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How does elevated ozone reduce methane emissions from peatlands?

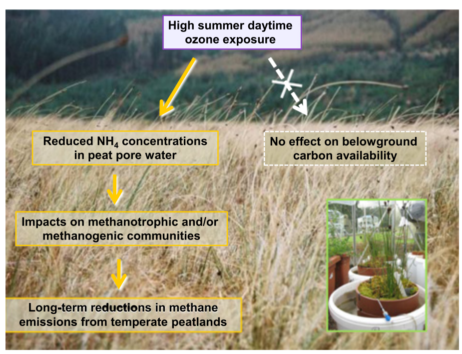
Sylvia Toet [a,⁎], Viktoria Oliver [a,1], Phil Ineson [b], Sophie McLoughlin [a], Thorunn Helgason [b], Simon Peacock [c,2], Andrew W. Stott [d], Jeremy Barnes [c], Mike Ashmore [e]

[a] Environment Department, University of York, York YO10 5NG, UK
[b] Department of Biology, University of York, York YO10 5DD, UK
[c] School of Biology, Newcastle University, Newcastle upon Tyne NE1 7RU, UK
[d] Natural Environment Research Council Life Sciences Mass Spectrometry Facility, Centre for Ecology and Hydrology, Lancaster LA1 4AP, UK
[e] Stockholm Environment Institute, University of York, York YO10 5NG, UK

HIGHLIGHTS

- Effects of ozone on methane emissions, and mechanisms involved, are uncertain.
- We exposed peatland mesocosms to ozone for 2.5 years in open-top chambers.
- Elevated daytime summer, but not annual mean, ozone reduced methane emissions.
- Elevated ozone did, unexpectedly, not affect plant-derived carbon inputs.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of increased tropospheric ozone (O_3) pollution levels on methane (CH_4) emissions from peatlands, and their underlying mechanisms, remain unclear. In this study, we exposed peatland mesocosms from a temperate wet heath dominated by the sedge *Schoenus nigricans* and *Sphagnum papillosum* to four O_3 treatments in open-top chambers for 2.5 years, to investigate the O_3 impacts on CH_4 emissions and the processes that underpin these responses. Summer CH_4 emissions, were significantly reduced, by 27% over the experiment, due to summer daytime (8 h day^{-1}) O_3 exposure to non-filtered air (NFA) plus 35 ppb O_3, but were not significantly affected by year-round, 24 h day^{-1}, exposure to NFA plus 10 ppb or NFA plus 25 ppb O_3. There was no evidence that the reduced CH_4 emissions in response to elevated summer O_3 exposure were caused by reduced plant-derived carbon availability below-ground, because we found no significant effect of high summer O_3 exposure on root biomass, pore water dissolved organic carbon concentrations or the contribution of recent photosynthate to CH_4 emissions. Our CH_4 production potential and CH_4 oxidation potential measurements in the different O_3 treatments could also not explain the observed CH_4 emission responses to O_3. However, pore water ammonium concentrations at 20 cm depth were consistently reduced during the experiment by elevated summer O_3 exposure, and strong positive correlations were observed between CH_4 emission and pore water ammonium concentration at three peat depths over the 2.5-year study. Our results therefore imply that elevated regional O_3 exposures in summer, but not the small increases in northern hemisphere annual mean background O_3

⁎ Corresponding author.
E-mail address: sylvia.toet@york.ac.uk (S. Toet).
[1] Present address: The School of Biological Sciences, Aberdeen AB24 2TZ, UK.
[2] Present address: School of Agriculture, Food and Rural Development, Newcastle University, NE1 7RU, UK.

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concentrations predicted over this century, may lead to reduced CH_4 emissions from temperate peatlands as a consequence of reductions in soil inorganic nitrogen affecting methanogenic and/or methanotrophic activity.

1. Introduction

Tropospheric ozone (O_3) and methane (CH_4) are the second and third most important contributors to the human-induced greenhouse effect after carbon dioxide (IPCC, 2013). The concentrations of both gases in the background troposphere increased over the last century and, without strong emission control, are predicted to increase further during the 21st century (Dentener et al., 2006; Royal Society, 2008; Wild et al., 2012). Recently, increased attention has been paid to the importance of measures to control atmospheric O_3 and CH_4 concentrations, because of their relatively short atmospheric lifetimes compared to CO_2 (Shindell et al., 2012). There are also important feedbacks between these two gases, since CH_4 emissions have contributed significantly to increases in global background O_3 concentrations (West and Fiore, 2005).

Ozone is also the most important gaseous air pollutant globally in terms of effects on ecosystem production and function (Ashmore, 2005) and northern hemisphere background levels of O_3 already exceed those at which significant effects on wild plant communities, crop yields and forest productivity can occur (Davison and Barnes, 1998; Avnery et al., 2011; Ainsworth et al., 2012). Global modelling of O_3 effects on CO_2 uptake and sequestration suggest that these indirect effects may be as important as the direct effects of O_3 on radiative forcing (Sitch et al., 2007). However, these simulations do not consider the possibility that O_3 may affect CH_4 fluxes from managed and unmanaged wetlands. Methane emissions from natural wetlands may have contributed significantly to recent increases in global CH_4 levels (Kirschke et al., 2013), whilst predicted future releases of CH_4 from Arctic permafrost thawing could be large enough to substantially increase tropospheric O_3 levels (Isaksen et al., 2014).

We have previously reported (Toet et al., 2011) that exposure to environmentally-relevant levels of elevated O_3 in the daytime decreased summer CH_4 emissions from temperate peatland mesocosms by ca. 25%. In contrast, Mörsky et al. (2008) reported that open-field exposure of boreal peatland microcosms to a similar increase in O_3 concentration in Central Finland only caused a decrease in CH_4 emission at the end of the first growing season, which was lost in the three subsequent growing seasons. Recently, Willamson et al. (2016) reported both increases and decreases in CH_4 emissions from temperate upland bog mesocosms in response to increasing background O_3 exposures in a short-term summer experiment. Studies on rice paddies, all also elevating O_3 concentrations for 7-8 h in the daytime in summer, have demonstrated that CH_4 emissions were reduced in response to the pollutant (e.g. Bhatia et al., 2011; Zheng et al., 2011), but not in all cases (Kou et al., 2015). However, none of these previous peatland or paddy studies have explored the impacts of the small year-round increases in 24 h mean background O_3 concentrations that are now affecting many areas of the northern hemisphere (Royal Society, 2008), which may be significant since substantial CH_4 emissions to the atmosphere have been reported in winter from boreal bogs and fens (e.g. Alm et al., 1999). Therefore, there is a need to assess year-round, long-term effects of elevated background annual mean O_3 concentrations on CH_4 emissions, as well as simply for summer peak exposures.

Furthermore, the mechanistic basis of any effects of O_3 on CH_4 emissions remains uncertain. It is unlikely to be related to direct effects of O_3 on microbial populations below-ground, because ^{18}O labelling studies have shown that O_3 penetration into the soil is limited to the top few mm, especially in wet soils (Toet et al., 2009). Consequently, O_3 effects on microbial activity are more likely to be indirectly controlled by processes mediated through vascular plants. Although O_3 has been reported to have little effect on above-ground biomass of peatland vegetation (Mörsky et al., 2011; Toet et al., 2011; Willamson et al., 2016), allocation of vascular plant biomass into below-ground components may be reduced (Ashmore, 2005), leading to reductions in substrate availability for methanogens. The potential for such effects was shown by Jones et al. (2009), who found a rapid decrease in dissolved organic carbon (DOC) concentrations in fen mesocosms after O_3 exposure, with a change in molecular composition of DOC indicating a switch in the substrate for micro-organisms from root-derived carbon (C) to soil C; similar effects were not found in mesocosms dominated by *Sphagnum* moss. Such indirect effects of elevated O_3 in peatlands might be expected to affect CH_4 production, although both Rinnan et al. (2003) and Mörsky et al. (2008) reported that elevated O_3 had no significant effect on CH_4 production potential.

Elevated O_3 could also reduce CH_4 emissions indirectly by impacts on N cycling. This may be through reduced litter quantity or quality, although effects of O_3 on nitrification, denitrification, microbial biomass and plant uptake of N have also been reported (Wittig et al., 2009; Li et al., 2010; Bhatia et al., 2011; Pereira et al., 2011; Bassin et al., 2015). In nitrogen (N) poor systems such as peatlands, reduced below-ground allocation of N could cause reduced activity of heterotrophic soil micro-organisms, such as methanogens (Kanerva et al., 2007). However, lower availability of ammonium (NH_4), the dominant form of inorganic N in peatlands, could also promote methanotrophic activity (Keller et al., 2006), and O_3 has been reported to reduce soil NH_4 concentrations in meadows (Kanerva et al., 2006) and soybean crops (Pereira et al., 2011). A direct adverse effect of O_3 on methanotrophs in the top layers of the moss cover of peatlands may also play a role, with Raghoebarsing et al. (2005) showing CH_4 consumption by *Sphagnum* plants through partly-endophytic methanotrophs in hyaline cells and on stem leaves.

We report here results from a peatland mesocosm study carried out over 2.5 years in open top chambers (OTCs), with two major aims. The first was to test the hypothesis that increases in global background O_3 concentrations, as well as elevated O_3 exposure during summertime, may reduce CH_4 emissions from peatlands. Our second aim was to identify the mechanistic basis for any observed effects of elevated O_3 concentrations on CH_4 emissions, paying specific attention to the following hypotheses:

1. Elevated O_3 reduces plant C allocation below-ground, whilst not affecting overall above-ground plant productivity
2. Elevated O_3 reduces the contribution of recent photosynthate to CH_4 emission
3. Elevated O_3 reduces CH_4 production potentials
4. Elevated O_3 decreases aerobic CH_4 oxidation potentials associated with the top peat layer (including living *Sphagnum* moss)
5. Elevated O_3 increases the aerobic CH_4 oxidation potentials deeper down the peat profile due to reduced pore water NH_4 concentrations.

2. Materials and methods

2.1. Experimental design

Mesocosms were collected from the wetter parts of a wet heath in the south western part of the Isle of Skye, Scotland (NGR: SV409227, latitude 57°13′ N, longitude 6°18′ W, 16 m a.s.l.) where annual average air temperature was 6.6 °C and annual average precipitation 2825 mm over the period 1981–2010. The vegetation was dominated by the peat moss *Sphagnum papillosum* and the sedge *Schoenus nigricans*, with *Erica tetralix*, *Molinea caerulea* and *Narthecium ossifragum* regularly present