Project Number 282910

ÉCLAIRE

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

Seventh Framework Programme

Theme: Environment

D2.5 Manuscript on constitutive emission considered for ozone balance

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JUELICH

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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, PI Mentel) is to characterize impacts of climate change induced stresses on vegetation. In particular, 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 shall be determined. Following results were obtained so far in our studies:
Elevated temperature (heat- or thermal stress) has different impacts on BVOC emissions from plants. Emissions due to diffusion of BVOC out of the plants' storage organs (pool emissions) show bursts. Such bursts can increase emissions by up to an order of magnitude, they can last for weeks and the integral emissions during such pulses may be as large as emissions without stress over a whole vegetation period. Contrary, most emissions in parallel to biosynthesis of BVOC (*de-novo* emissions) are suppressed by heat and do not recover within time periods of days to weeks. This behaviour is independent of the BVOC emissions being constitutive or induced by biotic stress.
Soil moisture has no significant impacts on BVOC emissions as long as the relative water content is between 50% and 80%. Under conditions of drought when the relative water content falls below 40% pool emissions as well as *de-novo* are decreased.
Drought also impacts O_3 uptake and the O_3 forming potential of plants. Both quantities are reduced. 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.

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 at the scale some 10 km thereby increasing exposure downwind. Main objective within task 2.4 therefore is 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.

3. Activities:

Impacts of heat stress on constitutive emissions as well as on biotic stress induced emissions werestudied using European beech (*Fagus sylvatica*), Norway spruce (*Picea abies*), and Scots pine (*Pinus sylvestris*). Furthermore, impacts of biotic stress on the formation potential of secondary organic aerosol were determined as well as impacts of heat and drought stress on top of the biotic stresses.
Impacts of drought on constitutive emissions were studied using Holm oak (*Quercus ilex*), European beech, Norway spruce and Scots pine. Both, experiments regarding impacts of heat and drought were conducted in the laboratory under well-defined conditions. In case of Holm oak most experiments were made in collaboration with Silvano Fares and Giulia Carriero.
Uptake of O_3 was investigated for plants without and with drought stress. As species Holm oak, Aleppo pine (*Pinus halepensis*) and Grey poplar (*Populus x canescens*) were used. Ozone destruction in gas phase reactions with plant emitted BVOC was investigated using Holm oak.
The O_3 formation potential was determined in one experiment using Holm oak and in another experiment using a set of 5 different plants (two Aleppo pines, one Holm oak, one Palestine oak (*Quercus calliprinos*), and one Pistachio (*Pistacia palestina*)).

4. Results:

In many cases elevated temperatures had irreversible impacts on BVOC emissions whereby the impacts on *de-novo* emissions differed from the impacts on pool emissions. Most *de-novo* emissions decreased and did not recover within days to weeks. This behaviour was independent of the *de-novo* emissions being constitutive or induced by biotic stress. Examples of BVOC emissions where heat

impacts decreased the emissions were those of sesquiterpenes and phenolic BVOC originating downstream of the shikimarte pathway. The only *de-novo* emissions increasing with heat were those of green leaf volatiles (GLV). However, the heat-induced emission pulses were roughly two orders of magnitude lower than the parallel drops in *de-novo* emissions of sesquiterpenes and phenolic BVOC (measured for Norway spruce and Scots pine).
Pool emissions were strongly increased during and after heat application. Such increased emissions were caused by membrane damage of resin ducts and the increases were irreversible on time scales of days to weeks. Heat induced emission pulses stayed for weeks and the integral emissions during such pulses could be as high as constitutive pool emissions over a whole vegetation period.

Impacts of soil moisture on BVOC emissions were investigated for European beech, Norway spruce, Scots pine, and Holm oak. For all investigated species soil moisture expressed as relative water content (RWC) had no significant impacts on BVOC emissions as long as the RWC varied between 80% and 50%. Under conditions of drought when RWC fell below 40%, pool emissions as well as *de-novo* decreased with decreasing RWC for European beech, Norway spruce, and Scots pine. For Holm oak an increase was observed when RWC dropped from 40% to 20% and at the RWC lower than 20% the emissions dropped to zero.
Rates of transpiration and net photosynthesis also decreased with decreasing RWC and vice versa but no relationship was found between both quantities and BVOC emissions. The temporal behaviour of the plants responses in transpiration and net photosynthesis differed from the temporal behaviour in BVOC emissions preventing from using one of these quantities as a reference for describing the impacts of drought on BVOC emissions. So far RWC has proved to be the best reference for describing impacts of drought on BVOC emissions.

Dominant process of O_3 uptake by plants was found to be the diffusion through the plants' stomata. Ozone destruction on the plants surfaces was negligibly low and, for the strong monoterpene emitter Holm oak, O_3 losses due to gas phase reactions were lower than losses due to diffusion through stomata. As stomatal aperture decreased with proceeding drought stress, also O_3 uptake decreased with proceeding drought.

At elevated NO_x concentrations in the atmosphere plants may be a net source for O_3 because photochemical ozone formation from plant emitted BVOC is more efficient than ozone uptake by plants and ozone destruction in gas phase reactions together. Ozone formation from constitutive emissions was studied for a set of Mediterranean plants (two Aleppo pines, one Holm oak, one Palestine oak, and one Pistachio). In another experiment the O_3 formation was studied using an individual Holm oak. The results obtained in these measurements differed strongly and the reason for this difference is not understood yet.

In addition O_3 formation from atmospheric oxidation of the constitutive emissions from Holm oak was studied in dependence of drought stress. As expected, the ozone formation potential of the plant decreased with increasing drought due to the decreasing BVOC emissions.

5. Milestones achieved:

Basic mechanisms of ozone uptake in dependence of the plants water supply were determined as well as a characterization of the impacts of heat stress on the BVOC emissions from several tree species. A phenomenological description of drought impacts on constitutive monoterpene emissions was developed and it was shown that drought decreases the O_3 forming potential as well as the O_3 uptake by plants. From the work dealing with drought stress we also achieved a Master thesis of Iida Pullinen, University of Cologne.

6. Deviations and reasons:

It was aimed to publish our data on the ozone formation potential of constitutive plant emissions. So far we did not submit a manuscript because the results obtained in different experiments using either an individual plant or a set of plants as BVOC sources were inconsistent to each other. Obviously

some basic processes leading to O_3 formation from BVOC are not understood yet. We will submit a manuscript on that item when the discrepancy is understood.
Results on impacts of heat and drought on constitutive and stress induced emissions were obtained earlier than expected. We therefore first published our results of the impact of heat stress on BVOC emissions and impacts of heat and drought on the potential of plant emitted BVOC to form atmospheric aerosols. We propose to accept these two publications, the master thesis of Iida Pullinen as compensation for the still missing publication on the ozone formation potential.

7. Publications:

Kleist, E., Mentel, T. F., Andres, S., Bohne, A., Folkers,A., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R., and Wildt, J. (2012) Irreversible impacts of heat on the emissions of monoterpenes, sesquiterpenes, phenolic BVOC and green leaf volatiles from several tree species. Biogeosciences, 9, 5111–5123.

Mentel, Th. F. Kleist, E., Andres, S., DalMaso, M., Hohaus, T., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R., Uerlings, R., Wahner, A., and Wildt, J. (2013) Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks. Atmos. Chem. Phys. Discuss., 13, 7463-7502.

Pullinen, Iida (2012); The effect of drought on BVOC emissions from Holm oak (Quercus Ilex), European beech (Fagus Sylvatica L.), Norway spruce (Pinus abies L.) and Scots pine (Pinus sylvestris), master thesis, University of Cologne

8. Meetings:

No presentation of ECLAIRE results in meetings except of ECLAIRE internal meetings.
Some of the results were presented at RWTH Aachen University (Cheng Wu on March 22nd 2013).

9. List of Documents/Annexes:

Manuscript Kleist et al. BG, 2012
Manuscript Mentel et al. ACPD, 2013