempe, G. Liebezeit, V. Dethlefsen and U. Harms (eds.) *Biogeochemistry and Distribution of Suspended Matter in the North Sea and Implications to Fisheries Biology*. Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 65.

Kempe, S. and K. Pegler, 1991. Sinks and sources of CO_2 in coastal seas: the North Sea. *Tellus* **43B**:224-235.

Kempe, S., M. Pettine and G. Cauwet, 1991. Biogeochemistry of European rivers. Pp 169-211 In: E.T. Degens, S. Kempe and J. Richey (eds.) *Biogeochemistry of Major World Rivers.* SCOPE Report 42. J. Wiley & Sons Chichester, New York.

Lerman, A., F.T. Mackenzie, and R.J. Geiger, 1988. Environmental chemical stress effects in carbon and phosphorous cycles in Ecotoxicology. In S. Levin (ed.) *Ecotoxicology*, Wiley-Interscience, New York (Seiten heraussuchen, vermutlich SCOPE REPORT).

Liss, P. S. and L. Merlivat, 1986. Air-sea gas exchange rates: introduction and synthesis. pp 113-127 In: P. Buat-Menard (ed.) *The Role of Air-Sea Exchange in Geochemical Cycling.* D. Reidel, Dordrecht.

Meybeck, M., 1981. River transport of organic carbon to the ocean. pp 219-269 In: *Flux of Organic Carbon by Rivers to the Oceans.* Rep. CONF 8009140, part 2. US Dep. of Energy, Washington D.C.

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. *Am. J. Sci.* **282**:401-450.

Milliman, J.D. C. Rutkowski and M. Meybeck, 1995. River Discharge to the Sea: A Global River Index (GLORI). LOICZ Reports and Studies No. 2. pp. 125.

Milliman, J.D. and J.P.M. Syvitski, 1992. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. *J. Geol.* **100**:525-544.

Parkhurst, D.L., D.C. Thorstenson, and L.N. Plummer, 1980. *PHREEQE a computer program for geochemical calculations.* Water Resour. Invest. Rept. 80-96:210 pp. U.S. Geol. Survey, Washington D.C.

Pegler, K. and S. Kempe, 1988. The carbonate system of the North Sea: Determination of alkalinity and TCO_2 and calculation of PCO_2 and Silica (Spring 1986). pp 35-87 In: S. Kempe, G. Liebezeit, V. Dethlefsen and U. Harms (eds). *Biogeochemistry and Distribution of Suspended Matter in the North Sea and Implications to Fisheries Biology.* Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband **65**.

Pernetta, J. and J. Milliman. 1995. *Land-Ocean Interactions in the Coastal Zone: Implementation Plan.* IGBP Report No. 33,. IGBP, Stockholm, Sweden, 215 pp.

Pytkowicz, R.M., 1983. *Equilibria, Nonequilibria, and Natural Waters.* Vols. I, II. J. Wiley & Sons, New York. 353 pp.

Redfield, A.C., 1958. The biological control and chemical factors in the environment. *Amer. Sci.* **46**:206-226.

Richey, J.E., R.L. Victoria, E. Salati and B. R. Forsberg, 1991. The biogeochemistry of a major river system: The Amazon case study. Pp 57-74 In: E.T. Degens, S. Kempe and J. Richey (eds) *Biogeochemistry of Major World Rivers.* SCOPE Report 42. J. Wiley and Sons, Chichester, New York.

Rosenberg, R., R. Elmgren, S. Fleischer, P. Jonsson, G. Persson and H. Dahlin, 1990. Marine eutrophication case studies in Sweden. *Ambio,* **19(3):**102-108.

Smith, S.V. and F.T. Mackenzie, 1987. The ocean as a net heterotrophic system: implications from the carbon biogeochemical cycle. *Global Biogeochem. Cycles* **1(3)**:187-199.

Smith, S.V., J.T. Hollibaugh, S.J. Dollar and S. Vink, 1991. Tomales Bay metabolism: C-N-P stoichiometry and ecosystem heterotrophy at the Land-Sea Interface. *Est. Coast. Shelf Sci.* **33**:223-257.

Smith, S.V. and J.T. Hollibaugh, 1993. Coastal metabolism and the oceanic carbon balance. *Rev. Geophy.* **31**:75-89.

Tugrul, S., O. Basturk, C. Saydam and A. Yilmaz, 1992. Changes in the hydrochemistry of the Black Sea inferred from water density profiles. *Nature* **359**:137-359.

Walsh, J.J., E.T. Premuzic, J.S. Gaffney, G.T. Rowe, G. Harbottle, R.W. Stoenner, W.L. Balsam, P.R. Betzer and S.A. Macko, 1985. Organic storage of CO_2 on the continental slope off the mid-Atlantic bight, the southeastern Bering Sea, and the Peru Coast. *Deep-Sea Res.* **32(7):**853-883.

Wigley, T.M.L. and L.N. Plummer, 1976. Mixing of carbonate waters. *Geochim. Cosmochim. Acta* **40:**989-995.

Wollast, R., 1983. Interactions in estuaries and coastal waters. pp 385-407 In: B. Bolin and R.B. Cook (eds.) *The Major Biogeochemical Cycles and Their Interactions.* SCOPE Rep. 21. J. Wiley and Sons, Chichester, New York.

LOICZ
IGBP