GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 21, GB2030, doi:10.1029/2006GB002799, 2007

Nitrification amplifies the decreasing trends of atmospheric oxygen and implies a larger land carbon uptake

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Received 22 July 2006; revised 21 January 2007; accepted 23 February 2007; published 28 June 2007.

[1] Atmospheric O_2 trend measurements are used to partition global oceanic and land biotic carbon sinks on a multiannual basis. The underlying principle is that a terrestrial uptake or release of CO_2 is accompanied by an opposite flux of O_2. The molar ratio of the CO_2 and O_2 terrestrial fluxes should be 1, if no other elements are considered. However, reactive nitrogen produced by human activities (e.g., fertilizers, N deposition) is also being incorporated into plant tissues. The various reaction pathways of the terrestrial nitrogen cycle cause fluxes of atmospheric O_2. Thus the cycles of nitrogen, carbon, and oxygen must be linked together. We report here on previously unconsidered anthropogenic nitrogen-related mechanisms which impact atmospheric O_2 trends and thus the derived global carbon sinks. In particular, we speculate that anthropogenic-driven changes are driving the global nitrogen cycle to a more oxidized state, primarily through nitrification, nitrate fertilizer industrial production, and combustion of fossil fuels and anthropogenic biomass burning. The sum of these nitrogen-related processes acts to additionally decrease atmospheric O_2 and slightly increase atmospheric CO_2. We have calculated that the effective land biotic O_2:CO_2 molar ratio ranges between 0.76 and 1.04 rather than 1.10 (moles of O_2 produced per mole of CO_2 consumed) over the period 1993–2003, depending on which of four contrasting nitrogen oxidation and reduction pathway scenarios is used. Using the scenario in which we have most confidence, this implies a 0.23 PgC yr^{-1} correction to the global land biotic and oceanic carbon sinks of most recently reported estimates over 1993–2003, with the land biotic sink becoming larger and the oceanic sink smaller. We have attributed large uncertainties of 100% to all nitrogen-related O_2 and CO_2 fluxes and this corresponds up to ±0.09 PgC yr^{-1} increase in global carbon sink uncertainties. Thus accounting for anthropogenic nitrogen-related terrestrial fluxes of O_2 results in a 45% larger land biotic sink of 0.74 ± 0.78 PgC yr^{-1} and a slightly smaller oceanic sink of 2.01 ± 0.66 PgC yr^{-1} for the decade 1993–2003.

Citation: Ciais, P., A. C. Manning, M. Reichstein, S. Zaehle, and L. Bopp (2007), Nitrification amplifies the decreasing trends of atmospheric oxygen and implies a larger land carbon uptake, *Global Biogeochem. Cycles, 21*, GB2030, doi:10.1029/2006GB002799.

1. Introduction

[2] High-precision measurements of atmospheric oxygen trends are used to partition the uptake of anthropogenic CO_2 between land and oceans [see, e.g., *Keeling and Shertz*, 1992]. The quantification of the global carbon budget by the Third Assessment Report of the Intergovernmental Panel on Climate Change [*Prentice et al.*, 2001] rests upon atmospheric oxygen measurements. The underlying principle is that the dissolution of anthropogenic CO_2 into the ocean has no O_2 counterflux, whereas the uptake of CO_2 by terrestrial plants is mirrored by an opposing O_2 flux. The O_2 to CO_2 ratio in land biotic fluxes commonly used in carbon sink calculations is 1.10 ± 0.05 moles of O_2 produced per mole of CO_2 consumed [*Severinghaus*, 1995; *Manning and Keeling*, 2006]. Photosynthesis emits O_2 to the atmosphere and respiration is usually assumed to absorb atmospheric O_2 following this same ratio. Thus the mass of oxygen in the terrestrial biosphere decreases over time if photosynthesis exceeds respiration. However, determining the precise value of this ratio is problematic [*Manning and Keeling*, 2006; *Seibt et al.*, 2004], particularly for respiration, which could have large variations over temporal scales and ecosystem ranges [*Randerson et al.*, 2006]. Recent studies have suggested molar ratios between 1.0 and 1.1 [*Manning*, 2001; *Marca*, 2004; *Seibt et al.*, 2004; *Stephens et al.*, 2007], however these studies have not been very comprehensive.

[3] Although there is no oceanic O_2 counter-flux directly as a result of fossil fuel CO_2 emissions, there is an indirect effect caused by the fact that the global oceans have warmed [*Levitus et al.*, 2000]. The ocean warming signal, combined with changes in ocean dynamics and biology, has likely

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0886-6236/07/2006GB002799$12.00

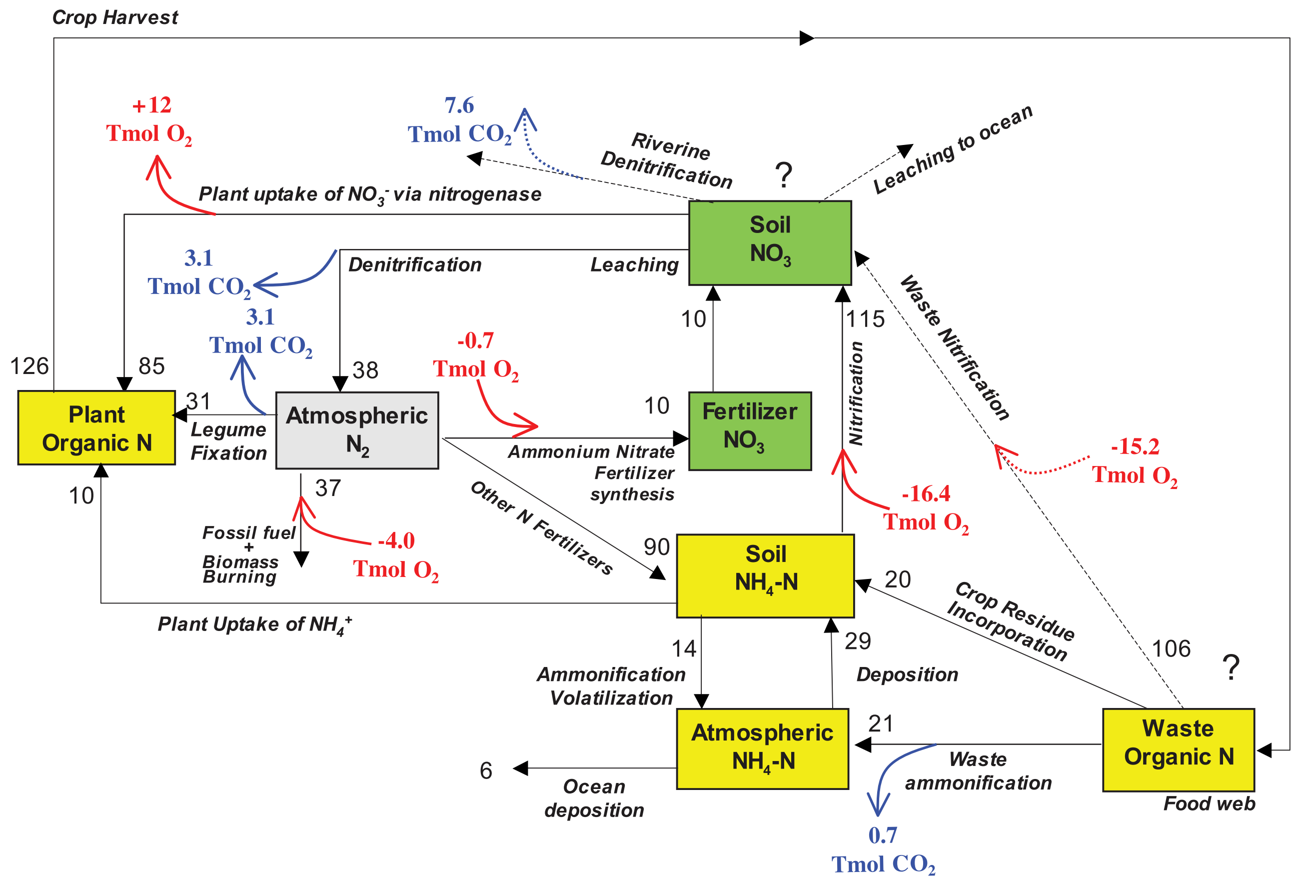


Figure 1. Component fluxes of the anthropogenic perturbation of the global nitrogen cycle fluxes (all fluxes are changes between present day and pre-industrial). Denitrification of groundwater or soil nitrate ions into N_2O rather than into N_2 is a small flux, not shown in the figure (see text). **In red** are the nitrification oxidizing reactions causing net uptake of O_2 from the atmosphere (see Table 1). **In blue** are the denitrification reactions causing a release of CO_2 to the atmosphere. **In black** are all other perturbation fluxes of nitrogen that are neutral with respect to O_2 and CO_2. Nitrogen perturbation fluxes are expressed in TgN yr^{-1}, and where applicable, the associated fluxes of O_2 or CO_2 are expressed in Tmol yr^{-1}.

affected the air-sea O_2 flux over the last decades (for a review, see work by *Bender et al.* [2005]). This effect has been taken into account to correct O_2-derived global carbon budgets by introducing an oceanic O_2 outgassing flux derived from observed air-sea heat fluxes [*Bopp et al.*, 2002; *Keeling and Garcia*, 2002; *Plattner et al.*, 2002]. The corresponding ocean outgassing correction amounts to a decreased global land carbon uptake of 0.5 PgC yr^{-1} for 1993–2003 [*Manning and Keeling*, 2006].

[4] Here we report on mechanisms which alter the O_2 to CO_2 ratio of the terrestrial fluxes in response to anthropogenic activities. These mechanisms create a net sink of O_2 from the atmosphere, with less significant counterbalancing CO_2 emissions. They are a side consequence of the human-driven oxidation of the reactive nitrogen cycle (Figure 1). The mechanisms analyzed here imply a revision to the oxygen method to derive the global carbon budget.

2. Background

[5] Nitrogen fertilizer use has risen sharply over the past century. The mobilization of reactive N in fertilizers is thought to contribute to increased emission of nitrogen oxides and NH_4-N by soils, and thus to increased deposition from the atmosphere [*Frink et al.*, 1999]. Also, the combustion of liquid fossil fuels [*Marland et al.*, 2003] and biomass burning [*Mouillot et al.*, 2006] has increased dramatically over the second half of the past century, contributing to increased nitrogen oxides emissions. These human activities are progressively pushing the nitrogen cycle toward a more oxidized state [*Vitousek et al.*, 1997]. The oxidation of reactive nitrogen takes place by nitrification, nitrate fertilizer production, and combustion (equations (1) to (3) in Table 1). All of these oxidation processes cause an uptake of O_2 from the atmospheric reservoir, as first suggested by *Keeling* [1988]. In the opposite case, nitrogenase, a reduction of nitrate by plants to incorporate N in their tissues, requires electrons which can be supplied by the dissociation of water, contributing a source of O_2 to the atmosphere (equation (4) in Table 1 and *O'Neill* [1993]). Thirdly, the reduction of oxidized nitrogen by denitrification in anoxic environments consumes energy provided by organic material, releasing CO_2 to the atmosphere (equation (5) in Table 1 and *O'Neill* [1993]). Finally, CO_2 is

Table 1. Processes, Reactions, and Perturbation Fluxes (Changes Between Present-Day 1990s and Pre-Industrial 1860) Associated With Diverse Transformations of Nitrogen, With the Associated O_2 and CO_2 Atmospheric Fluxes

Equation Number	Process[a]	Reaction	N Flux, TgN yr^{-1}	O_2 Source, Tmol yr^{-1}	O_2 Sinks, Tmol yr^{-1}	CO_2 Source, Tmol yr^{-1}	Reference
		Reactions Causing O_2 Uptake					
(1)	Fabrication of ammonium nitrate fertilizers (Haber-Bosh)	$2NH_3 + \mathbf{2O_2} \rightarrow NO_3^- + NH_4^+ + H_2O$	10		0.7		G04
(2)	Change in nitrification[b]	$NH_4^+ + \mathbf{2O_2} \rightarrow H_2O + NO_3- + 2H^+$	115 to 221		16.4 to 31.6		Mass balance
(3)	Combustion of fossil fuel and antropogenic biomass burning	$2N + \mathbf{3O_2} \rightarrow 2\ NO_3$	37		4.0		G04
	Subtotal		***161***	***0***	***21.2 to 36.3***	***0***	
		Reactions Causing O_2 Release[c]					
(4)	Fertilizer nitrate uptake/reduction by plants (nitrogenase)	$HNO_3 + 2H_2O \rightarrow NH_4OH + \mathbf{2O_2}$	85	12			Mass balance
	Subtotal		85	***12***			
		Reactions Causing CO_2 Release					
(5)	Change in terrestrial and riverine denitrification[d]	$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + \mathbf{5CO_2} + 7H_2O$	38 to 144			3.4 to 12.9	G04
(6)	Ammonification of urea in anthropogenic waste	$CO(NH_2)_2 + 2\ H_2O \rightarrow 2\ NH_3 + \mathbf{CO_2} + H_2O$	21			0.7	G04
(7)	Change in biological fixation of atmospheric N_2 by terrestrial plants[e]	$3CH_2O + 3H_2O + 2N_2 + 4H^+ \rightarrow \mathbf{3CO_2} + 4NH_4$	31			1.6	G04
	Subtotal		***90 to 196***	***0***	***0***	***5.7 to 15.2***	
	Total			**+12**	**21.2 to 36.3**	**+5.7 to 15.2**	

[a]Anthropogenic nitrogen fluxes are inferred from the difference between late-1990s and 1860 nitrogen fluxes estimates of *Galloway et al.* [2004] cited as G04 in the Reference column.
[b]The low O_2 sink value assumes only nitrification of fertilizer nitrogen, the high value assumes that 100% of N in crop products waste and by-products gets nitrified, for example, in rivers (see text).
[c]The assimilation flux of nitrate by cultivated plants is deduced from mass balance considerations (fluxes given in Figure 1). It can be verified that the ratio of crop N to fertilizer N is 130%, in agreement with values from *Frink et al.* [1999].
[d]The lowest CO_2 source estimate is derived from G04 denitrification anthropogenic fluxes. The highest CO_2 source estimate assumes that 100% of the nitrates derived from waste (see footnote b) are denitrified before they reach the ocean repository. Therefore this higher estimate of the CO_2 flux is correlated with the pertaining higher O_2 sink in footnote b.
[e]Assumes that 100% of electrons required by biological fixation are supplied by organic molecules (CH_2O) electron donors.

also emitted to the atmosphere during the ammonification of urea (equation (6) in Table 1) and during biological fixation (equation (7) in Table 1). In the following, we show that the sum of the diverse fluxes of anthropogenic N is a net sink of atmospheric O_2. The perturbation of denitrification conversely translates into a source of CO_2. Overall, the CO_2 source is smaller than the O_2 sink. This decreases the O_2 to CO_2 molar ratio of land biotic fluxes from the 'normal' value of 1.10, and has an impact on the inferred carbon sinks using oxygen trend measurements.

[6] We assumed that during pre-industrial times, there was a balance between nitrogen oxidation and reduction processes [*Galloway et al.*, 2004], implying that the nitrogen-driven atmospheric O_2 and CO_2 fluxes were in balance, and the concentrations in equilibrium. In reality, if there was a pre-industrial imbalance in the nitrogen cycle [e.g., *Gruber*, 2004; *Lueker*, 2004], it may have been impacting the mean value of the ratio of O_2 to CO_2 fluxes, but not the trends in atmospheric O_2 and CO_2 caused by the anthropogenic perturbation of the carbon and oxygen cycles.

[7] The human perturbation of the nitrogen cycle is illustrated in Figure 1. The perturbation fluxes begin by nitrogen inputs from fertilizers to croplands, followed by nitrogenase and incorporation of N into crop tissues (proteins) and by passage through food webs. In the end, terrestrial and freshwater denitrification fluxes are also perturbed. Other perturbed nitrogen fluxes are associated with human-caused fires and fossil fuel combustion, as well as with an increasing rate of atmospheric N fixation reflecting legume cultivation. All of these processes transfer nitrogen from the atmospheric N_2 reservoir into reactive N pools (see *Galloway et al.* [2003] for a detailed description). Thus a shift is created to higher oxidation states of reactive nitrogen, principally by increasing the pool of nitrates in soils. Human activities further increase the mobility of nitrates, by modifying the transport of nitrogen in freshwater systems. In particular, the channeling of rivers and the suppression of wetlands would tend to reduce the exposure of nitrate ions to denitrification [see, e.g., *Meybeck and Ragu*, 1996]. If a large fraction of the additional nitrates produced by human activities are deposited or transported to the deep ocean, they will be sequestered on the order of 2000 years [*Brandes and Devol*, 2002].

[8] We produced estimates of the removal/addition of atmospheric O_2 via various oxidation/reduction channels of reactive nitrogen (Table 1). Most of the nitrogen fluxes are taken from the synthesis of *Galloway et al.* [2004]. Importantly, we look here only at the perturbation of the N fluxes, defined as the difference between the late 1990s and 1860 [*Galloway et al.*, 2004, Table 2]. Missing anthropgenic N fluxes to close the budget are inferred by mass balance calculations (from fluxes in Figure 1). The relevant fluxes of N, and their counterpart O_2 and CO_2 fluxes are estimated below.

3. Results

3.1. Oxygen Sinks From Fertilizer Use and Nitrification

[9] A removal of atmospheric O_2 is associated with the production of industrial fertilizers (equation (1) in Table 1) provided that N in fertilizers originates from the atmospheric N_2 reservoir. Today, the fabrication of 100 TgN yr^{-1} of industrial nitrogen fertilizers takes place via the Haber-Bosh process, using the atmospheric N pool [*Galloway et al.*, 2004]. This flux is divided into 10 TgN yr^{-1} of ammonium nitrate (NH_4NO_3) and 90 TgN yr^{-1} of other types of fertilizers containing NH_4-N. The industrial fabrication of ammonium nitrate is a direct sink of atmospheric O_2, equalling 0.7 TmolO_2 yr^{-1} (Figure 1 and equation (1) in Table 1). Most of the reactive NH_4-N nitrogen carried by other man-made fertilizers and added to cultivated soils is subject to nitrification (*Galloway et al.* [2004] and equation (2) in Table 1). The great majority of plants absorb nitrate preferentially to ammonium, because nitrate is more mobile than ammonium [*Recous et al.*, 1992; *Cox and Reisenauer*, 1973; *Crawford and Glass*, 1998]. Therefore most of the NH_4-N nitrogen in fertilizers is oxidized into nitrate by nitrifying bacteria in the soil before it can be fixed by plant roots. Only in acidic soils, the nitrification reaction could be inhibited. In that case, instead of NO_3^-, plants preferably use NH_4^+ or low-molecular organic nitrogen. A reasonable estimate of the nitrification channel is that 90% of the total NH_4-N nitrogen in fertilizers, that is a flux of 81 TgN yr^{-1}, gets nitrified by soil bacteria [*Killham*, 1994]. This flux must be diminished by losses through soil NH_3 emissions (14 TgN yr^{-1}; Figure 1 corresponding to the emissions terms called 'cro' and 'fer' in Table 2 of *Galloway et al.* [2004]) and augmented by the input of additional anthropogenic N from crop residues laid off to the soil. We estimated that this process of incorporation of crop residues to cultivated soils delivers annually 20 TgN yr^{-1} of reactive nitrogen to plants (estimated using a global crop harvest index of 0.8 and crop biomass C:N ratios given by *Goudriaan et al.* [2001]). This extra input of nitrogen to the soil is assumed to become mineralized into nitrates in one year. One must also account for the atmospheric deposition of NH_4-N (29 TgN yr^{-1}; Figure 1), an input to the soil NH_4-N pool which occurs very close to emission regions [*Warneck*, 1988]. An additional flux is due to N in organic form in by-products and waste.

[10] We made two extreme estimates of the effect of the anthropogenic nitrification flux on the O_2 budget. In the first one, all N in waste is assumed to get nitrified (106 TgN yr^{-1}) and all the nitrates produced are transported and stored into the ocean. This would increase the total nitrification O_2 uptake to an upper value of 31.6 Tmol O_2 yr^{-1} (Figure 1 and Table 1). The second extreme estimate considers that 100% of N in waste remains stored in organic form and thus has no impact on atmospheric O_2. In that case, the nitrification flux concerns only N delivered in fertilizers and it is of 115 TgN yr^{-1} (Table 1), implying an atmospheric O_2 uptake lower value of 16.4 Tmol O_2 yr^{-1}.

[11] Finally, one can observe that the anthropogenic biological fixation of 31 TgN yr^{-1} of atmospheric N_2 by legume cultivars (see Figure 1 and *Galloway et al.* [2004]) does not involve O_2, but emits CO_2 (see equation (7) in Table 1 and section 5). The nitrogen biological fixation process is thus neutral with respect to the atmospheric O_2 budget. However, the process of biological nitrogen fixation still acts as a positive feedback to the soil nitrification oxygen

sink by increasing N in the biomass pool, and subsequently in the flux of crop residues addition (Figure 1).

3.2. Oxygen Sinks From Combustion Processes

[12] The high-temperature combustion of fossil fuel in engines produces NO_x ($NO_x = NO + NO_2$) and consumes atmospheric O_2 (equation (3) in Table 1). The associated flux is 33 TgN yr^{-1} after *Prather et al.* [2001] quoted in IPCC-TAR, implying an O_2 uptake of 3.5 $TmolO_2$ yr^{-1}. Additionaly, wildfires emit NO_x and remove O_2 by the same equation (3) in Table 1. Since we are concerned here only by the human perturbation of N fluxes, the anthropogenic component of biomass burning must be separated from the natural one. Following the recent biomass burning history reconstructed by *Mouillot et al.* [2006], we estimated that the anthropogenic share represents 60% of the total biomass burning N emission. From the total biomass burning N emissions (that is NO_x) reported by *Prather et al.* [2001] of 7 TgN yr^{-1}, we therefore derived an anthropogenic NO_x source of 4 TgN yr^{-1}. The total fossil plus anthropogenic biomass burning source of N to the atmosphere is of 37 TgN yr^{-1}.

[13] The NO_x compounds emitted by fossil fuel and anthropognic biomass burning are transformed into nitric acid, and further deposited as nitrates a few days after emissions [*Warneck*, 1988]. The current NO_x deposition flux is 24.8 TgN yr^{-1}, while its spatial distribution and the fate of deposited ions remain uncertain [see *Lamarque et al.*, 2005]. We estimated that the 37 TgN yr^{-1} of NO_X emissions cause a sink of 4 Tmol O_2 yr^{-1} (Figure 1 and equation (3) in Table 1). This oxygen uptake is likely to be underestimated because it ignores NO_x emissions produced by the combustion of biofuels and non-road transport, which may account for 2% of the emissions.

[14] Altogether, the combustion of fossil fuels, the burning of biomass by human activities, the industrial production of ammonium nitrate, and the nitrification of fertilizers N in soils produce a total sink of 21.2 to 36.3 $TmolO_2$ yr^{-1} (see Table 1). This O_2 uptake is equivalent to 3% of the annual uptake caused by fossil fuel combustion over the period 1993–2003. Thus it remains a small flux.

3.3. Oxygen Sources From Plant Nitrogen Use

[15] Once taken up by plant roots, nitrate ions have to be transformed into amino-acids before they can be incorporated into proteins to be used for enzymes and other plant tissues. The nitrate assimilation (= reduction) by the plant can be represented as

$$HNO_3 + 8H^+ + 8e^- \rightarrow NH_4OH + 2H_2O.$$

[16] In this process, the oxygen in the nitrate is transferred to water. Electrons needed for the reduction come via the oxidation of $NADPH_2$ to $NADPH^+ + H^+$ and the $NADPH^+$ has to be recycled (reduced) to $NADPH_2$ in the plant cell again. In plant cells there is often a surplus of electrons. Depending on where the nitrate assimilation takes place, the electrons for the reduction of $NADPH^+$ can come (1) from mitochondrial dissimilation of carbohydrates, resulting in a release of CO_2, (2) from fermentation processes that do not release any gases, or (3) directly from the photooxidation of H_2O ($H_2O \rightarrow 2H^+ + 2e^- + 1/2\ O_2$). Only this third source of electrons causes a release of O_2 to the atmosphere. In the extreme case where all the electrons could come from this channel, one can write as the overall equation for nitrate assimilation as

$$HNO_3 + 2H_2O \rightarrow NH_4OH + 2O_2.$$

[17] This corresponds to equation (4) in Table 1. Hence, per mole of NO_3^- reduced, two moles of O_2 are net-released to the atmosphere. The amount of nitrate incorporated into plant proteins is inferred from mass balance calculations (from the fluxes in Figure 1). We estimate that 85 TgN yr^{-1} are reduced by nitrogenase, which causes a source of 12 Tmol O_2 yr^{-1}. This source offsets 33 to 57% of the nitrification and combustion O_2 uptake. It is likely to be an overestimate however, because we have assumed that all the electrons come from cell water, the third possible mechanism described above.

4. Impact on Global Carbon Sinks Estimates

[18] The existence of a sink of atmospheric O_2 from the global nitrogen cycle becoming more oxidised has an impact on global carbon sinks as determined from atmospheric O_2/N_2 and CO_2 trends [*Bender et al.*, 2005; *Keeling and Shertz*, 1992, 2005; *Manning and Keeling*, 2006]. The nitrogen reactions above act to decrease the oceanic carbon sink and increase the land biotic carbon sink by an equal amount. We recalculated these carbon sinks on the basis of recent atmospheric observations over 1993–2003 [*Manning and Keeling*, 2006]. We also employed the same calculation methodologies as given by *Manning and Keeling* [2006]. The results are reported in Table 2 and shown graphically in Figure 2.

[19] We find that including the nitrification and combustion reactions of O_2 uptake summed in Table 1 (equations (1), (2) and (3)) results in a land biotic sink of 0.74 ± 0.78 PgC yr^{-1} and an oceanic sink of 2.01 ± 0.66 PgC yr^{-1} (Table 2, second column). This is a 0.23 PgC yr^{-1} increase in the land biotic sink, and an equivalent decrease in the oceanic sink, compared to the *Manning and Keeling* [2006] 1993–2003 estimate. For the land biotic sink, this represents a relatively large 45% increase. These calculations are also illustrated in Figure 2a in vector diagram format, after *Keeling et al.* [1996]. The nitrogen correction is the short, vertical, green vector. (The figure caption provides details of all vectors shown). To compare these results with the results of *Manning and Keeling* [2006], one can imagine extending the horizontal vector (oceanic sink) until it intersects the typical land biotic sink vector (with O_2/CO_2 slope of 1.1). This intersection point illustrates the extension of the oceanic sink vector and shortening of the land biotic sink vector, in other words, the larger oceanic sink and smaller land biotic sink presented by *Manning and Keeling* [2006].

[20] In the third column of Table 2, we have added the less certain estimate from nitrate reduction (Table 1, equation (4)), which decreases the carbon sinks correction to 0.10 PgC yr^{-1}. In these calculations we have used our lower estimate for nitrifcation fluxes (Table 1), because of a CO_2 complicity

Table 2. The 1993–2003 Global Carbon Budget and Partitioning of Carbon Sinks Between the Land Biosphere and Oceans Inferred From Atmospheric O_2/N_2 and CO_2 Measurements, Without and With the Anthropogenic Nitrogen Corrections as Given in Table 1[a]

All Data in Pg C yr^{-1}	*Manning and Keeling* [2006]	Correction 1: Corrected for O_2 Uptake From Nitrification and Combustion	Correction 2: Corrected for O_2 Release From Nitrate Reduction + Correction 1	Correction 3a: Corrected for CO_2 Release + Correction 1 + Correction 2 − Low Estimate	Correction 3b: Corrected for CO_2 Release + Correction 1 + Correction 2 − High Estimate
Land biotic uptake	0.51 ± 0.74	**0.74 ± 0.78**	**0.61 ± 0.75**	**0.54 ± 0.76**	**0.59 ± 0.83**
Oceanic uptake	2.24 ± 0.61	**2.01 ± 0.66**	**2.14 ± 0.62**	**2.21 ± 0.63**	**2.16 ± 0.70**
Land biotic O_2:CO_2 ratio[b]	1.1	**0.76**	**0.92**	**1.04**	**0.95**

[a]Correction 1 uses the low O_2 sink estimate of 21.2 Tmol O_2 yr^{-1}; correction 2 uses this O_2 sink estimate and the O_2 source of 12 Tmol O_2 yr^{-1}; correction 3a uses the low O_2 sink estimate of 21.2 Tmol O_2 yr^{-1}, the O_2 source of 12 Tmol O_2 yr^{-1}, and the low CO_2 source estimate of 5.7 Tmol CO_2 yr^{-1}; and correction 3b uses the high O_2 sink estimate of 36.3 Tmol O_2 yr^{-1}, the O_2 source of 12 Tmol O_2 yr^{-1}, and the high CO_2 source estimate of 15.2 Tmol CO_2 yr^{-1}. Uncertainties have been estimated by propagation of errors, assuming 100% uncertainty on both the nitrogen-related O_2 fluxes and the nitrogen-related CO_2 fluxes reported in Table 1. As in work by *Manning and Keeling* [2006], all calculations use global fossil fuel emissions of 6.48 ± 0.4 Pg C yr^{-1} and an observed global average atmospheric CO_2 increase of 3.73 ± 0.1 Pg C yr^{-1}.

[b]Units are moles of O_2 produced per mole of CO_2 consumed.

explained in section 5. Because of the uncertainty in the literature for nitrogen fluxes, we conservatively assumed 100% uncertainties on all nitrogen fluxes used in our global sink calculations. These uncertainties were propagated to the oceanic and land biotic sink estimates given in Table 2. For other parameters, we used the same uncertainties given by *Manning and Keeling* [2006].

5. Additional Effects and Caveats

[21] A key question is whether the fluxes of O_2 associated with reactive nitrogen reactions in Table 1 are accompanied by any fluxes of CO_2. If this is the case, the O_2:CO_2 ratio of the fluxes must then be examined. For photosynthesis, a global average ratio of 1.10 moles of O_2 produced per mole of CO_2 consumed is typically used in global carbon budgeting calculations from atmospheric O_2 measurements [*Manning and Keeling*, 2006; *Severinghaus*, 1995]. However, this value has not been well-defined, and even its uncertainty (±0.05) is little more than a guess [*Severinghaus*, 1995]. If there were one or more sources of CO_2 caused by nitrogen transformations and associated with the sink of O_2 caused by nitrification, they also must be taken into account in correcting for carbon sinks. The existence of CO_2 sources and O_2 sinks caused by nitrogen fluxes will also change the O_2:CO_2 molar ratio of global land biotic fluxes from the expected value of 1.1 Therefore we searched the scientific litterature to investigate the fate of oxidized nitrogen produced by human activities, looking for reactions susceptible to cause CO_2 fluxes to the atmosphere.

5.1. Denitrification and CO_2 Emissions

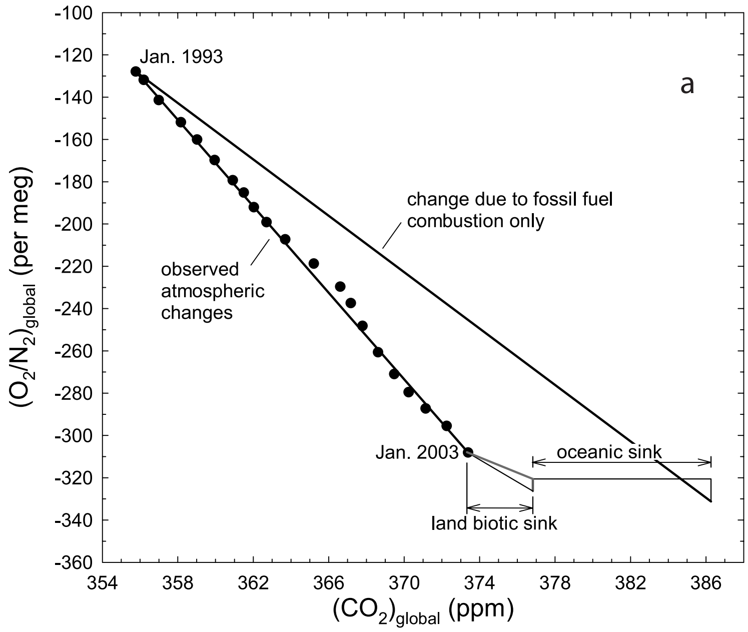
[22] Denitrification emits CO_2 to the atmosphere from the reaction of nitrate or nitrite ions with a substrate of decaying organic matter (equation (5) in Table 1). The very mobile NO_3^- and NO_2^- ions produced by fertilizer additions to croplands pass through several filters during their transport from land to ocean. In freshwater systems, they can be denitrified in anoxic groundwaters, in wetlands, foodplains or estuaries [*Galloway et al.*, 2004]. First, the flux of soil nitrates leached from cultivated soils contributes to anthropogenic denitrification. Leaching was estimated to represent up to 40% of the total fertilizer input globally. There is a large uncertainty in this estimate. We assumed (very)

Figure 2. Vector diagram showing oceanic and land biotic carbon sinks derived from atmospheric observations of O_2/N_2 and CO_2 over the period 1993–2003. (a) Scenario 1 and (b) scenario 3b (as given in Table 2). Solid circles are shown every 6 months and are annual mean O_2/N_2 ratio and CO_2 concentration measurements averaged from three stations in the Scripps Institution of Oceanography flask sampling network, namely Alert Canada, La Jolla U.S.A., and Cape Grim Tasmania. A solid line vector is drawn from the first annual average in January 1993 to the last in January 2003. The expected change in atmospheric O_2/N_2 ratio and CO_2 concentration from fossil fuel combustion, if no other processes were involved, is shown by the long, labeled vector (with a slope of 1.40 moles of O_2 consumed per mole of CO_2 produced). From the fossil fuel endpoint, the short vertical vector indicates oceanic O_2 outgassing as discussed in the text. From this vertical vector, the horizontal vector indicates the calculated oceanic carbon sink. From the end of the oceanic carbon sink vector, the short vector (vertical in Figure 2a, diagonal in Figure 2b; green in color versions) shows the nitrogen corrections. From this vector, the "typical" land biotic carbon sink vector is shown, with slope 1.10, returning to the atmospheric observations average point for January 2003. The vector sum of the nitrogen correction vectors and the typical land biotic sink vector is also shown (connecting the January 2003 observation point with the oceanic sink vector; red in color versions). This vector represents the net land biotic carbon sink taking into account anthropogenic nitrogen fluxes as discussed, and has slope 0.76 moles of O_2 produced per mole of CO_2 consumed in Figure 2a and 0.95 in Figure 2b. We verified that denitrification and fertilizer production, respectively a source and a sink of atmospheric N_2, induce negligible changes in the large atmospheric N_2 reservoir, and therefore do not impact the O_2/N_2 ratio.

conservatively that 90% of the leached fertilizer nitrates (38 TgN yr^{-1} deduced from mass balance in Figure 1) are presently denitrified before reaching the ocean [*Galloway et al.*, 2004]. This assumption leads to a lower end estimate of CO_2 emission of 3.4 TmolC yr^{-1}. Second, the nitrogen incorporated into crop biomass and then harvested, passes through food webs, just as carbohydrates do (Figure 1). Animal and human metabolism produce excretions and waste, which return reactive nitrogen to the environment. An additional denitrification flux could come from the transformation of N in excetions and organic waste (Figure 1). There are large uncertainties on the fate of N in waste. If we follow the extreme case of section 3.1 that 100% of waste N is nitrified and further assume that it is all denitrified, we would obtain a denitrification flux of 106 TgN yr^{-1}. This, together with the leached fertilizer nitrates, would give an upper end estimate of CO_2 emissions of 12.9 TmolC yr^{-1} (Table 1).

5.2. Other Nitrogen Fluxes Causing CO_2 Emissions

[23] Excretion products are mineralized into nitrate, urea or ammonia, the latter via the ammonification reaction (equation (6) in Table 1). Ammonification of decaying organic nitrogen causes no loss of CO_2. However, ammo-



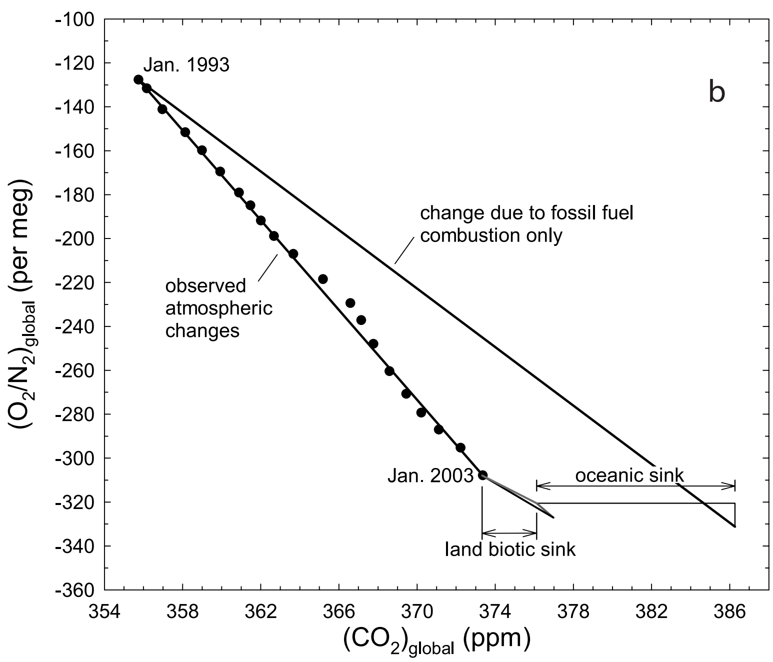


Figure 2

nification of urea (see Figure 1) causes a source of CO_2 of 0.7 TmolC yr^{-1}. Note that the NH_4-N vented to the atmosphere during ammonification gets deposited to the surface after a few days. Some of this reactive nitrogen may just be nitrified and provoke a supplementary fixation of atmospheric O_2 (Figure 1). Finally, the biological fixation of N requires electrons that must be supplied by carbohydrates (equation (7) in Table 1). Thus the small (and uncertain) increase in biological fixation since pre-industrial times [*Galloway et al.*, 2004] induces a source of CO_2 of 1.6 TmolC yr^{-1}.

5.3. Denitrification and Nitrous Oxide Emissions

[24] Denitrification emits mostly N_2 (96%) to the atmosphere and a very small flux of N_2O (4%). Thus the atmospheric pool of N_2O is currently increasing owing to fertilizer denitrification in agricultural soils. Such an excess of atmospheric N_2O will sequester atmospheric oxygen, owing to the long atmospheric lifetime of N_2O with respect to its photolysis in the stratosphere (110–170 years in the work by *Mahlman et al.* [1986]). We estimated the net anthropogenic emissions of N_2O to be 2.1 TgN yr^{-1} after the Table 1 of *Galloway et al.* [2004]. This flux causes a tiny sink of O_2 of 0.1 Tmol O_2 yr^{-1}, a negligible flux in the context of this analysis, and thus not considered further.

5.4. Ocean Nitrogen Cycle

[25] Another source of uncertainty may arise from the ocean nitrogen budget. Recent studies have challenged its stability with respect to N sinks (including biological N_2-fixation) estimated to be 265–294 TgN yr^{-1} and N sources (mainly water column and benthic denitrification) estimated to be 275–482 TgN yr^{-1} (see *Gruber* [2004] for a review). This imbalance, if asserted, may lead to a net CO_2 outgassing from the ocean [*Gruber*, 2004] that may impact the atmospheric budget without any counterpart on the O_2 budget. However, uncertainties of the ocean source and sink terms here are so large that it is therefore unclear whether such an imbalance exists today. Thus we have decided to leave those potential fluxes apart.

5.5. Summary Effects of N-Related CO_2 Emissions on Carbon Sinks

[26] We estimated net CO_2 emissions from anthropogenic changes in the nitrogen cycle since preindustrial times in the range from 5.7 to 15.2 TmolC yr^{-1} (Table 1). This total flux was estimated very conservatively with respect to the possible impact on the oceanic and land biotic carbon sinks. In other words, a less conservative estimate would result in a larger sinks correction. Note that our high estimate of the CO_2 emissions from waste denitrification is correlated with the high estimate of the O_2 sink from waste nitrification (see caption of Table 1). If N in waste is not nitrified, it cannot be later denitrified. Thus in Table 2, the fourth column (scenario 3a), we provide a low estimate of the N-related correction to the carbon sinks given both a lower O_2 sink and a lower CO_2 source, and in the fifth column (scenario 3b) we provide a high estimate given both a higher O_2 sink and a higher CO_2 source. In both scenarios, the CO_2 source is less than the O_2 uptake, and the O_2:CO_2 molar ratio for these nitrification/denitrification fluxes is 1.6, compared to the 'normal' terrestrial ratio of 1.1 for carbon reduction (photosynthesis) and oxidation (respiration) fluxes. The corresponding corrections to the 1993–2003 global oceanic and land biotic carbon sinks taking into account all of these processes, and using the high estimates above (which are nevertheless conservative), is a 0.08 PgC yr^{-1} increase in the land biotic sink, and an equivalent decrease in the oceanic sink (see Table 2, fifth column). Figure 2b illustrates scenario 3b in vector format, with the green vector showing the nitrogen correction with a slope (O_2/CO_2 molar ratio) of 1.6.

[27] It is worth noting that our definition of the land biotic carbon sink is the net effect from all terrestrial processes. Thus while adding nitrification processes result in an increase in the inferred carbon sink, denitification and biological fixation have a counteracting effect, diminishing the overall influence from anthropogenic nitrogen changes. This net terrestrial effect is illustrated by the red vectors in Figures 2a and 2b, which have slopes (O_2/CO_2 molar ratios) of 0.76 and 0.95 respectively (see also Table 2).

6. Discussion

[28] Incorporating anthropogenic changes in the nitrogen cycle in the global O_2 budget has the effect of decreasing the moles of O_2 produced per mole of CO_2 consumed (or vice versa) in terrestrial fluxes. We calculate that the land biotic O_2:CO_2 molar ratio typically used in global carbon budgeting calculations effectively must be changed from 1.10 to a range between 0.76 and 1.04, depending on which of the 4 scenarios summarized in Table 2 is used. It is important to realize that our corrections to the oceanic and land biotic sinks (Table 2) rest on the assumption that, globally, nitrification exceeds denitrification. We estimated indeed that anthropogenic nitrification is up to 3 times larger than its denitrification counterpart, on the basis of the nitrogen budgets established by *Galloway et al.* [2004] for 1860 and the early 1990s (their Table 1). Yet it is fair to say that this estimate is uncertain. In particular, changes in denitrification remain very poorly understood. For instance, the chanelling of rivers (Mississipi, Rhine) and the suppression of natural wetlands [*Meybeck and Ragu*, 1996] could decrease freshwater denitrification. On the other hand, the establishment of dams and the cultivation of rice could have increased regional denitrification [*Vitousek et al.*, 1997]. It is certain that the delivery of nitrate to rivers has dramatically increased in response to agricultural use of fertilizers. It is also widely observed that this has resulted in a massive input of new nitrate to the coastal seas [e.g., *Green et al.*, 2004], causing eutrophication and hypoxia. A particularly striking example is the gulf of Mexico, off the Mississipi Delta (see for instance http://oceanservice.noaa.gov/products/pubs_hypox.html). The consequences of such changes in nitrogen input by rivers to the coastal seas for atmospheric O_2 fluxes are not well understood. On the one hand, hypoxia could stimulate denitrification and enhance CO_2 emissions in the coastal zone. On the other hand, the subsurface oxygen minimum caused by eutrophication could be advected from the coastal

sea to the open ocean by seasonal water mass exchanges (e.g., the shelf pumping mechanism observed for carbon in the North Sea by *Thomas et al.* [2005]).

7. Conclusions

[29] We have shown that the human perturbation of the global N cycle results in nitrogen-related oxidation pathways dominating over reduction pathways, with more reactive nitrogen being cycled through the land biota. This oxidative imbalance creates a net uptake of atmospheric O_2 and a smaller source of atmospheric CO_2. These fluxes are part of the terrestrial carbon and oxygen cycles, but have not been accounted for in previous studies. When accounting for these fluxes, the value of the land biotic O_2:CO_2 ratio used in global carbon budgeting must be changed. Using estimates of (anthropogenic) nitrogen-related fluxes from the scientific literature, we calculate that the land biotic O_2:CO_2 molar ratio used in global carbon budgeting calculations should be decreased from the typically used value of 1.10 to between 0.76 and 1.04, depending on different possible anthropogenic nitrogen flux scenarios presented here. Using the fluxes from the scenario which we can report with least uncertainty (scenario 1 in Table 2), we calculate a modified land biotic ratio of 0.76. This results in changes to the global carbon sinks as recently inferred from atmospheric O_2 trends over the period 1993–2003, increasing the land biotic sink by 0.23 PgC yr^{-1} (a 45% correction) to 0.74 ± 0.78 PgC yr^{-1}, and decreasing the oceanic sink by the same amount to 2.01 ± 0.66 PgC yr^{-1}. There are large uncertainties associated with the magnitude of each nitrogen-related O_2 and CO_2 flux, primarily owing to insufficient knowledge of the fate of reactive nitrogen in ecosystems and freshwater systems. Assuming errors of 100% on each flux yields a range of uncertainties on global carbon fluxes of up to ± 0.09 PgC yr^{-1} greater than when nitrogen fluxes are not considered, as seen in the different columns in Table 2. However, we have been conservative on the side of minimizing the O_2 uptake from, for example, fossil fuel burning, plant reduction of nitrate from cell water, and CO_2 emissions from denitrification. Therefore our final corrections to the global oceanic and land biotic carbon sinks are also on the conservative side.

[30] In the future, rising fertilizer production and use is anticipated, which will further increase nitrification. In addition, river management and shrinking wetland areas will act to decrease denitrification. Therefore one may anticipate that the anthropogenic nitrogen fluxes will likely continue to consume atmospheric oxygen at even larger rates than today.

[31] **Acknowledgment.** We thank Ralph Keeling, who kindly provided a copy of his Ph.D. dissertation, where some of the O_2 fluxes decoupled from those of CO_2 were discussed.

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