Effects of climate change on air pollution impacts and response strategies for European ecosystems

Project Number 282910

ÉCLAIRE

Effects of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems

Seventh Framework Programme

Theme: Environment

D2.6 Manuscript on stress induced emissions considered in ozone balance

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Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	☐
RE	Restricted to a group specified by the consortium (including the Commission Services)	☐
CO	Confidential, only for members of the consortium (including the Commission Services)	☐

1. Executive Summary

Aim of task 2.4 (JUELICH (Mentel) is to characterize impacts of climate change induced stresses on trace gas exchange between atmosphere and vegetation. In particular, the derivation of a holistic ozone balance considering the interaction of all involved steps: impacts of heat- and drought stress on emissions of biogenic volatile organic compounds (BVOC), on the uptake of ozone (O_3) and nitrogen oxides (NO_x), and on the O_3 forming potential.

Elevated temperature (heat- or thermal stress) induced pulses of pool monoterpene emissions. Monoterpene emissions in parallel to their biosynthesis (*de-novo* emissions) were suppressed. Emissions induced by biotic stress (SIE) emissions are of *de-novo* nature. Dominant SIE emitted from the investigated species were those of sesquiterpenes and phenolic BVOC. According to their *de-novo* nature, emissions of sesquiterpene and phenolic BVOC were suppressed by thermal stress.

Drought and thermal stress impact O_3 uptake and the O_3 forming potential of plants. O_3 uptake is mainly reduced by drought induced closure of stomata; the O_3 forming potential is mainly reduced by reduction of BVOC emissions. Thermal stress increases the O_3 forming potential of conifers under BVOC limiting conditions and decreases the O_3 forming potential of *de-novo* emitters and conifers under biotic stress.

2. Objectives:

BVOC emissions have positive and negative effects on O_3 exposure and uptake. On the one hand, gas phase reactions of ozone with BVOC have the potential to destroy O_3 locally and therefore decrease exposure. On the other hand, their participation in atmospheric photochemistry can cause O_3 formation. The latter is dependent on the abundance of nitrogen oxides NO_X as shown in Figure 1.

Main objective was the determination of the O_3 balance for plants: Ozone uptake by the plants themselves, O_3 losses in gas phase reactions with BVOC, and O_3 formation in the presence of NO_x and BVOC have to be determined. Impacts of heat- and drought stress for plants on the ozone balance have to be characterized by determining their impacts on the individual processes affecting the O_3 balance.

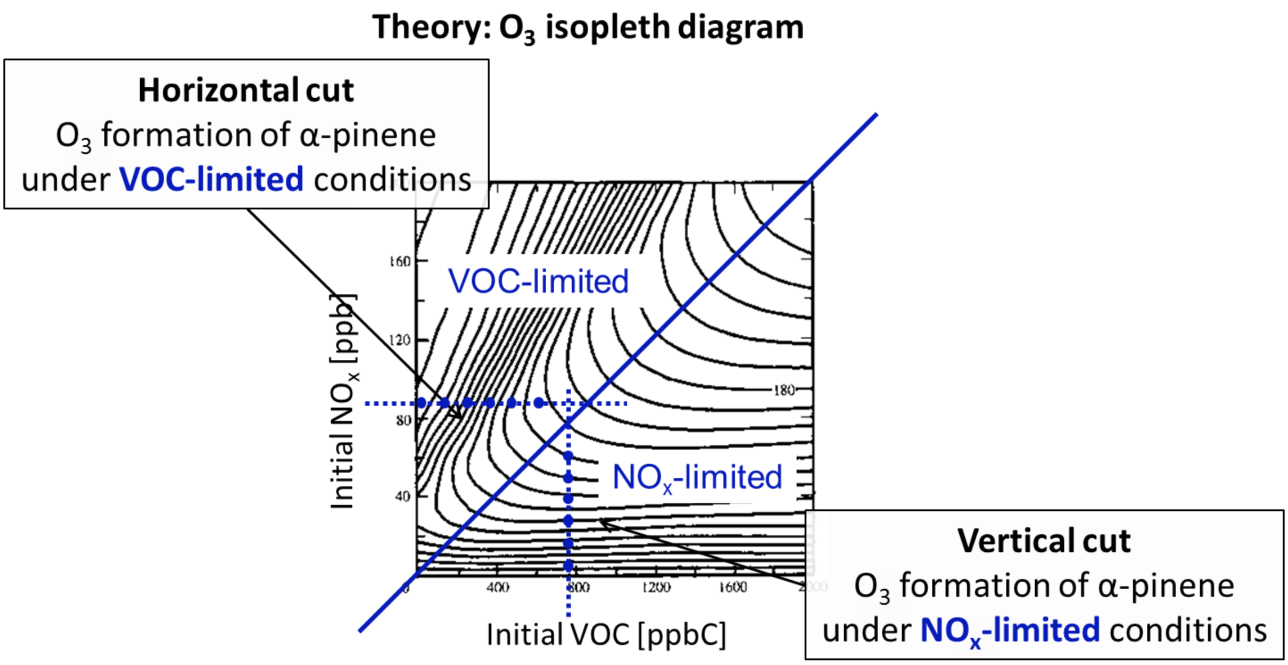

Figure 1: O_3 isopleth diagram, city mix (Jeffries and Crouse, 1990)

3. Activities:

The experimental activities during 2013 and early 2014 focused on generating the requirements for implementing the soil moisture dependence of *de-novo* monoterpene emissions in models. Measurements were conducted for:

a) Finding other usable reference quantities aside from the fraction of transpirable soil water.
b) Controlling for interdependencies of individual factors when using a factorial approach.

The experiments on ozone formation were conducted in 2014 and 2015 with α-pinene as individual ozone precursor to determine:

a) Ozone formation potential under NO_X limited conditions
b) Ozone formation potential under BVOC limited conditions.

The experimental setup is sketched in Figure 2.
By modelling the results obtained with α-pinene with state of the art models it is aimed to simulate the changes of trace gas uptake on photochemical ozone formation (e.g. lowered uptake of NO_X or changes of BVOC emissions from plants as a consequence of heat or drought periods as future stress scenarios for vegetation).

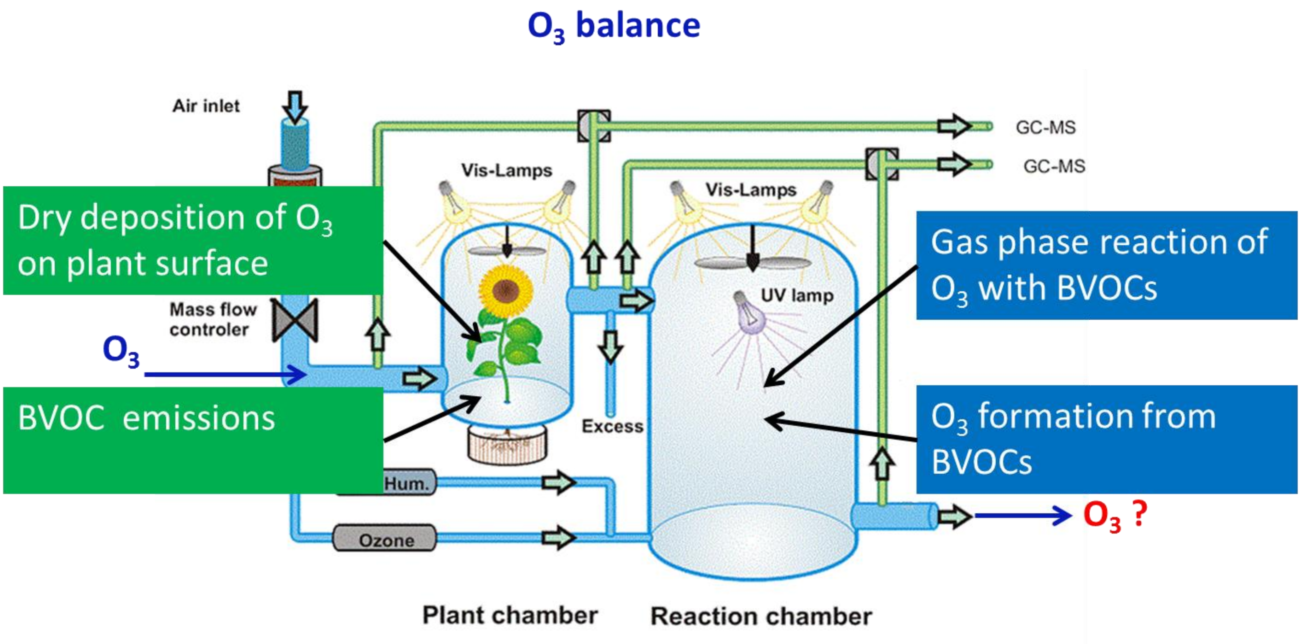

Figure 2: Experimental Setup for determination of the O_3-balance.

4. Results:

The impacts of plants on the ozone balance was investigated by measuring:

1. The uptake of O_3 by plants through the plants' surface,
2. Losses of ozone in reactions with the emitted BVOC
3. Photochemical ozone production from the emitted BVOC

All three processes were investigated for plants without stress and for plants under heat and drought stress.

1. Dominant pathway of ozone losses on the plants surface is the diffusion of O_3 through the stomata. Losses on the cuticle or stem of the plants are negligible. Uptake is diffusion limited and hence dry deposition depends on stress to the plants, particularly on drought.
2. Losses of ozone by gas phase reactions with plant emitted BVOC depend on the BVOC emission strengths and on the average number of double bonds. The former is substantially changed by drought and heat.

3. In case of VOC-limited O_3 production, O_3 production rates are linearly related to the BVOC emission rates.

Combining these results leads to the following qualitative statements.

In clean air with low NOx concentrations plants are always a sink of tropospheric O_3. For strong BVOC emitters as Holm oak and at stress free conditions uptake through the stomata contribute to at least 70 % to the total O_3-losses, gas phase reactions contribute to a maximum of 30%.
At high NOx conditions, plants switch from a sink to a source of O_3. A ratio of O_3 formation rate over BVOC loss rate, in the range of 2–3 ppb/ppb, was observed for α-pinene as individual BVOC and for BVOC mixtures from Holm oak and Norway spruce.

A qualitative assessment regarding the role of plants for O_3 balance at high NOx conditions was obtained by calculating the ratio of O_3 uptake fluxes over BVOC emission fluxes ($\Phi(O_3)/\Phi(BVOC)$). The lower this ratio, the more likely the plant is to be a source of O_3 at high NOx conditions. $\Phi(O_3)/\Phi(BVOC)$ strongly depends on environmental variables such as light intensity, temperature and stresses.
As long as high temperatures do not impose thermal stress $\Phi(O_3)/\ \Phi(BVOC)$ decreases. Moderate temperature increases also increase the role of plants as potential O_3 source. When temperature exceeds certain thresholds causing irreversible changes of BVOC emissions, constitutive *de-novo* monoterpene emissions decrease and pool emissions increase. This attenuates the role of *de-novo* emitters as a potential O_3 source and increases the ozone formation potential of pool emitters.

Drought causes stomatal closure and changes of BVOC emissions. At moderate drought $\Phi(O_3)$ / $\Phi(BVOC)$ decreases coherently leading to higher ozone formation potential of plants. Severe drought stress diminishes the total performance of a plant and diminishes its impacts on the O_3 balance, as shown in Table 1.

Table 1: effect of mild and severe drought stress on O_3 balance

	Remark	Plant chamber		Ozone balance
		O_3 loss flux [nmol m^{-2} s^{-1}]	BVOC flux [nmol m^{-2} s^{-1}]	Net O_3 flux [nmol m^{-2} s^{-1}]
Case 1	Standard	2.5 ± 0.1	3.9 ± 0.2	8.4
Case 2	Mild drought	1.4 ± 0.1	6.0 ± 0.3	15.4
Case 3	Severe drought	0.6 ± 0.1	0.2	-0.04

All results are described in a PhD thesis (Emissions of Biogenic Volatile Organic Compounds and Ozone Balance under Future Climate Conditions, Cheng Wu, RWTH Aachen). The thesis reflects the current understanding of the holistic ozone balance. A manuscript could not be produced yet because of experimental difficulties (see **6. Deviations and reasons**).

5. Milestones achieved:

Milestone 6: O_3 balance data for Mediterranean and Boreal forest species for input in models

Basic mechanisms of ozone uptake in dependence of the plants' water supply were determined for Mediterranean and Boreal species proving that the main ozone losses appear by uptake through the plants stomata. As drought or heat cause stomatal closure, ozone losses by dry deposition on plant surfaces decrease as a function of stomatal closure.
Losses of ozone by gas phase reactions with plant emitted BVOC depend on the average number of double bonds and the BVOC emission strengths. The latter is substantially changed by drought and heat.
Photochemical ozone production is also determined by the BVOC emission strengths. Under BVOC limiting conditions the change of ozone formation with changing BVOC emissions can be linearly approximated by a yield of about 2-3 ozone molecules produced by one emitted monoterpene.

The gas phase balance of ozone is controlled by the abundance of NO_X. It changes from a maximum loss of ~1 - 1.5 ozone molecules per emitted monoterpene at low NO_X conditions to a gain of 2-3 ozone molecules produced per emitted monoterpene.

6. Deviations and reasons:

All results are described in the manuscript of PhD thesis (Emissions of Biogenic Volatile Organic Compounds and Ozone Balance under Future Climate Conditions, Cheng Wu, RWTH Aachen), which can be supplied on request. Delays occurred due to an issue with ozone measurement and UV absorption interference in the measurement process. The total ozone balance was calculated (completing MS6), but this took one more year of doctoral work than planned. A peer review paper is in preparation, but will require further characterisation of the interference experienced before it can be submitted, it is therefore anticipated to be submitted after the project has finished. However no knock-on effects are expected as MS6 has already been delivered and all necessary scientific information is in the PhD thesis manuscript.

7. Publications:

PhD thesis, Cheng Wu (2015): Emissions of biogenic volatile organic compounds and ozone balance under future climate conditions (available on request).

Wu, C., Pullinen, I., Andres, S., Carriero, G., Fares, S., Goldbach, H., Hacker, L., Kasal, T., Kiendler-Scharr, A., Kleist, E., Paoletti, E., Wahner, A., Wildt, J., and Mentel, T. F.: Impacts of soil moisture on de novo monoterpene emissions from European beech, Holm oak, Scots pine, and Norway spruce, Biogeosciences, 12, 177-191, 10.5194/bg-12-177-2015, 2015.

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Bergström, R., Hallquist, M., Simpson, D., Wildt, J., and Mentel, T. F.: Biotic stress: a significant contributor to organic aerosol in Europe?, Atmos. Chem. Phys., 14, 13643-13660, 10.5194/acp-14-13643-2014, 2014.

Mentel, T. F., Kleist, E., Andres, S., Dal Maso, M., Hohaus, T., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R., Uerlings, R., Wahner, A., and Wildt, J.: Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks, Atmospheric Chemistry and Physics, 13, 8755-8770, 10.5194/acp-13-8755-2013, 2013.

Wildt, J., Mentel, T. F., Kiendler-Scharr, A., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., Müsgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R., and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by NOx, Atmos. Chem. Phys., 14, 2789-2804, 10.5194/acp-14-2789-2014, 2014.