

Effects of ozone on net primary production and carbon sequestration in the conterminous United States using a biogeochemistry model

By B. FELZER^{1*}, D. KICKLIGHTER¹, J. MELILLO¹, C. WANG², Q. ZHUANG¹ and R. PRINN², ¹*The Ecosystems Center, Marine Biological Laboratory, 7 MBL St., Woods Hole, MA 02543, USA;* ²*Joint Program on the Science and Policy of Global Change, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA*

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ABSTRACT

The effects of air pollution on vegetation may provide an important control on the carbon cycle that has not yet been widely considered. Prolonged exposure to high levels of ozone, in particular, has been observed to inhibit photosynthesis by direct cellular damage within the leaves and through possible changes in stomatal conductance. We have incorporated empirical equations derived for trees (hardwoods and pines) and crops into the Terrestrial Ecosystem Model to explore the effects of ozone on net primary production (NPP) and carbon sequestration across the conterminous United States. Our results show a 2.6–6.8% mean reduction for the United States in annual NPP in response to modelled historical ozone levels during the late 1980s–early 1990s. The largest decreases (over 13% in some locations) occur in the Midwest agricultural lands, during the mid-summer when ozone levels are highest. Carbon sequestration since the 1950s has been reduced by 18–38 Tg C yr⁻¹ with the presence of ozone. Thus the effects of ozone on NPP and carbon sequestration should be factored into future calculations of the United States' carbon budget.

1. Introduction

Changes in atmospheric composition during the 20th century have directly affected vegetation and soils and therefore the global carbon cycle. These changes have also indirectly affected the biota through influences on climate. While biogeochemical models have been used to study the potential beneficial effects of CO₂ fertilization (e.g. Cao and Woodward, 1998; McGuire et al., 2001) or nitrogen fertilization (e.g. Townsend et al., 1996), on terrestrial ecosystems across the globe, the damaging effects of air pollution on ecosystems have only been studied for specific sites, regions and vegetation types. Over 90% of this damage may be the result of one air pollutant, tropospheric ozone (Adams et al., 1986). The importance of these effects has not been considered in the context of larger, continental-scale or global carbon dynamics.

Tropospheric ozone is the product of photochemical reactions of carbon monoxide (CO), methane (CH₄) and other hydrocarbons in the presence of NO_x (NO + NO₂). Hydrocarbons are the product of fossil fuel emissions, solvent use, chem-

ical manufacturing and volatile organic carbon (VOC) emissions from natural vegetation. The primary source of NO_x in the troposphere is the combustion of fossil fuel, but it is also produced through the burning of biomass, lightning and microbial and geochemical processes in soils (Mauzerall and Wang, 2001). The destruction of ozone in the troposphere is also determined by the concentrations of NO_x, CO, CH₄ and non-methane hydrocarbons (NMHCs) (e.g. Lui et al., 1987; Lin et al., 1988). Ozone can also be transported into a region by local winds and downward from the stratosphere (Oltmans and Levy, 1994).

In the conterminous United States, ozone values reach their maximum in early spring (Singh et al., 1978) to late summer (Logan, 1989), depending upon favourable meteorological or pollution conditions. Industrial continental regions tend to have maximum ozone values in the late afternoon and minimum values in the early morning hours, whereas marine and high latitude sites have maximum ozone values before sunrise and their lowest values in the afternoon (Oltmans and Levy, 1994). Background ozone levels in unpolluted air can be anywhere from 20 to 60 parts per billion (ppb) (Seinfeld, 1989; Lefohn et al., 2001). Polluted regions contain ozone levels as high as 400 ppb (Seinfeld, 1989).

*Corresponding author.
e-mail: bfelzer@mbl.edu

The effects of ozone on vegetation have been studied in both the laboratory and the field (Beyers et al., 1992; Fuhrer et al., 1997; Heck et al., 1984a,b; Lindroth et al., 2001; Lyons et al., 1997; McLaughlin and Downing, 1995; Noormets et al., 2001; Pell et al., 1990; 1993; Pye, 1988; Tjoekler et al., 1995; Zheng et al., 1998). Ozone affects vegetation by direct cellular damage once it enters the leaf through the stomata, so that ozone uptake is a function of both ambient ozone levels and stomatal conductance (Mauzerall and Wang, 2001). The cellular damage is probably the result of changes in membrane permeabilities and may or may not result in visible injury or reduced growth or yield (Krupa and Manning, 1988). A secondary response to ozone is possibly a reduction in stomatal conductance, as the stomata close in response to increased internal CO₂ (Reich, 1987). Stomata generally open in response to light and warmth and close in response to aridity, water stress and high CO₂ (Mauzerall and Wang, 2001). It has been suggested that the decrease in stomatal conductance caused by ozone is similar in magnitude to that caused by increases in CO₂ above pre-industrial levels (Taylor and Johnson, 1994). Tjoekler et al. (1995) found a decoupling of photosynthesis from stomatal conductance as a result of long-term exposure to ozone. Such a decoupling implies that ozone-induced reductions in photosynthesis would also be accompanied by decreased water use efficiency (WUE), resulting in even larger reductions in productivity, particularly at arid sites (Ollinger et al., 1997).

There have been few process-based modelling studies on the effects of ozone on vegetation. Reich (1987) developed a linear model using the experimental results of earlier studies to determine how two groups of trees (pines and hardwoods) and crops respond to ozone. His results show that crops are the most sensitive to ozone and pines the least sensitive. Ollinger et al. (1997) used this model in the PnET-II forest ecosystem model to study the effects of ozone on hardwoods in the northeastern United States for the late 1980s to early 1990s. They found a reduction in net primary production (NPP) of between 3 and 16%, with less of a reduction on drier sites due to the lower stomatal conductance that generally occurs at these sites. Ollinger et al. (2002) later applied their ozone algorithms to a version of PnET (PnET-CN) that includes N cycling to evaluate the interactive effects of CO₂, O₃ and N deposition within the context of historical changes in land use for the hardwoods in the northeastern United States. They found that ozone counteracted the effects of increased CO₂ and N deposition on forest growth and carbon storage in this region.

The current study expands the work of Ollinger et al. (1997; 2002). We incorporate the Reich (1987) and Ollinger et al. (1997) algorithms into an extant biogeochemical model, the Terrestrial Ecosystem Model (TEM 4.2) to explore the effect of ozone on net primary production and carbon sequestration across the conterminous United States during the 20th century, in the context of changing atmospheric CO₂ concentrations, climate, land cover and agricultural management.

2. Methods

To conduct this study, we first modified TEM 4.2 to include the effects of ozone on vegetation and developed a spatially explicit historical ozone data set for the conterminous United States. We then conducted a series of simulations to partition the relative effects of ozone and other environmental factors. Finally, we estimated the uncertainty in our results associated with the errors in the ozone parameters. Below we describe these procedures in detail.

2.1. Model description

The TEM is a process-based biogeochemistry model that simulates the cycling of carbon, nitrogen and water between vegetation, soils and the atmosphere. Vegetation incorporates carbon by the uptake of atmospheric CO₂ during photosynthesis (i.e. gross primary productivity, GPP). Soils obtain both organic carbon and nitrogen from litterfall that results when plant tissue dies. Carbon returns to the atmosphere through autotrophic respiration (R_A) from vegetation and heterotrophic respiration (R_H) associated with the decomposition of soil organic matter. A pool of available soil inorganic nitrogen provides the source of nitrogen to the vegetation and is replenished by nitrogen mineralization of soil organic nitrogen that results from decomposition (Raich et al., 1991). Thus, nitrogen is recycled within the ecosystem. Nitrogen from vegetation is divided into labile and structural components, which are the result of resorption of nitrogen from dying tissues and mobilization of nitrogen to create new tissues (Tian et al., 1999). TEM is run at a 0.5° × 0.5° resolution, consisting of 3305 grids for the conterminous United States. Further details of the model are described in Raich et al. (1991) and Tian et al. (1999, 2003).

In this study a new version of the TEM, TEM 4.3, has been developed by modifying TEM 4.2 (Tian et al., 2003) to include the effects of ozone on plant growth and to incorporate a new agriculture scheme. Specifically, the calculation of GPP has been modified from the original equation (Raich et al., 1991; Tian et al., 1999) to include the effects of ozone on photosynthesis: (eq. 1)

$$\text{GPP} = C_{\max} f(\text{PAR}) f(\text{LEAF}) \\ \times f(T) f(Ca, Gv) f(\text{NA}, \text{O}_3) f(\text{O}_3)_t \quad (1)$$

where C_{\max} is the maximum rate of C assimilation, PAR is photosynthetically active radiation, LEAF is the leaf area relative to the maximum annual leaf area, T is the mean monthly air temperature, Ca is the atmospheric CO₂ concentration, Gv is the relative canopy conductance, O₃ is ozone and NA is the feedback of nitrogen availability on carbon assimilation. The multiplier $f(\text{O}_3)_t$ describes the direct effects of ozone on GPP for the current month, while the multiplier $f(\text{NA}, \text{O}_3)$ applies the effect of ozone to nitrogen uptake in order to maintain a constant ratio of carbon to nitrogen (C:N) during the production of new plant tissue.

Table 1a. Values of sensitivity coefficient a for eq. (2)

	a coefficient
Deciduous trees and other vegetation types	2.6×10^{-6} ($\sigma = 2.3 \times 10^{-7}$)
Coniferous trees	0.7×10^{-6} ($\sigma = 2.45 \times 10^{-7}$)
Crops	3.9×10^{-6} ($\sigma = 5.27 \times 10^{-7}$)

As cellular damage inhibits photosynthesis, the demand for nitrogen will also be reduced. Because the TEM interlinks the carbon and nitrogen cycles, reductions in carbon uptake without concurrent reductions in nitrogen uptake cause large shifts in the C:N toward less N-limiting conditions. Lindroth et al. (2001) shows that it is still questionable whether the C:N is affected by exposure to ozone.

Similar to the uptake of carbon dioxide, the uptake of ozone by vegetation is dependent upon moisture conditions. To simulate the influence of moisture conditions on ozone uptake, we modify eq. (1) in Ollinger et al. (1997) to be dependent upon the relative rate of evapotranspiration to potential evapotranspiration:

$$f(O_3)_{AOT40} = (1 - EET/PET) + \{EET/PET[1 - (agAOT40)]\} \quad (2)$$

where $f(O_3)_{AOT40}$ is the ratio of ozone-exposed to control photosynthesis and has a value between 0 and 1, EET/PET is the ratio of evapotranspiration to potential evapotranspiration (value between 0 and 1), a is an empirically derived ozone response coefficient (Table 1a), g is the mean stomatal conductance in mm s^{-1} , and AOT40 is an ozone index based on accumulated hourly ozone values above a threshold of 40 ppb in ppb-hr. The coefficients for conifers (based on pines) and crops are based on the regressions of the Reich (1987) uptake-response curves, and the coefficient for hardwoods was derived by Ollinger et al. (1997) for the AOT40 index (Table 1a). The dependence on stomatal conductance occurs because uptake is equal to dose (or AOT40) multiplied by stomatal conductance. Under moist conditions (i.e. EET is equal to PET), eq. (2) collapses to eq. (1) used in Ollinger et al. (1997).

Similar to Ollinger et al. (1997), we assume a linear relationship between canopy conductance (g) and GPP as follows:

$$g = b + cGPP_{\text{init}} \quad (3)$$

where GPP_{init} is the gross primary production expected with no ozone effects and the values of the coefficients b and c are shown in Table 1b. These parameter values allow a range of canopy conductances of 1–5 mm s^{-1} for woody vegetation and 2–14 mm s^{-1} for herbaceous vegetation (Korner et al., 1979).

It is uncertain how quickly cells damaged by episodic exposure to ozone are able to recover or are replaced from one month to the next (Pye, 1988). In order to account for some persistent damage from past ozone exposure during the lifespan of a leaf,

Table 1b. Values of canopy conductance coefficients b and c for eq. (3)

	b coefficient (mm s^{-1})	c coefficient ($\text{mm s}^{-1} \text{gC}^{-1} \text{m}^{-2}$)
Woody	1.0 ($\sigma = 0.33$)	0.0080782 ($\sigma = 0.0013464$)
Herbaceous	2.0 ($\sigma = 0.0$)	0.0402712 ($\sigma = 0.0044746$)

we compound the current month's ozone effect ($f(O_3)_{AOT40}$) by half of the previous month's total ozone effect ($f(O_3)_{t-1}$) for each month with a positive net primary production (NPP) to determine the total ozone effect of the current month ($f(O_3)_t$) on GPP:

$$f(O_3)_t = f(O_3)_{AOT40} - 0.5 + 0.5 f(O_3)_{t-1} \quad \text{if NPP} > 0.0 \quad (4)$$

$$f(O_3)_t = f(O_3)_{AOT40} \quad \text{if NPP} < 0.0$$

Thus, ozone damage from each month continues to affect the plant during the lifespan of the leaf. The diminishing effect from each previous month accounts for some recovery and replacement of cells from month to month. We also perform two sets of experiments assuming no compounding effects (complete cellular repair) and a full compounding effect (no cellular repair) to provide an estimate of the error inherent in these assumptions.

To ensure that the effect of ozone does not change the C:N, the amount of N entering the vegetation, nitrogen uptake by plants (NUPTAKE), is reduced by multiplying it by $f(O_3)_t$ as well. The influence of NUPTAKE on GPP as represented by $f(\text{NA})$ is described elsewhere (McGuire et al. 1992; Pan et al., 1998) and is dependent on whether nitrogen availability or other environmental factors limit photosynthesis during a particular month. The multiplier $f(\text{NA}, O_3)$ is the same formulation as the multiplier $f(\text{NA})$, but NUPTAKE used in the multiplier has been modified by $f(O_3)_t$ as described above.

To estimate the net assimilation of CO_2 into plant tissues (i.e. plant growth), we calculate NPP as follows:

$$\text{NPP} = \text{GPP} - R_A \quad (5)$$

To estimate carbon sequestration by the ecosystem, we calculate net carbon exchange (NCE) as follows:

$$\text{NCE} = \text{NPP} - R_H - E_c - E_p \quad (6)$$

where E_c is carbon emission during the conversion of natural ecosystems to agriculture, and E_p is the sum of carbon emission from the decomposition of agricultural and wood products (McGuire et al., 2001). For natural vegetation, E_c and E_p are equal to 0, so NCE is equal to net ecosystem production (NEP).

In addition to these revisions needed to incorporate the effects of ozone, TEM 4.3 also includes a new scheme to estimate NPP in agricultural ecosystems. In TEM 4.2, a spatially explicit, empirically derived relative agricultural productivity (RAP) database

CASTNET + EPA/AIRS sites

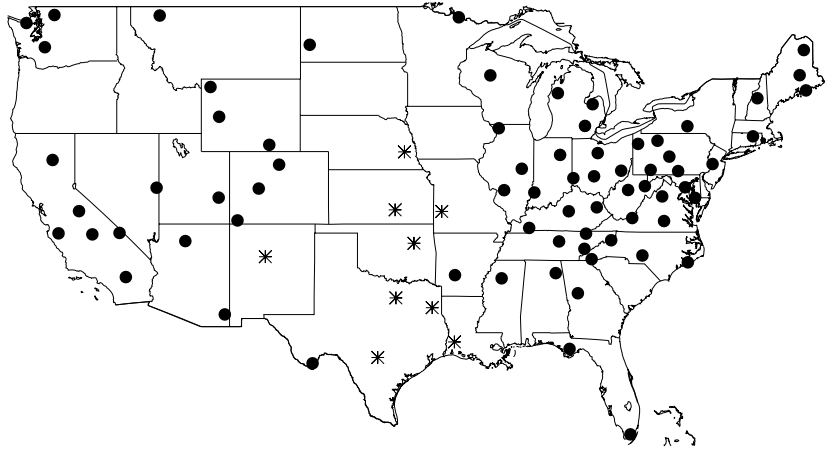


Fig. 1. Location of CASTNET (filled circles) and AIRS (asterisks) sites containing hourly ozone data for the United States.

was used to infer the effects of agricultural practices on crop productivity (McGuire et al., 2001). Agricultural production was determined by simply multiplying the NPP of the original natural vegetation by a RAP value for the appropriate grid cell. In TEM 4.3, agricultural productivity is no longer dependent upon the productivity rates of the original natural vegetation. Instead, the model uses grassland parametrizations to describe the carbon and nitrogen dynamics of crop plants. The soil organic matter dynamics of croplands, however, are still based on the parametrizations of the original natural vegetation. As in McGuire et al. (2001), 40% of vegetation carbon in crops is assumed to be removed during harvest, and the remaining vegetation carbon is transferred to the soil organic carbon pool. Although the effects of different agricultural practices on crop productivity are not explicitly considered in TEM 4.3, two switches have been added that allow the model to estimate crop productivity if nitrogen is not limiting (i.e. optimum fertilization) and to estimate crop productivity if water is not limiting (i.e. optimum irrigation). Thus, the model can discern a range of crop productivities based on optimum agricultural management versus no management in the context of changing environmental conditions. The revisions are described in more detail in the Appendix. As with previous versions, TEM 4.3 is calibrated to each ecosystem using carbon and nitrogen pools obtained from the literature and previous studies (Raich et al., 1991; McGuire et al., 1992)

2.2. Data set development

Climatological data sets used by TEM in this study include the cloudiness, historical air temperature and historical precipitation data sets used by McGuire et al. (2001). The model also uses spatially explicit data sets of soil texture, elevation and pre-disturbance natural vegetation (McGuire et al., 2001). Historical changes in cropland distribution are prescribed using the data set developed for the McGuire et al. (2001) study.

To account for the effects of ozone on terrestrial carbon dynamics, we have developed a spatially explicit data set of historical changes in the AOT40 index. First, hourly ozone data for the conterminous United States have been obtained from 71 stations of the Environmental Protection Agency's (EPA) Clean Air Status and Trends Network (CASTNET) and nine rural stations from the EPA's Aeronometric Information Retrieval Service (AIRS) (Fig. 1). The CASTNET sites are also located in rural regions away from urban emissions and are managed by both EPA and the National Park Service (NPS). The AIRS data have been chosen to fill in missing regions from the CASTNET data set and include sites in Texas, Louisiana, New Mexico, Oklahoma, Kansas, Missouri and Nebraska. Rural sites have been used to provide a more accurate measure of the ozone levels over the $0.5^\circ \times 0.5^\circ$ TEM grids. As observed in other studies (Lefohn and Runeckles, 1987; Lin et al., 2001), the addition of urban sites actually decreases the estimated ozone concentrations in the affected regions. The hourly ozone data are averaged for the 3-year period of 1998–2000. The AOT40 index is calculated directly from the averaged hourly data for each site on a monthly basis. This index is the sum of the amounts by which ozone mole fractions exceed 40 ppb during daylight hours (07:00–19:00 UTC). The site data for each month are then interpolated to a $0.5^\circ \times 0.5^\circ$ grid using a thin plate spline interpolation.

The resulting seasonal AOT40 signal averaged over the entire United States (Fig. 2) shows that during these 3 years, ozone levels are highest during August with a secondary peak in May and a minimum during the winter months. The spatial pattern of AOT40 is different between August and May (not shown). During August, AOT40 values are greater in the South and West, while May AOT40 values are greater across the Northern, Southwest and Southeast United States. This regional pattern is consistent with greater photochemical production of ozone in the Southern United States. The maps for March, April and May (Fig. 3a)

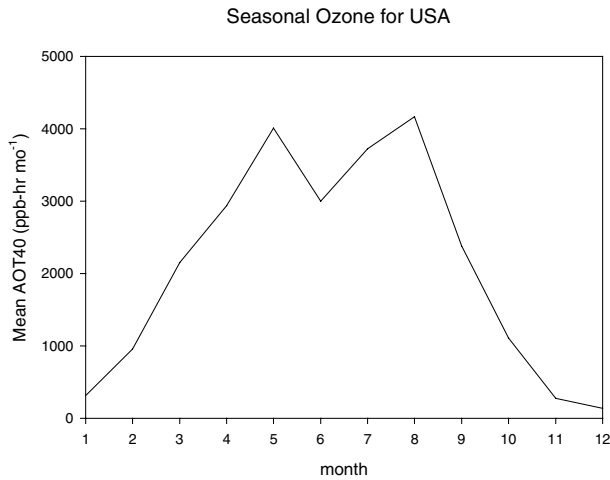
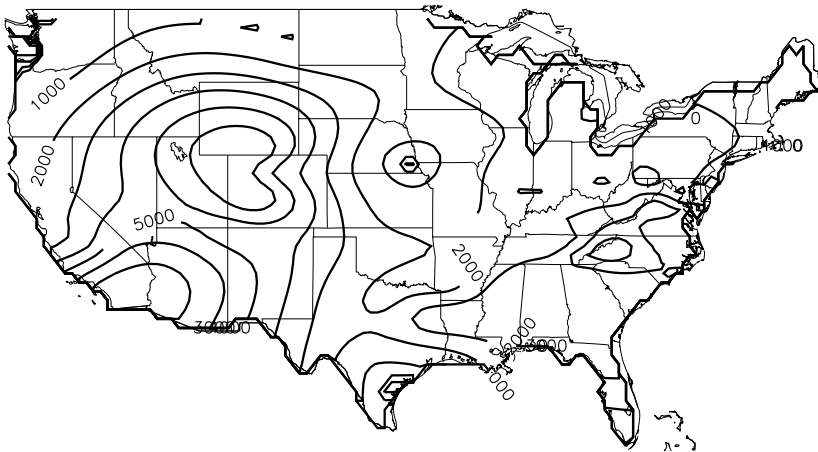


Fig. 2. Monthly mean of AOT40 (ppb-hr mo⁻¹) based on the $0.5^\circ \times 0.5^\circ$ interpolation of the CASTNET and AIRS data for 1998–2000.

and June, July and August (Fig. 3b) show highest AOT40 levels spreading eastward from the Los Angeles (LA) basin in the Southwest (consistent with Fiore et al. 1998) and in the region of the Southern Appalachians in the Southeast. The maximum in the Southwest is in part the result of transport from the LA urban centre and natural VOC emission from chaparral, whereas the maximum in the Southeast is a factor of both transport from the Midwest and high natural VOC levels from local forests.

Because atmospheric ozone concentrations have changed over time, we have developed a historical ozone data set to consider the effects of these changes on terrestrial dynamics. During recent decades, ozone levels have been fairly stable in rural locations within the United States (Lefohn and Shadwick, 1991; Fiore et al., 1998), with some reductions in urban areas due to reduced VOC emissions (Fiore et al. 1998; Lin et al., 2001). Therefore, we have held ozone levels constant at the climatological

MAM AOT40 (climatological ozone)



JJA AOT40 (climatological ozone)

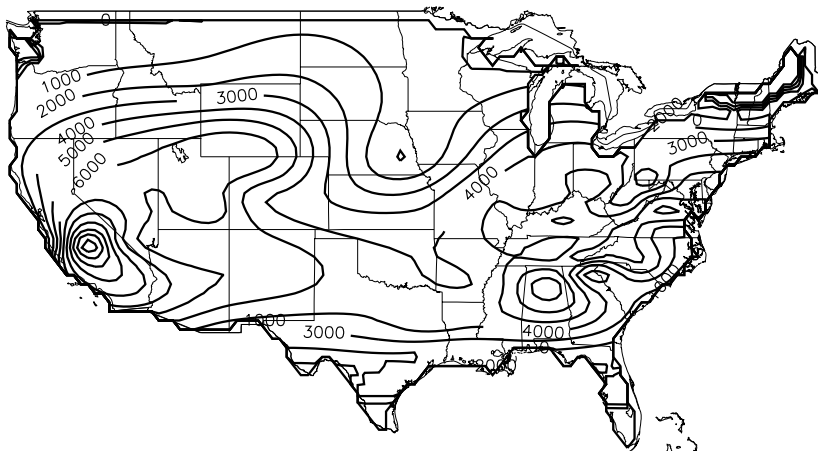


Fig. 3. Mean of AOT40 (ppb-hr) based on the $0.5^\circ \times 0.5^\circ$ interpolation of the CASTNET and AIRS data for 1998–2000 during (a) March, April and May and (b) June, July and August.

values from 1976–1995. Prior to 1976, we decreased ozone levels by 1.6% yr⁻¹ backward from 1975 to 1860, consistent with the historical trend developed by Marenco et al. (1994).

To scale the AOT40 data set to 1860, the hourly ozone data set is reduced by the method described above, and the AOT40 index is calculated from the newly reduced hourly ozone data. To simplify this process, we reduce the hourly ozone values from the sites with the maximum AOT40 value for each month, and then recalculate the AOT40 values based on these values to create representative historical AOT40 curves for each month. The AOT40 values at each grid point from 1976 are then reduced for each month based on these representative AOT40 curves. The result is that during the winter and early spring, AOT40 does not become positive until the 1950s, whereas during the summer and autumn, it becomes positive in the 1920s. Prior to 1923 there is no effect of ozone on vegetation during any month. Effectively, however, the effect of ozone is negligible prior to 1950.

2.3. Experimental design

To examine the relative effect of ozone on net primary production and carbon sequestration by terrestrial ecosystems in comparison with other environmental factors, we have devised seven model simulations. The first simulation is a reference run, “REF”, where we assume that terrestrial ecosystems are covered by natural vegetation and atmospheric CO₂ and ozone concentrations along with climate remain constant at the 1860 values throughout the simulation (Table 2). The second simulation examines the effect of CO₂ fertilization using historical atmospheric CO₂ concentrations (Keeling et al., 1995; Etheridge et al., 1996) (denoted CARBON). We then examine the influence of CO₂ fertilization and climate variability (Jones, 1994; Hulme, 1995) on terrestrial carbon dynamics in the third simulation (denoted CLIMATE). In the next two simulations, we examine the influence of CO₂ fertilization, climate variability and change in land use with and without optimal nitrogen fertilization (F) on crop productivity, (denoted LAND and LANDF, respectively). The final simula-

tions include the influence of CO₂ fertilization, climate variability, change in land use with and without nitrogen fertilization, and ozone (denoted OZONEF and OZONE, respectively). In this experimental scheme, the effects of ozone are determined with and without agricultural management. We expect that the simulations with optimal fertilization application (LANDF, OZONEF) will represent the best response of NPP and carbon storage to agricultural management, whereas the simulations without fertilizer applications (LAND, OZONE) will represent the effects of no agricultural management. As neither ozone nor fertilization significantly affects terrestrial carbon dynamics until the 1950s, we focus our analysis on the time period 1950 to 1995. The model experiments without ozone are conducted to examine how the effects of CO₂, climate and change in land use on terrestrial carbon dynamics compare with the effect of ozone.

For each simulation, carbon and nitrogen dynamics of terrestrial ecosystems are initialized to equilibrium conditions assuming the land is covered with the original natural vegetation. The model is then run in transient mode for 120 years using the historical climate data during the initial 40 years to initialize terrestrial carbon and nitrogen dynamics to a dynamic equilibrium state before starting our historical analysis from 1860 to 1995. If a grid cell was cultivated in 1860, the grid cell is converted during the first year of this 120-year spin-up period and allowed to come back to a dynamic equilibrium state.

2.4. Uncertainty analysis

There are several sources of error that contribute to uncertainty in our analysis. Direct ozone damage to photosynthesis itself is dependent upon the vegetation sensitivity (coefficient *a*) and canopy conductance (coefficients *b* and *c*). We address the errors associated with these terms with a formal uncertainty analysis described below. We address the uncertainty due to the issue of cell recovery and replacement with two sets of sensitivity experiments including no and complete cell recovery or replacement from month to month. We address the uncertainty of agricultural management by performing simulations with no agricultural management and with optimal nitrogen fertilization for all agricultural grids. Other sources of uncertainty include our assumption of no effect of ozone on C:N, the indirect effects of reduced stomatal conductance and uncertainty in the existing ozone data sets. We address these issues more thoroughly in section 4.

We have conducted an uncertainty analysis to evaluate the error in NPP and NCE due to the empirically derived ozone response coefficient (*a*, *b* and *c*) in eqs. (2) and (3). The multiplier $f(O_3)_t$ determines the effect of ozone in TEM 4.3, and the magnitude of this effect depends upon *a*, *b* and *c*. We have used the means and standard deviations of *a* for hardwoods, conifers and crops and *b* and *c* for woody and herbaceous vegetation (Tables 1a, b) to develop six Gaussian distributions, which are the probability distribution functions (PDFs) that

Table 2. Experimental set-up, showing application of CO₂, climate (temperature and precipitation), land use (agriculture), F (fertilization) and O₃

Simulation	Environmental factors				
	CO ₂	Climate	Land use	F	O ₃
REF	Constant	Constant	Constant	No	0
CARBON	Historical	Constant	Constant	No	0
CLIMATE	Historical	Historical	Constant	No	0
LAND	Historical	Historical	Historical	No	0
LANDF	Historical	Historical	Historical	Yes	0
OZONE	Historical	Historical	Historical	No	Historical
OZONEF	Historical	Historical	Historical	Yes	Historical

describe the uncertainty of each of the coefficients. From these PDFs, we have applied a Latin Hypercube (Morgan and Henrion, 1992) to generate 10 random combinations from 10 equally distributed probability bins to develop a random Monte Carlo scheme (Clark, 1961). These 10 combinations then constitute 10 individual simulations that are used as the basis for uncertainty statistics. This analysis is performed on the ozone experiment without agricultural management (OZONE).

3. Results

3.1. Effects of ozone on net primary production

The effects of ozone on NPP averaged over the conterminous United States result in a $2.6 \pm 0.34\%$ (1σ from our uncertainty analysis) decrease in annual NPP without agricultural management to a 6.8% decrease with agricultural management (Table 3). The largest effect of ozone on NPP (Figs. 4a and b) occurs during the summer months, with the largest monthly decrease of 4.3–8.7% in August (Table 3). During the winter months, when productivity and ozone levels are low in many parts of the United States, there is very little effect of ozone on NPP (Figs. 4a and b).

The inclusion of nitrogen fertilization provides a huge benefit to vegetation production, with an increase of 46.2% in NPP. This increase is reduced to 39.8% if ozone damage is considered (Table 3). These simulations therefore show that the productivity benefits of fertilization are partially offset by the effect of ozone. With optimal fertilization, crop plants do not experience the nitrogen limitations imposed on natural vegetation during the summer and are therefore responsible for a large proportion of the carbon uptake (i.e. GPP) during this time. Since the reduction in NPP is primarily the result of the imposed linear reduction on GPP (eqs. (1) and (2)), when fertilization is applied, the larger GPP contributes to the larger effect of ozone (Fig. 4c).

The reductions in NPP (Fig. 5a) show decreases of over 6% throughout the Midwest, with smaller decreases throughout the eastern two-thirds of the United States. With fertilization, there are substantially larger decreases in the Midwest, with addi-

tional agricultural lands in the Great Plains and South showing large decreases in production resulting from ozone exposure (Fig. 5b). These additional areas represent a combination of regions with high ozone exposure (i.e. large AOT40) and a large proportion of the area in cropland or abandoned cropland, which occur primarily in the eastern two-thirds of the United States (Fig. 6). The regional and seasonal pattern of NPP reduction (Fig. 7a) shows significant percentage decreases in the Northeast, Southeast, Midwest and Plains regions. These regions have a combination of agricultural lands (which are more sensitive to ozone exposure), high ozone levels and less drought stress than the western United States. The addition of fertilization produces much larger decreases in NPP (up to 13%) over all regions of the country, with the largest effects in the Midwest, Plains, Northeast and Southeast (the large percentage changes in the West represent relatively small differences due to low productivity). The largest ozone effects occur in midsummer (July or August) in most cases. Several factors are responsible for this midsummer peak. Ozone levels themselves are largest in August throughout the southern United States, yet they are highest in May in much of the northern United States. However, because of the ozone compounding, the actual ozone levels that damage the plant will be greater in the late summer than the early spring. The effect of ozone is also dependent upon canopy conductance and, therefore, GPP. As shown in Fig. 2c, GPP is highest in June and, with fertilization, higher in August than in May.

3.2. Effects of ozone on carbon sequestration

From 1950–1995, we estimate that 1640 Tg C ($35.6 \text{ Tg C yr}^{-1}$) were stored in terrestrial ecosystems without optimal agricultural management and 9372 Tg C ($203.7 \text{ Tg C yr}^{-1}$) with optimal agricultural management. Ozone exposure decreased carbon sequestration by 810 Tg C ($17.6 \pm 2.3 (1\sigma) \text{ Tg C yr}^{-1}$) without agricultural management and by 1762 Tg C ($38.3 \text{ Tg C yr}^{-1}$) with optimal agricultural management (Table 4). This reduction is due primarily to a reduction in vegetation carbon without agricultural management and soil carbon when agricultural management is assumed. At the grid-cell scale, significant reductions in carbon sequestration ($>9 \text{ g C m}^{-2} \text{ yr}^{-1}$) (Fig. 8) occur throughout most of the region where NPP has also been reduced. The difference in pattern between the NPP percentage differences and NCE differences are the result of using percentages, because lower NCE in agricultural lands increases the percentage difference, resulting in seemingly larger effects in croplands. The overall similarity in the actual differences or percentage differences implies that NPP dominates the NCE response.

3.3. Relative importance of the effects of ozone on NPP and carbon sequestration

A comparison of the annual NPP for the different simulations shows that the reduction in NPP due to ozone partly

Table 3. Comparison of mean annual net primary productivity (NPP) and mean monthly NPP during August for the period 1989 to 1993 among different scenarios

Scenario	Annual NPP (Tg C yr ⁻¹)	August NPP (Tg C month ⁻¹)
REF	3461	440
CARBON	3669	488
CLIMATE	3611	460
LAND	2642	348
OZONE	2574	333
LANDF	3864	527
OZONEF	3599	481

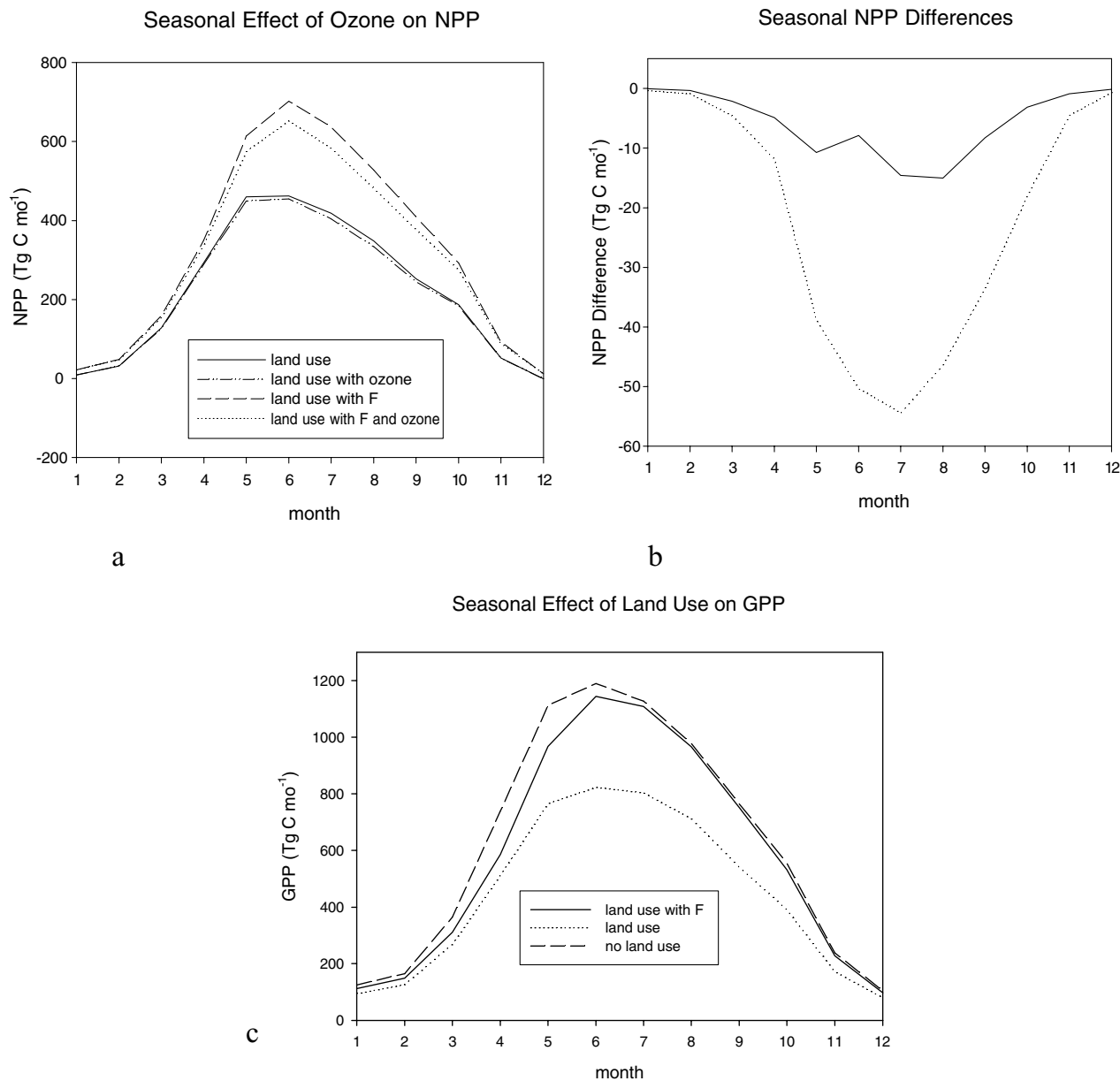
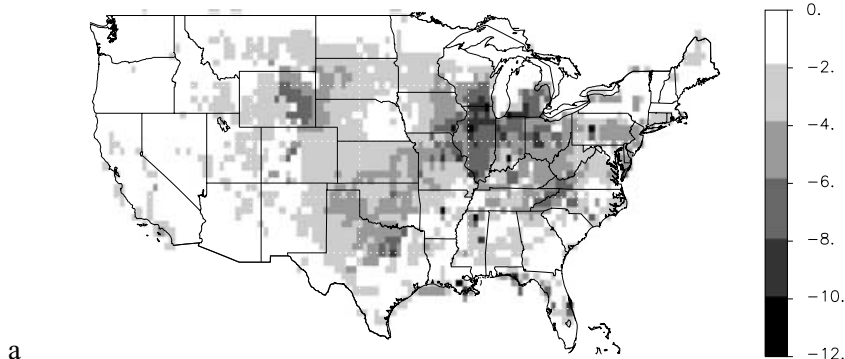


Fig. 4. (a) Mean monthly NPP from 1989–1993 over the United States for CO₂+climate+land use with nitrogen fertilization (F) with ozone (OZONEF) (dotted), and without ozone (LANDF) (dashed), CO₂+climate+land use with ozone (OZONE) (dashed with dots), and without ozone (LAND) (solid) in Tg C month⁻¹, showing the decrease of NPP due to ozone exposure. (b) NPP differences in Tg C month⁻¹ between the experiments with and without ozone in (a). (c) Mean monthly GPP from 1989–1993 over the United States for CO₂+climate+land use with fertilization (LANDF) (solid), CO₂+climate+land use (LAND) (dotted), and CO₂+climate (CLIMATE) (dashed) in Tg C month⁻¹, showing the shift in peak photosynthesis due to nitrogen fertilization.

compensates for the effects of CO₂ fertilization on NPP (+6.0% mean 1989–1993) (Table 3, Fig. 9a). The reduction is also significantly larger when fertilization is applied, showing that ozone damage can offset some of the gains resulting from intensive agricultural management. The climate effect on NPP is dominated by year-to-year variability. This variability also influences the

effects of land-use change and agricultural management. Overall, the magnitude of the ozone effect (–2.6 to –6.8%) is greater than the long-term trends caused by climate variability (–1.6%, CLIMATE–CARBON), but less than the influence of agricultural management (+46.2%, LANDF–LAND) and change in land use (–26.8%, LAND–CLIMATE) (Table 3, Fig. 9a).

Annual % difference NPP
(1989–1993) No Fertilization



Annual % difference NPP
(1989–1993) Optimal Fertilization

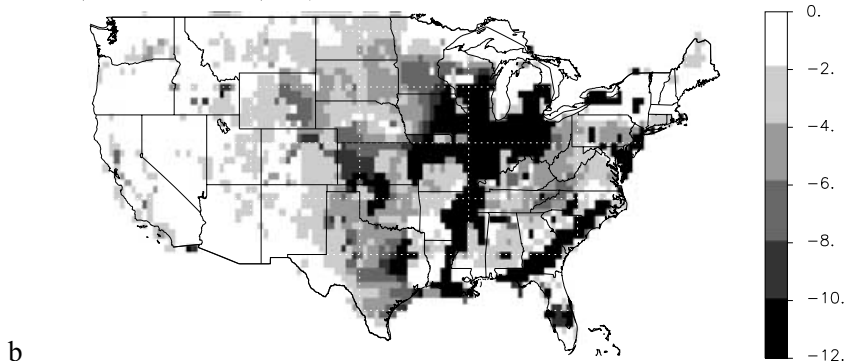


Fig. 5. (a) Map of mean annual NPP percentage difference between CO_2 +climate+land use with ozone (OZONE) and without ozone (LAND) for the years 1989–1993. (b) Map of mean annual NPP percent difference between CO_2 +climate+land use with fertilization with ozone (OZONEF) and without ozone (LANDF) for the years 1989–1993. The largest decrease is -33.7% (corresponding to $-316.6 \text{ Tg C yr}^{-1}$) and the largest increase is 3.6% (increases occur in 22 grid cells with most $<1.0\%$). The most significant decreases in NPP occur in the eastern half of the United States, where productivity is the highest, and in agricultural lands.

Agricultural Land (1995)

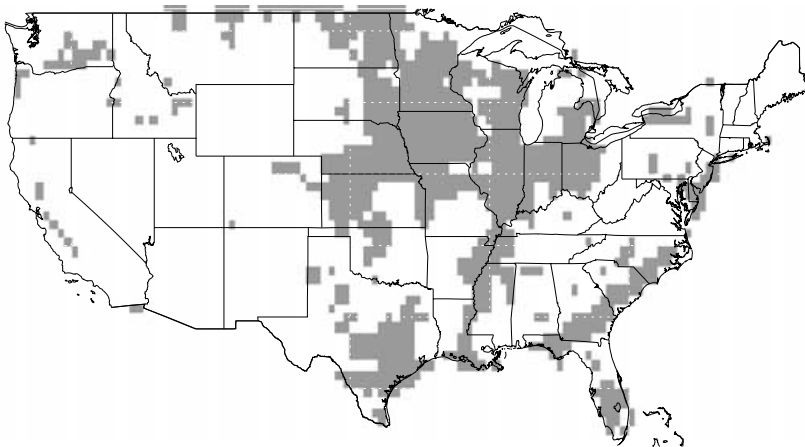


Fig. 6. Map of croplands during 1995.

Likewise, over the period 1950–1995, carbon sequestration is predicted to have increased as a result of optimal nitrogen fertilization, climate and CO_2 fertilization, but decreased as a result of change in land use (includes effects of land conversion, har-

vest of crops and abandonment of cropland) and ozone exposure (Table 4). The relative importance of these factors, however, has changed over this period (Fig. 9b). While the effect of CO_2 is increasing with time, the effect of ozone is only increasing slightly,

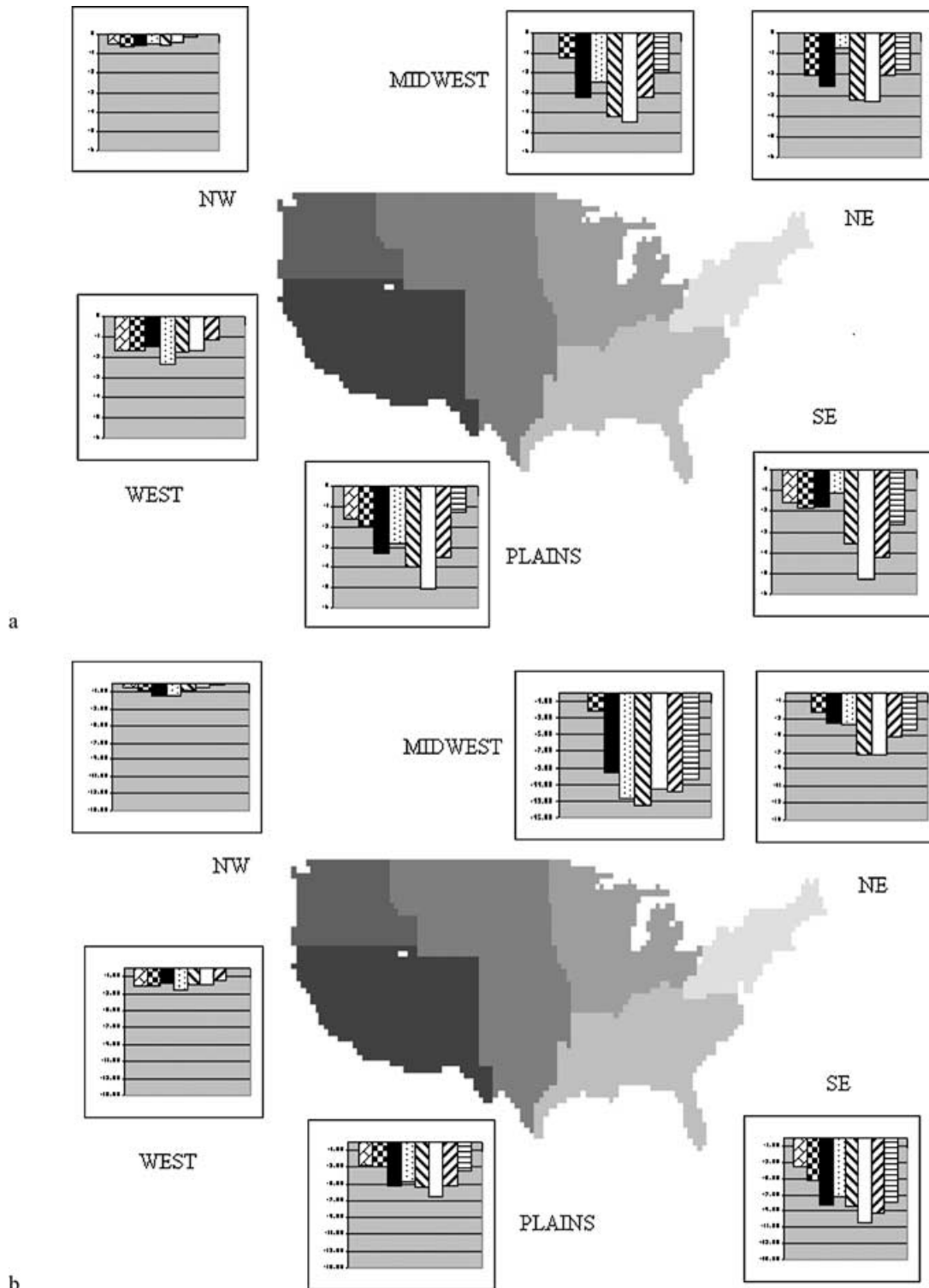


Fig. 7. (a) Regional and seasonal decreases in percentage NPP between CO₂+climate+land use with ozone (OZONE) and without ozone (LAND) for 1989-1993 (range is from 0 to -6, and gridlines are at 1% intervals). Largest decreases are in the range of 4-5%. (b) Regional and seasonal decreases in percentage NPP between CO₂+climate+land use with fertilization with ozone (OZONEF) and without ozone (LANDF) for 1989-1993 (range is from 0 to -15%, and gridlines are at 2% intervals starting at -1%). Largest decreases occur during midsummer and are in the range over 13%. March = diagonal brick, April = checkerboard, May = solid black, June = polka dots, July = back diagonals, August = white, September = forward diagonals, October = horizontal lines.

Table 4. Partitioning of cumulative changes in carbon storage (differences between the different model experiments) between 1950 and 1995 among effects attributable to CO₂ fertilization, climate variability, cropland establishment and abandonment, agricultural management and ozone exposure (units = Tg C)

Effect	Vegetation carbon	Soil organic carbon	Products	Total carbon storage
CARBON-REF	1609	1099	0	2708
CLIMATE-CARBON	12148	-410	0	838
LAND-CLIMATE	-30	-1452	-424	-1906
OZONE-LAND	-591	-215	-4	-810
Total (no F)	2236	-978	-428	830
LANDF-LAND	325	7081	326	7732
F × ozone	-27	-877	-48	-952
Total with F	2534	5226	-150	7610

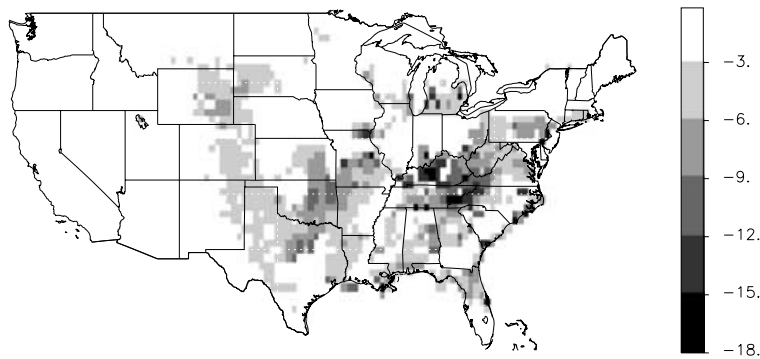
though in an opposite direction. If ozone levels were to rise in the future, the reduction in carbon sequestration caused by ozone will continue to partially counterbalance the future benefits of CO₂ fertilization. In general, the reduction of NPP and NCE by

ozone is larger when the vegetation is most productive, as occurs when croplands are fertilized.

4. Discussion

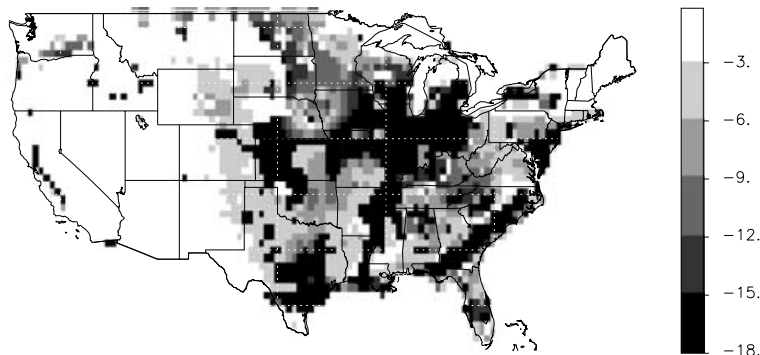
These results expand upon the site-specific modelling of Ollinger et al. (1997, 2002) to provide estimates of the effects of ozone on net primary production and carbon sequestration on a continental scale. The magnitude and even timing of the reduction of NPP and NCE due to ozone are somewhat dependent upon whether or not nitrogen fertilization is applied to croplands. The effect of ozone partially discounts the effects of increased CO₂ fertilization. Below, we examine how our simulated effects of ozone for different vegetation types compare with observational estimates, while also looking at the issue of the ozone measurements themselves. We then compare the results of this study with those of Ollinger et al. (1997, 2002) and other modelling studies and provide further insights into important mechanisms affecting carbon sequestration in the conterminous United States. Finally, we explore the major uncertainties and further research required to address these uncertainties.

Annual NCE difference (gC/m²/yr)
(1950–1995) No Fertilization



a

Annual NCE difference (gC/m²/yr)
(1950–1995) Optimal Fertilization



b

Fig. 8. (a) Map of annual NCE difference between CO₂+climate+land use with ozone (OZONE) and without ozone (LAND) for the years 1950–1995 in g C m⁻² yr⁻¹. (b) Map of annual NCE difference between CO₂+climate+land use with fertilization with ozone (OZONEF) and without ozone (LANDF) for the years 1950–1995 in g C m⁻² yr⁻¹. The largest decrease is -38.3 g C m⁻², and there are a few grids (15) with an increase in NCE no larger than 0.55 g C m⁻². The largest total C sequestration during this time period is decreased significantly in the eastern United States as a result of ozone exposure.

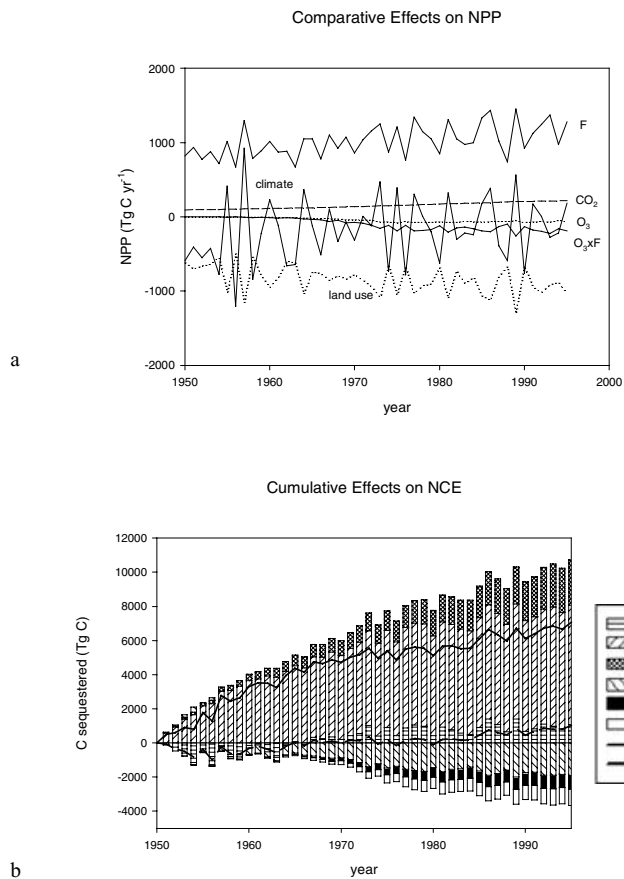


Fig. 9. Transient NPP and NCE responses from 1950–1995, showing how the effect of ozone compares with other disturbances. (a) Effect of CO₂ fertilization (CARBON–REF), climate variability (CLIMATE–CARBON), land use (LAND–CLIMATE), agricultural management (LANDF–LAND), ozone (OZONEF–LANDF) and the cross terms between ozone and nitrogen fertilization on NPP. (b) Cumulative carbon sequestration from each of the factors in (a). All units in (Tg yr⁻¹).

4.1. Comparison of simulated effects of ozone with observational studies

We develop a single measure of the magnitude of the effect of ozone by taking the ratio of the percentage biomass change to the ozone dose in ppm-hr for deciduous and coniferous trees and percentage yield change to the ozone dose in ppm-hr for crops. We then compare a range of results from laboratory and open top chamber (OTC) experiments against a range of TEM results using all of the 3305 United States grids. Note that it is impossible to compare specific sites with TEM grids because the OTC experiments apply an artificial ozone dose that is unrelated to the environmental ozone concentration that is forcing TEM at a particular grid cell. We use the observational studies compiled for trees by Pye (1988) and for crops by Heck et al. (1984b). For the model results, changes in biomass are calculated as the difference between NPP and carbon in litterfall. Crop yield is calculated directly in TEM as the carbon flux in the 40% of crop biomass harvested for agricultural products. Using the original CASTNET data set, we develop a linear relationship between AOT40 and dose in ppm-hr to convert our AOT40 values to dose:

$$\text{dose} = 1.32 \times \text{AOT40} + 13694 \quad r^2 = 0.92 \quad (7)$$

It is important to realize that while this relationship exists for the ozone concentrations measured over the United States, it is completely different for the laboratory experiments that went into the Reich (1987) model (as discussed in the following section). While the observational data are all laboratory or OTC experiments, conducted from weeks to months, the TEM results are based on the mean annual biomass changes during the period 1989–1993.

Overall, the values from our modelling study are in the same range as the experimental values (Fig. 10; Pye, 1988; Heck et al., 1984b). For all vegetation types except fertilized crops, the model medians are less negative than those calculated from observations. Deciduous trees and crops are more sensitive to ozone than coniferous trees in both simulations and experiments. There is considerable overlap in the ranges for all three vegetation types. The lower sensitivity of coniferous trees is entirely consistent with the Reich (1987) model that serves as the basis for TEM 4.3. For deciduous trees, the TEM 4.3 results contain a small number of grid cells with increases in biomass, which skews the maximum end of the range from the experimental

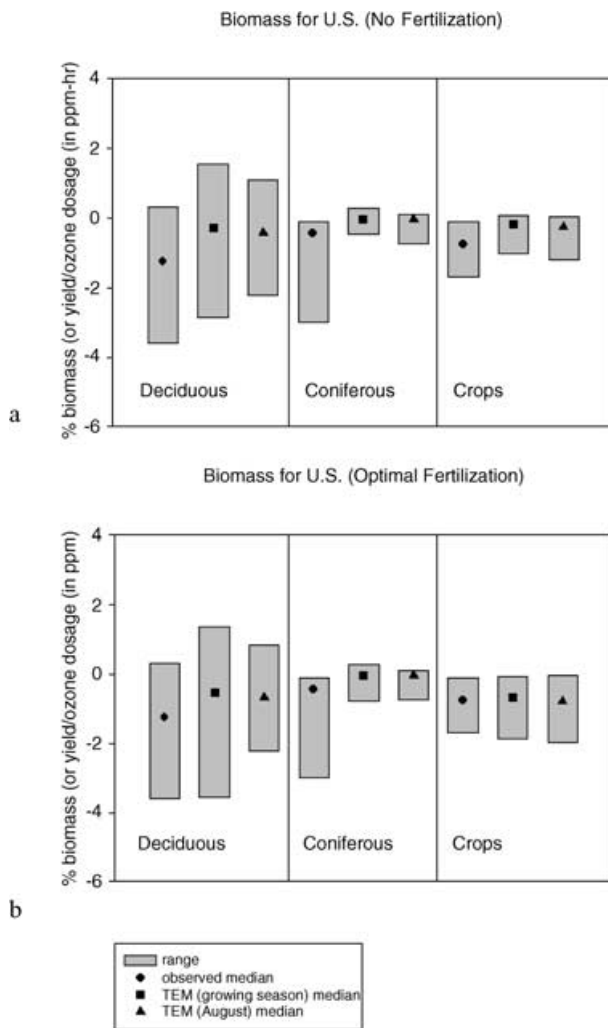


Fig. 10. Ratio of percentage change in biomass for trees or yield for crops to the increase in ozone dosage in ppm (a) with fertilization (F) and (b) without F (tree gridpoints may be abandoned cropland and therefore affected by fertilization). Observational data for trees are from Pye (1988) and include only the statistically significant data. Observational data for crops are from Heck et al. (1984b); 7 hours per day mean ozone concentrations are multiplied by the number of hours over the season to derive dosages. The TEM 4.3 results are based on NPP—carbon litterfall as a measure for biomass of trees and C flux coming into agricultural products as a measure for crop yield.

values (which also contain some biomass increases); although as evident in the median, most grid cells experience a decrease in biomass as a result of ozone exposure.

One source of uncertainty in this comparison is due to the seasonal differences between controlled experiments and model output. The observational data are mostly the result of seedlings grown under controlled, experimental conditions, rather than mature trees in a natural setting. Therefore, a comparison of model data with the observational data can be done using any month

during the growing season for the model data, all of which yield different values (the mean from May to September is used here). For example, if we use August values from TEM 4.3 to represent the month of maximum ozone exposure (Fig. 10), we get different values for both the ranges and the medians.

Another source of error lies in the spatial difference between laboratory experiments and actual canopy systems. The TEM results contain values from all grid cells within the range of a vegetation type, whereas the observed range is based on a very limited number of site-specific data. Fuhrer et al. (1997) caution that even exposure–response relationships derived from OTC experiments do not necessarily represent the effect of ozone over larger areas because of spatial variation in external atmospheric and environmental conditions which may change ozone uptake. Much of the experimental data used in these comparisons are from laboratory experiments, which are even more loosely tied to canopy systems. The FACE (Free Air CO₂ Enrichment Facility) study in northern Wisconsin (Isebrands et al., 2001; Lindroth et al., 2001; Noormets et al., 2001) illustrates the complexity of modelling the effects of ozone on vegetation, even for a specific tree species. In this study, seedlings of aspen and birch were analysed using free air fumigation techniques to determine the effects of CO₂ and O₃ together and independently on photosynthesis, stomatal conductance and N cycling. In different aspen clones, photosynthesis changed from +1% to –11% with equivalent ozone exposures (Noormets et al., 2001). In terms of biomass increment, Isebrands et al. (2001) also showed considerable variation between different aspen clones, in the final year varying from +17.0% to –28.8%. Even excluding the one ozonophilic clone, the range is from –20.0% to –28.8%.

4.2. Ozone measurements

Most experiments studying the effects of ozone on photosynthesis or biomass, including those used in Reich (1987), use ozone units of either concentration or dose, which is the mean ozone concentration multiplied by time of exposure. Note that dose as used here and by Reich (1987) is distinct from uptake, which includes stomatal conductance. Because dose depends upon both ozone concentration and time of exposure, it is very difficult to develop a point-to-point relationship between dose and AOT40 or any other index; i.e. for any given dose value, there can be any number of corresponding AOT40 values. It is therefore impossible to simply convert the Reich (1987) curves from dose to AOT40 or any other index without the original hourly data. Ollinger et al. (1997) used the original data in Reich (1987) to derive the correlation between ozone uptake and photosynthesis using the AOT40 index, rather than dosage. We use the coefficient for hardwoods, along with the slopes from the Reich (1987) uptake response curves, to develop the coefficients for conifers and crops. Our estimated uncertainties in these coefficients result in relatively minor errors in the NPP and NCE calculations.

Other ozone indices, such as the SUM06 index (sum of all ozone values greater than 60 ppb), may also be used instead of AOT40. However, a new set of correlations from the laboratory data (e.g. SUM06 versus photosynthesis) are required to develop a correlation based on another index. Lefohn et al. (1988) argue that indices like the W126 index, which account for, though give lower weighting to, lower ozone concentrations, are most appropriate. This argument would actually preclude the use of both the SUM06 and AOT40 indices. However, Lefohn et al. (2001) also argue that 60 ppb is a better threshold for the background ozone levels over the United States than 40 ppb, although there is other evidence that this “background” includes an important anthropogenic component from intercontinental transport of pollution (Marenco et al., 1994; Wang and Jacob, 1998). In any case, Fuhrer et al. (1997) have argued that the AOT40 index is more appropriate as a measure of ozone damage to vegetation based on laboratory and even some field data (McLaughlin and Downing, 1995) of exposure–response relationships. Especially in the case of crops, they believe that ozone values between 40 and 60 ppb contribute to yield damage.

4.3. Comparison with estimates of ozone damage from other modelling studies

Ollinger et al. (1997) considered only the effects of climate and ozone for the period 1987–1992, and they found an annual NPP reduction of 3–16%, with a mean reduction of 7.4% for 64 specific sites in the northeastern United States. Based on an additional simulation with ozone but no land use, we found a reduction of 3.8% in annual NPP for the same time period for deciduous trees in the Northeast region, which is in the lower end of their range.

In their more recent study, Ollinger et al. (2002) incorporated the effects of N deposition and land use history (both agriculture and timber harvest) into the PnET model for the same sites in the Northeast United States. TEM 4.3, while including croplands and abandonment, does not include timber harvest or N deposition. They found that including ozone offset some of the increase in NPP (from 17.4% to 12.0%) and NCE (12% lower) caused by CO₂ fertilization over the period 1860–1995 for the Northeast region. Our simulations with all disturbances included except agricultural management (LAND) show a 12.6% increase in NPP without ozone and an 8.4% increase with ozone over this same period for deciduous trees. NCE for the same period and region is 15.8% lower with ozone. Ollinger et al. (2002) also found that for carbon sequestration, the effects of N deposition offset the effects of ozone exposure, and that for net primary production, the combined enhancement by CO₂ and N deposition were equally offset by the combined negative effects of ozone exposure and land use disturbance. We found that ozone exposure and land disturbance (without optimal agricultural management) together only compensate for the effects of CO₂ fertilization.

Our study, however, has extended the analysis of the effects of ozone from the Northeast United States to other regions of the conterminous United States, where the effects of ozone are sometimes greater. Over the entire United States from 1860–1995 (without agricultural management), NPP decreases by 6.3% without ozone and 8.7% with ozone (due to conversion to cropland). The addition of fertilization creates substantial increases in NPP, although these are somewhat lower with ozone exposure. Because of cropland abandonment in the early 1800s, carbon has accumulated in the forests of the northeastern United States over the period 1860–1995. In other parts of the conterminous United States, carbon has generally been lost from terrestrial ecosystems because of conversion of natural vegetation to agricultural land prior to 1950. Ozone enhanced these historical carbon losses by 5.7% (and by 27.0% with agricultural management). However, in more recent times (1950 to 1995), carbon has also been sequestered in these other parts of the conterminous United States, though less sequestration has occurred with exposure to ozone.

Another class of process-based models has been used to assess the effects of ozone on vegetation at the tree physiological scale, rather than the ecosystem scale. These models are based on single trees and normally operate at the hourly time step, allowing for the direct computation of the effects of the diurnal ozone cycle (Constable and Friend, 2000). These models can also account for carbon allocation between roots, stems, and leaves, thereby accounting for differential ozone effects on each of these compartments (Constable and Friend, 2000). The TREGRO model, for example, reduces mesophyll conductance to simulate the effects of ozone. Yun et al. (2001) used TREGRO to show that the effects of ozone on aspen are highly dependent upon external environmental conditions and can even be more sensitive with less ozone exposure as a result, which is similar to our findings because of the ozone dependency on GPP. The effects of ozone on aspen were also studied using the tree physiological model ECOPHYS, which includes the effects of ozone on photosynthesis and stomatal conductance. Martin et al. (2001) found that there are substantial differential effects on leaves, roots and stems, with stem dry matter and diameter, leaf biomass and area and root growth being most sensitive to ozone exposure. Combining the TREGRO model with the stand-level ZELIG model for loblolly pine and yellow poplar, Laurence et al. (2001) showed that accounting for competition within the stand could lead to much greater responses than for individual trees.

4.4. Relative role of ozone in carbon sequestration in the conterminous United States

We estimate that ozone reduced carbon sequestration in the conterminous United States during the 1980s by between 18.7 and 35.4 Tg C yr⁻¹. For the same period Pacala et al. (2001) estimates that total carbon sequestration for the conterminous United States was 300 to 580 Tg C yr⁻¹. Since they used both field data

inventory and inverse modelling approaches, their estimates include the effect of ozone, although they were unable to separate it out. Based on our simulations, we estimate that in the absence of ozone pollution the carbon sink estimated by Pacala et al. (2001) would have been at least 3–12% higher. Other estimates of the carbon sink for the United States during the 1980s include 80.0 Tg C yr⁻¹ (Schimel et al., 2000), 310 Tg C yr⁻¹ (Birdsey and Heath, 1995) and 150–350 Tg C yr⁻¹ (Houghton et al., 1999). These studies all omit some of the terms included by Pacala et al. (2001), especially those involving storage in reservoirs and exports and imports. In the absence of an ozone effect, these sinks would be anywhere from 5–44% higher.

4.5. Relative effects of ozone on carbon storage in vegetation and soils

Carbon accumulation in vegetation from 1950–1995 occurred as a result of CO₂ fertilization, climate warming and agricultural management, but decreased with ozone exposure and change in land use (Table 4). As expected, the detrimental effects of ozone on GPP resulted in reduced vegetation carbon. Regrowth of natural vegetation after cropland abandonment offsets some of the decrease resulting from conversion of land to agriculture during this time period. Agricultural management increases carbon in vegetation by increasing the standing stocks of crops, and the addition of nitrogen to these ecosystems enhances the regrowth of vegetation after abandonment of cropland.

Carbon accumulation in soils occurs as a result of CO₂ fertilization and agricultural management, while reductions occur as a result of ozone, climate variability and change in land use (Table 4). With CO₂ fertilization, the litterfall contains more carbon because of the increased vegetation carbon. Climate warming increases decomposition, resulting in a loss of soil carbon. Land use reduces soil carbon each year because 40% of the crops are harvested and removed from the system. The reason why soil organic carbon increases so much with fertilization is because the vegetation that remains behind after harvesting contains more vegetation carbon, which accumulates in the soil every year. However, we assume no tillage, and under more realistic conditions most agricultural lands are tilled, breaking up soil aggregates that allow decomposition to increase and thus reducing the amount of carbon in the soil.

4.6. Future studies to address a number of uncertainties

To improve our understanding of the effects of ozone exposure on terrestrial carbon dynamics, we have identified six key uncertainties in this study that should be addressed in future studies of ozone damage to vegetation:

1. *Direct ozone effect.* Ozone damage to photosynthesis depends upon the vegetation type according to the Reich (1987) and Ollinger et al. (1997) linear assumptions (*a* coefficient) and

the canopy conductance (*b* and *c* coefficients). Crops are more sensitive to ozone exposure than trees because both the sensitivity of crops to ozone exposure and the stomatal conductance of crops are larger. Through a Latin Hypercube approach we have shown that the uncertainty of these coefficients contributes only slightly to the overall uncertainty of the results. However, experimental studies also show that the ozone response varies widely between different vegetation species or even within the same species, so that there is considerable uncertainty in the overall linear model.

2. *Indirect ozone effect.* We have not included the indirect effect of ozone on reduced canopy conductance, though we have accounted for the effect of moisture limitations. However, we are developing a more physically-based method of computing canopy conductance that will enable us to model these processes. These indirect effects are liable to be small because reduced canopy conductance will result in less ozone damage, but offsetting this potential increase in photosynthesis will be a lower CO₂ uptake.

3. *Ozone compounding.* There is still considerable uncertainty as to how quickly damaged cells are repaired and replaced from month to month. Although there is evidence for some accumulative effects from prolonged ozone exposure (Reich, 1987), the literature is not clear on how large this accumulative effect is (Pye, 1988). We have assumed a 50% reduction each month, but we could have equally assumed no repair or complete repair. We have run additional experiments which result in a reduction of NPP by 10.2% (without F) and 20.4% (with F) with no repair and 1.3% (without F) and 3.8% (with F) with complete repair. The reductions in NCE for the 1980s are -86.0, -129.6, -9.6 and -19.6 Tg C yr⁻¹ for the four cases, respectively. Clearly this uncertainty is large and will significantly affect any effort to model the effects of ozone on vegetation. We also note that we have treated deciduous and coniferous trees similarly. If we assume a 2–3 year lifespan for typical needles, the ozone damage to coniferous trees will be even greater than we have currently modelled, making our estimates for coniferous trees conservative (and thus helping to explain the underestimates in Fig. 10).

4. *Agricultural management.* Clearly there is a huge uncertainty introduced by agricultural management, including irrigation and nitrogen fertilization, which increases GPP and therefore, canopy conductances and the magnitude of the effect of ozone in both croplands and even abandoned croplands. Thus, the land use history is important when calculating the effect of ozone on carbon stocks (see also Ollinger et al., 2002). In this study, we have assumed optimal nitrogen fertilization, which is a realistic upper bound for the United States. We did not consider the effects of irrigation because of the limited use of irrigation in the conterminous United States (according to the U.S. Department of Agriculture (1997) only 16.5% of agricultural lands are irrigated). By reducing drought stress effects and increasing productivity in arid regions, we expect that irrigation will produce an even larger ozone effect in these areas. We also have

not assumed any tillage, which would decrease the amount of carbon stored in soils, and thus possibly reduce the magnitude of the effect of ozone.

5. *C:N*. We have assumed that ozone exposure does not affect the C:N of vegetation. As mentioned previously, there have been studies both confirming and rejecting this argument. If ozone affects carbon more than nitrogen, the system could move towards less N-limiting conditions, which could result in changes in the carbon and nitrogen dynamics of the ecosystem. For example, decreases in C:N could lead to increased decomposition and net N mineralization, which would result in more available N and therefore allow more N uptake by vegetation. In this case, enhanced nitrogen availability may compensate for the effects of ozone on productivity.

6. *Ozone (AOT40) data set*. The network of ozone monitoring stations in the United States, even when accounting for the AIRS stations, is still underrepresented in the Great Plains (see Fig. 1). We chose to use rural stations and non-urban stations in metropolitan regions to better represent ozone patterns in both rural and metropolitan regions. While urban areas contain less ozone than outlying rural areas, the entire metropolitan region contains higher ozone levels than far-outlying rural regions.

5. Conclusions

This research has explored the effects of tropospheric ozone on NPP and NCE over the United States during the latter half of the 20th century. Tropospheric ozone resulted in a reduction of about 2.6–6.8% in annual NPP over the United States during the late 1980s to early 1990s. The largest reductions occur in midsummer, when peak accumulated ozone levels coincide with peak productivity, especially in croplands. The reduction in NPP is largest in the eastern United States, corresponding to regions with both moderate to high ozone levels and agricultural lands.

Carbon sequestration in the conterminous United States since the 1950s has been reduced by 17.6–38.3 Tg C yr⁻¹ as a result of ozone exposure. The largest reductions in carbon sequestration coincide with regions of decreased NPP, with decreases >9 g C m⁻² yr⁻¹ common in some areas. The decrease in NCE is due to reduced carbon accumulation in both vegetation and soils.

The effects of ozone on net primary production within the conterminous United States are similar in magnitude to those of CO₂ fertilization and climate variability, but less than the effects of changes in land use and agricultural management. In terms of carbon sequestration, the negative effect of ozone is similar in magnitude to that of change in land use, while it offsets the positive effects of climate variability, CO₂ fertilization, and nitrogen fertilization. Ozone damage will diminish many of the yield and carbon storage gains of fertilization, which is a particularly important consideration for developing countries like China, that have high ozone levels and intensive agricultural management to support a growing population. Clearly these effects should be considered in future estimates of greening due to CO₂ fertiliza-

tion and carbon sequestration, especially in ozone-rich regions such as Europe and China. The developing world, in particular, will have to consider the effects of ozone on carbon sequestration to accurately estimate their obligations under international agreements.

6. Acknowledgments

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7. Appendix: Improvements in the Simulation of Agricultural Carbon and Nitrogen Dynamics by the Terrestrial Ecosystem Model

In version 4.2 of the Terrestrial Ecosystem Model (TEM), initial attempts have been made to incorporate the effects of human activities, particularly row crop agriculture, on terrestrial carbon and nitrogen dynamics (McGuire et al., 2001). These effects include: (1) the loss of carbon and nitrogen from ecosystems associated with conversion of forests to agricultural fields; (2) the changes in carbon and nitrogen stocks and fluxes associated with agricultural practices; (3) the loss of carbon as a result of the decomposition of agricultural products or wood products that were obtained during conversion; and (4) the sequestration of carbon associated with regrowth of natural vegetation when agricultural fields were abandoned. To simulate the changes in carbon stocks and fluxes associated with change in land use, we have used an approach similar to that described in the Terrestrial Carbon Model (Houghton et al., 1983; Melillo et al., 1988) except that initial biomass levels and the recovery of the biomass of natural vegetation after agricultural abandonment varied on a 0.5° × 0.5° grid cell basis in response to spatial and temporal variations in environmental conditions. To simulate carbon dynamics in agricultural ecosystems, we have used the relative agricultural productivity (RAP) approach of Esser (1995) where simulated agricultural productivity was a multiplier of the original natural vegetation. The RAP multiplier varies spatially and attempts to incorporate the effects of agricultural practices and their variation across the surface of the earth. The RAP multiplier can be greater than 1.0 in areas where agricultural fields are irrigated and fertilized, but the NPP of natural vegetation is constrained by moisture-limitations (e.g. California). However,

the RAP multiplier is generally less than 1.0 because most areas have less intensive management. While the RAP approach has been useful in examining the relative effects of human activities on historical changes in terrestrial carbon dynamics, the approach is limited in examining potential future changes, especially if changes in albedo and greenhouse gases associated with change in land use have an influence on future climate.

To improve our ability to assess the effects of agricultural activities on future terrestrial carbon dynamics, we have replaced the RAP approach with a more process-based approach. First, we use the extant grassland parametrizations of TEM 4.2 to simulate vegetation dynamics (e.g. gross primary production, respiration, nitrogen uptake, litterfall) of crop plants. As in TEM 4.2, soil organic matter dynamics in crop fields are parametrized based on the type of the original natural vegetation. Unlike TEM 4.2, we now use growing-degree days above 5 °C (GDD) to determine when crops are planted (GDD = 300) and harvested (GDD = 2000). The GDD approach allows us to simulate variations in the timing of planting and harvest of crops across a region. In addition, the simulation of multiple crops within a year is possible by resetting GDD to zero whenever a crop is harvested in areas with favourable climatic conditions. Similar to TEM 4.2, we assume that 40% of the vegetation biomass is removed from the fields during harvest and the remaining biomass enters the soil organic matter pools.

While our process-based approach allows us to consider the effects of changing atmospheric CO₂ concentrations and climatic conditions on crop metabolism and agricultural productivity, the evaluation of the effects of management (e.g. irrigation, application of fertilizers and pesticides) on agricultural productivity still requires the development of additional time-varying spatially explicit data sets that describe these activities. However, if we assume that the purpose of irrigation and fertilization is to alleviate water and nitrogen limitations, respectively, of crop plants, we can estimate the optimum effects of various management strategies if we run TEM for croplands without water and/or nitrogen limitations. To maintain mass balance, we calculate how much water and nitrogen are required to alleviate these limitations and then add these amounts to the crop ecosystem as irrigation and fertilizer, respectively.

To determine the amount of irrigation required, we determine both potential evapotranspiration (PET) and estimated evapotranspiration (EET) for a grid cell as described in Pan et al. (1996) and examine the relationship between these two variables. If EET is less than PET, then water availability is limiting crop production. To overcome this limitation, we subtract EET from PET and add this amount as irrigation to supplement precipitation.

To determine the amount of nitrogen fertilizer required, we determine nitrogen uptake by crops as described by McGuire et al. (1992) for both of the situations where nitrogen availability is limiting productivity (NUPTAKE) and where nitrogen availability is not limiting productivity (NUPTAKE_p) during a

particular month. If NUPTAKE is less than NUPTAKE_p, we then subtract NUPTAKE from NUPTAKE_p and add this amount to the ecosystem as N fertilizer. We apply fertilization only after 1950 to account for historic fertilization trends.

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