

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

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[1] Atmospheric O₂ 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 CO₂ is accompanied by an opposite flux of O₂. The molar ratio of the CO₂ and O₂ 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 O₂. 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 O₂ 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 O₂ and slightly increase atmospheric CO₂. We have calculated that the effective land biotic O₂:CO₂ molar ratio ranges between 0.76 and 1.04 rather than 1.10 (moles of O₂ produced per mole of CO₂ 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 O₂ and CO₂ 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 O₂ 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.

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1. Introduction

[2] High-precision measurements of atmospheric oxygen trends are used to partition the uptake of anthropogenic CO₂ 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 CO₂ into the ocean has no O₂ counterflux, whereas the uptake of CO₂ by terrestrial plants is mirrored by an opposing O₂ flux. The O₂ to CO₂

ratio in land biotic fluxes commonly used in carbon sink calculations is 1.10 ± 0.05 moles of O₂ produced per mole of CO₂ consumed [*Severinghaus*, 1995; *Manning and Keeling*, 2006]. Photosynthesis emits O₂ to the atmosphere and respiration is usually assumed to absorb atmospheric O₂ 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 O₂ counter-flux directly as a result of fossil fuel CO₂ 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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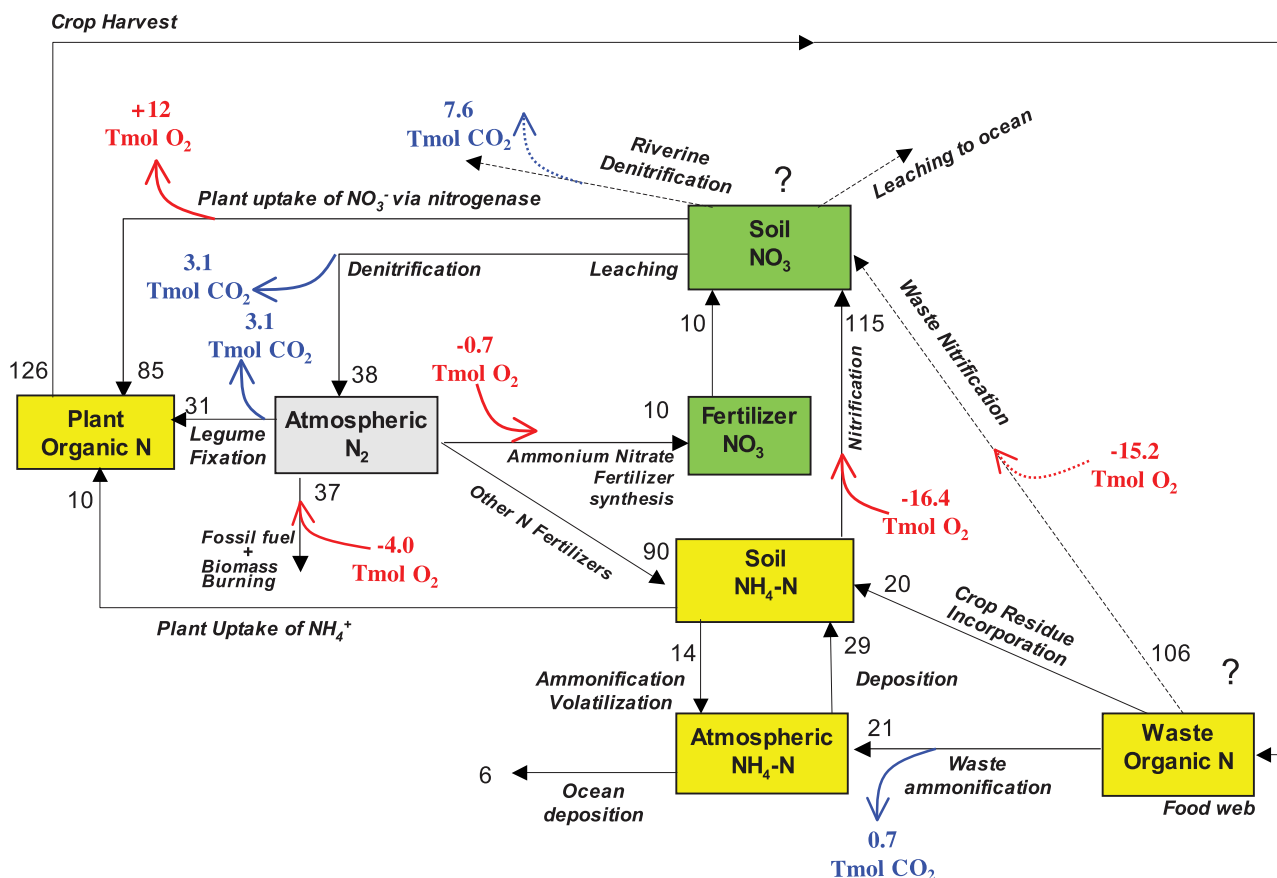


Figure 1. Component fluxes of the anthropogenic perturbation of the global nitrogen cycle fluxes (all fluxes are changes between present day and pre-industrial). Denitrification of groundwater or soil nitrate ions into N₂O rather than into N₂ is a small flux, not shown in the figure (see text). **In red** are the nitrification oxidizing reactions causing net uptake of O₂ from the atmosphere (see Table 1). **In blue** are the denitrification reactions causing a release of CO₂ to the atmosphere. **In black** are all other perturbation fluxes of nitrogen that are neutral with respect to O₂ and CO₂. Nitrogen perturbation fluxes are expressed in TgN yr⁻¹, and where applicable, the associated fluxes of O₂ or CO₂ are expressed in Tmol yr⁻¹.

affected the air-sea O₂ flux over the last decades (for a review, see work by *Bender et al.* [2005]). This effect has been taken into account to correct O₂-derived global carbon budgets by introducing an oceanic O₂ 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 O₂ to CO₂ ratio of the terrestrial fluxes in response to anthropogenic activities. These mechanisms create a net sink of O₂ from the atmosphere, with less significant counterbalancing CO₂ 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 NH₄-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 O₂ 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 O₂ 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 CO₂ to the atmosphere (equation (5) in Table 1 and *O'Neill* [1993]). Finally, CO₂ 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 O₂ and CO₂ 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
<i>Reactions Causing O₂ Uptake</i>							
(1)	Fabrication of ammonium nitrate fertilizers (Haber-Bosch)	$2\text{NH}_3 + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{NH}_4^+ + \text{H}_2\text{O}$	10		0.7		G04
(2)	Change in nitrification ^b	$\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_3^- + 2\text{H}^+$	115 to 221		16.4 to 31.6		Mass balance G04
(3)	Combustion of fossil fuel and anthropogenic biomass burning	$2\text{N} + 3\text{O}_2 \rightarrow 2\text{NO}_3$	37		4.0		
	Subtotal		161	0	21.2 to 36.3	0	
<i>Reactions Causing O₂ Release^c</i>							
(4)	Fertilizer nitrate uptake/reduction by plants (nitrogenase)	$\text{HNO}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} + 2\text{O}_2$	85	12			Mass balance
	Subtotal		85	12			
<i>Reactions Causing CO₂ Release</i>							
(5)	Change in terrestrial and riverine denitrification ^d	$4\text{NO}_3^- + 5\text{CH}_2\text{O} + 4\text{H}^+ \rightarrow 2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O}$	38 to 144			3.4 to 12.9	G04
(6)	Ammonification of urea in anthropogenic waste	$\text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$	21			0.7	G04
(7)	Change in biological fixation of atmospheric N ₂ by terrestrial plants ^e	$3\text{CH}_2\text{O} + 3\text{H}_2\text{O} + 2\text{N}_2 + 4\text{H}^+ \rightarrow 3\text{CO}_2 + 4\text{NH}_4$	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	

^aAnthropogenic 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.

^bThe low O₂ 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).

^cThe 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].

^dThe lowest CO₂ source estimate is derived from G04 denitrification anthropogenic fluxes. The highest CO₂ 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 CO₂ flux is correlated with the pertaining higher O₂ sink in footnote b.

^eAssumes that 100% of electrons required by biological fixation are supplied by organic molecules (CH₂O) 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 anthropogenic 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-Bosch 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 $0.7 \text{ TmolO}_2 \text{ yr}^{-1}$ (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 $31.6 \text{ Tmol O}_2 \text{ yr}^{-1}$ (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 $16.4 \text{ Tmol O}_2 \text{ yr}^{-1}$.

[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 ($\text{NO}_x = \text{NO} + \text{NO}_2$) 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 $3.5 \text{ TmolO}_2 \text{ yr}^{-1}$. Additionally, 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 anthropogenic 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 $4 \text{ Tmol O}_2 \text{ yr}^{-1}$ (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 $36.3 \text{ TmolO}_2 \text{ yr}^{-1}$ (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.

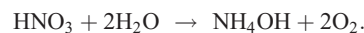
3.3. Oxygen Sources From Plant Nitrogen Use

[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



[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 $\text{NADPH}^+ + \text{H}^+$ 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 ($\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^- + 1/2 \text{O}_2$). 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



[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 $12 \text{ Tmol O}_2 \text{ yr}^{-1}$. 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 $0.74 \pm 0.78 \text{ PgC yr}^{-1}$ and an oceanic sink of $2.01 \pm 0.66 \text{ PgC yr}^{-1}$ (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 nitrification 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 O₂/N₂ and CO₂ Measurements, Without and With the Anthropogenic Nitrogen Corrections as Given in Table 1^a

All Data in Pg C yr ⁻¹	<i>Manning and Keeling [2006]</i>	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

^aCorrection 1 uses the low O₂ sink estimate of 21.2 Tmol O₂ yr⁻¹; correction 2 uses this O₂ sink estimate and the O₂ source of 12 Tmol O₂ yr⁻¹; correction 3a uses the low O₂ sink estimate of 21.2 Tmol O₂ yr⁻¹, the O₂ source of 12 Tmol O₂ yr⁻¹, and the low CO₂ source estimate of 5.7 Tmol CO₂ yr⁻¹; and correction 3b uses the high O₂ sink estimate of 36.3 Tmol O₂ yr⁻¹, the O₂ source of 12 Tmol O₂ yr⁻¹, and the high CO₂ source estimate of 15.2 Tmol CO₂ yr⁻¹. Uncertainties have been estimated by propagation of errors, assuming 100% uncertainty on both the nitrogen-related O₂ fluxes and the nitrogen-related CO₂ 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 CO₂ increase of 3.73 ± 0.1 Pg C yr⁻¹.

^bUnits are moles of O₂ produced per mole of CO₂ 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 O₂ associated with reactive nitrogen reactions in Table 1 are accompanied by any fluxes of CO₂. If this is the case, the O₂:CO₂ ratio of the fluxes must then be examined. For photosynthesis, a global average ratio of 1.10 moles of O₂ produced per mole of CO₂ consumed is typically used in global carbon budgeting calculations from atmospheric O₂ 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 CO₂ caused by nitrogen transformations and associated with the sink of O₂

caused by nitrification, they also must be taken into account in correcting for carbon sinks. The existence of CO₂ sources and O₂ sinks caused by nitrogen fluxes will also change the O₂:CO₂ molar ratio of global land biotic fluxes from the expected value of 1.1. Therefore we searched the scientific literature to investigate the fate of oxidized nitrogen produced by human activities, looking for reactions susceptible to cause CO₂ fluxes to the atmosphere.

5.1. Denitrification and CO₂ Emissions

[22] Denitrification emits CO₂ 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 NO₃⁻ and NO₂⁻ 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 O₂/N₂ and CO₂ 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 O₂/N₂ ratio and CO₂ 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 O₂/N₂ ratio and CO₂ 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 O₂ consumed per mole of CO₂ produced). From the fossil fuel endpoint, the short vertical vector indicates oceanic O₂ 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 O₂ produced per mole of CO₂ 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 N₂, induce negligible changes in the large atmospheric N₂ reservoir, and therefore do not impact the O₂/N₂ 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 $3.4 \text{ TmolC yr}^{-1}$. 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 excretions 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 $12.9 \text{ TmolC yr}^{-1}$ (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-

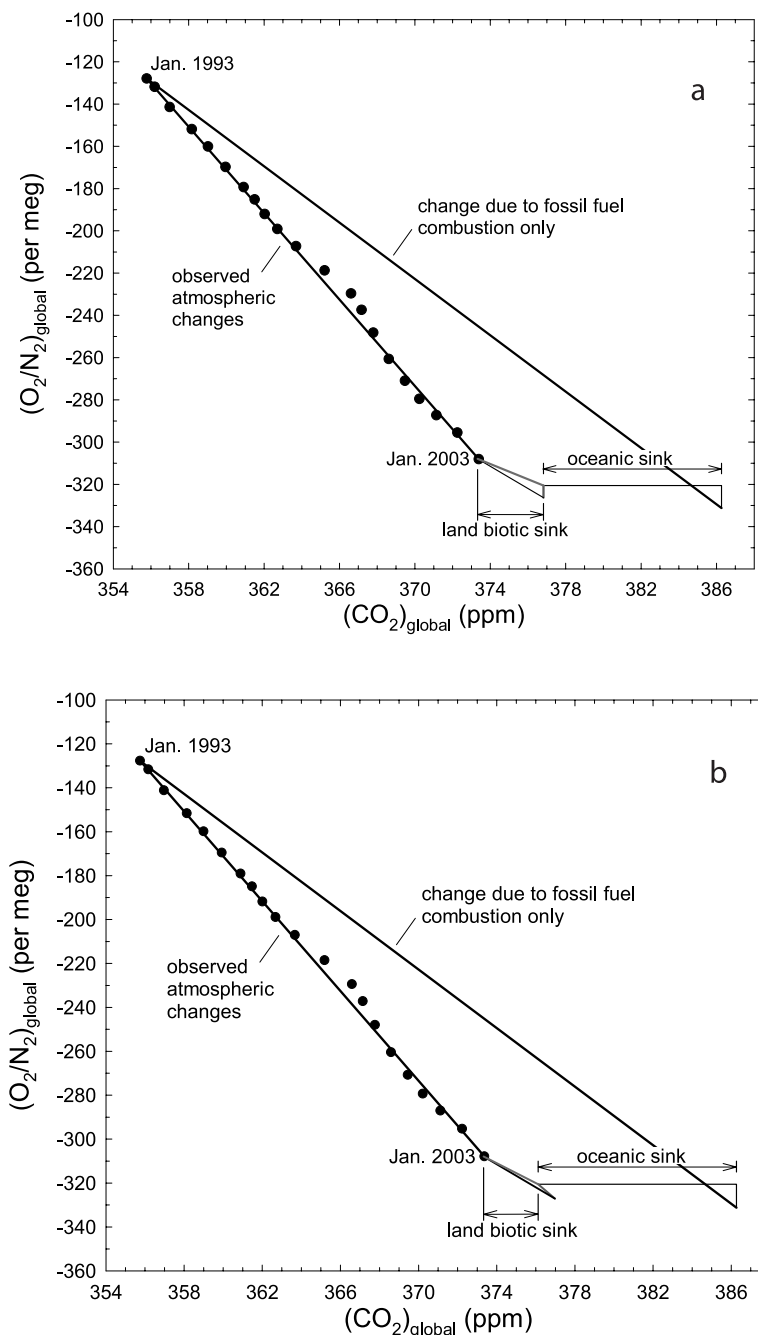


Figure 2

nification of urea (see Figure 1) causes a source of CO_2 of $0.7 \text{ TmolC yr}^{-1}$. Note that the $\text{NH}_4\text{-N}$ 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 $1.6 \text{ TmolC yr}^{-1}$.

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 $0.1 \text{ Tmol O}_2 \text{ yr}^{-1}$, 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 $265\text{--}294 \text{ TgN yr}^{-1}$ and N sources (mainly water column and benthic denitrification) estimated to be $275\text{--}482 \text{ TgN yr}^{-1}$ (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 $15.2 \text{ TmolC yr}^{-1}$ (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 $\text{O}_2\text{:CO}_2$ 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 ($\text{O}_2\text{:CO}_2$ 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, denitrification 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 ($\text{O}_2\text{:CO}_2$ 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 $\text{O}_2\text{:CO}_2$ 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 channelling of rivers (Mississippi, 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 Mississippi 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 O₂ and a smaller source of atmospheric CO₂. 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 O₂:CO₂ 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 O₂:CO₂ 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 O₂ 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 O₂ and CO₂ 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 O₂ uptake from, for example, fossil fuel burning, plant reduction of nitrate from cell water, and CO₂ 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.

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