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Is carbon within the global terrestrial biosphere becoming more oxidized? Implications for trends in atmospheric O₂

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Abstract

Measurements of atmospheric O₂ and CO₂ concentrations serve as a widely used means to partition global land and ocean carbon sinks. Interpretation of these measurements has assumed that the terrestrial biosphere contributes to changing O₂ levels by either expanding or contracting in size, and thus serving as either a carbon sink or source (and conversely as either an oxygen source or sink). Here, we show how changes in atmospheric O₂ can also occur if carbon within the terrestrial biosphere becomes more reduced or more oxidized, even with a constant carbon pool. At a global scale, we hypothesize that increasing levels of disturbance within many biomes has favored plant functional types with lower oxidative ratios and that this has caused carbon within the terrestrial biosphere to become increasingly more oxidized over a period of decades. Accounting for this mechanism in the global atmospheric O₂ budget may require a small increase in the size of the land carbon sink. In a scenario based on the Carnegie–Ames–Stanford Approach model, a cumulative decrease in the oxidative ratio of net primary production (NPP) (moles of O₂ produced per mole of CO₂ fixed in NPP) by 0.01 over a period of 100 years would create an O₂ disequilibrium of 0.0017 and require an increased land carbon sink of 0.1 Pg C yr⁻¹ to balance global atmospheric O₂ and CO₂ budgets. At present, however, it is challenging to directly measure the oxidative ratio of terrestrial ecosystem exchange and even more difficult to detect a disequilibrium caused by a changing oxidative ratio of NPP. Information on plant and soil chemical composition complement gas exchange approaches for measuring the oxidative ratio, particularly for understanding how this quantity may respond to various global change processes over annual to decadal timescales.

Keywords: chemical and elemental composition of organic matter, ecosystem respiration, global carbon cycle, plant allocation

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Introduction

Observed changes in atmospheric O₂ and CO₂ levels during the 1990s have been used to infer a net land carbon sink (Keeling & Shertz, 1992; Bender *et al.*, 1994; Keeling *et al.*, 1996; Battle *et al.*, 2000; Prentice *et al.*,

2001). The basis for this conclusion is that atmospheric O₂ levels decreased more slowly than expected from the oxidation of fossil fuels consumed during the decade, and that a net land carbon sink creates O₂ (and could thus account for the difference between the observations and the fossil fuels) (Keeling, 1988; Keeling *et al.*, 1996). Ocean exchange, while being an equally valid sink mechanism from the perspective of explaining the growth rate of CO₂, cannot solely account for the slow

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Table 1 List of abbreviations used in the paper

Symbol	Description
F_{ab}	Atmosphere to biosphere flux; here assumed to be equal to net primary production. For the Carnegie–Ames–Stanford Approach model used here, $F_{ab} = -55.4 \text{ Pg C yr}^{-1}$
F_{ba}	Biosphere to atmosphere return flux; here assumed to be equal to heterotrophic respiration, fire emissions, and other losses
F_{ff}	Fossil fuel emissions; for the 1990s we assumed fossil emissions were 6.3 Pg C yr^{-1}
F_{net}	The net land carbon flux: $F_{net} = F_{ab} + F_{ba}$. This quantity is solved for from Eqns (4) and (5). Note that a sink has a negative sign
F_{oc}	The net ocean carbon flux. This quantity is solved for from Eqns (4) and (5). Note that a sink has a negative sign
O_{outgas}	The net flux of O_2 from the ocean surface; we used a value of $0.4 \text{ ppm } O_2 \text{ yr}^{-1}$ from Plattner <i>et al.</i> (2002) in Fig. 1
R	The oxidative ratio of organic matter. Defined as the moles of O_2 consumed and the moles of CO_2 released from the complete oxidation of the carbon within an organic compound under fully aerobic conditions. It is also equivalent to the O_2 released and CO_2 consumed during the construction of the organic compound
R_{ab}	Oxidative ratio associated with the atmosphere to biosphere flux (F_{ab}); assumed to be 1.050 in Fig. 1 based on data in Table 2
R_{ba}	Oxidative ratio associated with the biosphere to atmosphere flux (F_{ba}); assumed to be 1.050 in Fig. 1a and 1.05175 in Fig. 1b
R_{ff}	Oxidative ratio associated with the fossil fuel emission (F_{ff}). In Fig. 1 this was assumed to be 1.38
R_{net}	Oxidative ratio associated with the net land carbon sink (F_{net})

O_2 decrease because air–sea gas exchange of CO_2 is thought to be mostly decoupled from oxygen production or consumption on decadal timescales (Keeling, 1988). The use of O_2 and CO_2 to partition carbon sinks, however, does require correcting for changes in past climate and their effects on ocean circulation, O_2 and N_2 solubility, and ocean biogeochemical cycles (Bopp *et al.*, 2002; Keeling & Garcia, 2002; Plattner *et al.*, 2002). Recent estimates of O_2 degassing from ocean warming have lowered the size of the land carbon sink inferred for the 1990s by approximately $0.5\text{--}0.7 \text{ Pg C yr}^{-1}$ (from the original 1.4 Pg C yr^{-1} estimate reported in the 2001 IPCC budget), but have not altered the fundamental conclusion that the terrestrial biosphere is a net sink for carbon (Bopp *et al.*, 2002; Plattner *et al.*, 2002).

Here, we explore how changes in the stoichiometry of terrestrial biomass may also contribute to trends in atmospheric O_2 . Atmospheric exchange of O_2 with terrestrial ecosystems is commonly expressed in terms of a net carbon flux from the atmosphere to the ecosystem (F_{net}) and the oxidative ratio (R_{net} ; a molar O_2 to CO_2 ratio; (Keeling, 1988)) that corresponds to this flux:

$$\frac{dO_2}{dt} = -R_{net}F_{net}. \quad (1)$$

For these fluxes, the sign convention is positive into the atmosphere and negative into the terrestrial biosphere (Table 1). This representation can be expanded as a difference between the two one-way components:

$$\frac{dO_2}{dt} = -(R_{ab}F_{ab} + R_{ba}F_{ba}) \quad (2)$$

where F_{ab} is the atmosphere-to-biosphere carbon flux (here assumed to be equal to net primary production (NPP)), R_{ab} is the oxidative ratio related to NPP (moles of O_2 released per mole of CO_2 fixed in NPP), F_{ba} is the biosphere-to-atmosphere return flux (here assumed to be equal to a combination of heterotrophic respiration, fires, and other losses), and R_{ba} is the oxidative ratio related to the return flux (moles of O_2 consumed per mole of CO_2 released). When an ecosystem is at steady state, F_{ab} and F_{ba} have the same magnitude. The carbon in F_{ba} , however, is always offset in time from newly assimilated carbon in F_{ab} because of time delays controlled by plant tissue lifetimes, rates of litter and soil organic matter (SOM) decomposition, and the disturbance regime. Newly assimilated carbon often flows into starch reservoirs (comprised of glucose polymers) within chloroplasts. Export of this carbon from mesophyll cells within a leaf often occurs via sucrose (Schober *et al.*, 2000). The production glucose, starch, and sucrose is associated with an R value of 1.0. The R_{ab} associated with NPP can be substantially higher than 1.0, however, because of the synthesis of longer-lived plant biochemicals that are more reduced (i.e. have a lower oxygen content like lignin and lipids) (Penning de Vries *et al.*, 1974; Poorter & Villar, 1997).

By replacing the sum of F_{ab} and F_{ba} with the net terrestrial flux (F_{net}), Eqn (2) can be rewritten in terms of net and disequilibrium components, analogous to equations developed to describe carbon isotope exchange (e.g. Tans *et al.*, 1993):

$$\frac{dO_2}{dt} = -(R_{ab}F_{net} + (R_{ba} - R_{ab})F_{ba}). \quad (3)$$

Combining terrestrial ecosystem exchange (Eqn (3)) with ocean and fossil fuel components, the changes in global atmospheric CO₂ and O₂ are then described by the following equations:

$$\frac{d\text{CO}_2}{dt} = F_{\text{ff}} + F_{\text{net}} + F_{\text{oc}}, \quad (4)$$

and

$$\begin{aligned} \frac{d\text{O}_2}{dt} = & -R_{\text{ff}}F_{\text{ff}} - (R_{\text{ab}}F_{\text{net}} + (R_{\text{ba}} - R_{\text{ab}})F_{\text{ba}}) \\ & + O_{\text{outgas}}. \end{aligned} \quad (5)$$

where F_{ff} represents fossil fuel carbon emissions (label 1 in Fig. 1a), F_{oc} represents the net ocean carbon flux (label 2 in Fig. 1a), R_{ff} represents the oxidative ratio related to F_{ff} , and O_{outgas} represents the O₂ flux from the ocean surface as a result of changes in the ocean's heat budget (label 4 in Fig. 1a). F_{oc} is assumed not to influence ocean-atmospheric O₂ exchange and so is absent from Eqn (5) and is represented by a horizontal line (label 2) in Fig. 1a (Keeling *et al.*, 1996).

In Eqn (5), if R_{ba} is equal to R_{ab} as commonly assumed, then the disequilibrium forcing term, $(R_{\text{ba}} - R_{\text{ab}})F_{\text{ba}}$, disappears. With this assumption, the terrestrial biosphere can be represented graphically by a net flux vector (label 3 in Fig. 1a) and R_{net} is the same as R_{ab} . However, if R_{ba} and R_{ab} are different, this may have an impact on atmospheric O₂ because this difference is multiplied by the gross flux, F_{ba} . For example, assuming that R_{ab} is 1.05 and F_{ba} is 60 Pg C yr⁻¹ (Cramer *et al.*, 1999), then an decrease in atmospheric O₂ equivalent to that caused by 1 Pg C yr⁻¹ net land source could be generated by a difference of 0.0175 between R_{ba} and R_{ab} (with R_{ba} greater than R_{ab} ; Fig. 1b). When the disequilibrium forcing term is included, very small differences between R_{ba} and R_{ab} have the potential to cause relatively large changes in atmospheric O₂, with consequences for the inferred land/ocean carbon sink partitioning.

Although an offset between R_{ba} and R_{ab} of 0.0175 would be challenging to directly measure in atmosphere and ecosystems studies that sample O₂ (Manning *et al.*, 1999; Luecker, Keeling & Dubey, 2001; Seibt *et al.*, 2004), this would, nevertheless, represent a major perturbation to both the global atmospheric oxygen cycle and to the oxidation state of carbon within the terrestrial biosphere. Disequilibria of a smaller magnitude may develop, however, by small year-to-year trends in R_{ab} whose effects are allowed to accumulate because of time delays between fixation and the return flux. This is analogous to the observation that small year-to-year increases in NPP (less than 0.1% yr⁻¹), when sustained over a number of years, can lead to a carbon sink (Thompson *et al.*, 1996) or that small year-to-year decreases in atmospheric δ¹³C (less than

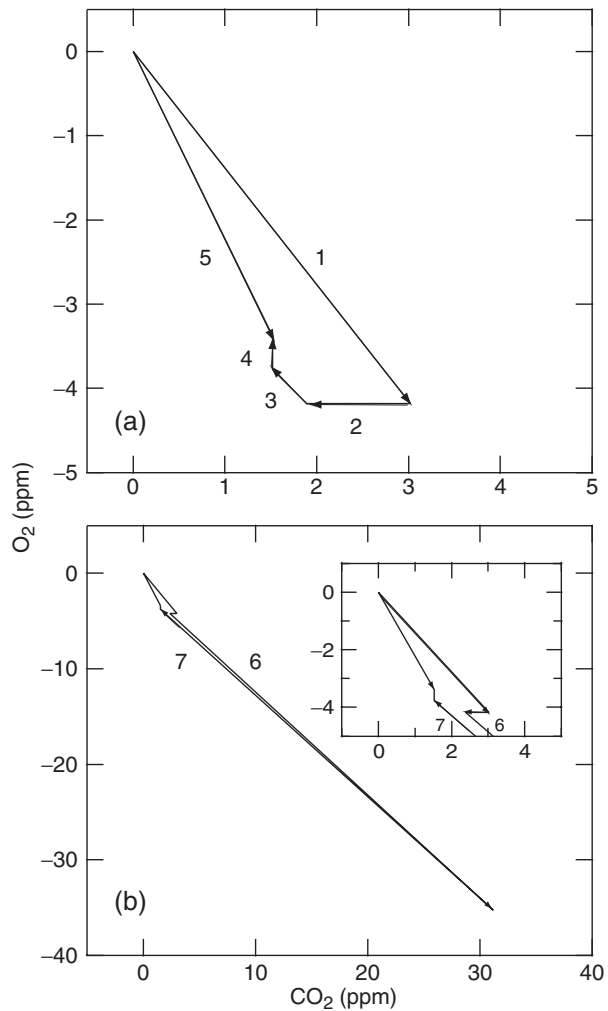


Fig. 1 (a) A vector diagram of the global oxygen cycle, with contributions from fossil fuels (1), ocean exchange (2), a net land carbon sink (3), ocean outgassing (4), and observations (5) during the 1990s (Keeling *et al.*, 1996, Prentice *et al.*, 2001). In this diagram, the observed atmospheric trend was 1.52 ppm yr⁻¹ for CO₂ and -4.18 ppm yr⁻¹ for O₂ (Prentice *et al.*, 2001), the O₂ outgassing rate was 0.4 ppm yr⁻¹ (Plattner *et al.*, 2002), the oxidative ratio of fossil fuels was 1.38, and the oxidative ratio of the net land carbon sink was 1.05. This leads to a sink partitioning of -0.8 Pg C yr⁻¹ for land and -2.3 Pg C yr⁻¹ for the oceans. (b) Same as (a), but with an oxidative disequilibrium between the biosphere to atmosphere return flux (6) and NPP (7). Note the change in scale. In (b), R_{ba} was greater than R_{ab} by 0.0175. This increased the land carbon sink by 1 Pg C yr⁻¹, and decreased the ocean sink by the same amount (to -1.8 Pg C yr⁻¹ for land and -1.3 Pg C yr⁻¹ for the oceans). The inset shows the other components of the budget in more detail.

0.025‰ yr⁻¹) can lead to an isotopic disequilibrium between the atmosphere and the terrestrial biosphere of 0.3‰ or between the atmosphere and the oceans of 0.6‰ (Tans *et al.*, 1993; Fung *et al.*, 1997; Gruber & Keeling, 2000).

Here, we investigate the hypothesis that changing plant cover over the global land surface is causing a decrease in the oxidative ratio of NPP. From a mass balance perspective, this is the same as the carbon within the terrestrial biosphere becoming more oxidized over time, and removing O_2 from the atmosphere as a consequence. We first show how a gradual decrease in the oxidative ratio of NPP (R_{ab}) can generate an O_2 sink that is proportional to the size of the time delay between NPP and heterotrophic respiration. We also show how these same time delays can lead to a divergence between the oxidative ratio measured in an ecosystem study (for e.g. R_{ba} measured with a Keeling plot approach) and the appropriate value to assign to the net carbon sink (R_{net}). We then discuss the most likely ways that human activities are increasing the oxygen content of the global terrestrial biosphere. In our analysis, we focus on NPP as the input flux because we are interested in the part of gross terrestrial ecosystem exchange that ultimately affects the net carbon balance of ecosystems on annual and decadal time scales. Over diurnal to seasonal timescales, other processes, including varying levels of nitrate uptake and reduction by plants, nitrification and denitrification within the soil, and soil diffusion may contribute to observed variability in measured oxidative ratios at the ecosystem scale (Seibt *et al.*, 2004).

Methods

Impact of a terrestrial biosphere O_2 disequilibrium on flux partitioning

We used several simple reservoir models and the Carnegie–Ames–Stanford Approach (CASA) biogeochemical model (Potter *et al.*, 1993; Field *et al.*, 1995) to estimate how trends in R_{ab} would affect our understanding of the carbon cycle. With these carbon models the size of the disequilibrium depends directly on the mean residence time (and the age distribution) of the carbon within the terrestrial biosphere and the rate of change of R_{ab} (e.g. Randerson *et al.*, 1999). For a given trend in R_{ab} , longer carbon residence times cause a larger offset between R_{ab} and R_{ba} .

With a one-pool box model, we assumed that global NPP was 60 Pg C yr^{-1} and that the turnover time of carbon within the terrestrial biosphere was 20 years. With the CASA model, global NPP was $55.4 \text{ Pg C yr}^{-1}$ and was estimated in each $1^\circ \times 1^\circ$ grid cell using a light use efficiency model and satellite NDVI (Field *et al.*, 1995, 1998). The age distribution of the return flux from CASA (Fig. 2) was controlled by the global distribution of NPP across the land surface, the contemporary spatial distribution of biomes (including agriculture),

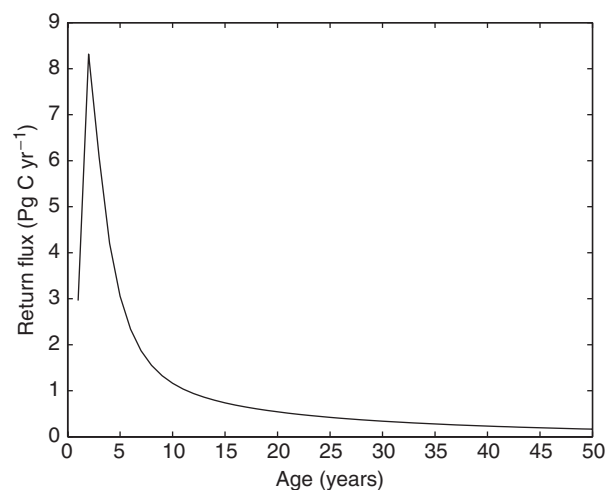


Fig. 2 Age distribution of the return flux from the biosphere to the atmosphere as estimated from the Carnegie–Ames–Stanford Approach model and starting with an annual cohort of carbon fixed during net primary production (NPP). This age distribution was created by tracking the annual cohort as it cycled through different plant and soil carbon pools within the model. Approximately 2.9 Pg C of the initial 55.4 Pg C cohort was emitted back to the atmosphere in the same year as the initial fixation. The greatest carbon loss occurred in the following year, with 8.3 Pg C emitted primarily as a result of fine root and leaf litter decomposition. Over 89% of the initial NPP cohort had returned to the atmosphere after a period of 50 years.

fixed plant tissue lifetimes, separate and fixed plant allocation schemes for woody and herbaceous vegetation, and variable rates of decomposition for metabolic and structural litter and microbial, slow, and passive soil carbon pools. Decomposition rates depended on substrate quality (the lignin to nitrogen ratio of incoming plant material), temperature, and soil moisture (Parton *et al.*, 1993; Schimel *et al.*, 1994).

Using both the one-pool box model and CASA, we assessed the size of the O_2 sink (and equivalent size of the apparent CO_2 source) that would occur as a result of linearly decreasing R_{ab} over a period of 100 years by 0.01 (an annual rate of -0.0001 per year). We chose the 100-year timescale because humans have substantially modified global vegetation cover over the past century (Houghton, 1994; Ramankutty & Foley, 1999; Achard *et al.*, 2002). We chose the cumulative change in R_{ab} of 0.01 units because this change is less than half of the mean difference between the oxidative ratios of herbaceous and woody plants from a survey by Poorter & Villar (1997) (Table 2), and thus, represents a scenario that is ecologically plausible. We chose a decrease in R_{ab} because humans are favoring plants (such as herbaceous crops) that have lower oxidative ratios (see the ‘Disturbance hypothesis’).

Table 2 Chemical composition and related oxidative ratios (*R*) of herbaceous and woody plant parts

	Lipid (mg g ⁻¹)*	Lignin (mg g ⁻¹)	Protein (mg g ⁻¹)	Soluble phenolics (mg g ⁻¹)	Carbohydrates (mg g ⁻¹)	Organic acids (mg g ⁻¹)	Minerals (mg g ⁻¹)	<i>R</i> (mol O ₂ mol ⁻¹ CO ₂)
Herbaceous leaf	45	44	222	44	429	83	101	1.031
Herbaceous stem	25	67	120	18	592	60	101	1.018
Herbaceous root	19	43	119	5	574	27	94	1.025
Woody leaf	56	113	131	88	320	51	56	1.054
Woody stem	38	231	55	93	732	30	9	1.041
Woody root	21	277	100	76	641	17	35	1.051
<i>R</i> for each chemical class [†]	1.37	1.14	1.13	1.05	1.00	0.68	–	

Chemical composition was taken from Poorter & Villar (1997).

*Number of observations for each class of chemical compound and the percentile distribution around the mean are given in Table 1 of Poorter & Villar (1997). Note that the chemical composition of the different plant organs does not sum to 100%. This is because some of the studies used in the Poorter & Villar (1997) analysis only reported a subset of chemical compounds. To compute *R* for each plant organ, the *R* values for each chemical class were weighted by their mass abundance. We did not use the mineral fraction in this calculation.

[†]To construct *R* we assumed that lipids had a composition of 13.5% palmitic acid (C₁₆H₃₂O₂), 3.0% stearic acid (C₁₈H₃₆O₂), 37.0% oleic acid (C₁₈H₃₂O₂), and 46.4% linoleic acid (C₁₈H₂₈O₂) based on the composition of corn oil from Bressani (1990), yielding an *R* value of 1.37. This was similar to the mean composition of corn oil used by Penning de Vries *et al.* (1974) (C₉₄H₁₆₅O₁₀) that yields an *R* value of 1.39. We assumed that lignin had an elemental mass ratio of 63.9% C, 6.2% H, and 25.8% O based on the composition of Kraft lignin from eucalyptus (Caballero *et al.*, 1997), yielding an *R* value of 1.14. Note that this value is more oxidized than coniferyl alcohol (C₁₀H₁₂O₃) that is thought to be a key constituent of lignin (with an *R* value of 1.15), but is more consistent with the chemical procedure often used to obtain the lignin fraction. For protein we used the data from Penning de Vries *et al.* (1974) for zein protein from corn (and assumed that the building block for N was atmospheric N₂) to obtain an *R* value of 1.13. Note that the elemental composition of Rubisco (including the large and small subunits) is C_{1.0}H_{1.93}O_{0.48}N_{0.27}S_{0.008} (J. Evans, personal communications, 2005). This yields an *R* value of 1.251, assuming atmospheric N₂ as the N source and sulfate as the S source. For carbohydrates, we assumed both structural (cellulose) and nonstructural carbohydrates (starch) had a chemical formula of C₆H₁₀O₅ and an *R* value of 1.0. Organic acids were assumed to have a mean composition of 30% citric acid (C₆H₈O₇), 30% aconitic acid (C₆H₆O₃), 20% oxaloacetic acid (C₆H₄O₅), 10% malic acid (C₄H₆O₅), and 5% oxalic acid (C₂H₂O₄) following from Penning de Vries *et al.* (1974), yielding an *R* value of 0.68. Soluble phenolics include simple phenols, phenylpropenes, lignans, coumarins, chromones, flavonoids, tannins, quinines, and alkanoids (Waterman & Mole, 1994). Although phenol is highly reduced (*R* = 1.16), most of the building blocks for these classes of phenols have more OH groups and are considerably more oxidized (Waterman & Mole, 1994). We assigned this class the chemical composition of ferulic acid (C₁₀H₁₀O₄) with an *R* value of 1.05 because this is an example of one of the more ubiquitous classes of phenolic substances (Waterman & Mole, 1994). Minerals were assumed to consist largely of silicon and potassium (Latshaw, 1924; Penning de Vries *et al.*, 1974) and were not used to calculate the mass-weighted *R* values.

Within each model run, *R*_{ab} decreased as a linear function of time, *t*, according to the equation

$$R_{ab}(t) = R_{ab}(0) + t \times L, \quad (6)$$

where at the initial steady-state *R*_{ab}(0) was set equal to 1.05 based on observations summarized in Table 2. *L* has units of the oxidative ratio per unit time and was set at -0.0001 per year in both the one-pool box model and CASA model runs. *R*_{ba} was computed at each time step in the one-pool and CASA model runs by convolving the distribution of carbon flux ages from the model (e.g. Fig. 2) with the prior history of *R*_{ab} through that time step and assuming constant levels of NPP. This approach has been employed in the past with terrestrial ecosystem models to efficiently calculate the δ¹³C disequilibrium and ocean carbon and isotope fluxes (Joos *et al.*, 1996; Randerson *et al.*, 1999).

Using values of *R*_{ba} obtained from the simulations described above, we then assessed the size of the atmospheric O₂ sink (and apparent CO₂ source) caused by the linear decrease in *R*_{ab} using Eqns (4) and (5).

Differences between the oxidative ratio of the sink and the return flux

To demonstrate how *R*_{ba} may diverge under some conditions from the oxidative ratio appropriate for representing a net carbon sink within an ecosystem (*R*_{net}), we made a second simple reservoir model. In this model, 2/3 of NPP within an ecosystem was allocated to a pool with a turnover time of 2 years (representing NPP allocated to leaves and fine roots) and 1/3 of NPP was allocated to a pool with a turnover time of 30 years (representing NPP allocated to wood) (Fig. 3). The 2-year pool was assigned an *R* of 1.06, while

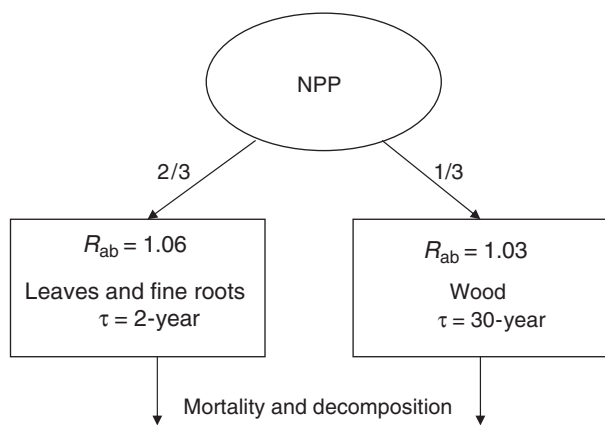


Fig. 3 A simple model of forest net primary production and allocation with two pools that have very different rates of turnover. This model is used to illustrate how the oxidative ratio of the net carbon sink (R_{net}) within an ecosystem may diverge under some conditions from the oxidative ratio of the return flux (R_{ba}).

the 30-year pool was assigned an R of 1.03. Heterotrophic respiration arising from these pools is assumed to occur with the same oxidative ratio. Note that this range in R is wider than the mean leaf and mean stem difference for woody plants in Table 2, but is well within the variation of the observations (Poorter & Villar, 1997). A carbon sink was generated in this simple model by increasing NPP in proportion to atmospheric CO_2 over the last 2 centuries according to the equation

$$F_{\text{ab}}(t) = F_{\text{ab}}(0) \left[1 + \beta \ln \frac{\text{CO}_2(t)}{\text{CO}_2(0)} \right], \quad (7)$$

where β was set equal to 0.3, corresponding to a 20% increase in NPP for a doubling of atmospheric CO_2 levels. The model was assumed to be in steady state in 1765 with CO_2 levels at 277 ppm and with NPP at $100 \text{ g C m}^{-2} \text{ yr}^{-1}$.

Results

Impact of a terrestrial biosphere O_2 disequilibrium on flux partitioning

With the one-pool box model described in the Methods section 'impact of a terrestrial biosphere O_2 disequilibrium on flux partitioning', a sustained linear decrease in R_{ab} by 0.0001 per year caused a disequilibrium ($R_{\text{ba}} - R_{\text{ab}}$) of 0.0019 after 100 years. This disequilibrium was equivalent to a $0.113 \text{ Pg C yr}^{-1}$ terrestrial carbon source in terms of impacts on global atmospheric O_2 levels (obtained via Eqns (4) and (5)). With the CASA model, the linear decrease in R_{ab} caused a disequilibrium ($R_{\text{ba}} - R_{\text{ab}}$) of 0.0017 after 100 years (Fig. 4a). This latter disequilibrium was equivalent to a $0.095 \text{ Pg C yr}^{-1}$

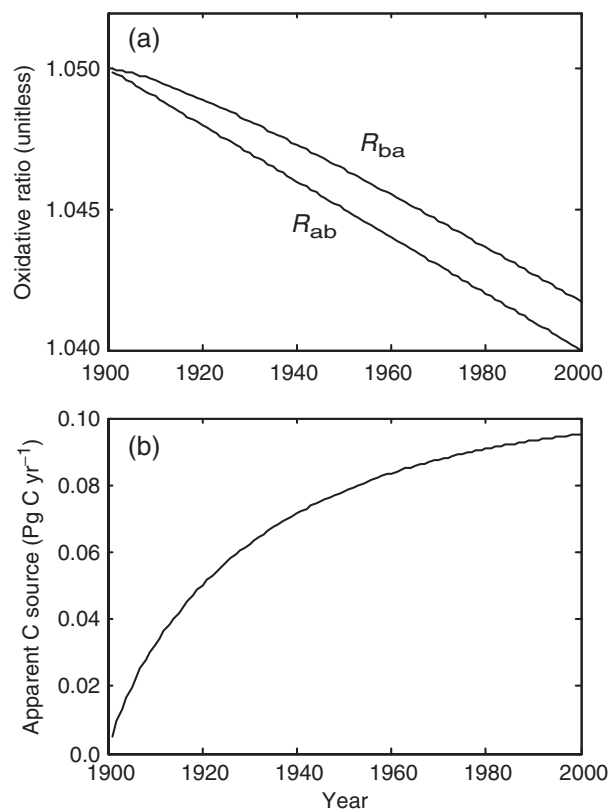


Fig. 4 (a) A small sustained decrease in the oxidative ratio of net primary production (NPP) (R_{ab}) can generate an oxidative ratio disequilibrium because of a delayed response of the oxidative ratio of the return flux (R_{ba}). After a period of several decades, the disequilibrium (i.e. the difference between R_{ba} and R_{ab}) starts to reach steady state. The size of the disequilibrium at steady state depends both on the turnover time of carbon within the terrestrial biosphere and the rate of change of R_{ab} . (b) An oxidative ratio disequilibrium caused by a decrease in R_{ab} has the same impact on atmospheric O_2 as a net land carbon source. After a period of 100 years, the size of the apparent carbon source would be approximately 0.1 Pg C yr^{-1} , assuming a linear decrease in R_{ab} of 0.0001 per year and using the resulting disequilibrium in Eqn (4) and (5). The apparent carbon source from the disequilibrium has the effect of requiring a larger terrestrial carbon sink in the equations required to balance the global atmospheric budgets of CO_2 and O_2 .

terrestrial carbon source in terms of impacts on global atmospheric O_2 levels (Fig. 4b).

Differences between the oxidative ratio of the sink and the return flux

The sensitivity of R_{ba} to time delays also has implications for ecosystem studies that are designed to quantify the oxidative ratio appropriate to assign to the net carbon source or sink. Specifically, the oxidative ratio associated with an annual carbon sink within an eco-

system (R_{net}) may be substantially offset from that associated with the return flux (R_{ba}) because these two fluxes originate from different carbon pools within the ecosystem. For example, using the model described in Fig. 3, the appropriate value to assign to R_{net} for the carbon sink within the ecosystem (caused by the increases in NPP) was 1.035 in the year 2000, while R_{ba} (as might be measured using a Keeling Plot approach during the night within a plant canopy) was 1.050, reflecting a much greater contribution from the rapid turnover of the leaf and fine root pool (Fig. 5). In this example, 84.7% of the carbon accumulation that accounted for the annual carbon sink resided in the slow pool, while only 15.3% resided in the fast pool. With this simple model, changing the turnover time of the fast pool from 2 years to 1 year caused even more of the net carbon sink to reside in the slow pool (92.2%) and caused R_{net} to decrease to 1.032. This change had a negligible effect on R_{ba} because R_{ba} was controlled primarily by the fractions of NPP allocated to the two pools, and this allocation pattern did not change between the simulations.

Discussion

The disturbance hypothesis

We hypothesize that increasing levels of disturbance across multiple biomes in recent decades has caused R_{ab} to decrease. In the tropics, this includes wide-scale replacement of woody vegetation with pastures and crops (Houghton, 1994; Ramankutty & Foley, 1999; Achard *et al.*, 2002). In the boreal biome, this includes an increase in fire activity and tree mortality that is decreasing the mean stand age of forests (Kurz & Apps, 1999; Kasischke & Stocks, 2000) and increasing the abundance of deciduous tree species and herbaceous plants (Chapin *et al.*, 2000a). Globally, this includes an increase in the success of invasive species (Dukes & Mooney, 1999; Chapin *et al.*, 2000b) and increased disturbance of agricultural soils by plowing and grazing during the the 20th century (Ramankutty & Foley, 1999). These activities often increase the oxidation state of carbon in plant and SOM via mechanisms described below. This increases the oxygen content of the remaining biomass, causing a small sink of atmospheric O_2 that has not been typically accounted for in atmospheric budgets. At a regional scale, fire suppression or agricultural abandonment (e.g. Goodale *et al.*, 2002; Hurtt *et al.*, 2002) could have the opposite effect even though at the global scale human activity is contributing to net deforestation.

Within a plant, lipids and lignin compounds have carbon that is more reduced. These compounds have

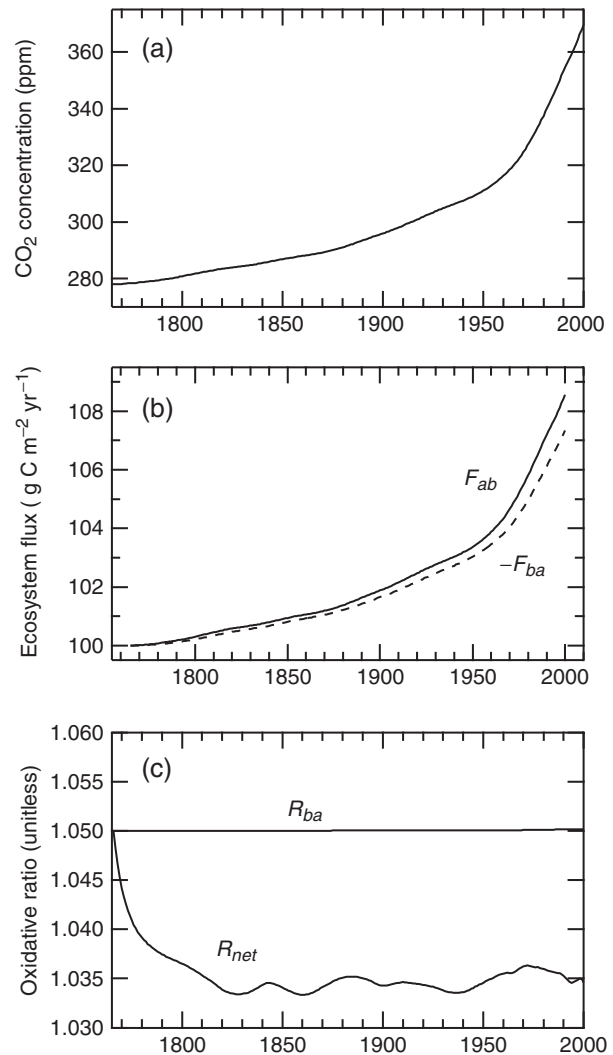


Fig. 5 (a) Smoothed atmospheric CO_2 concentrations from Keeling *et al.* (1989) and Etheridge *et al.* (1996) used as inputs to the simple ecosystem model described in Fig. 3. (b) Response of net primary production (NPP) to increasing levels of atmospheric CO_2 , assuming a β of 0.3 (—; F_{ab}). The magnitude of the return flux lags behind NPP because of the turnover times of terrestrial biosphere pools (---; F_{ba}). Note that the sign of F_{ba} is reversed from that described in the text in order to show both F_{ab} and F_{ba} on the same graph. This delay is responsible for the carbon sink (F_{net}) that is represented in (b) by the difference between the two lines. (c) The oxidative ratios associated with the carbon sink (R_{net}) and the return flux (R_{ba}) diverge early in the simulation because most of the carbon sink resides in the wood pool, whereas most of the respiration flux comes from the leaf and fine root pool.

larger R values (1.37 and 1.14, respectively) and are more costly to build as compared with other compounds such as cellulose and starch (that have oxidative ratios near or equal to 1.0) (Penning de Vries *et al.*, 1974; Poorter, 1994). On average, the leaves, stems, and roots

of woody vegetation have higher concentrations of lipids and lignin than herbaceous vegetation (Table 2). As a result, the expansion of agriculture and grazing during the 20th century probably caused a decrease in the oxidative ratio of the remaining plant biomass within these ecosystems.

In boreal regions, disturbance levels may also be increasing. In boreal forests of Canada, for example, mortality from insects and fires has increased in recent decades, causing a decrease in the stand age distribution and a small net carbon source (Kurz & Apps, 1999). Within the boreal biome, herbaceous plants and deciduous trees are frequently found in greater abundance in early stages of succession (Chapin *et al.*, 2000a) and tend to have less lignin as compared with evergreen conifers (White, 1987). As a result, a decrease in boreal stand age may cause a decrease in the oxidative ratio of NPP at a landscape scale. Based on elemental abundance and chemical composition data, deciduous hardwood species (oak and beech) have an oxidative ratio that is approximately 0.02 less than evergreen conifers (pine and spruce) (Browning, 1963; Gaur & Reed, 1995).

Within the soil, more recalcitrant components of SOM such as humic acids and humins tend to be more reduced than recent inputs from plants (Kang *et al.*, 2003; Killops & Killops, 2005). Enhanced degradation of these recalcitrant compounds from plowing and other forms of disturbance would cause a disequilibrium ($R_{ba} > R_{ab}$), as they were replaced in the soil by younger and more oxidized root inputs. This disequilibrium within soils would have a similar effect on atmospheric O_2 levels as the one caused by a shift in plant functional types described above.

Evidence for the disturbance hypothesis from plant construction cost data

Plant construction cost data is closely linked with the heat of combustion and the oxidation state of carbon within a plant tissue (McDermitt & Loomis, 1981; Williams *et al.*, 1987; Gary *et al.*, 1995). Construction costs, however, decrease with increasing mineral content of a plant tissue, whereas oxidative ratios are independent of mineral concentration – leading to a divergence between these two quantities under conditions of high mineral accumulation. Allowing for this limitation, construction cost data may serve as a useful proxy for oxidative ratios under some circumstances. In boreal forests, leaves from early successional species have lower construction costs and are consistent with the tissue chemistry and elemental composition data described above (P'Yankov *et al.*, 2001). Leaf construction costs from other biomes show similar trends. For example, recently disturbed Mediterranean ecosystems

have lower leaf-level construction costs than mature vegetation (Navas *et al.*, 2003). Other studies show that deciduous and semideciduous leaves have lower construction costs than co-occurring evergreen species (Eamus *et al.*, 1999; Villar & Merino, 2001). Invasive species may also reinforce a downward trend in R_{ab} . For example, lower construction costs associated with plant tissues of invasive species may contribute, in some instances, to their success in competing with slower growing native species (Baruch & Goldstein, 1999; Nagel & Griffin, 2001). More generally, plants that establish earlier in succession may use more oxidized carbon compounds (that are cheaper to build) to more rapidly achieve canopy dominance (and more effectively compete for light).

Implications

A decrease in R_{ab} from increasing levels of disturbance would increase the oxygen content of terrestrial biomass and represent a previously neglected sink of atmospheric O_2 . Accounting for this additional O_2 sink mechanism would require a small increase in the land carbon sink in equations used to describe the global atmospheric CO_2 and O_2 budgets. In the results section we showed how a downward trend in R_{ab} by 0.0001 per year is equivalent to carbon source of 0.1 Pg C yr^{-1} after a period of 100 years to illustrate, in a simple way, the links between a changing oxidative ratio of NPP and ensuing O_2 disequilibria. Although errors introduced in regional to global atmospheric O_2 budgets from this disequilibrium are likely to be small, they may be equal in magnitude or larger than errors introduced from using incorrect values of R_{net} . For example, changing from a R_{net} value of 1.1 to 1.0 in the global budget described in Fig. 1a causes the land carbon sink to increase from 0.76 to $0.83 \text{ Pg C yr}^{-1}$. The change in the inferred land carbon sink ($0.07 \text{ Pg C yr}^{-1}$) is the same magnitude as that induced by a trend in R_{ab} of 0.0001 per year over a period of several decades (e.g. Fig. 4). Past ecosystem studies have been partly motivated by an attempt to reduce uncertainties associated with R_{net} ; our analysis suggests that accounting for disequilibria may be equally important, although more challenging to directly measure.

A quantitative estimate of the size of the global oxidative ratio disequilibrium is outside the scope of this preliminary study. There is an abundance of C, H, and N elemental composition data available for leaves and stems (that are often used to assess construction costs), but fewer direct measurements of O (Keeling, 1988). More importantly, analysis of disturbance impacts on atmospheric O_2 requires an understanding of whole ecosystem elemental composition, including

wood, root, and SOM components. The elemental composition of wood of fast and slow growing tropical tree species is particularly relevant for such an estimate, given the large carbon stocks in tropical forests and their vulnerability to harvesting and land-use change. In general, information on whole ecosystem elemental composition is sparse, and has not been widely synthesized along axes of succession, disturbance regime, or responses to changing resource availability. One complicating factor is that a decrease in plant construction costs (from increased levels of disturbance) is likely to be accompanied by increased rates of tissue turnover (Williams *et al.*, 1989; Kikuzawa, 1991; Cordell *et al.*, 2001) and decomposition. More rapid turnover of these tissues would limit carbon accumulation in these pools, weakening the overall impact of a changing terrestrial biosphere oxidative ratio on atmospheric O₂ levels.

Any ecosystem level synthesis would also require careful assessment of the oxidation state of carbon in SOM and its response to these same drivers. A key uncertainty linked with SOM involves quantifying how the oxidative ratio shifts through the different stages of decomposition. As proteins, starch, and organic acids are degraded rapidly, more of the carbon storage in litter and SOM over years to decades may occur via lignin accumulation (Berg & Meentemeyer, 2002). Over centennial to millennial timescales, recycling of organic matter through microbial biomass may lead to the accumulation of humic acids and humins that have even higher oxidative ratios (Kang *et al.*, 2003; Killops & Killops, 2005).

The observations presented in Table 2 also suggest that the R_{net} appropriate to assign to the plant component of a net land sink on annual to decadal timescales is less than or equal to 1.05, even though recent atmospheric observations of CO₂ and O₂ correlations provide evidence for substantially higher values (Severinghaus, 1995; Luecker, Keeling & Durbey, 2001; Seibt *et al.*, 2004). Syntheses of elemental abundance data support the proximate chemical analysis data presented in Table 2. For example, the mean elemental mass composition of wood from 29 observations compiled by Gaur & Reed (1995) was 49.9 ± 2.0% C, 6.1 ± 0.4% H, 42.9 ± 1.9% O, 0.2 ± 0.3% N, and 0.9 ± 1.2% ash, yielding a mean R value of 1.043 ± 0.023 (with the assumption of atmospheric N₂ as the initial source of the organic N). R decreases to 1.040 assuming NH₄⁺ was the initial source and increases to 1.046 assuming NO₃⁻ was the initial source. These observations from stems and wood are particularly relevant for global studies given that the accumulation of woody biomass has been implicated as playing a major role in the northern hemisphere carbon sink (Goodale *et al.*, 2002) and that the loss of woody biomass

contributes substantially to a tropical source (Houghton, 1994; Achard *et al.*, 2002).

Concurrent gas exchange observations of O₂ and CO₂ have the potential to provide substantial insight about the physiological and biogeochemical transformations that are occurring within ecosystems over short timescales. Over annual to decadal timescales, these approaches should match estimates of the oxidative ratio derived from the accumulation (or loss) of biomass from the system and its elemental composition (Severinghaus, 1995). Even though this latter (mass balance) approach has received less attention recently, it is probably a robust approach for determining the R_{net} value appropriate for use in global atmospheric studies on annual to decadal timescales (Keeling, 1988).

Other possible drivers of O₂ disequilibrium

Other global change processes may also contribute to trends in R_{ab} . For example, at the level of an individual plant, any factor that changes the allocation of NPP between leaves, stems and roots has the potential to induce a change in R_{ab} (Table 2). Alternately, any process that alters the chemical composition (e.g. the lignin or lipid content) of different plant organs could have a similar effect. At the level of an ecosystem or biome, a trend in R_{ab} may be caused by changing the distribution of plant functional types that have different chemical compositions. Disequilibria can also be caused by a change in the chemical composition of SOM that affects R_{ba} (Keeling, 1988).

Elevated levels of atmospheric CO₂ are increasing levels of plant growth in many ecosystems (Koch & Mooney, 1996; DeLucia *et al.*, 1999) and are altering the response of ecosystems to other aspects of global change (Shaw *et al.*, 2002; Kaakinen *et al.*, 2004). There are also small systematic changes in chemical composition, with higher levels of starch in high-CO₂ grown plants (Griffin *et al.*, 1996; Poorter *et al.*, 1997; Wullschlegel *et al.*, 1997; Kaakinen *et al.*, 2004). However, the additional starch will easily decompose and may not play a significant role in the decomposition of the more resistant plant material (e.g. Hirschel *et al.*, 1997).

The effect of human-induced changes in the global nitrogen cycle (Vitousek *et al.*, 1997) on R_{ab} may be even more challenging to assess. The potential for increased levels of N to cause a net carbon sink (and a net O₂ source) within terrestrial ecosystems is well established (Holland *et al.*, 1997) although recent work also shows that added N can also lead to a loss of carbon from ecosystems (Mack *et al.*, 2004). In terms of O₂ disequilibrium, the consequences of increased N availability may be indirect, through a shift in plant allocation and species composition. Often, increased availability of soil

resources, including N, leads to increased allocation to stems and leaves (Stitt & Krapp, 1999; Poorter & Nagel, 2000). If increased levels of N stimulate greater stem growth in both herbaceous and woody species, this could drive a decrease in R_{ab} (Table 2). The opposite could occur, however, if leaf allocation exceeded that of stem allocation or if woody plants increased their abundance at the expense of herbaceous plants. These indirect mechanisms are compelling because they amplify the effects of added N within an ecosystem – typically N concentrations are relatively low in the plant tissues that account for much of terrestrial carbon storage over annual to decadal timescales (e.g. the boles and stems of trees, coarse woody debris, etc.).

Conclusions

Here, we examined for the first time levels of disequilibrium between R_{ab} and R_{ba} within the terrestrial biosphere that would have an impact on our interpretation of O_2 measurements used for land and ocean carbon sink partitioning. This type of disequilibrium can be sustained by a small trend in the R_{ab} of terrestrial NPP because of time delays between NPP and the return flux. In contrast with isotopic disequilibria that are driven by a changing atmospheric isotopic ratio, oxidative ratio disequilibria may be induced by a change in the chemical composition of plants and soils. These changes in tissue chemistry can occur either from a change in the abundance of plant functional types within a biome or from a shift in allocation within individual species to different plant compounds. At a global scale, we hypothesize that increasing levels of disturbance (caused largely by human activity) is the primary mechanism affecting the contemporary oxidative ratio of the terrestrial biosphere and that this is causing R_{ab} to decrease.

More generally, our work suggests that because different classes of chemical compounds are involved with terrestrial carbon storage over diurnal, seasonal, decadal, and millennial timescales, there is no single value of R_{net} appropriate to assign to a net land carbon source or sink. Instead this value depends on the time interval of the flux estimate (and the corresponding oxidation state of the carbon pools involved with the storage). Given that wood is one of the primary terrestrial carbon storage reservoirs that can respond over decadal timescales, it is likely that R_{ab} appropriate for multiyear global atmospheric O_2 analyses is less than or equal to 1.05. A critical issue for future work is to reconcile mass balance and flux based approaches for estimating the oxidative ratio. In this regard, special consideration needs to be given to measurements of whole ecosystem elemental composition in tropical ecosystems, including

areas that have undergone transformations associated with land clearing for agriculture and grazing.

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