Coupling of the Perturbed C–N–P Cycles in Industrial Time

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Abstract. Coupling of the C–N–P biogeochemical cycles is effected by the dependence of the land and aquatic primary producers on the availability of N and P. In general, the Redfield ratios C:P and N:P in the reservoirs supplying nutrients for primary production on land, in the oceanic coastal zone, and in the surface ocean differ from these ratios in the land phytomass and aquatic plankton. When N:P in the source is higher than in primary producers, this results in a potential accumulation of some excess nitrogen in soil water and coastal water, and increased denitrification flux to the atmosphere. The oceanic coastal zone plays an important role in the coupled C–N–P cycles and their dynamics because of its intermediate position between the land and oceanic reservoirs. These coupled cycles were analyzed for the last 300 years of exposure to four human-generated forcings (fossil fuel emissions, land use change, chemical fertilization of land, and sewage discharge to the coastal zone) and global temperature rise. In the period from 1700 to 2000, there has been a net loss of C, N, and P primarily from the land phytomass and soil humus, despite the rise in atmospheric CO_2, increased recycling of nutrients from humus, chemical fertilization, and re-growth of forests on previously disturbed land. The main mechanisms responsible for the net loss were increased riverine transport to the coastal zone of dissolved and particulate materials and, for N, increased denitrification on land. The oceanic coastal zone gained N and P, resulting in their accumulation in the organic pool of living biomass and dissolved and reactive particulates, as well as in their accumulation in coastal sediments from land-derived and *in situ* produced organic matter. Pronounced shifts in the rates and directions of change in some of the major land reservoirs occurred near the mid-1900s. Denitrification removes N from the pool available for primary production. It is the strongest on land, accounting for 73–83% of N removal from land by the combined mechanisms of denitrification and riverine export.

Key words: C–N–P cycles; coupled cycles; C:N:P ratios, denitrification; human perturbations; land environment; ocean coastal zone; primary production; cycle dynamics

1. Introduction

The concept of the coupled biogeochemical cycles is rooted in the ubiquitous occurrence of the major nutrient elements carbon, nitrogen, and phosphorus in living organisms on land and in waters. The coupling of the biogeochemical cycle of carbon to those of other elements is well established in the need of primary producers to use other nutrient elements in

addition to carbon. The availability of nitrogen, phosphorus, and more than a dozen trace elements is a general condition for land and aquatic primary producers to be able to photosynthesize organic matter and perpetuate life. Nitrogen and phosphorus follow carbon as the main constituents of living organic matter, and their close linkage to the carbon cycle has been long recognized in their important role as a "growth limiting nutrient", a nutrient element whose insufficient abundance in the environment limits primary production.

The very large number of studies of photosynthesizing organisms and natural ecosystems produces evidence for a somewhat variable role of nitrogen or phosphorus as a "limiting nutrient" under different environmental conditions (e.g., Schlesinger, 1997). From considerations of natural abundance, atmospheric or mineral sources, and chemical speciation of N and P in natural waters, phosphorus is the more likely growth-limiting element on a global and long time scale (e.g., Smith, 1984; Tyrrell, 1999; Guidry and Mackenzie, 2003).

The very large amount of work on global and regional carbon cycles is supported by a more limited number of studies of the nitrogen and phosphorus cycles at time scales comparable to those of the carbon cycle, from geological to centuries-long temporal scales of the industrial age, and from global to subcontinental spatial scales (e.g., Black and Shimmield, 2003; Blackburn and Sorensen, 1988; Cole et al., 1993; Galloway and Cowling, 2002; Galloway et al., 1995a,b; Howarth et al., 1996; Krug and Winstanley, 2002; Mackenzie et al., 2002; Peierls et al., 1991; Seitzinger and Kroeze, 1998; Tiessen, 1995; Turner et al., 2003; Vitousek et al., 1997; Wollast, 1993, 1998). Most workers usually consider the atmosphere, land and ocean as big reservoirs, with variable subdivisions. The separate role of the oceanic coastal zone has received much less attention despite its importance as the reservoir proximal to land and receiving direct inputs from the land and atmosphere (e.g., Chen et al., 2003; Chen, 2004; Lerman et al., 2002; Liu et al., 2000; Mackenzie et al., 2002; Mantoura et al., 1991; Rabouille et al., 2001; Smith and Mackenzie, 1987; Smith and Hollibaugh, 1993; Ver et al., 1999; Wollast, 1993, 1994, 1998; Wollast and Mackenzie, 1989). The oceanic coastal zone has been estimated as occupying 7–10% of total ocean surface area ($26–36 \times 10^6$ km^2) to a mean depth of 130 m, making its volume about 0.25 to 0.34% of total ocean volume. This coastal zone receives horizontal transports of C, N, and P from land, input of the same nutrients by upwelling from intermediate oceanic depths, exchange of CO_2 with the atmosphere, and atmospheric deposition of N. As the coastal zone is an active site of biological primary production in the ocean, the role of this reservoir in controlling the dynamics of the C, N and P cycles is distinct and different from the roles of the land and open ocean. Because the volume of the coastal zone is

smaller than the volumes of the land and oceanic reservoirs, it has been more pronouncedly affected by the environmental forcings of the last 300 years, as discussed in the next section.

In this paper we examine first the human forcings on C–N–P coupled biogeochemical cycles in the past 300 years (1700–2000) of industrial time, and the C:N:P ratios in the major cycle reservoirs and their relationships to primary production on land and ocean coastal waters and other inter-reservoir pathways. Based on model analysis, we discuss the changes in the major reservoir sizes that occurred as a result of human perturbations. Such changes are behind the net transfers of C, N, and P between the big domains of land, oceanic coastal zone, atmosphere, and open ocean. Further, we demonstrate the role of denitrification, primarily on land and in the coastal zone, as an important mechanism that is one of the two branches of a flux–fork that removes nitrogen from land to the atmosphere and by runoff to the ocean. Our results also confirm the view that the oceanic costal zone is, despite its relatively small size, an important reservoir intermediating the C–N–P cycle dynamics between the adjacent reservoirs of land, atmosphere, and open ocean.

2. Environmental forcings

In the last 300 years, the global cycles of carbon, nitrogen and phosphorus were perturbed primarily by the following five forcings:

(1) Emissions of C and N to the atmosphere from fossil fuel burning and, more recently, by such activities as CO_2 emissions due to cement production and N emissions due to industrial and transportation activities.

(2) Land-use activities. Prior to the start of the Industrial Revolution about the year 1850, land-use activities were primarily those of wood-fuel combustion for food preparation, heating, construction, biomass burning for metal and clay pottery production, and forest clearing for agricultural land-use. At the present time, these activities include the conversion of land for food production (grazing land, agricultural land), for urbanization (building human settlements, roads, and other structures), for energy development and supply (building dams, hydroelectric plants, and mining of fossil fuels), and for resource exploitation (mining of metals, harvest of forest hardwood) (Mackenzie, 1998). The consequences of these actions are manifested by increased deforestation, reforestation, logging, shifting cultivation, desertification and salinization, local flooding, loss of wetlands, and changes in the chemical and biological properties of aquatic systems (Meyer and Turner, 1994). The main effects of the changing land-use activities are: first, as a direct perturbation when CO_2 and N-gases derived from land-use changes are

emitted to the atmosphere and some of the nutrients are released to the continental reservoirs; second, changing land-use activities are responsible for a major mechanism of material transfer from land to the coastal zone owing to soil erosion, mineral dissolution, and surface water runoff.

(3) Application of inorganic chemical fertilizers containing N and P to croplands. The cropland area of the world is about 9.4% of the continental area (14×10^6 km^2; Schlesinger, 1991) or about 12% of the land area that is covered by vegetation. A global average application of inorganic fertilizers is in part taken up by the land biomass and in part leached into soil and groundwaters and into surface runoff from land.

(4) Municipal sewage containing organic forms of C, N, and P has been so far a relatively small but an increasing perturbation owing to the growth of the urban population and generally inadequate practices of sewage treatment in many parts of the world. Both sewage and a more recent phosphorus input through the use of detergents are perturbations linked to population growth and its geographic distribution. The pathways of release of municipal sewage may include releases into rivers and other continental waters, croplands, and the oceanic coastal zone.

(5) The fifth forcing is a climatic perturbation of global temperature rise of about 1 K in the last three hundred years.

A summary of the C, N and P forcings due to the four human-generated processes considered above is given in Table I. The biggest carbon perturbation is fossil-fuel emissions, followed by land-use changes. However, for nitrogen, releases due to land use changes and addition of chemical fertilizers are greater than fossil-fuel and industrial emissions. Similarly, land-use changes are the biggest source of phosphorus release from the land surface. It should be stressed that land-use changes as a whole are primarily responsible for the increased transport of organic carbon, nitrogen, and

Table I. Summary of C, N and P perturbations in the period 1700–2000

Perturbation	Time period	C		N		P	
		(10^{12} mol)	Gtons	(10^{12} mol)	Gtons	(10^{12} mol)	Gtons
Emissions (fossil fuel and industrial)	1850–2000	23,333	280	90.6	1.27	–	–
Land-use change	1700–2000	16,667	200	451.0	6.3	72.8	2.26
Chemical fertilizers	1920–2000	–		156.6	2.2	18.0	0.56
Sewage	1700–2000	774	9.3	132.7	1.9	8.4	0.26
Detergent	1945–2000	–	–	–	–	1.1	0.03

(from data in Ver et al., 1999, and Mackenzie et al., 2001). 1 Gton $= 10^9$ ton $= 10^{15}$ g.

phosphorus from soils and land surface in general to the oceanic coastal zone and for the release of N and P that are reutilized as nutrients driving primary production.

3. Model Analysis

Our analysis of the C–N–P system is based on the model *TOTEM* (*T*errestrial *O*cean a*T*mosphere *E*cosystem *M*odel) described in detail elsewhere (Mackenzie et al., 2001, 2002; Ver et al., 1999). *TOTEM* is a process-based Earth system model of the global coupled biogeochemical cycles of carbon, nitrogen, phosphorus, and sulfur (C–N–P–S) that recognizes the dependence of the carbon cycle on the cycles of nitrogen, phosphorus, and sulfur. The model treats the four environmental domains of the atmosphere, land, oceanic coastal zone, and open ocean as a system of 14 reservoirs, recognizing the coastal zone as a domain that receives inputs from the land, atmosphere, and open ocean, and exchanges its contents with the atmosphere and open ocean. The essential feature of the model is manifested in the coupling between the C–N–P–S cycles at every biologically mediated transfer process, such as photosynthesis, autorespiration, decay, and burial of organic matter. This provision for the diverse, process-based biogeochemical interactions among the four element cycles in the four environmental domains of land, atmosphere, coastal ocean, and open ocean (including the sediments of the latter two domains) distinguishes *TOTEM* from other models dealing with single-element cycles. Sensitivity tests of the model show robustness of the trends in reservoir and flux changes during the years 1700–2000 and projections into the 21st century. Validation of the model is in the agreement of its results for atmospheric CO_2 with those reported in the literature from various measurements and projections into the near future. Such changes as about 20% in the C:N:P ratios of land phytomass or humus, and $< 50\%$ changes in the rate parameters determining the major fluxes confirm the trends predicted by the model, although the atmospheric CO_2 values may differ by up to a few tens ppmv CO_2 from those reported as ''best'' results. The coupled cycles approach is critical to modeling the responses of biogeochemical systems to global change because an anthropogenic or natural source of one of these elements, such as fossil fuel burning or humus respiration, is often a source of all three other elements.

Earlier model analyses of the coupled C–N–P cycles in the Earth surface environment using *TOTEM* (Mackenzie et al., 2001, 2002; Ver et al., 1999) focused mainly on the perturbations of the fluxes between the reservoirs, caused by the human forcings (Table I), and on the cumulative effects of the forcings passing through the individual reservoirs. The time scale of these forcings, extending to the year 1700, represented the choice of a starting point of analysis. The magnitudes of the forcings and computed

changes in the fluxes for the period of 300 years (1700–2000), with pro-
jections to the first half of the 21st century, were justified by the very good
agreement of the *TOTEM*-computed atmospheric CO_2 content and the
reported values for the 300-year period and projections for the 21st century
(IPCC IS92a, Houghton et al., 1996), where the differences between the
different projection models and *TOTEM* give estimated atmospheric CO_2
concentration in the year 2040 as 475–495 ppmv. Furthermore, the rates of
CO_2 uptake by the oceans and land phytomass as computed by *TOTEM*
agree with the estimates by other investigators for the decades of the 1980s
and 1990s (Bruno and Joos, 1997; Hudson et al., 1994; Keeling et al., 1996;
Quay et al., 1992; Sarmiento et al., 1992; Siegenthaler and Sarmiento,
1993); a more detailed discussion of the different estimates is given in Ver
et al., 1999), and the *TOTEM*-calculated riverine fluxes of dissolved inor-
ganic N and P agree with the values compiled by Meybeck (1982) and
Meybeck and Ragu (undated, UNEP).

The sources of data for fossil fuel and industrial emissions and emissions
due to land-use changes have been documented in Mackenzie et al. (2001,
2002) and Ver et al. (1999). Some of the other data sources and specific
mechanisms assumed in the model and germane to this paper are summarized
below.

In *TOTEM*, the C:N:P ratio for land biomass is 510:4:1 and the initial
C:N:P ratio in soil humus is 140:6.6:1 (Table II). For the coastal and

Table II. C:N:P atomic ratios in land phytomass and soil humus

	C	N	P	Reference
Vascular land plants	822	9	1	Deevey (1973)
	510	4	1	Delwich and Likens (1977)
	2057	17	1	Likens et al. (1981)
Northern to tropical coniferous and deciduous forests	3213–3595	19	1	Vitousek et al. (1988), cited in Schlesinger (1991)
Woody gymnosperms	387–1160	24–71	1	Bowen (1979); P content 1–3 g kg^{-1} dry organic matter
Woody angiosperms	580 or less	13–42	1	Bowen (1979); P content 2 g kg^{-1} dry organic matter
Herbaceous vegetables	116 or less	6.6–17	1	Bowen (1979); P content 10 g kg^{-1} dry organic matter
Soil organic matter (humus)	140	6.6	1	Likens et al. (1981)
	258	17	1	Freney and Williams (1983)
	278	17	1	Stevenson (1982), mean of organic components of soils

Table III. C:N:P atomic ratios in oceanic reservoirs

Environmental medium	C	N	P	Reference
Particulate organic				
Marine phytoplankton	108	15.5	1	Murray (1994)
	106	15	1	Parsons and Takahashi (1973)
	80	15	1	Dyrssen (1977), cited in Chen et al. (1996)
Zooplankton	103	16.5	1	Murray (1994)
Plankton mean	106	16	1	Murray (1994), Redfield et al. (1963)
	122 ± 18	16	1	Chester (2000), Takahashi et al. (1985)
	126	15.7	1	Chester (2000), Watson and Whitfield (1985)
Marine benthic plants	550	30	1	Atkinson and Smith (1983)
Suspended organic matter	366	47.6	1	Chen et al. (1996)
Particulate organic (surface)	105	1.9	1	Mackenzie et al. (1993); Ver (1998)
Particulate organic (deep)	106	13	1	Mackenzie et al. (1993); Ver (1998)
Remineralization of organic matter in water column	135 ± 18	13 ± 1	1	Li et al. (2000)
Dissolved inorganic				
Surface ocean (100 m)	1312	0.7	1	Mackenzie et al. (1993); Ver (1998)
Deep ocean	710	12	1	Mackenzie et al. (1993); Ver (1998)
Dissolved organic				
Surface ocean (100 m)	106	6.3	1	Mackenzie et al. (1993); Ver et al. (1999)
Deep ocean	106	7.6	1	Mackenzie et al. (1993); Ver et al. (1999)
Marine sediments	250	20	1	Ingall and Van Cappellen (1981)
	$\sim$200–600		1	$(C:P)_{org}$, sources cited by Anderson et al. (2001)
	up to $\sim$3800		1	$(C:P)_{org}$, Anderson et al. (2001)
	up to $\sim$420		1	$C_{org}:P_{reactive}$, Anderson et al. (2001)

open-ocean biota, the ratio is 106:16:1 (Table III). For the two quantitatively smaller perturbations, fertilizer inputs were calculated from data of Smil (1991) and FAO, as reported by Ver et al. (1999). For the organic sewage perturbation in the model, sewage discharges into the coastal zone are based primarily on considerations involving the short residence time of water in rivers and the historical proximity of many large urban agglomerations to the coastal zone. Sewage C, N, and P are routed directly to the coastal zone in *TOTEM*. Sewage data are from Billen (1993) and Caraco (1995), adjusted for population growth, as given in Mackenzie et al. (2001). Detergent data were taken from the United Nations Population Division (1995), adjusted for population growth.

In this paper, the results of the model analysis are focused on net changes in the C, N, and P masses of the more important land and coastal reservoirs, and some of the major fluxes for the same 300-year period.

4. C:N:P Ratios in Biogeochemical Reservoirs

The concept of coupling between the biogeochemical cycles of C, N, and P is rooted in the C:N:P ratios of the biotic and biota-modified reservoirs, known as the Redfield or RKR ratios after the work of Redfield, Ketchum, and Richards (Redfield et al., 1963). In this paper we discuss the coupling between the C–N–P cycles as evidenced by the C–N–P contents of their major reservoirs and by the values of their C:N:P *molar* or *atomic* ratios. We address this issue with reference to the various biogeochemical mechanisms that are responsible for the inter-reservoir transfers of materials in the C–N–P cycles. Furthermore, we present an overview of the cumulative changes in the coupled C–N–P cycles that are due to the major forcings, as summarized in Table I.

After the original work of Redfield et al. (1963) established for the oceanic plankton the C:N:P molar ratio at close to 106:16:1, later work has shown that in land plants the C:N and C:P ratios are considerably higher, indicating a greater efficiency of land plants to sequester atmospheric carbon. Relative abundance of N and P in the source reservoirs (e.g., soil water, continental fresh waters, and ocean surface water) and in chemical forms that can be used by primary producers is believed to determine, at least to some extent, the roles of the two elements as a "limiting nutrient", as well as the C:N:P ratios in the living organic matter of different taxa. Sterner and Elser (2002, pp. 120–132, 320–332) summarized the C:N:P ratios in terrestrial and aquatic ecosystems and discussed their differences between different taxa and their dependence on environmental conditions of growth. Depending on the relative availability of inorganic N and P in the environment or in culture media, the N:P ratios in marine phytoplankton can vary within wide limits, with a transition

from P-limited to N-limited growth occurring in the N:P range of 20–50 (Geider and La Roche, 2002).The C:N:P ratios of the land and oceanic reservoirs are summarized in Tables II and III. It should be noted that the ratios reported for the higher or vascular land plants in Table II vary greatly, both in their C:P and N:P molar ratios. There is also variation in the mean ratios for soil organic matter (humus), particularly in the C:P values. As most of the estimates of the reservoir masses are based on carbon in primary producers on land and in the ocean, and CO_2 in the atmosphere, modeling the role of N and P in the global carbon cycle is constrained by the variation in the C:N:P ratios of reactive reservoirs such as land plants and soil humus. A lower C:N:P ratio in plants would require relatively more N and P to sustain primary production, and these two nutrient elements would have to be available in greater amounts from remineralization of soil organic matter and, for P, from chemical weathering of soil and crustal minerals. Thus, given the uncertainties in the mean C:N:P ratios for the plant and soil reservoirs, results of modeling of the interactive C–N–P cycles would be anticipated to give only the directions and relative magnitudes of change from the past to the future.

Although the reported C:N:P ratios for oceanic phytoplankton and zooplankton vary within narrower limits than those for land plants (Table III), the value of C:N:P = 106:16:1, as reported by Redfield et al. (1963) is commonly used as the mean value for aquatic plankton, oceanic as well as fresh-water. However, recently Li et al. (2000) have derived a new molar formula for the remineralization of marine plankton equivalent to a C:N:P ratio of 135:13:1 based on a two end-member mixing model of waters of the subtropical North Pacific gyre, and Li and Peng (2002) have shown that these ratios vary somewhat from ocean basin to ocean basin (Table III). The higher C:N:P ratio in suspended organic matter (Chen et al., 1996) includes both living and dead organic matter and zooplankton, as well as organic matter of terrestrial origin. In marine sediments, Anderson et al. (2001) distinguish between the C:P ratios in organic matter, $(C:P)_{org}$, and the ratio of organic C to reactive P, $C_{org}:P_{reactive}$, where the latter is a sum of three forms of phosphorus: $P_{reactive} = P_{oxide-associated} + P_{authigenic} + P_{organic}$. In various sedimentary environments, the ratios $(C:P)_{org}$ are usually considerably higher than the ratios $C_{org}:P_{reactive}$ (Table III).

It should also be noted that although C:P ratios in marine sediments vary widely, the C:N:P ratios in soil humus and marine sediments, as given in Tables II and III, are similar, which might indicate similarity between the microbial diagenetic processes in the two sedimentary environments. In general, bacteria have C:N:P ratios very similar to the material they consume.

A summary diagram of the main land and oceanic coastal reservoirs, and their C:N:P ratios and interreservoir fluxes is shown in Figure 1.
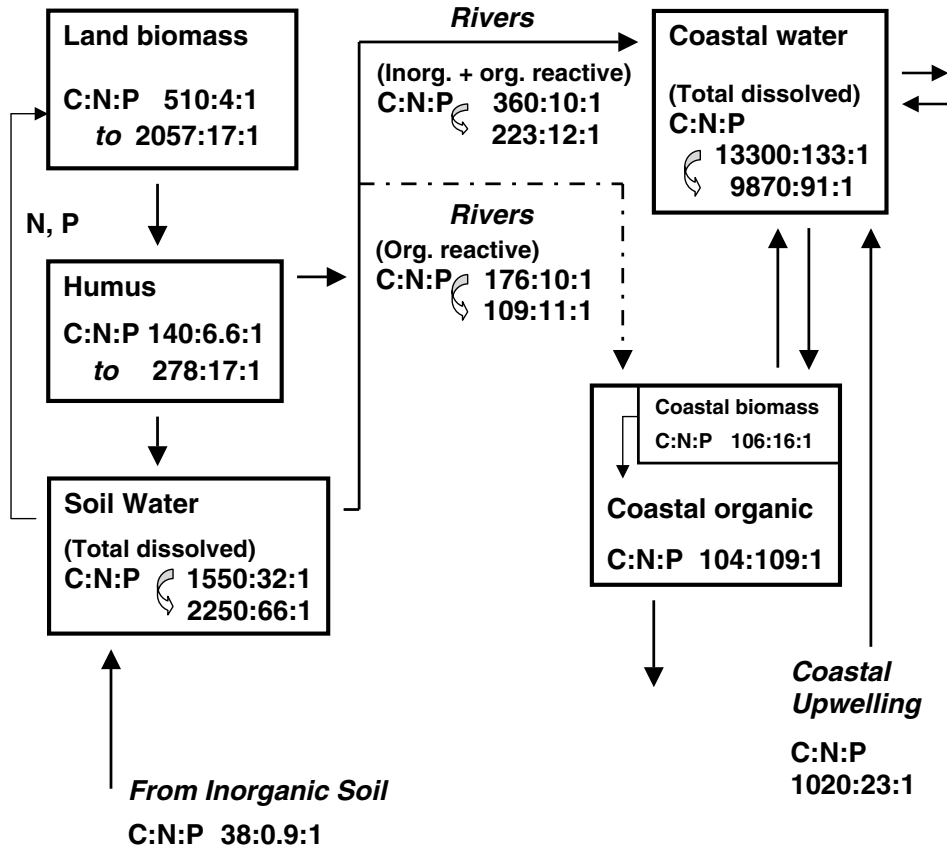
Figure 1. C:N:P molar ratios in land and coastal oceanic reservoirs. From Table IV, Ver (1998), Ver et al. (1999), and sources cited therein. For land biota and humus, ranges of C:N:P ratios are shown. Curved arrow in soil water, rivers, and coastal water shows model-calculated change from year 1700 to 2000. For riverine fluxes, C:N:P in organic reactive species and in inorganic plus organic reactive are shown, as defined in the text.

For land plants and humus, the C:N:P ratios are shown within their ranges according to various estimates, as given in Table II. The major transport fluxes shown are from inorganic soil to soil water, upwelling from the deeper ocean to the coastal zone, and riverine transport from land to the coastal zone. The coastal organic reservoir includes all the organic forms of C, N, and P in the coastal ocean: the biomass of primary producers, dissolved organic species (DOC, DON, DOP), and particulate organic reactive forms of the three elements. The particulate material transported by rivers consists of inorganic (PIC, PIN, PIP) and organic fractions (POC, PON, POP). The latter is divided into 50% refractory, that is deposited in coastal sediments, and 50% reactive (Smith and Hollibaugh, 1993), that is transported to the

coastal organic reservoir. Thus organic reactive C:N:P in rivers (Figure 1) is the sum of dissolved organic and reactive particulate fractions. In soil water and coastal water reservoirs, dissolved C, N, and P are inorganic forms. In coastal water, the mass of C corresponds to its concentration of $(1.85 \pm 0.25) \times 10^{-3}$ mol C kg^{-1}.

Land plants derive their C from atmospheric CO_2, and some of this carbon is returned to the atmosphere through remineralization of humus, as indicated by the lower C:N ratio in humus than in the biomass. The N:P ratios in plants and humus are comparable within the wide range of reported data (Table II). Land plants obtain most of their nutrient N and practically all of P from soil water. The higher N:P ratios in soil water indicate that some excess of N, above the needs of primary production, can be transported to the atmosphere by denitrification and by overland water flow to the coastal zone.

In the coastal zone, the main input of the nutrients (C, N, P) is by oceanic upwelling from intermediate depths, followed by riverine flow. The C:P and N:P ratios in the upwelling flux to coastal water (Figure 1) are considerably higher than in the Redfield ratio of coastal primary producers, indicating that excess C and N are brought to coastal water and N is at least in part lost by denitrification to the atmosphere, and C in some upwelling areas as CO_2 also evades to the atmosphere.

It should be noted that the changes in the C:P and N:P ratios in soil water and coastal water reservoirs from the year 1700–2000 reflect differences in the reservoir mass changes, as also given in Table IV: in soil water, P decreases relative to C and N, but in coastal water P increases faster than the other two elements.

5. Results of Environmental Perturbations

In this section, we discuss how the five major forcings of the C–N–P biogeochemical cycles have affected reservoir sizes and flux rates with particular attention to the changing riverine output of materials to the coastal ocean and the partitioning of denitrification between the land and the ocean during the past 300 years. The analysis is based on numerical simulations of the coupled cycles using the model *TOTEM*.

5.1. C, N, AND P RESERVOIRS

Among the four forcings of the global environment, as listed in Table I, fossil fuel emissions add CO_2 and N-oxides (and S-oxides) to the atmosphere, and wet and dry deposition on land and in the coastal zone returns some of the emitted N (and S) to the surface. The effects of land-use

Table IV. C, N, and P masses of major land and coastal reservoirs and their change from year 1700 to 2000. Coastal and ocean biota reservoirs include biomass and dissolved and particulate reactive organic components

Reservoir and mass	Year 1700 (10^{12} mol)	Year 2000 (10^{12} mol)	Change (10^{12} mol)	Change (%)
C atmosphere	49,017	66,376	17,359	35.41
C land biota	49,800	47,291	−2509	−5.04
C humus	20,500	17,665	−2835	−13.83
C inorganic soil	59,800	58,744	−1056	−1.77
C soil water	248	214	−34	−13.77
C coastal organic	367	492	125	34.07
C coastal water	6,000	6,204	204	3.40
C coastal sediments	207,000	208,113	1113	0.54
C org coast seds		*770*[1]		
	41,900–107,700[2]			
C ocean organic	3820	3851	31	0.81
C surface ocean (100 m)	65,640	67,871	2231	3.40
N land biota	391	384	−7.1	−1.81
N humus	976	786	−190.0	−19.47
N inorganic soil	123	121	−2.5	−2.01
N soil water	5.1	6	1.1	22.04
N coastal organic	386	514	127.8	33.10
N coastal water	60	57	−2.9	−4.77
N coastal sediments	2280	2338	58.1	2.55
N org coast seds		*62*[1]		
	3350–8620[2]			
N surface ocean (100 m)	35	32.6	−2.4	−6.85
N ocean biota	213	215	1.8	0.83
P land biota	98	95	−2.29	−2.35
P humus	147	121	−26.44	−17.98
P inorganic soil	1150	1142	−7.66	−0.67
P soil water	0.16	0.09	−0.07	−40.81
P coastal organic	3.5	4.8	1.27	36.37
P coast water	0.45	0.63	0.18	39.67
P coast sediments	9200	9244	43.75	1.36
P org coast seds		*3.1*[1]		
	168–430[2]			
P surface ocean (100 m)	50	54	4.05	8.10
P ocean organic	36.1	36.4	0.30	0.83

[1]C organic from Rabouille et al. (2001), N and P from C:N:P = 250:20:1 (Ingall and Van Cappellen, 1990).
[2]Calculated from coastal zone surface area (28–36) $\times 10^6$ km^2), sediment thickness 1–2 m, porosity 40%, bulk sediment density 1900 kg m^{-3}, organic matter content 2.5 wt% (Trask, 1955), and organic matter composition $(CH_2O)_{250}(NH_3)_{20}(H_3PO_4)_1$ (Ingall and Van Cappellen, 1990).

changes are diverse: increased soil erosion by land-surface water runoff and transport of N and P to the coastal zone; increased rates of mineralization of soil organic matter that returns N and P to soil water where the two nutrients become, in part, available for plant growth and are, in part, transported to river flow; and increasing denitrification that returns N to the atmosphere. Increased use of N and P chemical fertilizers on land promotes photosynthetic production and increases riverine transport of the two elements from the leached fraction of the applied fertilizer to the coastal zone. The smaller forcing owing to sewage input, and the much smaller input of P-containing detergents (Table I) are, as mentioned previously, directed to the coastal zone in the model. These fluxes account for a higher addition of nutrient N and P to the coastal zone. If all or most of sewage remained on land, its effects would be similar to those of the N and P chemical fertilizers: partial increase in plant photosynthesis and partial removal by leaching to rivers and transport to the coastal zone. Thus the general picture of the land reservoirs contributing nutrients for bioproduction in coastal waters would not be greatly affected.

Net computed changes from year 1700 to 2000 in the land, coastal ocean, and surface open ocean reservoirs are given in Table IV.

The land biota reservoir, as given in Table IV, is characterized by the Redfield ratio C:N:P = 510:4:1, the coastal and open ocean plankton by the ratio 106:16:1, and soil humus by the ratio 140:6.6:1 (Table II). The reservoirs of coastal and open-ocean organic include the standing crop of the plankton as well as the reactive dissolved and particulate organic matter. Of the mass of C in coastal organic in Table IV, given as 367×10^{12} mol C, only 11% or 42×10^{12} mol C are represented by the living biomass. Of the total C in the ocean organic reservoir, 3820×10^{12} mol C, the living biomass accounts for 5.8% or 221×10^{12} mol C.

In the 300 year period since 1700, there has been net transfer of C, N, and P from land to the coastal ocean reservoirs, addition of C to the atmosphere from fuel emissions and land use changes (resulting in the documented increase of atmospheric CO_2 by 35%), and loss of N by denitrification from land, coastal water and sediments, and open ocean. The reservoir masses listed in Table IV were computed as explained in detail in Ver (1998) and Ver et al. (1999), and used in the model *TOTEM*. However, uncertainties associated with some of the estimated masses may be considerable depending on the choices of parameters that are used in calculating masses. The C, N, and P masses of coastal sediments (Table IV) are an example. The C, N, and P values in Table IV represent the total mass of both inorganic and organic C, N, and P as employed in *TOTEM*. A much lower value of organic C in Coastal sediments, 770×10^{12} mol C, was given by Rabouille et al. (2001) for the diagenetically reactive portion of the upper sediment column of the coastal zone during industrial time,

the 20th century. A different estimate, as explained in the footnote to Table IV, is based on an estimate of the reactive sediment thickness of 1–2 m in the coastal zone, containing 2.5 wt% organic matter. This estimate gives organic C as 20–50% of total C (2.07×10^{17} mol C), a higher value for organic N, and a much lower value for organic P. Although it is commonly cited that the soil humus C reservoir is about three times larger than C in land plants, the values for C, N, and P given in Table IV represent reactive humus that accounts for only a fraction of total organic matter in soil.

5.2. NET RESERVOIR CHANGES

Over the industrial period of human forcings of the last 300 years, the land reservoirs of biota (plants) and soil humus decreased (Table IV), to a large extent due to land use changes, including deforestation and faster rates of soil erosion. Significantly, the increase in atmospheric CO_2 and remineralization of organic matter releasing N and P to soil water were insufficient to counterbalance the reduction in the mass of terrestrial organic matter, as represented by its main constituents C, N, P.

The continental soil water is an aggregate reservoir defined to include the moisture in soil above the water table plus the water in the upper 10 m of the shallow groundwater reservoir. It is an important transition zone for the transport of nutrients and carbon between the organic and mineral realms and between the soil reservoir and atmosphere, rivers, and streams. Biochemical transformation reactions, such as terrestrial photosynthetic uptake, ammonification and volatilization, denitrification, and soil respiration, occur in the soil water reservoir. The physical transport and export via rivers to the coastal margin of organic and inorganic dissolved components originate from this reservoir. Because water is usually present as a reaction medium, the conceptual flux going from soil $\rightarrow$ soilwater $\rightarrow$ atmosphere, or from soil $\rightarrow$ soilwater $\rightarrow$ rivers and surface runoff is justified. Definition of the soil water reservoir does not imply the presence of 100%-saturated soils. The volume of this aggregate reservoir is calculated to be 0.121×10^6 km^3 (soil moisture = 0.065×10^6 km^3; upper 10 m of the shallow groundwater = 0.056×10^6 km^3) (Berner and Berner, 1987).

The masses of C, N, and P in the soil water reservoir are small relative to humus and land biota, such that small decreases in mass translate into relatively large percentage changes. With regard to the decrease in the mass of soil water C and P, this is likely attributable to the decrease in the humus reservoir, from which C and P are supplied to soil water, whereas the water flow rate from soil water to rivers remains unchanged in the model (no changes in atmospheric precipitation and evapotranspiration are included in
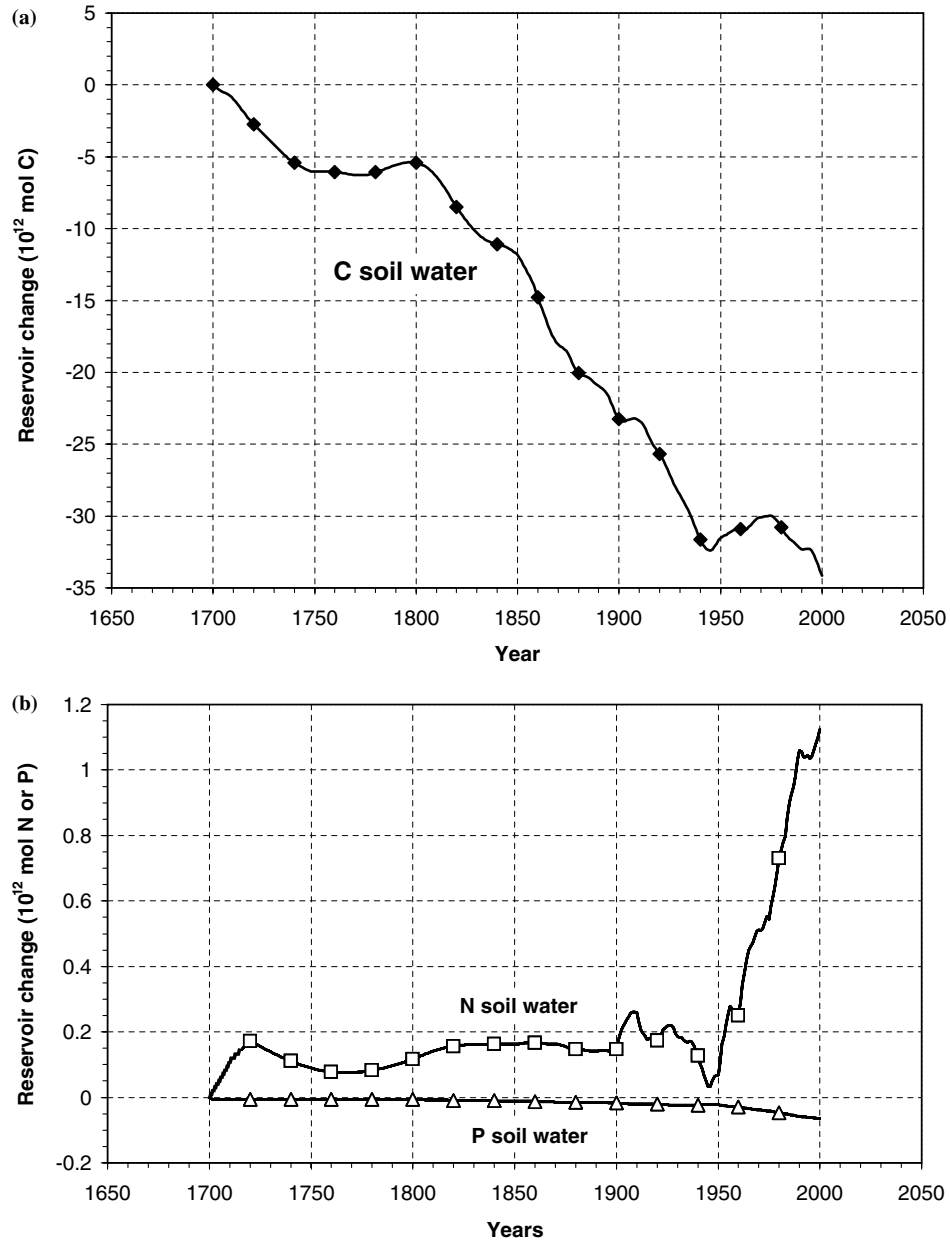
Figure 2. Changes in soil water, 1700–2000, normalized to 0 in year 1700. (a) Dissolved carbon. (b) Dissolved N and P. Note the difference in the vertical scale between (a) and (b).

the model). Although the decrease in the mass of humus affects N as well as C and P, an increase in N in soil water should be noted. This increase is the result of human activities, primarily land use change and application of
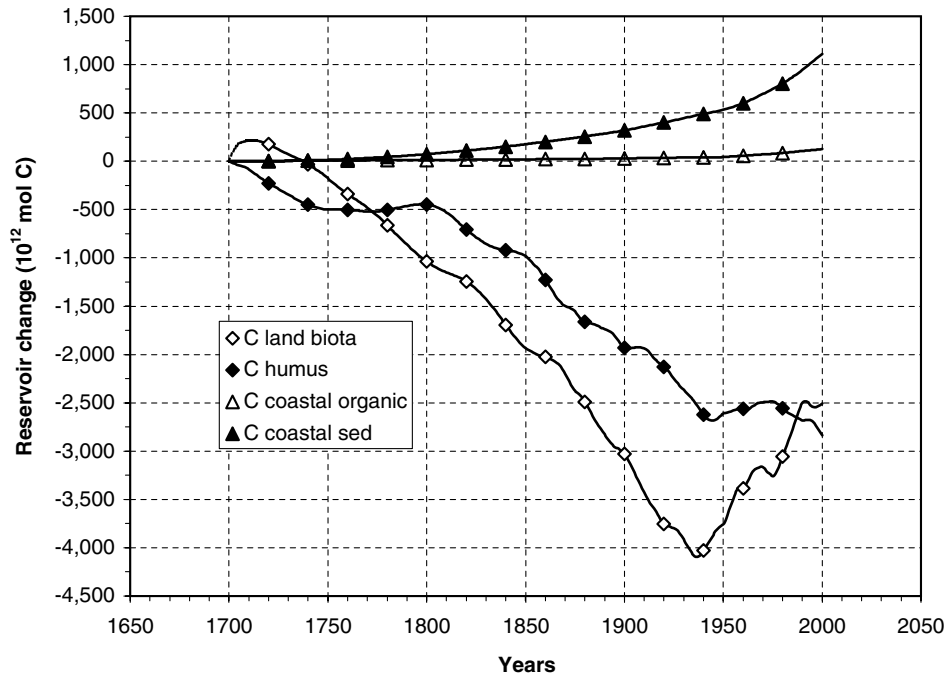
Figure 3. Changes in the C mass of land plants, humus, coastal organic reservoir, and coastal sediment, normalized to 0 in year 1700. (The initial rise in land biota C, from 1700 to about 1710, is a result of model run in the early years of the 300-year period starting with the approximate values of the initial quasi-steady state). Similarity in the loss of C from land biota and humus prior to changes in the trends near 1950 should be noted.

chemical fertilizers. The rates of change in the reservoir contents of C, N, and P have not been linear over the 300-year period. Changes in the C, N, and P of soil water are shown in Figure 2, all normalized to 0 in the year 1700. The decline in C of soil water is similar to the pattern of decline in C of soil humus that is shown in Figure 3.

The reversal in the decline of C in the land biota near the year 1950, also shown by the N and P trends (Figures 4 and 5), is probably due to fertilization of the land phytomass because of a combined negative feedback effect of rising atmospheric CO_2 and release of N and P from the humus and chemical fertilizers on land, and re-growth of phytomass in previously disturbed areas.

In the coastal zone, major changes occur in coastal sediments. At a 300-year time scale, input of nutrients from the open ocean to the coastal zone has probably not changed significantly, such that the increases in the coastal organic matter and sediment reservoirs are due to (1) increase in the flux of dissolved and reactive particulate N and P from land, (2) leaching of chemical fertilizers added to the land and input of sewage to the coastal zone,
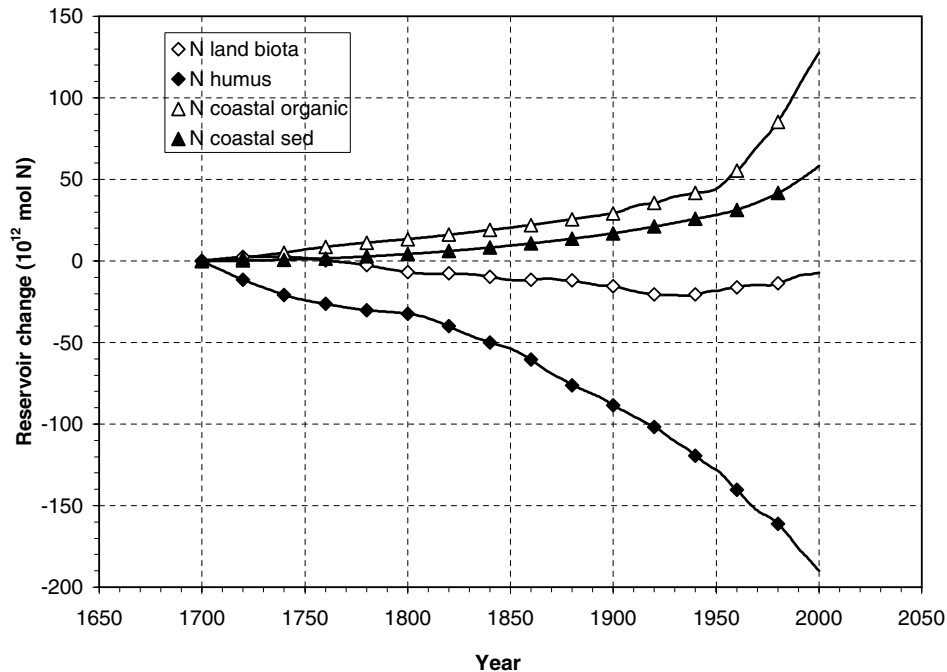
Figure 4. Changes in the N mass of land plants, humus, coastal organic reservoir, and coastal sediment, computed for the period from 1700 to 2000, normalized to 0 in 1700.

(3) increased net primary production in the coastal zone due to nutrient input, and (4) accumulation of land-derived as well as photosynthetically produced organic matter in the coastal zone.

6. Denitrification and Riverine Output from Land

Riverine output of nitrogen from land to the coastal zone and denitrification are the two major processes partitioning the flow of N between a form utilizable in primary production and a form that is returned to the atmosphere. Changes in the relative magnitudes of riverine output and denitrification over the last 300 years are important parameters in the global C–N–P coupled cycles.

Denitrification is the microbially mediated process of reducing NO_3^- and NO_2^- to NO_x, N_2O, and N_2. Bacteria of the genus *Pseudomonas* account for most of the conversion occurring in soils, aided by the enzyme nitrate reductase, but other genera have also been reported (Knowles, 1982; Tiedje et al., 1989). The general requirements for denitrification to occur are (1) bacteria that can perform denitrification; (2) suitable electron donors such as organic carbon compounds, reduced S compounds, or molecular hydrogen
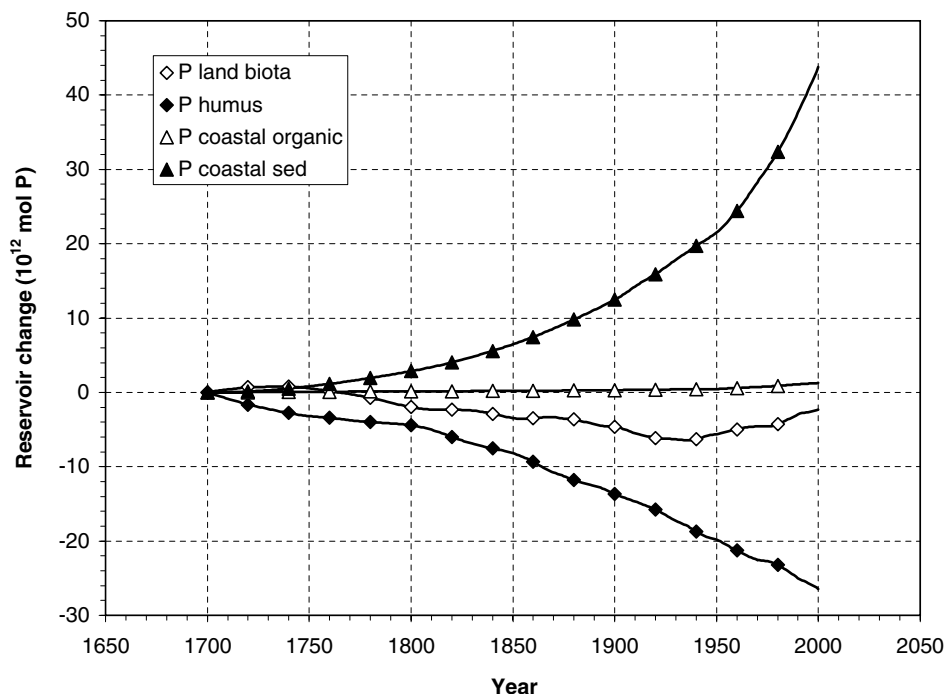
Figure 5. Changes in P mass of land plants, humus, coastal organic reservoir, and coastal sediment, computed for the period from 1700 to 2000, normalized to 0 in 1700.

(H_2); (3) N oxides as electron acceptors; and (4) anaerobic conditions or restricted O_2 availability (Stevenson, 1982). The following is an example of a denitrification reaction (Schlesinger, 1997):

$$5CH_2O + 4H^+ + 4 NO_3^- \rightarrow 5 CO_2 + 2 N_2 + 7 H_2O.$$
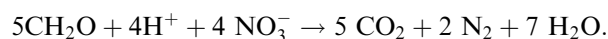
Because the residence times of NO_x and NH_3 gases in the atmosphere are very short (0.1 and 0.01 year, respectively), most of the terrestrial gaseous nitrogen loss as these compounds is balanced by the return fluxes of wet and dry deposition of N on land and the coastal zone. A good evidence that the nitrogen cycle was balanced in preindustrial time is the constancy of atmospheric N_2O concentration, near 285 ppbv, in the ice core records (Delmas, 1992; Kinzig and Socolow, 1994; Zhang, 2002), even if N_2O comprises but a small fraction of the products of denitrification (about 5% of total, Schlesinger, 1991). One estimate assigns to denitrification more than 60% of global N_2 and N_2O produced and emitted to the atmosphere, where N_2O production makes a small fraction of the total (Summer, 2000; Zhang, 2002).

Denitrification removes to the atmosphere inorganic N that may otherwise be available for primary production on land and in the hydrosphere. As most of the N and P needed in primary production on land is obtained from

remineralization of soil humus, the C:N:P ratio in the source reservoirs from which primary producers derive their C, N, and P indicates the presence of either excess or deficiency of one or more of the three nutrient elements. For example, from Table II, one of the C:N:P ratios in land plants is 510:4:1 and in soil humus 140:6.6:1. When humus of this composition is remineralized, for every 1 mol of phosphorus, $510 - 140 = 370$ mol C would be taken by new production from the atmosphere and there would be excess nitrogen of $6.6 - 4 = 2.6$ mol N that can be denitrified and transported to the atmosphere and/or removed by river flow to the coastal zone. In general, the preceding relationship between uptake of C in primary production and liberation of excess N applies when $(C:P)_{plants} > (C:P)_{humus}$ and $(N:P)_{plants} < (N:P)_{humus}$. If the signs between the preceding ratios were reversed, then there would be an excess of C and a deficiency of N in the source reservoirs relative to the primary producers on land or in waters. For example, the C:P ratios in coastal water and surface ocean (ratios of total dissolved C to total dissolved P), as given in Table IV, are higher than $C:P = 106:1$ in oceanic phytoplankton. However, the N:P ratio in surface ocean water at 0.7:1 is lower than its value in phytoplankton, about 16:1. An excess of C may be responsible for a greater transfer of CO_2 to the atmosphere, whereas a deficiency of N would suggest a higher rate of N fixation by oceanic bacteria. Clearly, the magnitudes of the N:P ratios in soils, coastal water, sediments, and open ocean are not by themselves responsible for denitrification that takes place as long as oxidized N-species are available, but these ratios control at least to some extent the pathways from source reservoirs to primary producers.

Denitrification rates vary temporally and spatially across ecosystems, as demonstrated in over 90 field and experimental measurements in temperate and tropical ecosystems (Firestone and Davidson, 1989). At soil temperatures ranging from 6 to 20°C, annual N_2O emissions from temperate soils range from 3×10^{-4} to 3×10^{-1} mol N m^{-2} yr^{-1} while in tropical soils where the soil temperature ranged from 16 to 30°C during measurement, annual N_2O emissions range from 10^{-3} to 10^{-1} mol N m^{-2} yr^{-1}. Low winter temperature limits N_2O production and emission in the temperate zone while in the tropical region, where the minimum temperature is high enough to maintain biological denitrification, other factors such as moisture and substrate organic matter availability and quality may control denitrification rates. The mean emission rates of N_2O from soils in the tropical and temperate climate zones are similar, 6.5×10^{-3} and 4.9×10^{-3} mol N m^{-2} yr^{-1}, respectively.

Reaction kinetics of denitrification has been variably treated as the Michaelis-Menten mechanism, zero order or first order reaction (e.g., Summer, 2000). Temperature dependence of biologically mediated reactions is often expressed as Q_{10}, that is a factor of increase or decrease in the

reaction rate for a 10 K temperature change. Such a temperature dependence, f_T, is parameterized in *TOTEM* as

$$f_T = Q_{10}^{\Delta T/10}. \tag{1}$$

There are few data dealing with the Q_{10} for denitrification. Of those reported in the published literature, a wide range of values for each climatic zone exists. For example, in temperate non-wetland forests, Q_{10} ranges from 2 to 5.1 (Baath and Soderstrom, 1988; Rolston et al., 1984; Ross and Cairns, 1978; Ross and Tate, 1993; Williams et al., 1992), while in boreal forests, Q_{10} ranges from 0 to 2.8 (Blackmer et al., 1982; Denmead et al., 1979; Mosier and Parton, 1985; Nadelhoffer et al., 1991). A mean Q_{10} value of 2.4 for soil respiration was reported by Raich and Schlesinger (1992). Following the Q_{10} value for microbial activity, a global mean Q_{10} value of 2.0 was chosen for *TOTEM* with due consideration given to the fact that the Q_{10} literature data for denitrification are biased towards temperate biomes.

In our model, denitrification rate on land is a temperature dependent first-order flux from soil water to the atmosphere (Mackenzie et al., 2001; Ver et al., 1999):

$$NF_{Sw10}(t) = kN_{Sw10} \times N_{Sw}(t) \times f_T, \tag{2}$$

where the first-order rate parameter is $kN_{Sw10} = 1.65$ year^{-1} and $N_{Sw}(t)$ is the N mass in soil water at time t; subscript Sw denotes soil water and subscript 10 the atmospheric reservoir. The effect of temperature is relatively small: for an approximately 1 K temperature rise from 1700 to 2000, at the value of $Q_{10} = 2$, the factor f_T is 1.07, corresponding to an increase in rate of 7%. Preindustrial value of denitrification on land, from *TOTEM*, is 8.42×10^{12} mol N year^{-1}, and it falls well within the range reported in the literature of 7.5 to 13.2×10^{12} mol N year^{-1}.

Besides the land, denitrification occurs in three other reservoirs, as taken in our model: coastal water, coastal sediments, and ocean surface water. For each of these reservoirs (*i*), denitrification flux to the atmosphere (subscript 10) was modeled as

$$NF_{i-10}(t) = kN_{i-10} \times N_i(t). \tag{3}$$

The rate parameters are as follows: for coastal water, $kN_{i-10} = 0.020$ yr^{-1}; for coastal sediments, $kN_{i-10} = 0.0016$ yr^{-1}, and for ocean water, $kN_{i-10} = 0.059$ yr^{-1}.

Computed denitrification rates from land, coastal zone (coastal water plus coastal sediments), and open ocean for the period from 1700 to 2000 are shown in Figure 6. The largest source of denitrification is the land, followed by the water and sediments in the coastal zone, and the surface
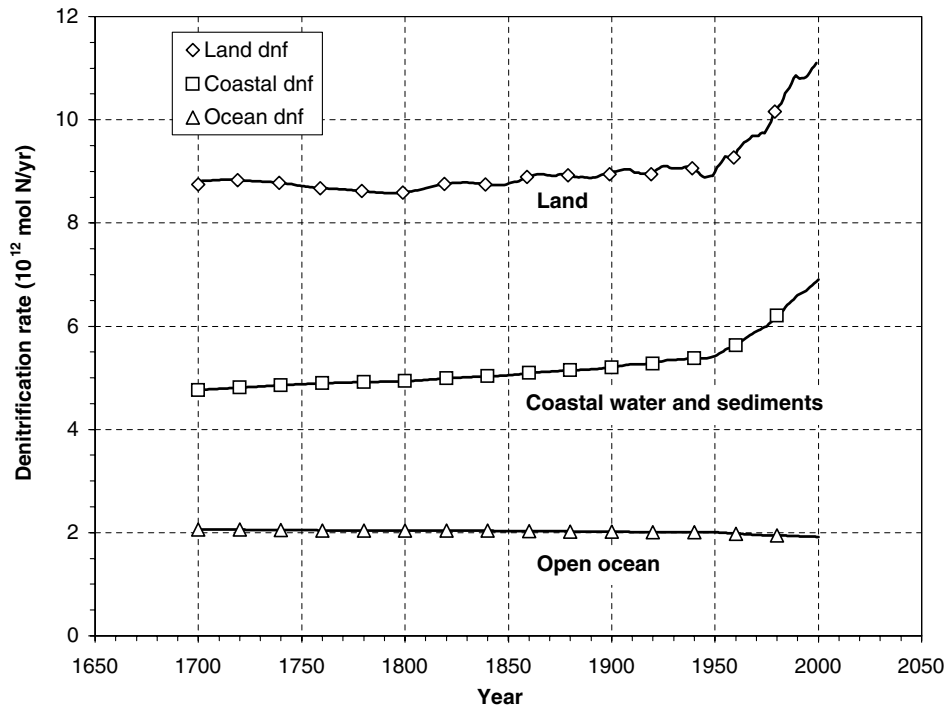
Figure 6. Denitrification rates from land, oceanic coastal zone (water and sediment), and surface ocean for 1700–2000.

open ocean. It should be pointed out that the starting point of the numerical simulation using *TOTEM* for the year 1700 for total terrestrial denitrification is in good agreement with the preindustrial estimates of Galloway et al. (1995), whereas the model estimate for preindustrial total ocean denitrification is on the low side in the range of their estimates. The strong increases in denitrification on land and in the coastal zone close to the year 1950 shown in Figure 6 reflect the increasing forcings of a growing global population, resulting in a consequently greater land use, fertilizer application, and sewage discharge.

Our results (Figure 6) indicate that denitrification from the global coastal zone increased from 4.8×10^{12} mol N yr^{-1} in 1700 to 6.9×10^{12} mol N yr^{-1} in 2000. A value of coastal denitrification for the water column and sediments of 5×10^{12} to 6.9×10^{12} mol N yr^{-1} was given by Wollast (1991), for a range of coastal zone area from 26×10^{6} to 36×10^{6} km^2. Model results of Seitzinger and Giblin (1996) and Seitzinger and Kroeze (1998) are in the range from 9×10^{12} to 34×10^{12} mol N yr^{-1}, depending on the areal size of the global coastal zone. A wide range of values has been reported from regional measurements of other investigators, cited above, from 0 to a high of

$(75 \pm 10) \times 10^{12}$ mol N yr^{-1} measured in the South Atlantic Bight and extrapolated to the global coastal zone (Mackenzie et al., 2002).

Nitrification on land and in waters and nitrogen fixation on land make N available for primary production. Denitrification is a process that removes N from the pool available for primary production on land and in continental and oceanic waters. Estimates of denitrification rates on land, in different sections and regions of the global coastal zone, and in the ocean are available in the literature (Devol, 1991; Gardner et al., 1993; Giblin et al., 1994; Hopkinson et al., 1991; Law and Owens, 1990; Lohse et al., 1993; Seitzinger, 1988; Seitzinger and Giblin, 1996; Seitzinger and Kroeze, 1998). It has been suggested by Van Mooy et al. (2002), in a discussion of remineralization of organic matter in the oceanic water column, that if organic matter had a C:N ratio of 61:16 instead of the Redfield ratio C:N = 106:16, then 9% more nitrogen would be lost by denitrification from the water column. To compare our global results with those of other investigators, the land and oceanic estimates of denitrification rates are summarized in Table V.

For the land, our model results are comparable to those of other investigators. For the ocean, our model taking into account coastal water and sediments, and the surface ocean layer gives results near the low end of the range of other estimates.

Export of reactive nitrogen by rivers is composed of total dissolved N and reactive particulate organic N; the latter is 50% of total particulate organic (Smith and Hollibaugh, 1993). Riverine export of nitrogen increased by a factor of more than 2, from 1.8 to 4×10^{12} mol N yr^{-1} between the years 1700 and 2000. At the same time, land denitrification increased by a smaller factor of 1.3 (Figure 6). The fraction of land denitrification of the total N related to denitrification and riverine export is shown as a function of time in Figure 7.

Table V. Denitrification rates on land and in the ocean, including water and sediments of the coastal zone (compiled by Zhang, 2002)

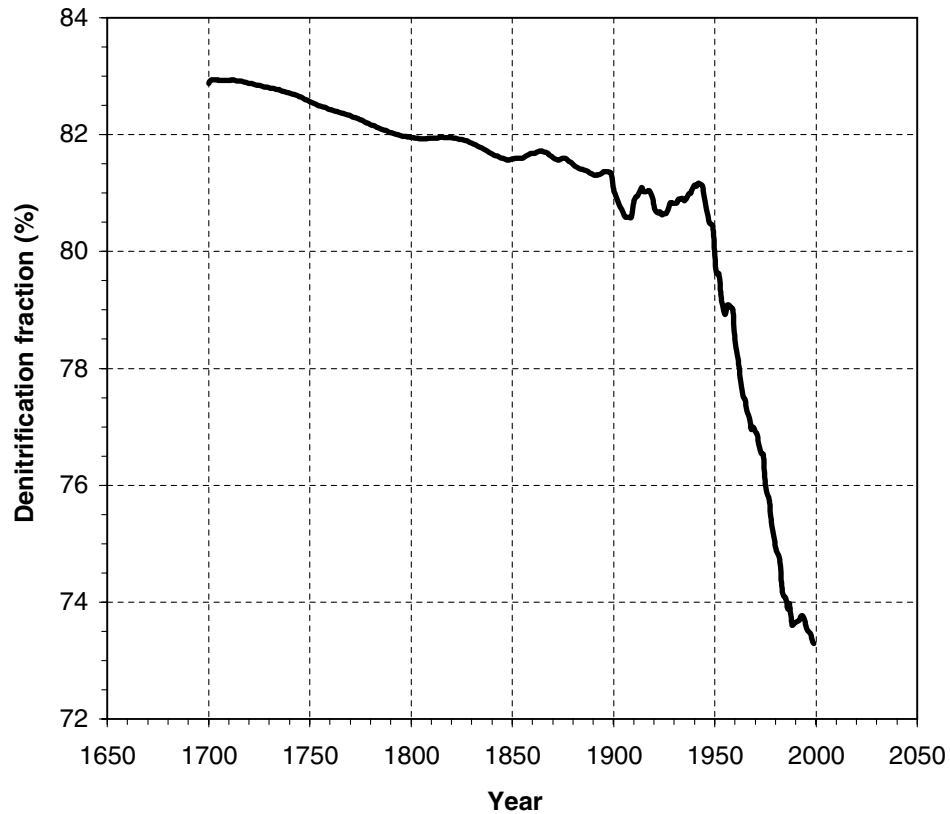| Sources	On land (10^{12} mol N yr^{-1})	Ocean (coastal water and sediments, open water) (10^{12} mol N yr^{-1})
Mackenzie et al. (1993)	14	
Wada and Hattori (1991)	7.6–11	
Berner and Berner (1996)	7.6–11.5	9.1
Schlesinger (1991)	> 9.3	
Galloway et al. (1995)	6.1–13.3	10.7–12.9
Gruber and Sarmiento (1997)		9.6–15.4
Soderlund and Svensson (1976)		6.5
This paper (1700–2000)	8.4–11.1	6.8–8.8

Figure 7. Land denitrification as a fraction of total N export from land (denitrification and transport of riverine total dissolved and organic reactive N to coastal zone).

The decline in the land denitrification fraction near the year 1950 reflects a smaller increase in denitrification rate, as shown in Figure 6, relative to a greater increase in the riverine transport of nitrogen from land. Denitrification has been less affected by human forcings than the transfer of nitrogen from land to the coastal zone and open ocean. Land to coastal zone transfer of the nutrients N and P has been the main factor in the redistribution of these elements and in their availability for biological production in the coastal zone.

7. Conclusions

The biogeochemical cycles of C, N, and P are coupled in their dynamics in the biologically mediated environmental reservoirs of primary producers on land, in the oceanic coastal zone, and in the surface open ocean, as well as in soils and sediment organic matter. In the last three-hundred years, these and other biogeochemical cycles have been perturbed by four human-generated

forcings (in order of decreasing importance: fossil fuel emissions, land use change, application of chemical fertilizers on land, and organic sewage discharge) and the global climatic forcing of temperature rise. The particular importance of the coastal zone in the dynamics of the C–N–P cycles is due to its intermediate location between the land and open ocean and its relatively small volume in comparison to the adjacent land and oceanic reservoirs.

The C:N:P Redfield ratios are constrained within fairly narrow limits for aquatic primary producers, but their estimates for the land phytomass and soil humus are considerably more variable. Nevertheless the C:N and N:P ratios in the transfer fluxes that maintain primary production on land and in coastal waters are higher than these ratios in land plants and oceanic plankton, indicating that there is an excess of available C and N relative to P for primary production.

While the increase in atmospheric CO_2 in the last 300 years, combined with the recycling of nutrient N and P in soils due to land use practices, and chemical fertilization might have been expected to result in a negative feedback and greater biological production, net effects of the major human forcings have been losses of C, N, and P from land and their transfer to the oceanic coastal zone and beyond, as indicated by our model analysis. Net losses of C, N, and P characterize the land phytomass, soil humus, and inorganic soil, and losses of C and P are indicated for the soil water reservoir. Superimposed on the general loss of materials for the past 300 years is the result that the trend was reversed for the land phytomass near the year 1950, possibly indicating that its increase in size in the second half of the 20th century was a combination of a negative feedback response to rising atmospheric CO_2 and effects of land fertilization (and perhaps re-growth of phytomass in previously disturbed areas). Net gainers of C, N, and P are the downcycle reservoirs of coastal organic matter that includes living biota, dissolved organic C, N, and P, and their reactive particulate forms, and coastal sediments where part of land-derived and *in situ* produced organic matter is stored.

Denitrification is a process that removes nitrogen from the pool available for primary production on land and in continental and oceanic waters, mostly in the form of nitrate, and returns it to the atmosphere as molecular nitrogen and, to a small extent, as nitrous oxide. The strongest denitrification flux is from land, followed by denitrification in coastal ocean water and sediments, both have increased with time during the past 300 years. Denitrification and riverine flow are the main mechanisms of N removal from land. However, in the course of the 300 years of human forcings and global temperature change, denitrification increased relatively less than riverine transport of dissolved and particulate N. As a result, according to our model analysis, the denitrification fraction of total N loss from land (the sum of denitrification and riverine export) decreased from about 83% in

preindustrial time to 73% in the year 2000, the rate of decrease becoming pronouncedly stronger near the year 1950.

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