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Century-scale nitrogen and phosphorus controls of the carbon cycle

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Abstract

In recent decades, humans have become a very important force in the Earth system, demonstrating that emissions (gaseous, liquid, and solid) are the cause of many of our environmental issues. These emissions are responsible for major global reorganizations of the biogeochemical cycles. The oceans are now a net sink of atmospheric CO_2, whereas in their preindustrial state they were a source; the trophic state of the coastal oceans is progressively moving toward increased heterotrophy; and the terrestrial realm is now vacillating between trophic states, whereas in preindustrial times it was autotrophic. In this paper, we present model calculations that underscore the role of human-induced perturbations in changing Earth's climate, specifically the role of anthropogenic nitrogen and phosphorus in controlling processes in the global carbon cycle since the year 1850 with projections to the year 2035. Our studies show that since the late 1940's emissions of nitrogen and phosphorus have been sequestered in the terrestrial living phytomass and groundwater. This nutrient-enhanced fertilization of terrestrial biota, coupled with rising atmospheric CO_2 and global temperature, has induced a sink of anthropogenic CO_2 that roughly balances the emission of CO_2 owing to land use change. In the year 2000, for example, the model-calculated terrestrial biotic sink was 1730 Mtons C/year, while the emission of CO_2 from changes in land use was 1820 Mtons C/year, a net flux of 90 Mtons C/year emitted to the atmosphere. In the global aquatic environment, enhanced terrestrial inputs of biotically reactive phosphorus (about 8.5 Mtons P/year) and inorganic nitrogen (about 54 Mtons N/year), have induced increased new production and burial of organic carbon in marine sediments, which is a small sink of anthropogenic CO_2. It is predicted that the response of the global land reservoirs of C, N, and P to sustained anthropogenic perturbations will be maintained in the same direction of change over the range of projected scenarios of global population increase and temperature change for the next 35 years. The magnitude of change is significantly larger when the global temperature increase is maximum, especially with respect to the processes of remobilization of the biotically important nutrients nitrogen and phosphorus.

Keywords: Nitrogen; Phosphorus; Carbon; Biogeochemical cycles

1. Introduction

Nearly 30 years ago, Bob Garrels, Fred Mackenzie, and Cynthia Hunt published the book, ''Chemical Cycles and the Global Environment: Assessing Human Influences (1975)''. To our knowledge, this was one of the early, if not the first, attempts to demonstrate quantitatively the role of human activities in contributing to and modifying the coupled biogeochemical cycles of the bioessential elements carbon, nitrogen, phosphorus, and sulfur on a global scale. In recent decades, humans have become an even more impor-

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tant force in the Earth system, demonstrating even more forcibly that emissions (gaseous, liquid, and solid) are the cause of many of our environmental issues. Owing to land use activities and fossil fuel combustion, the terrestrial respiration and decay flux of CO_2 to the atmosphere have increased by about 15%; the nitrogen fixation flux has more than doubled over its preindustrial rate; the mining of phosphate ores has led to emissions of four times more phosphorus to the surface environment than released by chemical weathering; and fossil fuel and biomass burning emissions have led to a doubling of the flux of sulfur to the atmosphere. These emissions are responsible for major global reorganizations of the biogeochemical cycles. The oceans are now a net sink of atmospheric CO_2, whereas in their preindustrial state they were a source; the trophic state of the coastal oceans is progressively moving toward increased heterotrophy; the terrestrial realm is now vacillating between trophic states, whereas in preindustrial times it was autotrophic; and the ocean-to-continent flux of sulfur has been completely reversed. In addition, a plethora of environmental problems have developed because of human interference in the global cycles, including regional and global climatic change; photochemical smog and increases in tropospheric ozone levels; additions of contaminants and nutrients to ground, surface, and oceanic coastal waters; eutrophication of aquatic systems; and acid deposition.

In this paper, we present model calculations that underscore the roles of human-induced perturbations in changing Earth's climate and of anthropogenic phosphorus and nitrogen as controls on the carbon cycle since the year 1850 with projections to the year 2035. The calculations for the past and future represent numerical experiments run with the model Terrestrial Ocean aTmosphere Ecosystem Model (*TOTEM*; Mackenzie et al., 2001; Ver et al., 1999a). *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 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 most other models. 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.

Based on an analysis of model results, we conclude that emissions of nitrogen and phosphorus in the form of nitrogenous fertilizers and combustion products, phosphate fertilizers, and remobilized products from enhanced remineralization of organic matter have been sequestered in the terrestrial living phytomass and groundwater since about 1950. The enhanced fertilization of terrestrial biota induced by these "new" nutrients is a sink of anthropogenic CO_2 that roughly balances the emission of CO_2 owing to land use change. These anthropogenic nutrients are also continuously leached into aquatic environments. The enhanced discharge of inorganic bioavailable nitrogen and phosphorus to coastal waters via rivers and the atmosphere has led to increased new production and burial of organic carbon in marine sediments, a small sink of anthropogenic CO_2, and enhanced denitrification. In addition, because of changing land use practices during most of the 150-year time span since 1850, the soil humus reservoir has lost and will continue to lose organic material, including carbon, nitrogen, and phosphorus, now accumulating in transient continental water bodies and floodplains (Smith et al., 2001) to the coastal margin.

2. Past 150 years of carbon, nitrogen, and phosphorus fluxes

There is little doubt that the fluxes and reservoir masses of the elements of carbon, nitrogen, and phosphorus have been modified by human activities (Galloway and Melillo, 1998; Galloway et al., 1995; Garrels et al., 1975; Houghton et al., 1996; Mackenzie et al., 1993; Vitousek et al., 1997). These activities include fossil fuel burning, changes in land use, application of inorganic fertilizers to agricultural crop-

lands, and loading of municipal and industrial sewage in nearshore environments.

2.1. Historic pattern of human perturbations from 1850 to 2000

In this section, we discuss the past 150 years of nitrogen and phosphorus anthropogenic fluxes and some relevant carbon fluxes as calculated using *TOTEM*. The industrial production of inorganic nutrient fertilizers was not established until after the end of World War II in the late 1940's (Fig. 1A). With the increased production of nitrogen fertilizers through the Haber–Bosch process and increased mining of phosphate rock, the consumption of inorganic fertilizers in agriculture increased exponentially. Between 1950 and 1994, there was a sustained increase in global annual consumption of N and P fertilizers from 3 to 74 Mtons N and from 2.4 to 13 Mtons P, yielding average annual growth rates of 7% and 4%, respectively. Two notable global economic setbacks, which caused the collapse of world fertilizer consumption, are reflected within these trends: the oil crisis in the 1970s and the governmental and economic reorganizations in the countries of Central Europe, Former Soviet Union (FSU), and, to a lesser extent, Western Europe in the early 1990s. Between 1990 and 1994, fertilizer consumption decreased, yielding average annual negative growth rates of 2% N and 7% P. Increase in consumption by Asian countries during the latter period partly offset the significant decline by the European nations (United Nations FAO, 2000).

World fertilizer consumption after 1994 and towards the end of the 20th century has increased at an average annual rate of 2.5% for N and 3% for P.

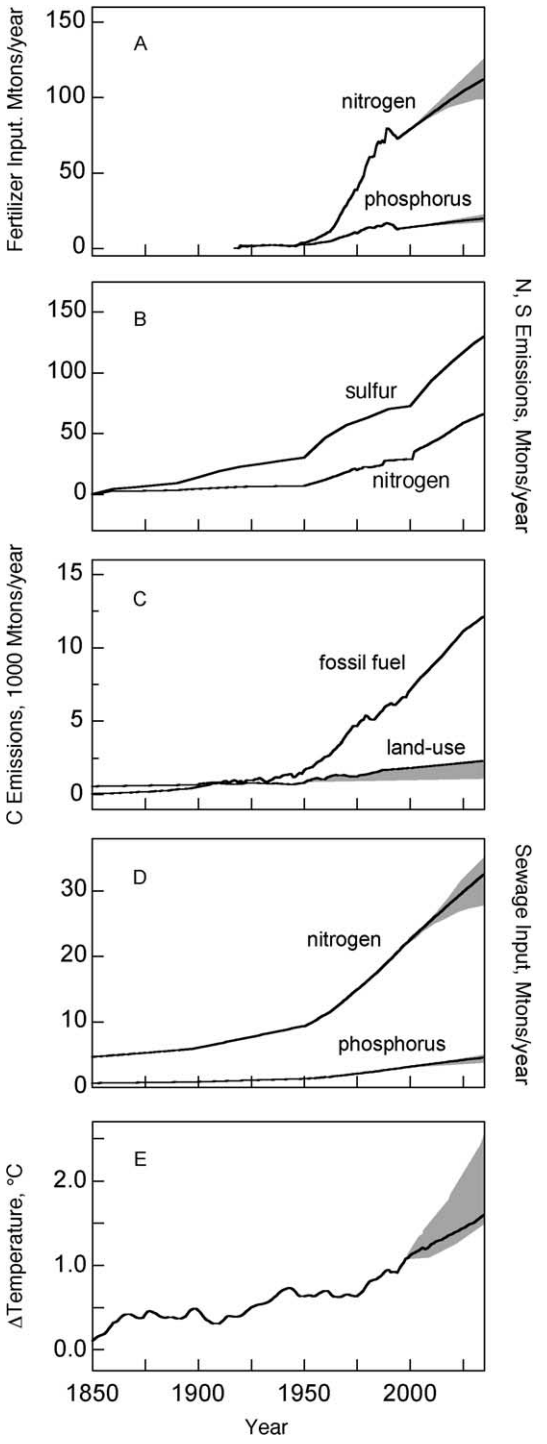

Fig. 1. Perturbations on Earth system simulated by *TOTEM* and projections to 2035 (A) inorganic N and P fertilizer application; (B) N and S emissions from fossil fuel burning and industrial activities; (C) CO_2 emissions from fossil fuel burning and land use activities; (D) municipal sewage and wastewater disposal; and (E) mean annual temperature variation. See text for description and sources of data. The shaded areas in (A) and (D) show the range of values of the perturbations calculated from the global population projections based on low and high fertility rates (United Nations Population Division, 2001); the shaded area in (C) shows the range of projections for emissions of CO_2 from land use change; in (E), the shaded area represents future global temperature from the Special Report on Emission Scenarios (SRES; Nakicenovic et al., 2000).

Note that these rates are much smaller relative to those for earlier decades. This small increase is mainly due to continued increased consumption in Asian and South American countries. Consumption in Western European nations has stabilized while that in the FSU has declined further.

Peak global consumption of nitrogen fertilizer was 80 Mtons N/year in 1989. Following the decline in the early 1990s, consumption reached this peak level again in 1998. World phosphate consumption today (2000, 14 Mtons) is still well below its 1989 peak of 17 Mtons.

Significant anthropogenic remobilization of nitrogenous combustion products from the burning of fossil fuels began with the Industrial Revolution in 1850 (Fig. 1B). The fate of anthropogenic N in the atmosphere is dictated by the short lifetime of the NO_x gases and their conversion products in the atmosphere. For these atmospheric components, ambient meteorological conditions during emission are important factors in their distribution and eventual deposition. The mechanisms for transfer to the terrestrial or nearshore surface ocean reservoirs include wet and dry deposition and sedimentation of large particles. In 1860, the annual rate of release of available nitrogen from this source was 0.4 Mtons (Dignon and Hameed, 1989). (By 2000, the anthropogenic emission of N combustion products had exponentially risen to 33 Mtons/year). Of this emission, it is estimated that about 60% was returned to the terrestrial realm while the rest was deposited onto coastal marine surface waters (Ver et al., 1999a).

Land use activities include the conversion of land for food production (grazing land, agricultural land), urbanization (building human settlements, roads, and other infrastructures), energy development and supply (building dams and other hydroelectric infrastructures, mining of fossil fuel), and resource exploitation (mining of metals, harvest of forest hardwood) (Mackenzie, 1998). Unlike fossil fuel burning or the agricultural use of inorganic fertilizer, these activities do not *add* material from sources external to the Earth system. Rather, these activities alter or enhance the process rate parameters for remineralization, weathering, denitrification, and biological uptake organic nitrogen and phosphorus storage is shifted from soil humus to terrestrial and oceanic phytomass; and inorganic N and P are transferred from land to the coastal margin and atmosphere (N only).

Land use activities affect the cycling of nitrogen and phosphorus by enhancing the remineralization of terrestrial organic matter, thus increasing the availability of nutrients in soilwater. This increased availability of nutrients, coupled with rising atmospheric CO_2 and warming temperatures, promotes enhanced productivity and storage of organic carbon in the terrestrial biota, thus increasing the drawdown of atmospheric CO_2. Furthermore, these activities enhance the rates of transfer of organic and inorganic material from land to the coastal zone owing to soil erosion, mineral dissolution, and surface water runoff.

Using data derived from the emission of CO_2 from land use activities, we estimate that 18 Mtons N/year and 7 Mtons P/year were being remobilized into inorganic forms on land in 1850 (Fig. 1C). These fluxes are equivalent to a CO_2 emission flux of 560 Mtons C/year. An additional 4 Mtons N/year and 3 Mtons P/year are transported to the coastal margin owing to anthropogenic effects on erosion and runoff, bringing the total effect from land use activities to 32 Mtons N/year and 10 Mtons P/year. Over the next 100 years from 1850 to 1950, the average annual growth rate of perturbational effects from land use activities was 1%. By 2000, the total overall effect of land use activities increased to 100 Mtons N/year and 50 Mtons P/year, with an average annual growth rate of the perturbation of 2% between 1950 and 2000.

2.2. Fluxes on land

We start with the fluxes involved with the cycling of N and P on land and relate these to the balance and redistribution of carbon. Fig. 2A is a balance diagram of major *anthropogenic* input fluxes of nitrogen and their redistribution among terrestrial reservoirs. Input from atmospheric deposition, leaching of fertilizer, and land use remobilization from humus and the living terrestrial phytomass are balanced by accumulation in the biomass and humus, export of dissolved and particulate N to the coastal oceans, and loss of N via denitrification and emission of gaseous N forms. This diagram and other balance diagrams to follow represent the balance of the anthropogenic sources and sinks of the elements. The natural background fluxes, which are not shown, define the starting point of the system at the quasi-steady state condition taken as the year 1700 in the model *TOTEM* (see Ver et al., 1999a).

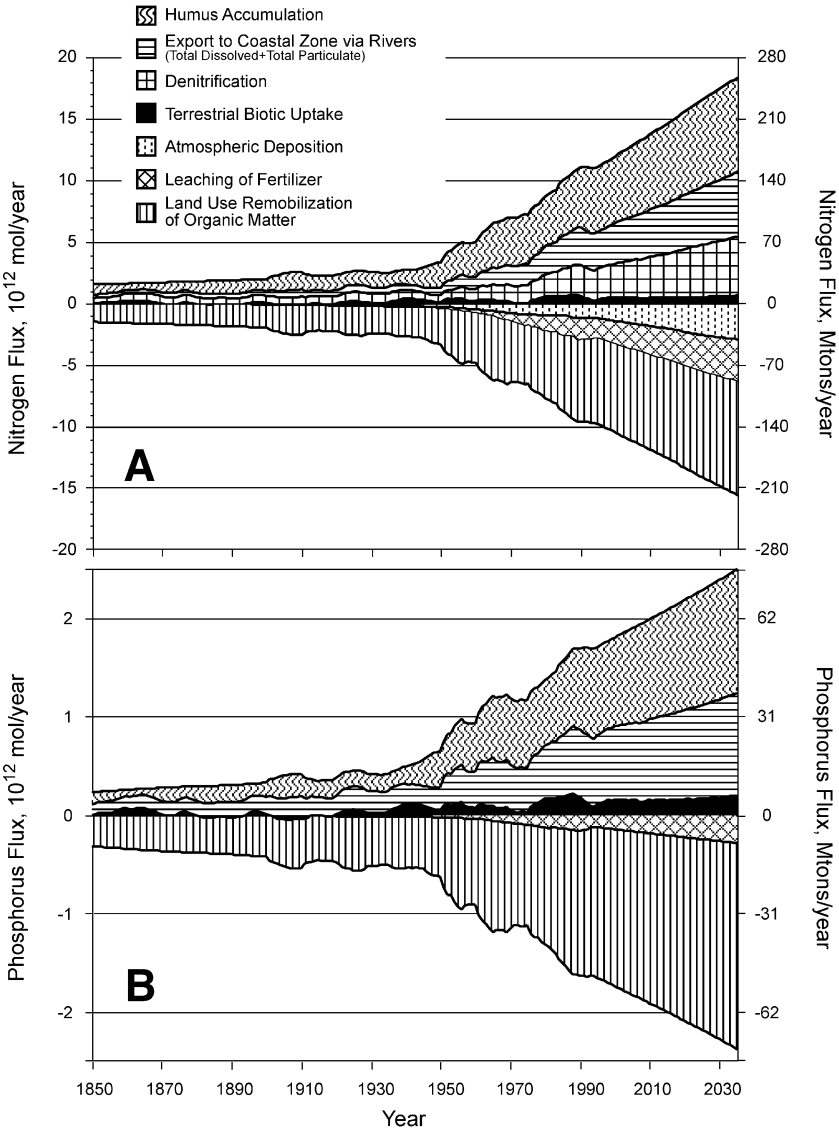

Fig. 2. The model-calculated partitioning of the human-induced perturbation fluxes on land of (A) nitrogen and (B) phosphorus for the period since 1850 to the present (2000) and projected to 2035 under the business-as-usual scenario, in units of 10^{12} mol/year and Mtons/year. The anthropogenic sources are plotted on the (−) side and the resulting accumulations and enhanced export fluxes are plotted on the (+) side. Note that the remobilization fluxes of P and N from land use activities are plotted separately from those for the terrestrial uptake flux, to highlight their opposing effects on the terrestrial organic reservoirs.

It can be seen from Fig. 2A that the anthropogenic mobilization of N in the Earth's surface environment became dramatically more important since the late 1940's following World War II as a result of the growing human population and its demand for resources to fuel the expanding global economy of the postwar years. In the year 2000, the total N mobilized on the Earth's surface by human activities was about 150 Mtons N/year. This rate was more than three times greater than that at the close of World War II (1950, 45 Mtons N/year) when much of the mobilized N was associated with land use activ-

ities (about 90%). Note that as the 20th century progressed, more of the anthropogenic emissions came from fertilizers and the combustion of fossil fuel. In the year 2000, land use activities accounted for 70% of the anthropogenically mobilized N while fertilizer application and atmospheric deposition accounted for 16% and 14%, respectively.

In the Earth surface system, the anthropogenic fluxes were redistributed into the environment by several processes. Increased application of nitrogenous fertilizers to croplands led to an increase in the export flux of N to the atmosphere including the emission of N_2 and N_2O via denitrification. The small temperature increase over the past 150 years may have also contributed to this enhanced denitrification flux. In addition, the application of N fertilizers to the landscape has resulted in the leaching of some of the nitrogen into aquatic systems as NO_3^- and NH_4^+ and an increase in the export of dissolved inorganic nitrogen (DIN) and total organic nitrogen (TON) to the coastal ocean. Finally, fertilizer N remaining in the soilwater, N from atmospheric deposition, and N remobilized by land use activities via the degradation of living phytomass and humus have led to the enhanced fertilization of the terrestrial phytomass, particularly in some forested areas of temperate North America and Europe (Matson et al., 1987; McGuire et al., 1995; United Nations FAO, 2001).

The case for phosphorus is similar to that for N with one very important exception: there is no major global flux of P as a gas species, although there is evidence to suggest that on a local or regional scale, the emission of phosphine, and perhaps polyphosphate gas, might be important (Devai and Delaune, 1995; Gassmann, 1994). On a global scale, humans have significantly perturbed the P cycle by the mobilization of nutrient P through land use activities and the application of phosphate fertilizer to croplands (Fig. 2B). For the past 150 years, changing land use practices have increased the remobilization of P into the environment from 6 Mtons P/year in 1850 to 28 Mtons P/year in 2000. Land use activities have also increased erosional loss of P from land from 3 to 22 Mtons P/year between 1850 and 2000. Additionally, the increased application of phosphate fertilizers since the close of World War II (Fig. 2B) provided a greatly enhanced source of anthropogenic P in the environment. At this time, the total perturbation on the P cycle was about 20 Mtons P/year, 96% of which came from the remobilization and erosional loss of P owing to land use activities. The perturbation from phosphate fertilizer leaching into the soilwater was small at about 0.7 Mtons P/year (4% of the total). By the year 2000, land use activities accounted for 92% of the total perturbation, about 50 Mtons P/year released to the environment. Phosphorus leaching from fertilizer application accounted for about 8% or about 5 Mtons P/year. This leaching flux represents 30% of the total of 15 Mtons of fertilizer P applied annually to croplands, golf courses, home lots, etc. Phosphorus leaching from these sources subsequently enters aquatic systems as dissolved inorganic and organic P (DIP, DOP) and as particulate P (PP). A portion of this P is exported to the coastal marine realm by river and groundwater discharges, while the rest is used in the fertilization of new phytomass (Fig. 2B).

Fig. 2 shows increasing transient accumulation of organic N and P in the terrestrial humus and phytomass reservoirs induced by enhanced fertilization of the biota over the past 150 years. Between 1850 and 2000, the rates of N accumulation increased from 12 to 84 Mtons/year while that of P increased from 4 to 33 Mtons/year. Note, however, that when other losses of N and P are accounted for, including remobilization and erosion of organic matter because of changes in land use practices, the net change in the terrestrial organic reservoirs of N and P over the past 150 years was calculated to be in the opposite direction, with N losses ranging from 8 to 20 Mtons/year and P losses ranging from 1 to 6 Mtons P/year (Fig. 3). The humus reservoir sustained losses over the entire 150-year period while the phytomass fluctuated between net gains and net losses.

In previous papers (Mackenzie et al., 2001; Ver et al., 1999a), we demonstrated that during the past 150 years, there has been a net overall loss of organic carbon from the terrestrial biota and soil humus reservoirs. This conclusion was based on calculations derived from results of *TOTEM* simulations. As shown in Fig. 3, the pattern of loss of N and P from these reservoirs is similar to that for organic carbon. From about 1850 to 1940, organic N and P, as well as C, were generally lost from both living phytomass and soils in the terrestrial realm. Since about 1940, the gain of N, P, and C from the fertilization of terrestrial biota fluctuated while soil organic C, N, and P

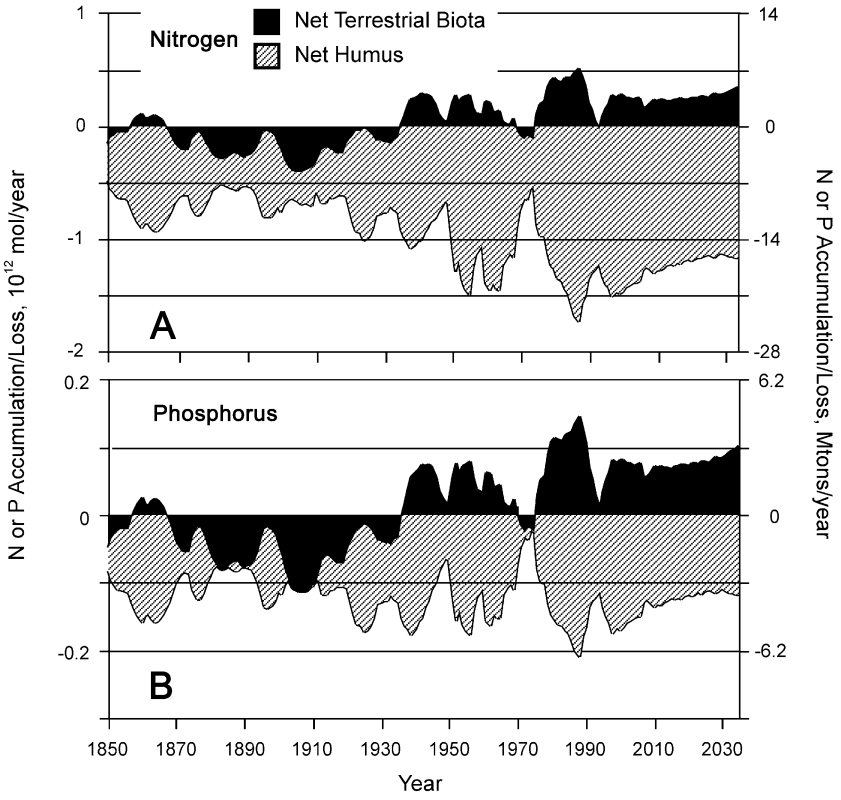

Fig. 3. The net accumulation (+) or loss (−) of (A) nitrogen and (B) phosphorus by the terrestrial organic reservoirs of living biota and humus for the period since 1850 to the present (2000) and projected to 2035 under the business-as-usual scenario, in units of 10^{12} mol/year and Mtons/year.

sustained continuous losses because of land use activities. Between 1850 and 1950, the terrestrial biota sustained net annual losses averaging about 1.5 Mtons N and 1 Mton P. These amounts are equivalent to about 220 Mtons C/year. This trend is reversed during the most recent 50 years (1950–2000), when the terrestrial biota gained about 3 Mtons N and 2 Mtons P/year, equivalent to about 300 Mtons C/year. The humus reservoir sustained net losses of C, N, and P throughout the entire period from 1850 to 2000, averaging about 15 Mtons N and 4 Mtons P, equivalent to about 170 Mtons C.

Nutrients remobilized from soil humus at a C:N:P molar ratio of 140:10:1 partly supported the fertilization of the terrestrial phytomass at a molar ratio of 510:4:1, a process especially evident from the pattern of net uptake of C, N, and P by the terrestrial biota since about 1950 (Fig. 3). It is believed that a major fraction of the remobilized organic matter was not remineralized but was redistributed on land and sequestered in artificial water bodies such as agricultural ponds and dammed reservoirs and in natural lacustrine sediments and river floodplains. This redistribution of anthropogenic carbon may constitute a sink for atmospheric CO_2 and must be accounted for in any budget of the carbon cycle (see, e.g., Smith et al., 2001; Stallard, 1998). The magnitude of the sink is still controversial but, in recent decades, may be on the order of 1000 Mtons C/year (Smith et al., 2001; Stallard, 1998). Model calculations show that some of the remineralized N and P were transported to the coastal ocean and other aquatic environments via river and groundwater discharges, stimulating new production and leading to enhanced burial of organic matter (Mackenzie et al., 1998a; Ver et al., 1999a,b). The enhanced burial of organic matter in aquatic environ-

ments also constitutes a sink, albeit small, for anthropogenic CO_2. The response of the N and P biogeochemical cycles in the coastal margin to perturbations from terrestrial processes is discussed in Section 2.3.

Table 1 shows a comparison of *TOTEM* calculations with present and previous estimates by the Intergovernmental Panel on Climate Change (IPCC) (Prentice et al., 2001) with respect to the response of the biogeochemical cycle of C to anthropogenic perturbations over the past two decades. The model-calculated accumulation and flux values for the decade of the 1980s agree very closely with those of the IPCC despite differences in the analytical approach and model structure. Our model results show that the major perturbations on atmospheric C in the 1980s were from fossil fuel emissions averaging 5380 Mtons C/year and emissions from land use change averaging 1525 Mtons C/year. This anthropogenic CO_2 was partitioned among the atmosphere (accumulation averaging 3140 Mtons C/year), oceans (uptake averaging 1625 Mtons C/year), and terrestrial phytomass (biotic uptake averaging 2135 Mtons C/year).

During the 1990s, the global C cycle sustained a 15% increase in the anthropogenic perturbations over that of the 1980s. According to IPCC estimates, the increased perturbation was redistributed among the ocean and terrestrial organic matter, with the atmosphere maintaining an accumulation rate equal to that of the 1980s. Although *TOTEM* results do not entirely agree with these IPCC estimates for the 1990s, our model-calculated fluxes are within the range of the reported uncertainty of $\pm 1\sigma$. *TOTEM* model calculations show increased accumulation of anthropogenic CO_2 in the atmosphere, averaging 4150 Mtons C/year and a 30% increase over the 1980s rate. The oceanic uptake of CO_2 also increased by 20% relative to its rate during the 1980s. A model-calculated decline in the terrestrial uptake implies that the net flux from the atmosphere to the terrestrial organic reservoirs was very small relative to that estimated by the IPCC (compare 87 Mtons C/year to 1400 or 700 Mtons C/year).

It is obvious from analysis of *TOTEM* results averaged for the decade of the 1990s that there is a discrepancy between our calculations of the atmosphere accumulation and net land–atmosphere flux and those of the IPCC. There are several potential reasons for these differences. Several biogeochemical, physical, and socio-economic factors not included in our model—such as changing fertilizer leaching rates, proportion of soil C lost during deforestation, changes in soil moisture and precipitation, and increased use of organic fertilizer–may have affected the response of the terrestrial organic C reservoirs to anthropogenic perturbations from the late 1980s to the end of the decade of the 1990s. For example, recent analysis of decades of U.S. Forest Service data indicates that increased efficiency and improvements in forest technologies, various conservation strategies, and recycling have contributed to revitalized forest growth in North America and Europe (Wernick et al., 1997). Forest plantations in the developed world increased from 45–60 to 80–100 million hectares for the period 1980–1995 (World Resources Institute, 2001). For the same period in the developing world, plantations

Table 1
Comparison of *TOTEM* calculations with IPCC estimates in Mtons C/year[a]

	1980s			1990s		
	TOTEM[b]	IPCC TAR[c]	IPCC SAR[d]	*TOTEM*	IPCC TAR	SRLULUCF[e]
Atmospheric increase	3140	3300 ± 100	3300 ± 100	4150	3200 ± 100	3300 ± 100
Fossil fuel/cement emissions	5380	5400 ± 300	5500 ± 300	6220	6400 ± 400	6300 ± 400
Ocean–atmosphere flux	−1625	−1900 ± 600	−2000 ± 500	−1985	−1700 ± 500	−2300 ± 500
Land–atmosphere flux[f]	−610	−200 ± 700	−200 ± 600	−87	−1400 ± 700	−700 ± 600
Land use change	1525	1700 (600–2500)	1600 ± 1000	1730	–	1600 ± 800
Terrestrial uptake	−2135	−1900 (−3800–300)	−1800 ± 1600	−1815	–	−2300 ± 1300

[a] Positive values are fluxes to the atmosphere; negative values are fluxes from the atmosphere.
[b] Terrestrial Ocean Atmosphere Ecosystem Model.
[c] IPCC Third Assessment Report (Houghton and Yihui, 2001).
[d] IPCC Second Assessment Report (Houghton et al., 1996).
[e] IPCC Special Report on Land Use, Land Use Change, and Forestry (SRLULUCF) (Watson et al., 2000).
[f] sum (a) + (b).

increased from 40 to 81 million hectares. Globally, forest plantations increased from 160 to 187 million hectares for the period from 1995 to 2000 (United Nations FAO, 2001). A rough calculation of the NPP and biomass of forest plantations yields maximum values of 1130 Mtons C/year and 56,000 Mtons of biomass C in 1995, and 1325 Mtons/year and 65,450 Mtons of biomass C in 2000. These NPP values, however, represent a very small fraction (2%) of the terrestrial biotic uptake flux calculated by *TOTEM* for the 1990s and about 10% of the terrestrial biomass. Thus, over the long term, a consideration of these managed forests in the model *TOTEM* could modify the model-calculated global C fluxes.

In Fig. 4, we show a sensitivity analysis of a few factors that might be responsible for the difference in *TOTEM*-calculated estimates for the 1990s and those of the IPCC. Note in particular that from the late 1950s (the start of the Mauna Loa observational record of atmospheric CO_2 concentrations) until the early 1990s, the *TOTEM*-calculated concentrations of atmospheric CO_2 fit remarkably well with the Mauna Loa observational data. In the mid and late 1990s, the fit is not as good and generally *TOTEM*-calculated concentrations overestimate the observed data. This does not seem to be a function of the land use CO_2 model we use in our calculations (see Fig. 4). Note, however, that an increase in the rate of leaching of inorganic N and P fertilizers into the soilwater can significantly affect the drawdown of CO_2 from the atmosphere. It is possible, but certainly difficult to prove, that some enhancement of the amounts of nutrients N and P made available for biotic uptake in the 1990s could explain some part of the discrepancy between the *TOTEM*-calculated atmospheric CO_2 concentrations and those of the IPCC for this time period.

2.3. Horizontal fluxes of C, N, and P from land to sea

It has been known for some time that because of human activities on land, the global fluxes of C, N, and P by rivers to the ocean have increased over time (Cole et al., 1993; Howarth et al., 1996; Meybeck, 1982, 1993; Peierls et al., 1991; Wollast, 1993; Wollast and Mackenzie, 1989). These increased fluxes result in part from changes in land use practices, including deforestation, conversion of forest to grassland, pastureland, and urban centers, and regrowth of forests. In addition, the application of fertilizers to croplands and the subsequent leaching of N and P into

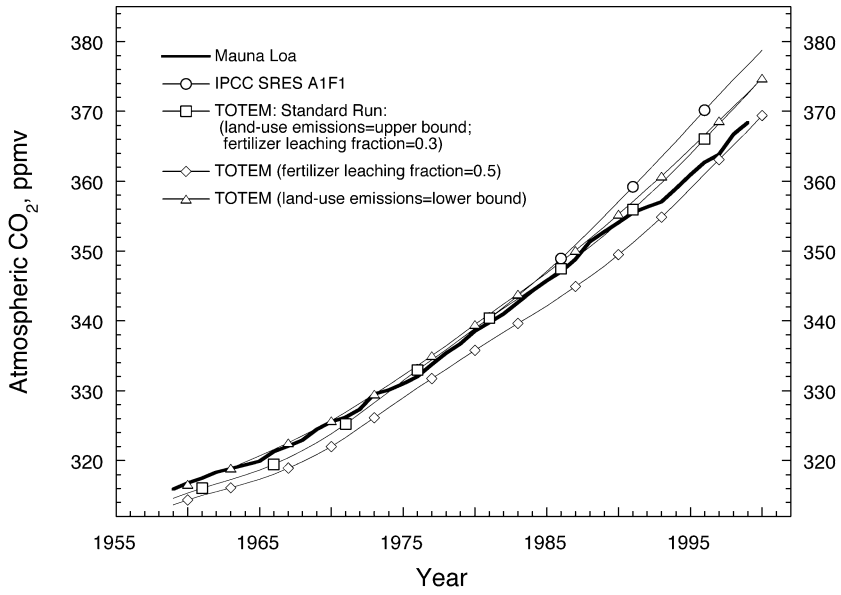

Fig. 4. A sensitivity analysis of the response of the atmospheric reservoir of carbon under selected model scenarios compared with observed data from Mauna Loa (Keeling and Whorf, 2001). The forcing functions tested were land use emission of CO_2 and inorganic fertilizer application. See also Fig. 1C for the range in values for land use emission of CO_2.

aquatic systems have also led to enhanced fluxes. Some estimates indicate that the riverine fluxes of C, N, and P have approximately doubled during the past several centuries (Meybeck, 1993). In addition, atmospheric fluxes of nitrogen from land to the sea have also increased (Dignon and Hameed, 1989; Galloway, 1990; Galloway et al., 1996; Hameed and Dignon, 1992; Vitousek et al., 1997). On a local or regional scale, these increased inputs to coastal marine waters have led to problems of eutrophication and degradation of coastal marine ecosystems.

Fig. 5 shows the model-calculated historical changes in the riverine C, N, and P fluxes that are reactive (total dissolved + reactive particulate fractions) and refractory (particulate inorganic and organic fractions), and from sewage loading onto coastal marine waters (see also Table 2 for summary). Also shown are historical changes in the accumulation flux of organic C in marine sediments and the exchange of N between the oceans and atmosphere. Notice in particular that these fluxes show a significant increase in magnitude after World War II, as the global peacetime economy expanded along with the population. The demand for resources to feed the population and to grow the economy led to a dramatic increase in the mobilization of C, N, and P into the surface environment of Earth. For example, the riverine TON flux remained almost constant between 1850 and 1950 with an average growth rate of 0.1% per year. Owing to increased anthropogenic activities on land especially after 1950, the growth rate of the riverine N fluxes now averages an order of magnitude greater, at 1.2% per year. Similar changes in rates are noted for riverine carbon and phosphorus fluxes after 1950.

2.4. Fate of nitrogen and phosphorus in the coastal zone

In this section, we discuss the fate of the anthropogenic N and P transported to the coastal ocean by the horizontal fluxes related to river and groundwater discharges and through the atmosphere. Carbon is not discussed in detail as the fate of this element in the global coastal zone has been discussed by the authors in a number of previous publications (Mackenzie et al., 1998a, 2000; Ver et al., 1998, 1999b). Fig. 6A and B shows the sources of anthropogenic N and P to the global coastal zone and the processes responsible for removal and dispersal of these elements in this region for the period between 1850 and 2035. Nitrogen and phosphorus inputs include riverine and groundwater fluxes of refractory particulate P (inorganic), refractory organic N and P (predominantly particulate), and reactive N and P (TDN, TDP, and the reactive fractions of PON and POP). Other sources of anthropogenic N and P are from direct sewage loading into coastal waters and the atmospheric deposition of N. These nutrients are dispersed throughout the coastal zone via biogeochemical and physical processes and are either removed from coastal zone waters or accumulate there in dissolved form. The removal processes involve deposition and accumulation in coastal marine sediments in both organic and inorganic forms, uptake by marine phytoplankton, and export to the open ocean. In addition, N is lost to the atmosphere by denitrification and emission of other gaseous N forms.

Model results show that while DIP is being depleted in the water column consistent with the accumulation of biomass in the coastal biotic reservoir, excess N is accumulating as DIN in the coastal water column or is volatilized to the atmosphere via denitrification at increasing rates. This finding confirms the idea that external phosphate inputs to oceanic waters control longer-term primary production, and that P is the ultimate limiting nutrient (ULN) in the global coastal ocean (see Tyrrell, 1999 and references therein for background on the biologists' versus geochemists' view of how oceanic primary production is controlled). Our findings are consistent with that of Tyrrell's (1999) model prediction of increased bioproductivity in the coastal ocean forced by a sustained increased input of inorganic P. Because there is no provision in *TOTEM* to distinguish between nitrogen-fixing and nonnitrogen-fixing phytoplankton to simulate the homeostatic control of nitrate and phosphate concentrations, increased input of inorganic N to the global coastal ocean causes an excess of DIN in our model.

Table 2 shows the increment of change in the input and output fluxes of anthropogenic N and P for the global coastal zone for the years 1850, 1950, and 2000. For comparison, initial values of the input and output fluxes are also shown (year 1700, the model-assumed quasi-steady state; Ver et al., 1999a) as well

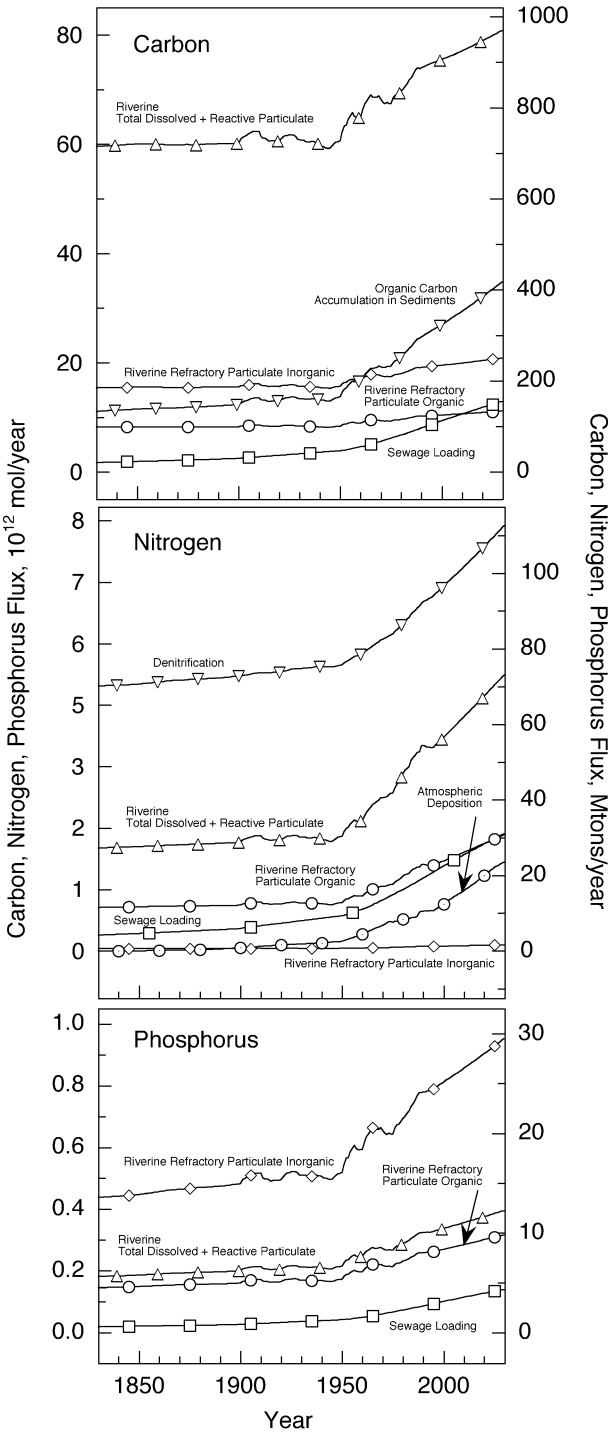

Fig. 5. *TOTEM* simulation results for the past, present, and predicted input and output fluxes of carbon, nitrogen, and phosphorus into or out of the global coastal margin, in 10^{12} mol/year and Mtons/year. Note that the flux values plotted here represent the total flux (initial value + response to perturbation). See also Table 2.

Table 2
Historical and future increment of change in fluxes of carbon, nitrogen, and phosphorus for the global coastal zone (see Fig. 5 for temporal trends and absolute flux values)

	Initial	ΔCarbon flux (Mtons/year)			
	1700	1850	1950	2000	2035
Input fluxes					
Riverine flux (total dissolved + reactive particulate)	695	24	32	210	287
Riverine flux (refractory particulate organic)	96	3	4	29	40
Riverine flux (particulate inorganic)	180	6	8	54	74
Sewage loading	0	23	47	113	163
Atmospheric deposition	–	–	–	–	–
Output fluxes					
Denitrification	–	–	–	–	–
Export to open ocean	5990	34	101	268	472
Accumulation in water column (organic)*	0	2	10	24	27
Accumulation in sediments	108	30	58	216	328
Accumulation in water column (inorganic)	0	2	7	50	60
	Initial	ΔNitrogen flux (Mtons/year)			
	1700	1850	1950	2000	2035
Input fluxes					
Riverine flux (total dissolved + reactive particulate)	25	3	5	32	51
Riverine flux (refractory particulate organic)	11	1	2	13	22
Riverine flux (particulate inorganic)	0.6	0.1	0.1	0.7	1
Sewage loading	0	5	9	22	32
Atmospheric deposition	0	0	2.6	12	25
Output fluxes					
Denitrification	67	4	9	30	49
Export to open ocean	163	0.8	2	6	24
Accumulation in water column (organic)*	0	2	9	30	35
Accumulation in sediments	3	2	4	14	22
Accumulation in water column (inorganic)	0	−0.1	−4	1	2
	Initial	ΔPhosphorus flux (Mtons/year)			
	1700	1850	1950	2000	2035
Input fluxes					
Riverine flux (total dissolved + reactive particulate)	5	0.8	2	5	8
Riverine flux (refractory particulate organic)	4	0.6	1	4	6
Riverine flux (particulate inorganic)	12	2	4	13	18
Sewage loading	0	0.7	1	3	5
Atmospheric deposition	–	–	–	–	–
Output fluxes					
Denitrification	–	–	–	–	–
Export to open ocean	17	1	2	6	9
Coastal organic matter accumulation in water column (organic)*	0	0.05	0.3	0.6	0.7
Accumulation in sediments	18	3	6	20	28
Accumulation in water column (inorganic)	0	0	−0.3	−0.8	−0.9

*Net increase in coastal biomass and organic matter in the water column.

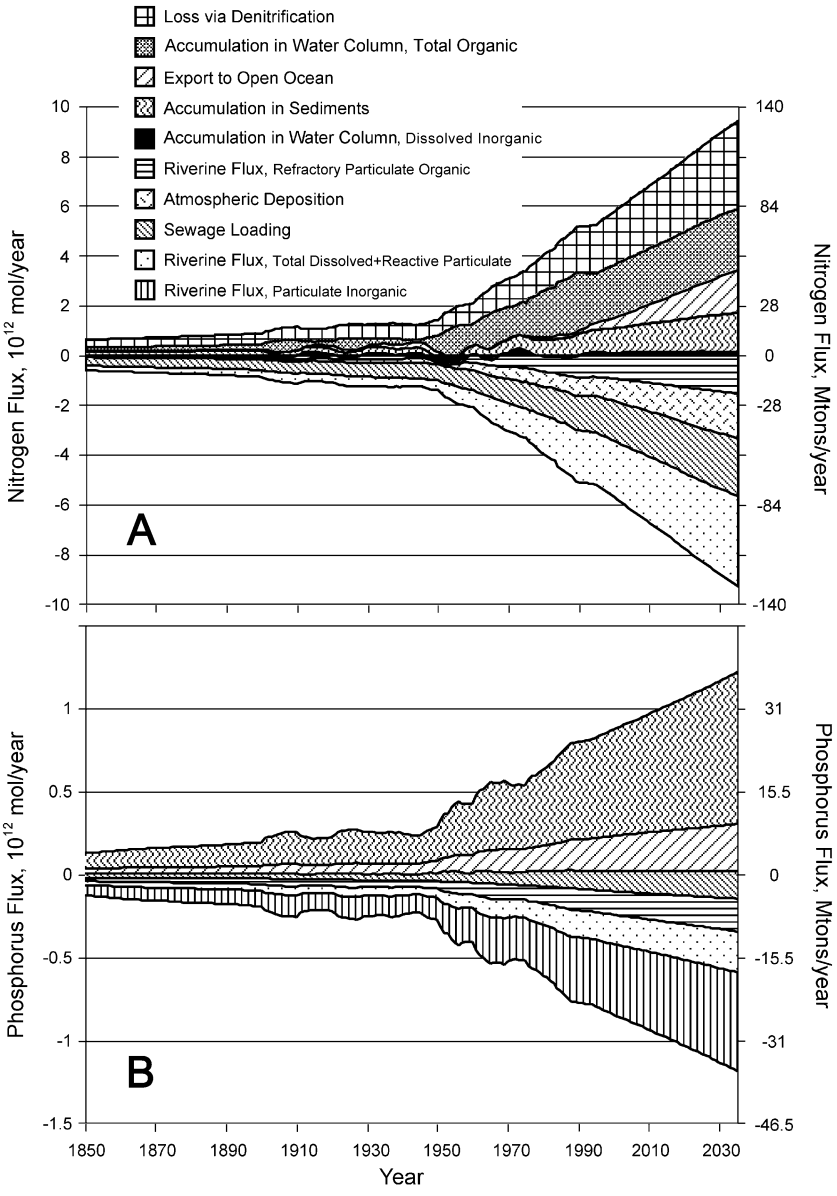

Fig. 6. The model-calculated partitioning of the human-induced perturbation fluxes in the global coastal margin of (A) nitrogen and (B) phosphorus for the period since 1850 to the present (2000) and projected to 2035 under the business-as-usual scenario, in units of 10^{12} mol/year and Mtons/year. See Fig. 2 for description of plot structure. See also Table 2 and Fig. 5.

as fluxes for carbon, as derived from previous numerical experiments using *TOTEM* (Mackenzie et al., 1998a, 2000; Ver et al., 1998, 1999b) and the projected magnitude of these fluxes in 2035 using a "business-as-usual" (BAU) scenario. Notice from both Fig. 6A and B and Table 2 the significant increases in the N and P input fluxes to the coastal zone, and hence output fluxes, during the last half of the 20th century. The rate of change of the total anthropogenic N and P inputs to the coastal zone for

the past 50 years prior to 1950 was 1% per year; over the most recent 50 years after 1950, the average rate of change was 2% per year.

2.5. Comparison of model calculations with observation for the year 2000

In this section, we explore how the numerical calculations using *TOTEM* fit with observational data and interpretations of the data for the latter part of the 20th century. We use the year 2000 of our model calculations as the basis for comparison. It should be kept in mind that the observational data and their interpretations have been made at various times during the past few decades and, therefore, one cannot anticipate that model calculations will fit exactly observational data. However, such a comparison might provide some confidence at least in the direction of the calculated trends.

Model-calculated historical trends for the global average concentrations of DIN, DIP, DOC, and POC in global rivers are shown in Fig. 7 (see also Table 2). Model results are consistent with derived global averages of observational data collected by Meybeck

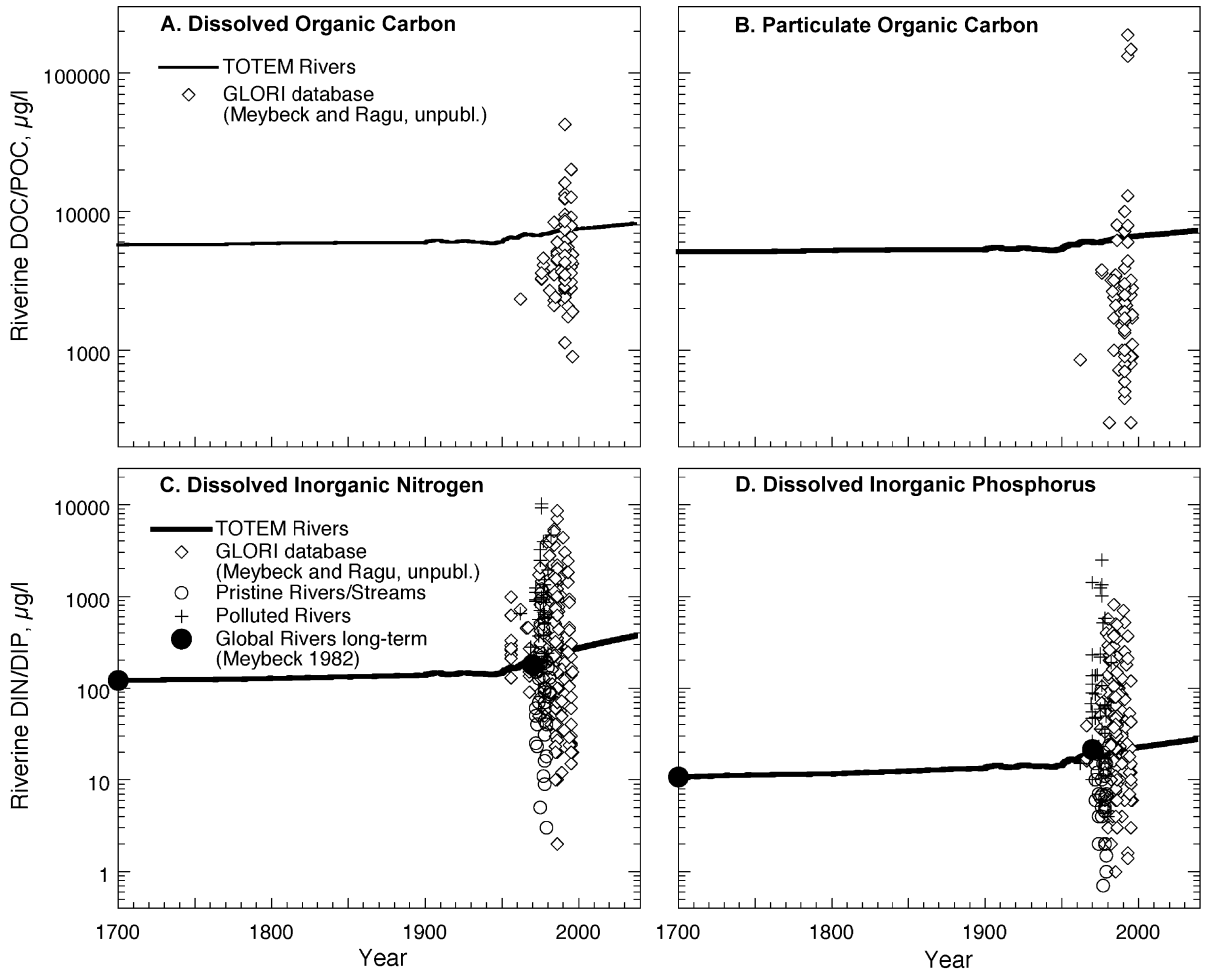

Fig. 7. A comparison of model-calculated historical and future (under the business-as-usual scenario) trends for the global average riverine concentrations of (A) DOC, (B) POC, (C) DIN, and (D) DIP and derived global average values and observational data collected by Meybeck (1982) and Meybeck and Ragu (unpublished data) from more than 450 rivers worldwide. Units are micrograms of the element per liter. Note the log scale of the elemental concentration on the *y*-axis.

(1982) and Meybeck and Ragu (unpublished data) from more than 450 rivers worldwide, and N and P values for selected rivers and streams, which have been classified as either pristine or polluted (Meybeck, 1982). Model predictions for organic C concentrations do not fit the observed data as well as that for inorganic N and P concentrations. This is consistent with the suggestion by Stallard (1998) and Smith et al. (2001) that about 1000 Mtons C/year of the organic matter lost from terrestrial reservoirs are sequestered in transient reservoirs such as agricultural ponds, dammed reservoirs, and natural lacustrine sediments. As noted earlier, significant changes occurred in the riverine delivery of organic and inorganic material from land during the period following the end of World War II.

Analysis of *TOTEM* global rates of denitrification from coastal marine sediments (Table 2) indicates that this removal process accounts for about 45% of the total nitrogen inputs to the global ocean, consistent with findings from various studies (Seitzinger and Giblin, 1996). Compared with rates measured in various coastal margins and predicted by other models (Table 3), *TOTEM*-calculated global denitrification rates fall within the lower bound of the range of estimates.

Table 3
Comparison of *TOTEM*-calculated rate of denitrification with various measured and model-derived values for the global coastal zone

	Denitrification (mmol N/m^2 day)
TOTEM-calculated	
Global average, 1970s	0.45
Global average, 1980s	0.47
Global average, 1990s	0.49
Measured values	
Massachusetts Bay (Giblin et al., 1994)	<0.48–5.12
Gulf of Mexico (Gardner et al., 1993)	1.0–3.36
South Atlantic Bight (Hopkinson et al., 1991)	6.4
Eastern North Pacific (Devol, 1991)	3.2
North Sea (Law and Owens, 1990)	0.0024–0.4
North Sea (Lohse et al., 1993)	0–0.6
Model-derived	
>45° N latitude (Seitzinger and Giblin, 1996)	0.9
20°–45° N (Seitzinger and Giblin, 1996)	2.6
0°–20° N (Seitzinger and Giblin, 1996)	1.42
Global average (Seitzinger and Kroeze, 1998)	1.2

3. Future of the nitrogen and phosphorus cycles

In this section, we forecast the future behavior of the global biogeochemical cycles of nitrogen and phosphorus and analyze the controls of these cycles on the future of the carbon cycle. The process changes in the global coupled C–N–P system are forced by sustained perturbation from changes in global surface temperature and human activities of fossil fuel burning, land use, sewage loading, and agricultural fertilizer use from the year 2000 to 2035. The magnitudes of these future perturbations (Fig. 1) are adopted and derived from many sources. Future emissions of gaseous C from fossil fuel burning are adopted from the IPCC IS92a or business-as-usual (BAU) emission scenario (Leggett et al., 1992), and emissions of gaseous N are calculated from the C emission values. Trends for the future emission of C and simultaneous remobilization of N and P from changes in land use activities are projected from Houghton (1983, 1991, 1995) and Houghton et al. (1998). Projections for future emissions of N and P from sewage loading of riverine and coastal waters and from the use of inorganic N and P fertilizer in agriculture are calculated from global population trends (United Nations Population Division, 2001). Lastly, future changes in global surface temperature are adopted from projections by the IPCC (Cubasch et al., 2001).

In order to investigate fully the range of possible future behavior of the biogeochemical cycles of N and P, we use three standard variant projections for global population by the United Nations Population Division (2001) based on low, medium, and high fertility rates and three projections for future global temperature by the IPCC using the emission scenarios of the Special Report on Emission Scenarios (SRES; Nakicenovic et al., 2000). World population was 6.1 billion in mid-2000 and is currently growing at an annual rate of 1.2%. By the year 2050, global population is expected to be between 7.9 (low variant) and 10.9 billion (high variant). Assuming the medium variant (the business-as-usual scenario, BAU), the global population is expected to be 9.3 billion in 2050. According to the IPCC projections, the globally averaged surface temperature is projected to increase by 1.4–5.8 °C over the period 1990–2100. These projections are greater than those published earlier by the IPCC Second Assessment Report (1.0–3.5 °C) because of changes

in the projected sulfur dioxide emissions (Cubasch et al., 2001).

It is interesting to note that the increase in global population is expected to occur mainly in less developed regions, principally in the continents of Asia and Africa, where the population is projected to increase steadily from 4.9 billion in 2000 to 8.2 billion in 2050 (medium variant). The population of the more developed countries is projected to change very little over the next 50 years as fertility levels are expected to remain below replacement level (Lutz, 1994). The projected increases in global population and the imbalance in the distribution of this increase have significant implications for the magnitude and variability of the human-induced forcings on the coupled C-N-P cycles from fossil fuel burning, deforestation, land use conversion, agricultural activities, and urbanization. For example, the rapid rates of population growth in Asia, accompanied by increased rates of economic development, industrialization, and land use change (Galloway and Melillo, 1998), are expected to modify significantly the biogeochemical cycles of C-N-P on land, thus contributing strongly to modification of the global cycles of these elements, particularly in the adjacent coastal margins (Hu et al., 1998; Mackenzie et al., 1998b; Skole et al., 1998; Vorosmarty et al., 1998). Thus, it is anticipated that over the next 50 years, the greatest impact from perturbations on land will be concentrated on about 60% of the global continental shelf area (excluding Antarctica and primarily in the global tropical and Northern temperate zones) owing to the fact that close to 85% of the global coastal population will be living at these boundaries (World Resources Institute, 1994).

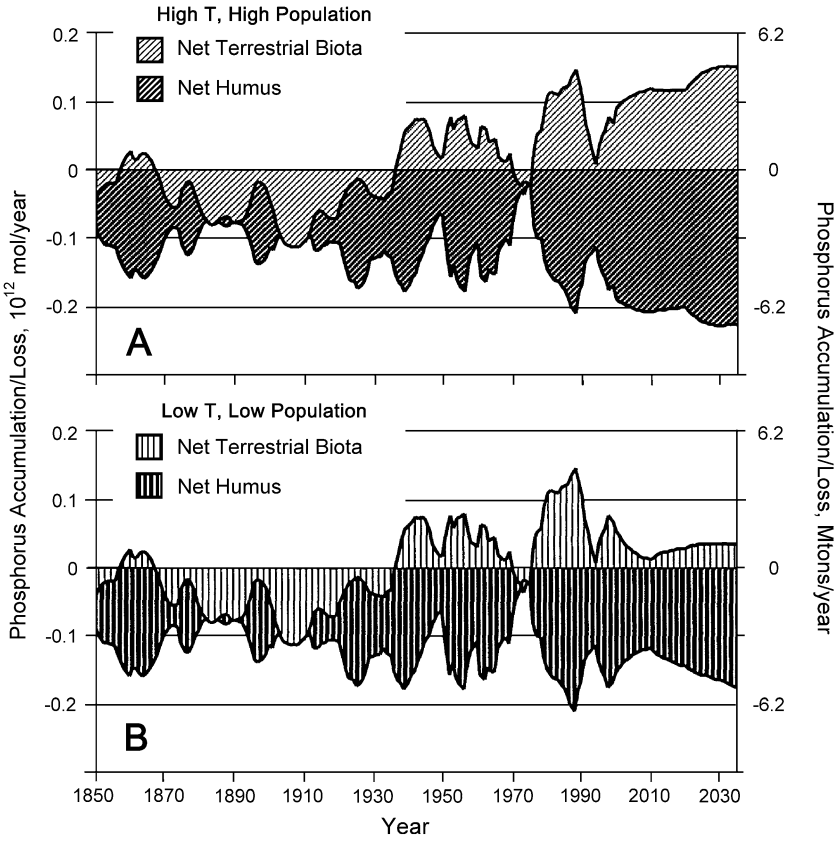

Fig. 8. Historical and comparison of the projected (2000–2035) net accumulation (+) or loss (−) of phosphorus by the terrestrial organic reservoirs of living biota and humus, in units of 10^{12} mol/year and Mtons/year. Simulation results under two scenarios are shown (A) high population/high temperature and (B) low population/low temperature.

3.1. Fluxes involving land reservoirs and between land and sea

Results from a *TOTEM* forecast of the coupled C-N-P biogeochemical cycles over the next 35 years show that sustained perturbation from human activities on land and from increasing global surface temperature will cause the continued loss of soil organic matter and enhanced fertilization of the terrestrial biosphere. Fig. 8 shows that over the range of projected scenarios of global population increase and temperature change for the next few decades, the response of the land reservoirs to the perturbations will be maintained in the same direction of change. Furthermore, the magnitude of change is significantly larger when the global temperature increase is maximum, especially with respect to the processes of remobilization of nutrients N and P.

The responses to the perturbations on land are transferred downcycle through the horizontal fluxes from land to sea. Thus, as shown in Fig. 6A and B, the direction of change is maintained with increased transport of N and P to the global coastal margin in organic and inorganic forms. Sewage loading of C, N, and P increases with global population, and atmospheric deposition of N on the coastal ocean surface increases with increased burning of fossil fuels and industrialization.

3.2. Horizontal fluxes and the coastal marine zone

Sustained perturbations on land projected over the next 35 years cause the increased delivery of reactive N and P to the global coastal margin (Figs. 6 and 7) and induce increases in the removal fluxes of denitrification, biomass accumulation, accumulation in coastal marine sediments, and export to the open ocean. Simultaneous fertilization of the coastal margin biota with increased sources of reactive N and P enhances bioproduction and the accumulation and removal of excess N in the water column. While

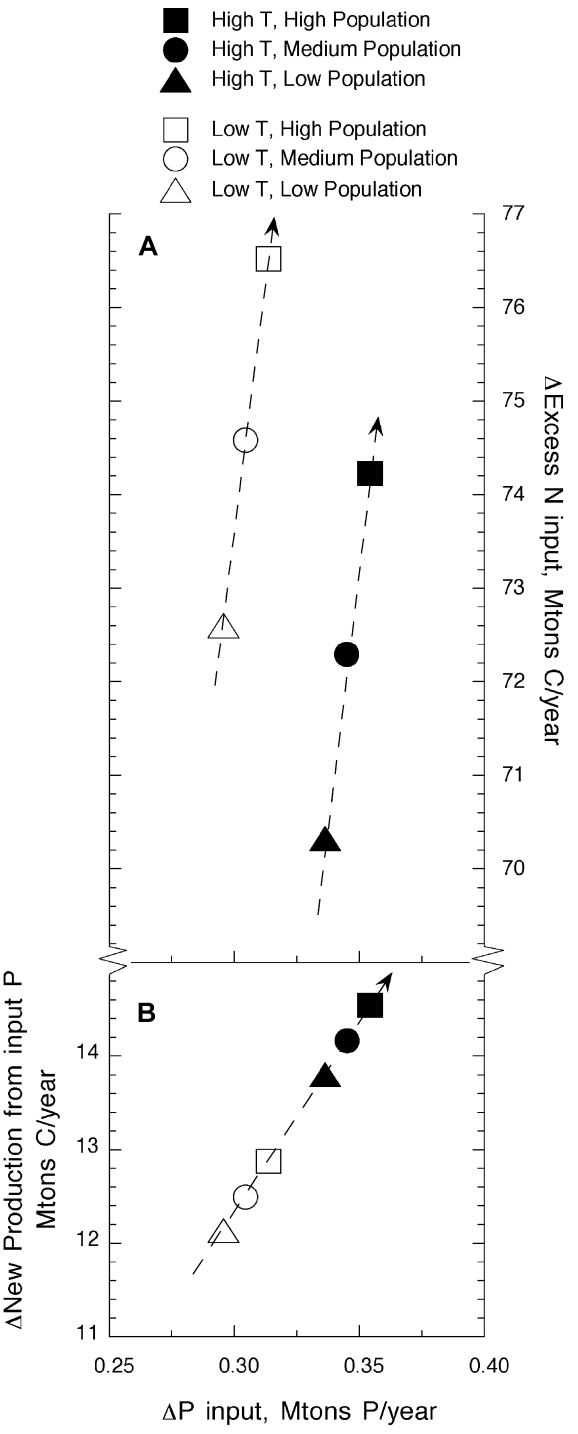

Fig. 9. The relationship between input of new dissolved inorganic phosphorus (DIP) to the global coastal margin in units of Mtons P/year and (A) excess available nitrogen and (B) new production, in units of Mtons C/year under six scenarios of projected global population and temperature. The dashed lines point in the direction of increasing anthropogenic perturbations.

denser human populations on land directly translate to proportionate increases in the remobilization fluxes of terrestrial N and P to the coastal margin, the response of N and P processes to higher global surface temperature is not symmetrical as indicated by Fig. 9. Here we show calculated new production (in units of Mtons C/year) owing to new sources of the limiting nutrient (in this case, P), the excess flux of the nonlimiting nutrient (N, in equivalent units of Mtons C/year), and their correlation with the changing input flux of reactive P. Model results represented in Fig. 9 suggest that new production in the global coastal margin is directly correlated with the rate of P input, regardless of the source of perturbation on land (increased human population or increased temperature). Note that with projected higher temperature change, significantly more P is delivered to the coastal margin from enhanced weathering on land. With the case of N, higher temperature change on land may result in enhanced loss of remobilized N via denitrification and gaseous emission, hence reducing the delivery flux to the coastal margin.

4. Conclusions

We have demonstrated the historical and future roles of anthropogenic N and P as controls on the carbon cycle and of human-induced perturbations in changing Earth's biogeochemical processes using model analysis of the coupled C-N-P global biogeochemical cycles. Emissions of N and P in the form of remobilized products from enhanced remineralization of organic matter, agricultural fertilizers, and combustion products have been sequestered in the terrestrial living phytomass and groundwater since the late 1940's. The enhanced fertilization of terrestrial biota induced by these sources of new nutrients and rising global temperature is a sink of anthropogenic CO_2 that roughly balances the emission of CO_2 owing to land use change. In the global aquatic environment, enhanced sources of biotically reactive phosphorus, the ultimate limiting nutrient, induced increased new production and burial of organic carbon in marine sediments, which is a small sink of anthropogenic CO_2. Excess nitrogen either accumulated in the water column or was removed via denitrification. Finally, over the range of projected scenarios of global population increase and temperature change over the next 35 years, the response of the land reservoirs to the perturbations will be maintained in the same direction of change. The magnitude of change is significantly larger when the global temperature increase is maximum, especially with respect to the processes of remobilization of nutrients N and P.

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