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1 How do increasing background concentrations of tropospheric ozone affect peatland
2 plant growth and carbon gas exchange?

3

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10

11 Abstract

12

13 In this study we have demonstrated that plants originating from upland peat bogs are
14 sensitive to increasing background concentrations of ozone. Peatland mesocosms
15 from an upland peat bog in North Wales, UK were exposed to eight levels of elevated
16 background ozone in solardomes for 4 months from May to August, with 24 hour
17 mean ozone concentrations ranging from 16 to 94 ppb and cumulative AOT_{024hr}
18 ranging from 45.98 ppmh to 259.63 ppmh. Our results show that plant senescence
19 increased with increasing exposure to ozone, although there was no significant effect
20 of increasing ozone on plant biomass. Assessments of carbon dioxide and methane
21 fluxes from the mesocosms suggests that there was no change in carbon dioxide
22 fluxes over the 4 month exposure period but that methane fluxes increased as
23 cumulative ozone exposure increased to a maximum AOT_{024hr} of approximately 120
24 ppm h and then decreased as cumulative ozone exposure increased further.

25

26 Key words: tropospheric ozone; methane; peatlands; wetlands; senescence

27

28 Highlights

- 29 • Peatland plant senescence is increased by season-long exposure to elevated
30 ozone but above and below ground plant biomass is not significantly affected.
- 31 • Methane emissions increase at low to moderate cumulative ozone exposure
32 but decrease as cumulative ozone exposure increases further.
- 33 • Dissolved organic carbon in the peat pore water and carbon dioxide exchange
34 are not significantly affected by increasing background ozone concentrations.

35

36 Introduction

37 Peat-forming wetlands are an important carbon storage ecosystem with global estimates
38 of carbon sequestration in the region of 20-30 gCm⁻²yr⁻¹ (Wieder, 2001). Carbon
39 dioxide is taken up by vascular plants and mosses during photosynthesis and, although
40 some is released back to the environment during plant respiration, the remainder is
41 stored in plant tissue or transported through the plant and released as exudates of
42 dissolved organic material (Schutz et al., 1991). Once the plants die, the carbon in their
43 tissues is not broken down and released to the atmosphere as peatland decomposition
44 rates are low so the plant material is laid down as peat. The low molecular weight
45 exudates such as sugars and amino acids form an energy source for bacteria and archaea
46 living in the peatland and their metabolism contributes to the carbon dioxide release
47 and to the release of methane. The dissolved carbon in the pore water can be exported
48 out of the peatland in streams and this can be an important loss point for carbon in the
49 peatland carbon cycle. The majority of peat-forming wetlands in northern Europe are
50 in upland areas where ozone concentrations are higher than adjacent low-lying areas
51 (Royal Society, 2008), and thus any changes that affect plant growth and carbon gas
52 exchange have the potential to affect carbon storage within peatlands.

53 Annual mean tropospheric ozone concentrations in Northern Europe are currently in
54 the region of 30-35 ppb, having increased from less than 20 ppb in the mid-20th century.
55 Although there has been little change in mean concentrations in the past decade
56 (Hartmann *et al.*, 2014), climate change and hemispheric transport of pollutants may
57 affect future ozone levels. One future scenario predicts that background ozone
58 concentrations in Northern Europe will continue to increase during the 21st century due
59 to hemispheric transport of ozone precursor molecules (Royal Society 2008).

60 Tropospheric ozone is a phytotoxic pollutant and wetland vascular plants have been
61 found to be relatively sensitive to elevated ozone concentrations (Franzaring *et al.*,
62 2000, Power & Ashmore, 2002, Williamson *et al.*, 2010) with symptoms including
63 premature senescence, reductions in photosynthesis and reduced biomass. However,
64 *Sphagnum* mosses have been shown to be relatively tolerant to elevated ozone
65 concentrations (Rinnan 2003) during both short term acute ozone fumigation (Potter *et*
66 *al.*, 1996a) and during longer term exposure with only *Sphagnum recurvum* showing a
67 reduction in shoot growth under elevated ozone (Potter *et al.*, 1996b).

68 Carbon dioxide uptake in wetland mesocosms takes place during photosynthesis and,
69 if plant growth is reduced by increasing background ozone, it may be expected that
70 carbon dioxide uptake would be reduced. Increasing tropospheric ozone
71 concentrations during short-term exposure was found to transiently increase the rate
72 of dark respiration (Niemi *et al.*, 2002, Rinnan *et al.*, 2003), possibly as a result of the
73 plants repairing ozone damaged tissues. Under a doubling in ambient ozone
74 concentrations Haapala *et al.*, (2011) showed that photosynthesis was reduced during
75 the first year of a four year exposure period but during the fourth year both
76 photosynthesis and total respiration showed a tendency to be higher than under
77 ambient conditions.

78 As wetland plants play a major role in methane emission from wetlands it is possible
79 that any damage to wetland plant functioning by ozone could have a secondary effect
80 on these. Two possible routes via which methane emissions are affected by plant
81 growth are: through the provision of a conduit for gas exchange via the aerenchyma
82 (Chanton et al., 1997; Ding et al., 2005; Greenup et al., 2000; Thomas et al., 1996)
83 and the exudation of low molecular weight compounds to provide an energy source
84 for microbes (Schutz et al., 1991). A range of wetland adapted species demonstrate
85 active pressurised gas flow from the leaves to the roots to allowed continued oxygen
86 supply in waterlogged soils, whereby air is forced downwards through the
87 aerenchyma as a result of the pressure generated through the gradient in temperature
88 and water vapour pressure. The return flow of gas is through the older leaves of the
89 plants as they are unable to support the pressure gradients required to force air down
90 into the roots (Mitsch and Gosselink 2000). Ozone-induced increased senescence
91 could increase the available pathways for gas release and hence the flow of methane
92 between the substrate and the atmosphere. Previous studies have shown that recently
93 fixed photosynthate is preferentially retained in leaves rather than transported through
94 the plant (Andersen, 2003; Grantz and Farrar, 1999, 2000), which could lead to a
95 reduction in root exudates meaning that there would be less energy available for
96 methanogens.

97 Previous published research on the effect of elevated ozone on methane emissions
98 from peatlands ranged from showing an increase when mesocosms were exposed to
99 100ppb ozone (Niemi *et al.*, 2002), a non-significant increase after 50 days exposure
100 to 200ppb ozone (Rinnan *et al.*, 2003), a transient decrease at ozone concentrations
101 double the current ambient (Morsky *et al.*, 2008) to a significant decrease in methane
102 emissions during the growing seasons of a two year exposure period (Toet *et al.*,

103 2011). A previous study investigating the impacts of elevated background ozone
104 using open top chambers showed that seasonal exposure of meadow mesocosms to
105 elevated ozone over a three year period did not change methane fluxes (Kanerva *et*
106 *al.*, 2007).
107 Here, we have studied the effects of increasing background ozone concentrations on
108 plant senescence, plant growth and carbon gas exchange in peatlands, an ecosystem
109 recognised as having the potential to exert profound changes to the planet's climate
110 through the storage of carbon and the emission of methane (Bridgham *et al.*, 2013,
111 Freeman *et al.*, 2001). By using a wide range of ozone treatments, we hoped to
112 increase our understanding of tropospheric ozone effects on plant growth and carbon
113 gas exchange from peatlands and shed some light on the conflicting results found in
114 other studies.

115

116 Materials and Methods

117 Ozone exposure:

118 Forty-eight mesocosms (diameter 16cm, depth 40cm) were collected from the
119 Migneint, a large area of oligotrophic, blanket bog in North Wales, UK (3°48.8' W,
120 52°59.6' N) dominated by the NVC vegetation type M6 (*Carex echinata-Sphagnum*
121 *recurvum/auriculatum* mire) (Buckton & Ormerod, 1997), following the method of
122 Freeman *et al.*, (1993) and exposed to ozone in specially constructed greenhouses
123 (solardomes), with 6 replicate mesocosms per ozone treatment. Mesocosms were
124 selected to ensure as uniform as possible vegetation cover, with the vascular plants
125 being *Juncus effusus* and *Carex echinata*. *Sphagnum* mosses were not identified to
126 species level but the majority of the *Sphagnum* present in the area sampled was
127 *Sphagnum fallax*. The water table was maintained within 2cm of the surface of the

128 mesocosms throughout the exposure period.

129 The solardome facility consists of eight hemispherical glass domes, 3 m in diameter
130 and 2 m tall, situated on an East-West line to minimise differences in shading as used
131 in previous experiments including: Hayes et al (2015), Hayes et al (2011), and Mills et
132 al (2009). Ozone was generated by passing oxygen (from a Workhorse 8 oxygen
133 generator, Ozone Industries Ltd.) through a G11 ozone generator (Ozone Industries
134 Ltd.). A computer-controlled (Lab-VIEW version 7) mass-flow controller system was
135 used to deliver ozone to the solardomes, where it was mixed with charcoal filtered air
136 and the fan system ensured two complete air changes per minute. The ozone
137 concentration in the centre of each of the solardomes was measured on a 30 minute
138 cycle by two API400 ozone analysers (Envirotech) with matched calibrations. Ozone
139 concentrations in one solardome were continually sampled to provide a feedback
140 system using a Model 49C ozone analyser (Thermo Electron) and the ozone supply to
141 all domes was adjusted accordingly.

142 The ozone profile used in the solardomes was based on concentrations measured at
143 the Snowdonia ozone monitoring site at Marchlyn Mawr, Wales, UK(4°03.4' W,
144 53°08.2' N) during a typical week with no marked ozone episodes but relatively high
145 background ozone: 31st May – 6th June 2006 (AA treatment) and with incremental
146 starting points. The target treatments consisted of a sub-ambient treatment (AA-20
147 ppb), a simulated ambient treatment (AA) and six treatments with increasing
148 background ozone (AA+12 ppb, AA+24 ppb, AA+36 ppb, AA+48 ppb, AA+60 ppb
149 and AA+72 ppb). These were applied as a continuous, repeated, weekly regime
150 designed to simulate increased background ozone concentrations. The exposure
151 period within the solardomes was from 9th May 2008 -2nd September 2008.

152

153 Gas and water sampling and analysis:

154 Gas exchange samples were taken fortnightly by placing a two litre transparent,
155 plastic chamber over the mesocosms and attaching with a rubber seal between the
156 headspace and the outer casing of the mesocosm to ensure that the soil structure was
157 not disturbed by the attachment of the chamber. A 30ml sample of the background
158 gas was taken at the moment of capping and a second sample of the gas within the
159 chamber was taken after one hour. The accumulation of methane and carbon dioxide
160 within the chamber was found to be linear over this time period when measured in a
161 preliminary experiment prior to the mesocosms being placed in the solardomes. Gas
162 samples were stored under positive pressure in airtight glass vials (Perkin Elmer) that
163 were evacuated prior to use and analysed within 24 hours of sample collection. Gas
164 samples were analysed for the concentration of methane and carbon dioxide using a
165 Perkin Elmer Gas Chromatograph (GC) fitted with a flame ionisation detector (FID)
166 to detect methane and a methaniser to convert carbon dioxide to methane. Gas
167 samples were pressurised with a known amount of nitrogen in the headspace
168 autosampler (Turbo-Matrix) and samples were injected into the GC at 23.2psi with
169 nitrogen carrier gas. Samples were passed through a Poropak QS ceramic column,
170 hydrogen flow was set at 45ml min^{-1} and airflow was set to 450 ml min^{-1} . The FID
171 (flame ionisation detector) temperature was 375°C .

172 Pore water samples were taken at three weekly intervals from the wetland mesocosms.
173 Samples were filtered through a $0.45\mu\text{m}$ cellulose acetate filter immediately following
174 collection. Total dissolved carbon was measured using a ThermaloxTM elemental
175 analyser. Samples were injected over a platinum-coated, mesh catalyst. Oxygen was
176 used as the carrier gas and thermal catalytic oxidation was used to oxidise carbon
177 compounds in the sample to carbon dioxide, which was detected and measured using

178 a non-dispersive infra-red detector.

179

180 Plant Growth:

181 During the growing season visible senescence on vascular plants growing in the
182 mesocosms was assessed at two week intervals. Vascular plant leaves were counted
183 as senesced if more than 25% of an individual leaf had died back and the percentage
184 of the entire plant that was senesced was calculated.

185 Above and below ground vascular plant and moss biomass present in the mesocosms
186 was measured following 16 weeks of ozone exposure. Plant biomass was harvested
187 and dried to constant mass at 65°C.

188

189 Statistical analysis:

190 Relationships between ozone exposure, plant senescence, plant biomass and methane
191 emissions were analysed using regression analysis in R v 2.14.2. Ozone exposure is
192 reported as accumulated hourly mean ozone concentration over 24 hours without a
193 threshold ozone concentration (AOT_{024hr}). This measure incorporated the effects of
194 elevated ozone throughout the night, rather than daylight hours as is more usually
195 used. It also included the potential effects of ozone in treatments that were below 40
196 ppb, which would be omitted if the more commonly used parameter AOT₄₀ had been
197 calculated. Use of AOT_{024hr} also allowed the cumulative effect of ozone to be
198 assessed, irrespective of the time scale of ozone exposure. Gas exchange and
199 senescence measurements are plotted grouped by cumulative ozone exposure; dome
200 mean values for senescence, carbon dioxide and methane fluxes measured through the
201 4 month ozone exposure were ordered by cumulative ozone dose and averaged by
202 each 20 ppm h increase in ozone exposure.

203

204 Results

205 Seasonal mean ozone concentrations ranged from 16 ppb in the lowest ozone
206 treatment to 94 ppb in the highest treatment, while AOT_{024hr} and daylight AOT₄₀
207 ranged from 45 to 260 ppm h and 0 to 73 ppm h respectively (Table 1).

208

209 Vascular plant species emerging or germinating in the mesocosms consisted of *Juncus*
210 *effusus*, *Carex echinata* and small quantities of *Poa triviata*. Although each
211 mesocosm did not have the same number of plants per species, there was no
212 significant difference in the species present across the eight ozone treatments. Using
213 combined data from all ozone treatments and assessments, vascular plant senescence
214 on the species growing in the mesocosms showed a positive relationship ($P < 0.05$)
215 with increasing AOT_{024hr} (Figure 1a), indicating senescence increased to a greater
216 extent in the mesocosms exposed to higher doses of background ozone. Elevated
217 background ozone over the 16 week period caused an increase in the percentage of
218 senesced vascular plant material from 5% in the lowest exposure to 25% in the
219 highest accumulated ozone exposure. There were no significant differences in
220 senescence seen in the individual vascular plant species present in the mesocosms so
221 senescence data was pooled across all vascular plant species for analysis and
222 presentation. After 16 weeks of ozone exposure there was a significant relationship
223 between ozone exposure and senescence, with the mesocosms exposed to higher
224 ozone showing higher vascular plant senescence (Figure 1b). In contrast, there was
225 no significant effect of ozone on vascular plant cover, above or below ground vascular
226 plant biomass (for all biomass combined and for individual species present in each
227 mesocosm) or *Sphagnum* spp. moss biomass (Table 2).

228 Methane fluxes showed an inverse polynomial relationship with accumulated ozone
229 exposure. At low to moderate AOT_{024hr} values (ranging from 0 – 120 ppm h)
230 methane fluxes increased as accumulated ozone exposure increased, whereas from
231 AOT_{024 hr} values of 120 ppm h to 220 ppm h methane fluxes decreased as AOT_{024hr}
232 values increased (Figure 2). When methane fluxes after 16 weeks of ozone exposure
233 were correlated with vascular plant senescence, vascular plant biomass and moss
234 biomass there was no correlation between methane fluxes and above or below
235 vascular plant biomass, vascular plant cover or moss biomass (Table 3). However,
236 there was a trend towards a significant correlation ($P = 0.08$) between vascular plant
237 senescence and methane fluxes (Table 3). Carbon dioxide fluxes did not show a
238 statistically significant change with increasing exposure to ozone and showed high
239 levels of variability within mesocosms exposed to similar levels of ozone, though
240 mesocosms showed a net uptake of carbon dioxide throughout the exposure period
241 (data not presented).

242 Dissolved organic carbon within the pore waters of the wetland mesocosms showed
243 no relationship with increasing exposure to elevated background ozone, remaining
244 unchanged over time and as ozone exposure increased (data not presented).

245

246 Discussion

247 This experiment has shown that elevating the background ozone throughout the
248 growing season increases vascular plant senescence and changes methane fluxes from
249 wetlands, although plant biomass, carbon dioxide fluxes and dissolved organic carbon
250 concentrations were unchanged.

251

252 The increase in vascular plant senescence caused by exposure to elevated ozone
253 agrees with published results showing that wetland plants were sensitive to mean
254 daily peak concentrations of ozone of 77 ppb, 80 ppb and 150 ppb respectively
255 (Franzaring *et al.*, 2000, Power & Ashmore, 2002, Williamson *et al.*, 2010). In this
256 study the linear relationship between AOT_{024 hr} indicates that vascular plants exposed
257 to lower concentrations of ozone for a longer time period showed similar levels of
258 senescence to those exposed to higher ozone concentrations for shorter time periods at
259 any given value of AOT_{024 hr}. This suggests that a growing season with moderately
260 high background tropospheric ozone could be as detrimental to plant health as one
261 where there are a small number of high peaks in tropospheric ozone.

262 Above and below ground vascular plant biomass was unaffected by increasing
263 exposure to ozone, a finding that agrees with published results from Toet *et al.* (2011)
264 who found that vascular plant biomass in wetland mesocosms was unaffected by two
265 years exposure to elevated ozone. However, this is in contrast to studies on other
266 semi-natural vegetation types where increasing ozone exposure reduced vascular plant
267 biomass with examples from grasslands (Barbo *et al.*, 1998; Hayes *et al.*, 2006; Ramo
268 *et al.*, 2006; Ramo *et al.*, 2007) and trees (Paakkonen *et al.*, 1996; Saleem *et al.*, 2001).
269 Similarly to the vascular plants in this study *Sphagnum* moss biomass was unaffected
270 by elevated ozone exposure, which agrees with previous studies showing that the
271 majority of *Sphagnum* species are relatively tolerant to ozone (Morsky *et al.*, 2011,
272 Toet *et al.*, 2011). In addition, as carbon dioxide fluxes were unchanged by increasing
273 ozone exposure, this suggests that ozone exposure does not have a significant impact
274 on wetland plant photosynthesis and respiration.

275 Methane emissions increased with increasing AOT_{024hr} to a maximum at
276 approximately 120 ppm h and then decreased as AOT_{024hr} continued to increase. It is

277 possible that effects of ozone on methane fluxes seen in published papers, ranging
278 from large increases through to decreases in methane emissions, are due to differences
279 in cumulative ozone exposure between experiments taking into account the ambient
280 ozone concentrations at the experimental sites used. The results of Lloyd (2004)
281 showed large increases in methane emission but the cumulative ozone exposure of the
282 highest treatment was an AOT0_{24hr} of 120 ppm h which coincides with the peak in
283 methane emissions shown in this experiment. The positive effects of ozone on
284 methane emissions shown by Niemi *et al.*, (2002) occurred at an estimated cumulative
285 ozone exposure of up to 48.8 ppm h in their highest ozone treatment, which, when
286 compared with an AOT0_{24hr} of 9.7 ppm h in their control exposure would be in the
287 range of the results in this experiment that show an increase in methane. The results
288 of Morsky *et al.*, (2008) and Toet *et al.*, (2011), showing a decrease in methane
289 emissions after exposing peatland mesocosms to increases in ozone above current
290 ambient concentrations of tropospheric ozone, potentially coincided with the
291 decreasing methane phase of the relationship found in our experiment. Using ozone
292 concentrations measured at the Snowdonia ozone monitoring site at Marchlyn Mawr
293 over a four month summer growing season the average ozone exposure (AOT0_{24hr})
294 between 2006 and 2010 was 101 ppm h, a value that is close to the ozone exposure
295 corresponding to the highest methane emissions seen in our study. This could be one
296 possible explanation for the decrease in methane emissions measured here and in
297 other studies under ozone concentrations above ambient levels, although it should be
298 remembered that the different studies took place in very different locations with
299 different ambient ozone characteristics.

300 The increase in methane fluxes from peatlands seen following exposure to low to
301 moderate accumulated levels of ozone in this study could either be due to an increase

302 in methanogenic activity, a decrease in methanotropic activity or an increase in the
303 release of methane through the aerenchyma of the vascular plants. Toet *et al.*, (2009)
304 showed that ozone does not diffuse more than a few millimetres into the substrate,
305 particularly in waterlogged soils, suggesting that it is unlikely that the change in
306 methane fluxes seen is a result of the direct impact of ozone on methanogenic or
307 methanotrophic bacteria. This is corroborated by results from Morsky *et al.*, (2008)
308 and Rinnan *et al.*, (2003) showing that exposure to elevated ozone had no impact on
309 potential methane production or consumption in peat taken from mesocosms.

310 Wetland vascular plants show two main types of gas exchange between the
311 atmosphere and their roots: passive diffusion and active pressurised flow (Brix *et al.*,
312 1992, Whiting & Chanton, 1993) and the major flow mechanism differs between
313 species (Roura-Carol & Freeman, 1999, Thomas *et al.*, 1996, Van der Nat *et al.*,
314 1998). Passive molecular diffusion occurs as a result of a concentration gradient
315 between the methane within the substrate and the atmosphere. If this were the
316 dominant gas exchange mechanism then an increase in methane production would
317 have to occur for methane emissions to increase. DOC concentrations were
318 unchanged by exposure to elevated ozone, which suggests that substrate availability to
319 methanogens is not increasing. However, active pressurised flow occurs because of a
320 pressure differential developing between green, photosynthesising leaves and older,
321 senescing leaves (Chanton & Whiting, 1996, Chanton *et al.*, 1997, Chanton *et al.*,
322 1993, Shannon *et al.*, 1996, Yavitt & Knapp, 1998) forcing the flow of methane into
323 the roots, through the aerenchyma and out through inter-cellular pore spaces in
324 senesced leaves. As the senesced leaf area was increased by elevated ozone, then the
325 lower pressure “leaky” leaf area is increased, thus there may be more gas flow
326 through plants resulting in more methane being transported from the peat to the

327 atmosphere. Senesced leaves are also unlikely to show any stomatal control and it has
328 been shown that methane emissions from *Carex* species are partially under stomatal
329 control (Morrissey *et al.*, 1993), which suggests that this could also be a factor behind
330 the increasing methane emissions seen in this experiment as many of the mesocosms
331 were dominated by *Carex echinata*. A further indication that the influence of elevated
332 ozone on methane fluxes may be under stomatal control comes from Mills *et al.*,
333 (2009) and Wagg *et al.*, (2012) who showed that grassland plants exposed to elevated
334 ozone lost their usual response to ABA and no longer had stomatal control when
335 exposed to extreme drought. The natural variation in species cover and composition
336 of the mesocosms means that further work would be required to further explore this
337 relationship and test the hypothesis that the change in methane emissions seen
338 following exposure to elevated background ozone is because of increased senescence
339 present on aerenchymatous vascular plants.

340 As a recent review by Rinnan *et al.*, (2013) concludes; methane and carbon dioxide
341 fluxes from peatland systems are under the control of many different factors including
342 temperature, water table height and fluctuation and light availability meaning that
343 there are many ways the impact of elevated tropospheric ozone on these carbon gas
344 fluxes may be masked. This study has provided a potential explanation for the
345 seemingly contradictory methane emissions from previous studies but further
346 investigation of the interactions between the factors that affect methane emission
347 would increase our understanding of the effect of ozone exposure on methane
348 emissions. We have shown that peatland ecosystems have the potential to be changed
349 by relatively low accumulations of tropospheric ozone, when considered over the
350 period of a growing season. Increases in plant senescence may affect the long-term
351 viability of sensitive peatland plants, and, although biomass was unaffected by

352 elevated background ozone over one growth season, it is possible that the increased
353 resources needed by the plants to replenish damaged tissue may have longer-term
354 implications for plant health and carbon sequestration by wetlands.

355

356 Conclusions:

357 Our results have shown that peatland plants are sensitive to increasing background
358 ozone concentrations, which adds new knowledge to previous published work
359 showing that peaks in tropospheric ozone also damage wetland plants. The gas
360 exchange measurements made during this study suggest that methane fluxes from
361 wetlands can be very sensitive to relatively small changes in background ozone
362 concentrations, and that the results from five separate studies on the impacts of
363 elevated ozone on methane fluxes fit within the pattern found in our study. We
364 hypothesize that there is a relationship between plant senescence resulting in changes
365 in methane fluxes ($P = 0.08$ in our study). Further work carrying out more intensive
366 gas exchange sampling from peatlands would indicate whether the effects we have
367 seen occur on a wider scale. Further understanding of the mechanism for how
368 changes in plant growth following ozone exposure are resulting in changes in methane
369 fluxes and the interactions between the factors that affect methane emission and
370 tropospheric ozone exposure are needed to fully assess the implications of
371 tropospheric ozone increases for global greenhouse gas budgets.

372

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376

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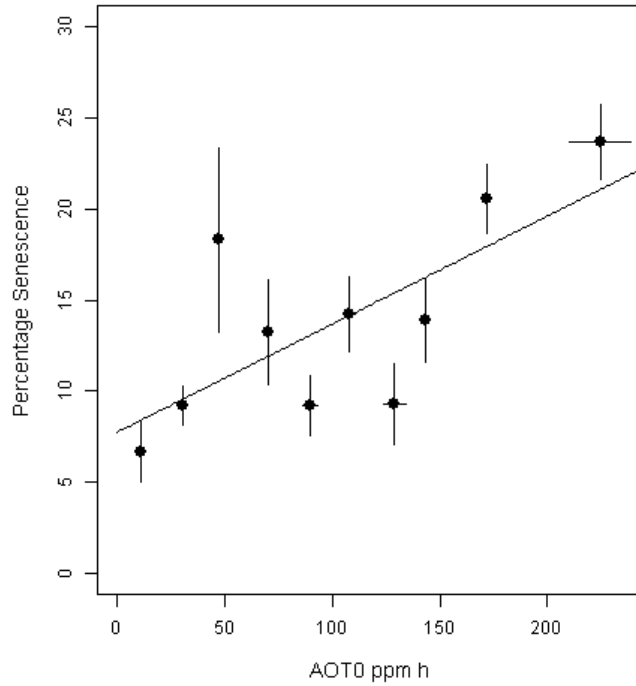


Figure 1a: Vascular plant senescence against AOT0 ppm h through the 16 week experimental period. $P < 0.05$, $R^2 = 0.509$, $F \text{ stat} = 8.30$. Error bars show the standard error of the mean for each data point with AOT0 meaned per 20 ppm h intervals.

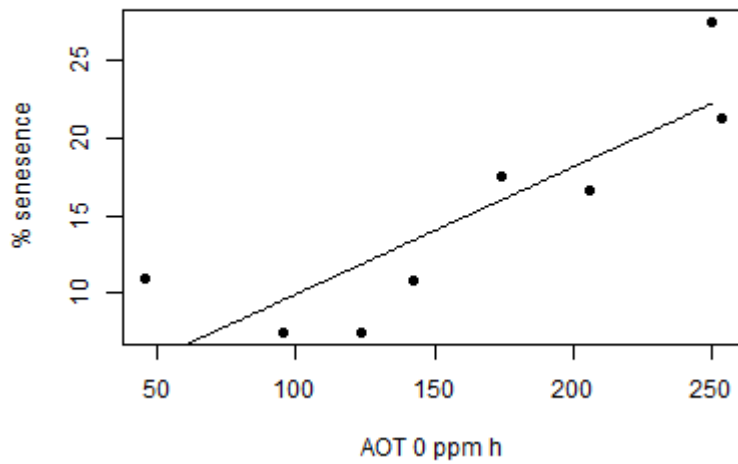


Figure 1b: Vascular plant senescence at the end of the 16 weeks of ozone exposure period. See Table 2 for statistical relationships.

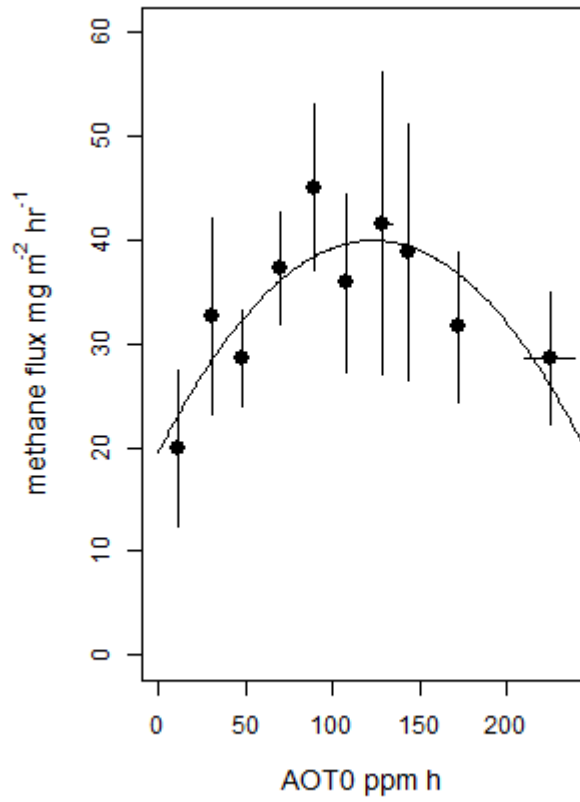


Figure 2: Methane flux plotted against AOT0 ppm h accumulated throughout the 16 week experimental period. $P < 0.01$, $R^2 = 0.719$, $F \text{ stat} = 8.93$. Values are shown as the mean \pm SE and where SE bars are not present variation was within the size of the points on the plot.