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LETTER

Sensitivity of global greenhouse gas budgets to tropospheric ozone pollution mediated by the biosphere

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Abstract

Tropospheric ozone (O_3), a harmful secondary air pollutant, can affect the climate via direct radiative forcing and by modifying the radiative forcing of aerosols through its role as an atmospheric oxidant. Moreover, O_3 exerts a strong oxidative pressure on the biosphere and indirectly influences the climate by altering the materials and energy exchange between terrestrial ecosystems and the atmosphere. However, the magnitude by which O_3 affects the global budgets of greenhouse gases (GHGs: CO_2, CH_4, and N_2O) through altering the land–atmosphere exchange is largely unknown. Here we assess the sensitivity of these budgets to tropospheric O_3 pollution based on a meta-analysis of experimental studies on the effects of elevated O_3 on GHG exchange between terrestrial ecosystems and the atmosphere. We show that across ecosystems, elevated O_3 suppresses N_2O emissions and both CH_4 emissions and uptake, and has little impact on stimulation of soil CO_2 emissions except at relatively high concentrations. Therefore, the soil system would be transformed from a sink into a source of GHGs with O_3 levels increasing. The global atmospheric budget of GHGs is sensitive to O_3 pollution largely because of the carbon dioxide accumulation resulting from suppressed vegetation carbon uptake; the negative contributions from suppressed CH_4 and N_2O emissions can offset only ~10% of CO_2 emissions from the soil–vegetation system. Based on empirical data, this work, though with uncertainties, provides the first assessment of sensitivity of global budgets of GHGs to O_3 pollution, representing a necessary step towards fully understanding and evaluating O_3–climate feedbacks mediated by the biosphere.

1. Introduction

Tropospheric ozone (O_3) is formed from the photochemical oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs), typically initiated by the hydroxyl radical (OH), in the presence of nitrogen oxides ($NO_x \equiv NO+NO_2$) (Leighton 1961). Its concentration has significantly increased since the industrial revolution and is projected to either continue to rise or to decline over the course of this century with considerable spatial variability, driven largely by trends in fossil fuel combustion (source of NO_x) and vegetation growth (source of VOCs) (Myhre *et al* 2013, Young *et al* 2013, Cooper *et al* 2014). In addition to severe damage to human health, what makes O_3 particularly important as a pollutant in the troposphere is its reactivity with biochemical systems—it can alter the metabolisms involved with the production and/or consumption of radiatively significant gases such as CO_2, CH_4, and N_2O (McLaughlin *et al* 2007, Zak *et al* 2011, Ainsworth *et al* 2012, Agathokleous *et al* 2016). All of these could largely contribute to changes in the atmospheric GHG budgets and affect climate (Sitch *et al* 2007). This paper provides the first assessment of the sensitivity of global budgets of CO_2, CH_4, and N_2O to tropospheric O_3 abundance resulting from the alterations of land-atmosphere exchange based on a meta-analysis of published experimental studies of O_3 impacts on the exchange of these three gases from varying ecosystems.

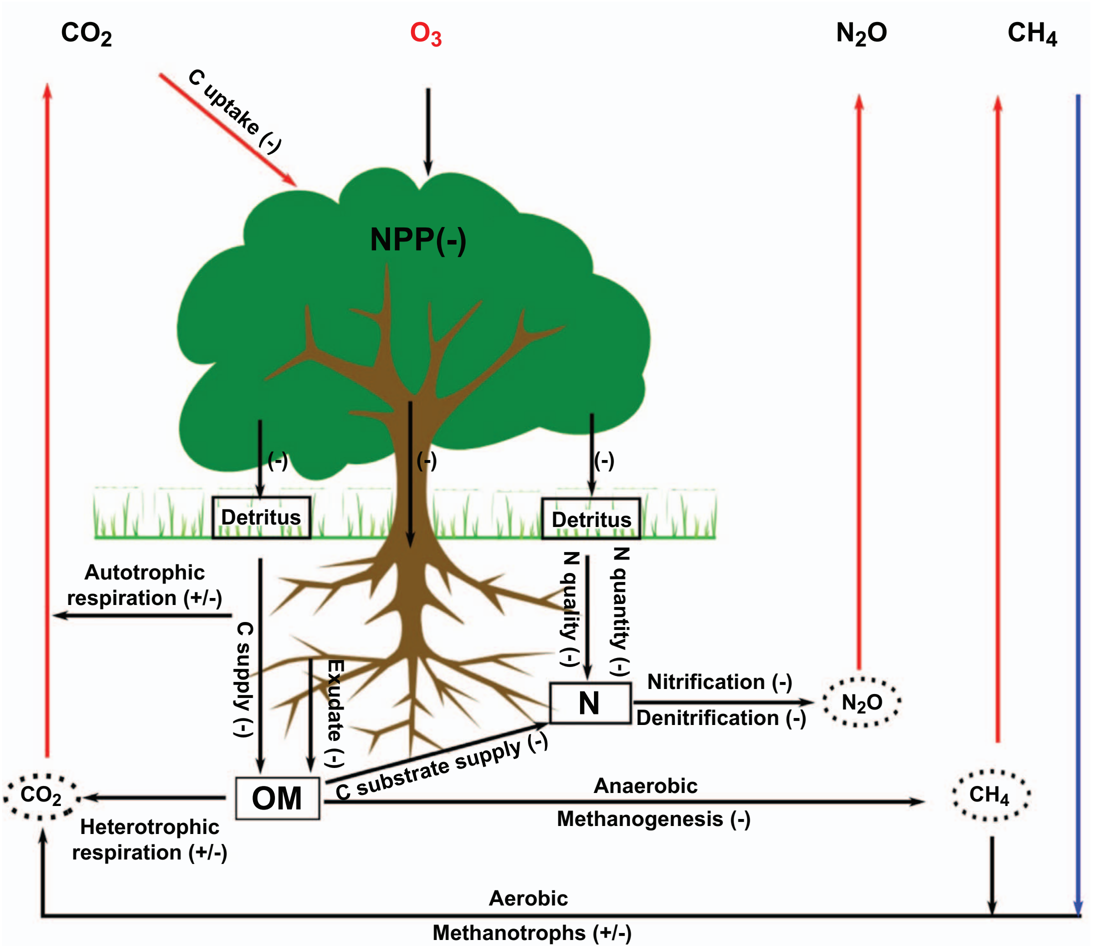

Figure 1. Schematic of processes by which O_3 influences GHG production and/or consumption. +/−signs denote positive and negative effect reported by different studies, respectively. The blue and red lines denote CH_4 consumption and emissions of CO_2, N_2O, and CH_4, respectively.

There are a myriad of mechanisms at different organizational levels by which the oxidizing capacity of O_3 affects terrestrial ecosystems. Ozone can directly depress photosynthesis by disturbing cellular biochemistry or indirectly by damaging stomatal function; in either case it alters carbon and water exchange (Ainsworth *et al* 2012). Ozone can also change secondary metabolism and tissue chemistry, which can affect carbon mineralization (Findlay *et al* 1996, Loya *et al* 2003, Valkama *et al* 2007). At the community level, O_3 exerts indirect effects on species composition through mediation of competitive relations (Wang *et al* 2016). Since O_3 does not penetrate soil (Blum and Tingey 1977), impacts on the processes responsible for the production and/or consumption of CO_2, CH_4, and N_2O in soils are mediated by these aboveground changes (figure 1). Changes in organic matter production, composition, and allocation, in turn, affect decomposition and carbon and nitrogen cycling, and alter rates of CO_2 and N_2O production and CH_4 production/consumption (Agathokleous *et al* 2016).

Independent empirical studies from different ecosystems around the world have been conducted to measure changes in the sources or sinks of GHGs in response to elevated O_3. These experiments feature different designs with regards to ecosystem type, fumigation method and duration, O_3 manipulation level, and other experimental factors (e.g. atmospheric CO_2 level). Such differences likely contribute to inconsistencies among different studies and complicate efforts to synthesize and interpret the results. Here, we conducted a meta-analysis (Hedges *et al* 1999, Gurevitch *et al* 2001) of the published literature to statistically synthesize and analyze all reported empirical findings and determine the sensitivity of CO_2, CH_4, and N_2O exchange between terrestrial ecosystems and the atmosphere to changes in O_3 pollution. These results allow for the first systematic assessment of the sensitivity in the budgets of GHGs to tropospheric O_3 concentration elevation that are based on empirical data.

2. Methods

2.1. Data collection

A search of published literature concerning O_3 influences on belowground processes was initially conducted in both the ISI Web of Science (Thomson Reuters, New York, NY, USA) and Google Scholar

(Google, Mountain View, CA, USA) with a range of search terms. Only those studies that reported results on soil respiration, CH_4 uptake/emission, and/or N_2O emission were selected. For example, the oft-cited study by Findlay *et al* (1996) examined litter decomposition, but was not included here because CO_2 emission values were not reported. Similarly, studies that only measured the respiration of soil surrounding roots or root respiration were not included. We did not include lab incubation studies, except for CH_4 uptake with a lack of field measurements. These three GHGs show seasonal variations in their fluxes that appear to be independent of O_3 impacts. Therefore, to avoid the potential variability and bias caused by a limited number of sampling dates, only those studies that repeatedly measured the fluxes at least one year (growing season) are included. In these cases, we either extracted the annual sum, or calculated the mean values for a whole year.

For effect size calculations, data including mean, standard deviation or standard error, and number of replicate for both control and treatment were extracted from text, tables, or graphs. The basic principles for data extraction from each individual study were as follows: To keep the independence of each observation, continuous observations within a single study were subjectively excluded to extract only one observation (i.e. the last year or growing season). However, different treatments (e.g. multiple manipulated levels of O_3, different plant community, and elevated CO_2 level) in one study were treated as independent observations (Gurevitch *et al* 2001), and thus were included. The papers with data presented only as graphs were digitized using Engauge Digitizer (http://digitizer.sourceforge.net/). In addition, the control and treatment O_3 level (ppb) were extracted either directly if reported or indirectly by converting the cumulative O_3 exposure measures (e.g. accumulative ozone exposure above a threshold of 0 and 40 ppb: AOT0 and AOT40). Categorical variables included ecosystem type (forest, cropland, rice paddy, grassland, and peat land), fumigation method (free air concentration enrichment—FACE and open top chambers—OTCs), fumigation duration, and CO_2 elevation. The categorical variables and the corresponding levels used by different response variables (soil respiration, CH_4 flux, and N_2O flux) depended on the data availability. The detailed information of these compiled data and the corresponding literature are listed in supporting information S1 available at stacks.iop.org/ERL/12/084001/mmedia.

2.2. Meta-analysis and meta-regression

First, the response ratio (RR) of O_3 elevation for each individual observation was calculated by response ratio:

$$\mathrm{RR} = \ln(X_\mathrm{t}/X_\mathrm{c}) \tag{1}$$

of which the sampling variance was computed by:

$$v = \frac{(SD_\mathrm{c})^2}{N_\mathrm{c}(X_\mathrm{c})^2} + \frac{(SD_\mathrm{t})^2}{N_\mathrm{t}(X_\mathrm{t})^2} \tag{2}$$

where X_c is the control mean, X_t is the treatment mean, SD_c is the control standard deviation, SD_t is the treatment standard deviation, N_c is the control replication number, and N_t is the treatment replication number.

The normalization of effect sizes under different O_3 manipulation levels to a same ΔO_3 followed a linear transformation procedure:

$$X_\mathrm{nt} = X_\mathrm{c} + \left(\frac{X_\mathrm{t} - X_\mathrm{c}}{\Delta O_3}\right)^* \Delta CO_3^* \tag{3}$$

where X_nt is the normalized value, X_c is the control mean, X_t is the treatment mean, ΔO_3 is the O_3 level difference between the treatment and control, and $\Delta O_3{}^*$ represents the O_3 level difference to which the effect sizes are normalized (i.e. a certain O_3 concentration interval between the current troposphere O_3 level and an elevated O_3 level: 10, 20, 30 and 40 ppb).

Meta-analysis of RR was performed by fitting to the random-effects model via the restricted maximum-likelihood (REML) method. The inverse-variance weighted mean of RRs and the standard error of the weighted mean were calculated. The detailed calculation procedures are fully described in references Hedges *et al* (1999) and Koricheva *et al* (2013). The unlogged mean RR and corresponding 95% confidence interval (CI) were further obtained. Percentage change due to elevated O_3 was calculated from the unlogged mean RR. The O_3 effect on a response variable was considered significant if the 95% CI did not overlap 1.

The meta-regression of RR with moderators was performed by fitting to the mixed-effects model via the REML method as well. An omnibus test with a chi-square distribution (Q_M) (Koricheva *et al* 2013) was conducted to show whether the moderator has a significant contribution to the total heterogeneity. For categorical moderator with a significant Q_M, the categorical group was subdivided and the inverse-variance weighted mean RR for each level was calculated. An omnibus test was further conducted, with a significance of Q_M indicating that the mean RR were different among the levels of this categorical moderator.

In addition, during the meta-analysis publication bias was tested by funnel plots (Jennions *et al* 2013), and Egger's regression test was further performed to test the plot asymmetry (Egger *et al* 1997). Q-Q normal plots were created to test whether the effect sizes fulfill the normality requirement (Wang and Bushman 1998). All calculation procedures described above were executed by R language using the 'metafor' package (Viechtbauer 2010).

2.3. Estimation of global GHG budget sensitivity

The meta-analysis results provide the average changes of each gas across the terrestrial ecosystems over the planet under a certain O_3 concentration interval between the current troposphere O_3 level and an elevated O_3 level (i.e. $\Delta O_3{}^*$ in ppb). We can give an approximate sensitivity estimate of the global GHG changes in response to this tropospheric O_3 level increase relative to today in a way as follows:

$$\Delta F = F_c^* \Delta A \tag{4}$$

where ΔF change (year^{-1}) represents the average change of each flux; F_c (year^{-1}) represents the strength of each flux under the current O_3 level; and ΔA (%), obtained from meta-analysis and dependent on O_3 level, denotes the average percentage change of each flux. The current strengths of the different fluxes are listed in table S1 in supporting information S2. It is noteworthy that the upscaling here has integrated the major ecosystem types, though still not yet a complete representation, across the land surface. This representativeness is much better than the previous global modelling studies that parameterized O_3 effects in global ecosystem models with strikingly limited O_3 response data. For example, in the study of O_3 impacts on global carbon cycling by Sitch *et al* (2007) O_3 response data for only a few European and North America species were extrapolated to represent all global vegetation types.

As for the determination of net flux of CO_2 into the atmosphere, our work only conducted a meta-analysis of soil respiration and thus the change in carbon uptake by terrestrial vegetation is necessary to complete the analysis. Previous meta-analysis of plant photosynthesis response to O_3 elevation for trees (Wittig *et al* 2007), wheat (Feng *et al* 2008), and soybeans (Morgan *et al* 2003), and studies comparing plants from multiple functional groups find a consistent 20% reduction (Reich and Amundson 1985, Volin *et al* 1998, Lombardozzi *et al* 2015). Moreover, the synthesis work by Lombardozzi *et al* (2013) did not find a significant correlation between photosynthesis response and O_3 level and agreed with the average 20% effect. Therefore, a constant 20% value is applied to constrain the global net primary productivity (NPP) to quantity the reduction of vegetation carbon uptake caused by different O_3 elevation levels. It is noteworthy that our meta-analysis of soil respiration also includes the autotrophic respiration by plant roots, which, however, is not included in the NPP term. This represents a small uncertainty. Note that for the CO_2 flux change a 50% reduction is further applied assuming 50% percent of the net accumulation of CO_2 from the terrestrial biosphere is sequestered by the ocean (Sabine *et al* 2004).

To describe the global GHG budget change, GWP (global warming potential) was used to calculate the GHG balance in units of CO_2 equivalents as follows:

$$\begin{aligned} \mathrm{GHG} = {} & \mathrm{F}_{\mathrm{CO_2-C}} * 44/12 + \mathrm{F}_{\mathrm{CH_4-C}} * 16/12 \\ & * \mathrm{GWP}_{\mathrm{CH_4}} + \mathrm{F}_{\mathrm{N_2O-N}} * 44/28 * \mathrm{GWP}_{\mathrm{N_2O}} \end{aligned} \tag{5}$$

where $\mathrm{F}_{\mathrm{CO_2}}-\mathrm{C}$, $\mathrm{F}_{\mathrm{CH_4}}-\mathrm{C}$, and $\mathrm{F}_{\mathrm{N_2}}\mathrm{O}-\mathrm{N}$ are annual changes of total soil CO_2 efflux, N_2O, and CH_4 as calculated by the above equation. The fractions 44/12, 16/12 and 44/28 were used to convert the mass of CO_2-C, CH_4-C and N_2O-N into CO_2, CH_4, and N_2O. $\mathrm{GWP}_{\mathrm{CH_4}}$ (Pg CO_2 equivalent (equiv.) per Pg CH_4) and $\mathrm{GWP}_{\mathrm{N2O}}$ (Pg CO_2 equiv. per Pg N_2O) are constants indicating integrated radiative forcing of CH_4 (28) and N_2O (265) in terms of a CO_2 equivalent unit over a period of 100 years (Ciais *et al* 2013).

3. Results

Collectively, 96 effect sizes (RRs) for soil respiration (CO_2 emission), N_2O emission, and CH_4 emission and uptake were compiled from peer-reviewed studies (supporting information S1). These studies were conducted in the Northern Hemisphere for ecosystems including forest, grassland, agricultural land, and peat land (figure S1 in supporting information S2). The data do not show publication bias based on funnel plots and Egger's tests (figure S2 supporting information S2) and fulfill the requirement of normality according to Q-Q plots (figure S3 in supporting information S2). Moreover, methodological differences, i.e. fumigation method and duration, among studies do not make a significant contribution to RR variability, with the exception of fumigation method for CH_4 emission (table S2 in supporting information S2). For these reasons, we conducted the analyses across the entire dataset.

Differing O_3 manipulation levels were adopted by different studies. We choose the absolute difference in experimental O_3 concentration between the treatment and control (hereafter referred to as ΔO_3) as a variable to describe the different studies. Meta-regressions between ΔO_3 and RR of different gases indicate that the RR of CO_2 and CH_4 (both emission and uptake) hold a significantly positive and negative linear relationship with ΔO_3, respectively, while the RR of N_2O is uncorrelated with ΔO_3 (figure 2). These results suggest that the magnitude of CO_2 and CH_4 responses depend on O_3 levels in the lower atmosphere. As for N_2O, based on limited data we can not exclude its dependence on O_3 levels. In this study, we temporarily treat N_2O response as being independent O_3 level. Therefore, to assess the sensitivity of terrestrial ecosystems in terms of GHG exchange to O_3 pressure, we test four ΔO_3 levels—10, 20, 30, and 40 ppb—to which RR were linearly normalized, except for N_2O. Meta-analyses were further conducted on these normalized RR.

First, GHGs from different ecosystems present differing sensitivities to changes in O_3 (table S3 in

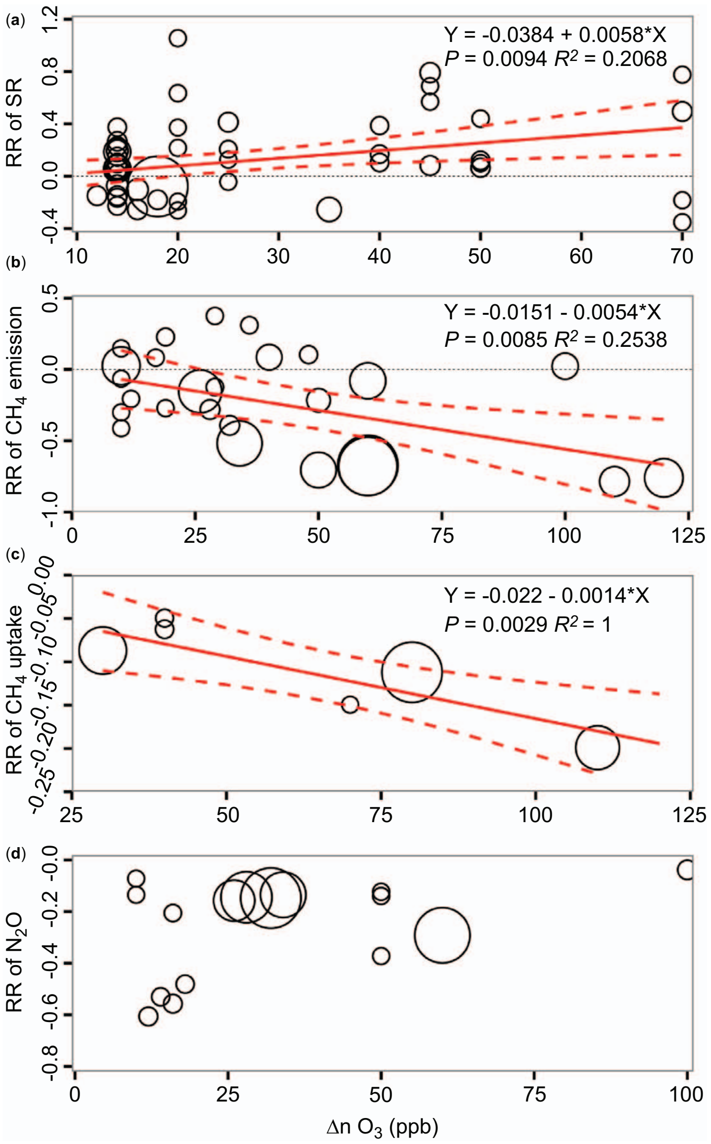

Figure 2. Meta-regression between RR and ΔO_3. (*a*)–(*d*) denote soil respiration, CH_4 emission, CH_4 uptake, and N_2O emission, respectively. The RR of N_2O is not statistically correlated with ΔO_3 (*d*). The size of the bubble is the relative weight of the RR in the random-effects meta-regression. Larger bubbles indicate study outcomes that contributed a greater overall weight in meta-regressions.

supporting information S2). The CO_2 effluxes from soils in both cropland and peat land, though with a similar magnitude, show a low sensitivity to increased O_3 (figure S4 in supporting information S2). By contrast, CO_2 effluxes from grassland soils display strong sensitivity to elevated O_3, with CO_2 flux diminished by from more than 10% (10 ppb) to more than 60% (20 ppb), and the forest shows a smaller but still significant response of 5% (10 ppb) to 30% (40 ppb) (figure S4 in supporting information S2). For CH_4 emissions, rice paddies present a significant reduction from almost 7% (10 ppb) to 25% (40 ppb), while the peat land does not show significant responses to O_3 elevation (figure S5 in supporting information S2). Similarly, O_3 enrichment shows a significantly different effect on the N_2O flux among the three ecosystems as well. Elevated O_3 results in a reduction of N_2O emissions by an average of 19% (statistically not significant), 16%, and 41% for cropland, rice paddies, and grassland, respectively (figure S6 in supporting information S2). Additionally, this meta-analysis indicates that O_3 and CO_2 elevations in combination have a larger influence on CO_2 and N_2O effluxes than O_3 alone (figures S4, S6 in supporting information S2). This may result from a carbon fertilization effect and associated protection of carbon fixation against elevated O_3 via stomatal closure (Sitch *et al* 2007, Valkama *et al* 2007).

Integrating the responses across these different ecosystems, we derived the average responses for each gas. For soil CO_2 efflux, the RR of CO_2 is positively correlated with O_3 level (figure 2(*a*)), but does not show a significant sensitivity to O_3 enrichment until ΔO_3 of 30 and 40 ppb, when soil respiration is stimulated by an average of about 12% and 15%, respectively (figure 3(*a*)). By contrast, CH_4 emissions are sensitive to O_3 across the full range of treatments, with an average of 6% (10 ppb), 11% (20 ppb), 14%

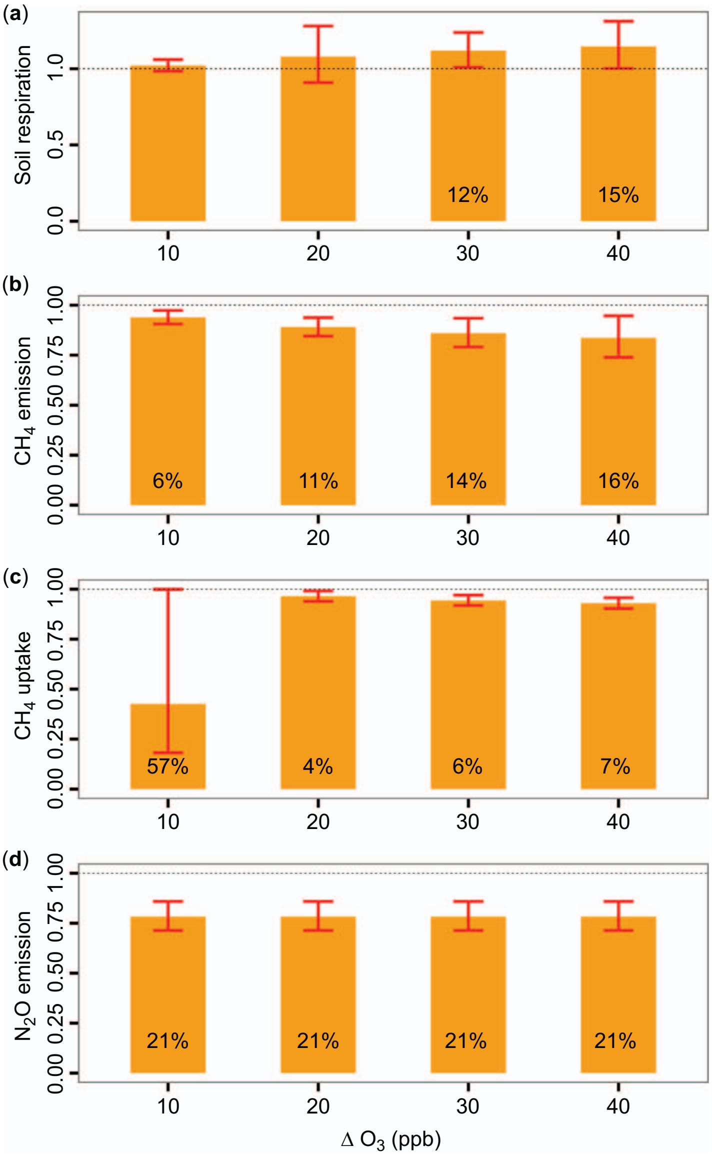

Figure 3. Meta-analysis of GHGs exchange across different ecosystems. (*a*)–(*d*) shows the meta-analysis results of soil respiration (*a*), CH_4 emission (*b*), CH_4 uptake (*c*), and N_2O emission (*d*) respectively, with mean and 95% confidence interval. The values are back-transformed from the RRs. The response is significant if the interval does not overlap 1(denoted by the dashed line). Values presented in this figure minus 1 multiplied by 100 correspond to the % change, with the negative and positive suggesting a decrease and an increase, respectively. Values listed on the bar are the mean of significant responses.

(30 ppb), and 16% (40 ppb) (figure 3(*b*)). Similarly, CH_4 uptake is sensitive to the dose of elevated O_3 with a large reduction seen initially but with low sensitivity to further increases in O_3 (figure 3(*c*)). Finally, the RR of N_2O emissions does not depend on O_3 manipulation level (figure 2(*d*)); elevated O_3 significantly decreases N_2O emission by an average of 22% regardless of the ΔO_3 level (figure 3(*d*)). Our meta-analysis suggests that the soil respiration of terrestrial ecosystems is rather insensitive to O_3 pressure, stimulating CO_2 release to the atmosphere only after large O_3 changes. These responses of CO_2, CH_4, and N_2O exchange occur primarily because of reduced carbon availability from inhibited photosynthesis and slower decomposition and nitrogen return from altered detritus quality (Findlay *et al* 1996, Andersen 2003, Grantz *et al* 2006, Kanerva *et al* 2006). However, it has also been postulated that O_3 pressure may stimulate mycorrhizal formation in fine roots and root nutrient acquisition and turnover (Scagel and Andersen 1997, Kasurinen *et al* 2004) or greater consumption of the carbon formed since the O_3 pressure because of changes in microbial activity and carbon quality (Loya *et al* 2003), which cause unsuppressed and even enhanced CO_2 efflux from soils.

Scaling up these average ecosystem-scale responses, we estimate the sensitivity of global budget of the three gases to enhanced O_3 (figure 4) As shown in figure 4(*a*), the contribution by suppressed N_2O flux to the global budget is consistently ~1.23 Pg CO_2 equiv. yr^{-1}. Increased O_3 of 10 and 20 ppb induce a decline of the current terrestrial natural CH_4 emission flux by an average of 6% and 11%, which contributes

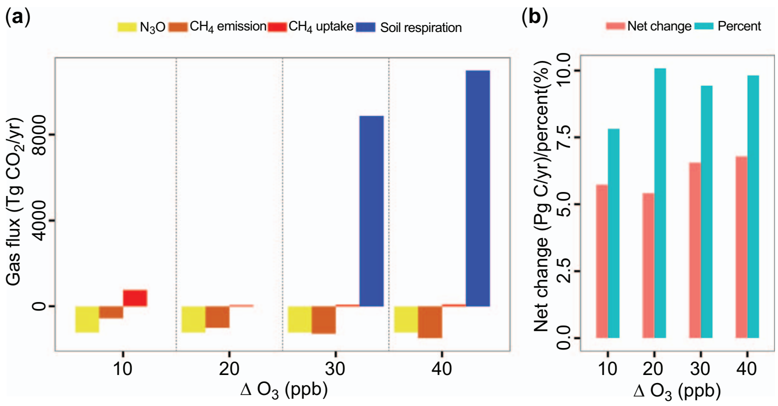

Figure 4. Sensitivity of global GHG budget change to O_3 change. (*a*) Shows the positive (enhanced soil respiration and suppressed CH_4 uptake) and negative contributions (suppressed N_2O and CH_4 emissions) to the atmospheric GHGs. (*b*) Shows the net global budget change and the percent of positive contributions offset by the negative contributions by accounting for the positive contribution from suppressed vegetation carbon uptake (that is, 22.0 Pg C yr^{-1}). All values are in CO_2 equiv. See table S4 in supporting information S2 for specific calculation and data source.

to a reduced balance of 0.6 and 1.0 Pg CO_2 equiv. yr^{-1}, while suppressed CH_4 uptake positively contributes 0.8 and 0.05 Pg CO_2 equiv. yr^{-1}. Global soil CO_2 efflux is insensitive to these small changes in O_3 ($\Delta O_3 = 10$ and 20 ppb). By contrast, in response to larger increases in O_3 ($\Delta O_3 = 30$ and 40 ppb) stimulated soil CO_2 emissions contribute an average of 4.4 and 5.5 Pg CO_2 yr^{-1}, respectively (figure 4(*a*)). At the same ΔO_3, suppressed CH_4 emissions contribute 1.3 and 1.5 Pg CO_2 equiv. yr^{-1}, while suppressed CH_4 uptake contributes only 0.07 and 0.09 Pg CO_2 equiv. yr^{-1} (figure 4(*a*)). This sensitivity analysis clearly shows that the soil system can be transformed from a sink into a source with O_3 level continuously increasing because of enhanced soil CO_2 emissions outweighing suppressed CH_4 and N_2O emissions. Taking into consideration O_3-suppressed CO_2 uptake by vegetation (which is about 44.0 Pg CO_2 yr^{-1}), plus the oceans' CO_2 sequestration, the O_3-induced net global GHGs budget change on average is approximately 21.0 (5.7), 19.8 (5.4), 24.0 (6.6) and 24.9 Pg CO_2 yr^{-1} (6.8 Pg C yr^{-1}) for the 10, 20, 30, and 40 ppb change in O_3, respectively (figure 4(*b*); table S4 in supporting information S2). These changes correspond to an annual increase of 12.73%, 12.00%, 14.55%, and 15.10% relative to the current net global budget (table S4 in supporting information S2). Additionally, under the four O_3 change levels the reduction in N_2O and CH_4 emissions offset at most about 10% of the O_3-induced net increase of CO_2 (figure 4(*b*)). Therefore, the sensitivity of terrestrial vegetation productivity to elevated O_3 predominate the global GHG budget change sensitivity.

4. Discussion

The overall exchange of GHGs between terrestrial ecosystems and the atmosphere is sensitive to tropospheric O_3 pollution, and significantly contributes to the atmospheric GHG accumulation. This matches the conclusion of a large buildup of CO_2 in the atmosphere derived from the modelling study by Sitch *et al* (2007), which, however, only considered the CO_2. For understanding the full range of interactions between the atmosphere and terrestrial processes, we need an integrative perspective (e.g. Tian *et al* 2016). Our results also suggest that suppressed CH_4 and N_2O emissions can offset a portion of the increased CO_2 emissions. This study clearly pinpoints the necessity for assessing surface-atmosphere exchange processes comprehensively in air quality–climate feedback analyses. Therefore, other possible feedback pathways mediated by biogenic volatile organic compounds (BVOCs) and soil nitrous oxides (NO_x) emissions should be investigated and fully incorporated into assessment of O_3–climate feedbacks (e.g. Hickman *et al* 2010).

It is important to note that these estimates of global GHG flux sensitivities come with uncertainties. First, GHGs from different ecosystems present differing sensitivities to changes in O_3 due to fundamental differences in vegetation composition. However, this study, as a pioneering work, integrates the different systems in an aggregate way, using the average responses disregarding the variations (though they are small relative to the sensitivities themselves). Moreover, uncertainties in the baseline estimates of the GHG fluxes will necessarily increase the magnitude of uncertainty of GHG fluxes sensitivity to O_3 exposure. Ecosystem-specific assessments are expected for future studies to tackle these uncertainties. A related question that should be addressed involves the impact of using different measures of O_3 dosage (e.g. AOT40 and O_3 flux) rather than O_3 concentration on estimates of ecosystem sensitivity. Second, the studied ecosystem types and independent observations that can be included in this meta-analysis are limited. For example, upland forest ecosystems generally act as a sink of CH_4 (e.g. Yavitt *et al* 1990), but no study is currently available of the O_3-sensitivities of these ecosystems. There is also a striking lack of experimental data from the Southern Hemisphere (figure S1 in supporting information S2). This problem is particularly important because many regions in the Southern Hemisphere are predicted to industrialize in the future, which could lead to higher O_3 levels in the vicinity of cities and hemisphere-wide. Clearly, more field measurements on CO_2, N_2O, and CH_4 fluxes around the world should be undertaken. Third, exchange of GHGs between the atmosphere and terrestrial ecosystems can be simultaneously influenced by other global change agents. To more fully and realistically evaluate O_3 impacts on GHGs, the combined impacts with other global change agents, e.g. nitrogen deposition and climate warming, need additional investigation.

5. Conclusion

By fully accounting for the three gases simultaneously, we find that with the O_3 level continuously increasing the whole soil system would be transformed from a sink into a source of GHGs. With an increase of O_3 concentration by 10 ppb, the global annual net atmospheric budgets would on average increase by ~12% (i.e. ~5 PgC yr^{-1}). However, in the global atmospheric budget suppressed CH_4 and N_2O emissions can offset a small portion (at most 10%) of the net CO_2 increase derived from changes in soil respiration and vegetation carbon fixation in terms of CO_2-equivalent. The sensitivity of global net GHGs budgets is still predominantly determined by the high sensitivity and thus a large magnitude of O_3-induced reduction in terrestrial vegetation carbon sequestration capability.

Natural systems with a high biodiversity, however, are increasingly suggested to be resilient to O_3 pressure. For example, the productivity and carbon stock of the temperate deciduous forest in the Eastern United States are shown to be unsuppressed by O_3 pressure (Wang *et al* 2016). The FACE study by Zak *et al* (2011), which included both O_3-tolerant and O_3-sensitive species or genotypes, also indicated unsuppressed net primary productivity after a long-term fumigation (11 years). Grassland ecosystems including temperate (Volk *et al* 2011), calcareous (Thwaites *et al* 2006), and alpine types (Bassin *et al* 2007) have also shown that the productivity is insensitive to elevated O_3. Hence, we postulate that the indirect role of O_3 (that is via altering the land–atmosphere exchange) on the Earth's radiative balance might be most significant on those managed systems that are of low diversity, e.g. agricultural and forest plantation systems. This means agricultural production practices would play a key role in mitigating O_3's indirect effects on global climate, reinforcing the conclusion that adoption of best practices in human-impacted ecosystems could mitigate climate change (Paustian *et al* 2016, Tian *et al* 2016).

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