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ÉCLAIRE

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

Seventh Framework Programme

Theme: Environment

D2.3 Assessment of primary and secondary BVOC exchange rates

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JUELICH

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PU	Public	X
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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 2.3 is quantifying BVOCs exchanges in field experiments and in response to combined environmental change and pollution scenarios (IPP-CNR). We demonstrated that isoprene (*i*) is oxidized to methyl vinyl ketone and methacrolein (i_{ox}) in leaves and that i_{ox}/i emission ratios increase with temperature, possibly due to an increase in ROS production under high temperature and light stress. A further experiment for quantifying i_{ox} compensation point is in progress. Campaigns for field measurements of BVOC exchanges are in progress at a Mediterranean Quercus ilex site.

Task 2.3 additionally aims at providing information on the reactivity of biogenic volatile organic compounds (BVOC) with other reactive nitrogen (NO) and oxygen species (ROS) within leaves (BAS-IFRG). In particular, the effect of ozone stress on changes in BVOC and NO emissions, as well as the ROS formation was studied. It was demonstrated that ozone slightly inhibited isoprene emission and significantly increased the emission of isoprene oxidation products methyl vinyl ketone (MVC) and methacrolein (MACR). Ozone stress also induced considerable emission of NO from leaves. These changes were correlated with higher amount of LOX emission and increased level of lipid peroxidation due to higher level of ROS.

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, 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) 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 were those of sesquiterpenes and phenolic BVOC. According to their *de-novo* nature, emissions of sesquiterpene and phenolic BVOC were suppressed by thermal stress.

Soil moisture had no significant impacts on BVOC emissions as long as soil moisture was high. Under conditions of drought both, *de-novo* type emissions and pool emissions were lower than at high soil moisture. While the fraction of transpirable soil water (FTSW) proved to be a usable reference quantity for describing the dependence of *de-novo* monoterpene emissions on progressing drought, it was inappropriate for describing the behaviour of these emissions during recovery from preceding droughts. Furthermore, responses of pool emissions to changes of soil moisture were not describable using soil moisture as reference quantity alone.

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 under BVOC limiting conditions.

2. Objectives:

Isoprene is postulated to mitigate oxidative damage during the stress-induced accumulation of reactive oxygen species (ROS) in the cell, but the in-planta products of isoprene-ROS reactions had not been detected. Concurrent measurements of BVOC and ozone fluxes at a Mediterranean Quercus ilex forest can provide information on the capacity of Mediterranean ecosystems to control tropospheric ozone pollution.

Biogenic volatile isoprenoids have a general role in stress protection. However, plants also emit NO under stressful conditions. Since isoprene is highly reactive, theoretically is possible that it could react with other gaseous compounds emitted by leaves. Therefore, one of the objectives within task 2.3 is to understand whether isoprene is involved in the regulation of NO and ROS formation within leaves.

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:

Partner CNR detected the products of isoprene-ROS reactions in plants by using pyruvate-2-^{13}C leaf and branch feeding and individual branch and whole mesocosm flux studies (Jardine et al., 2014). A further experiment for investigating the compensation point of i_{ox} has been postponed to 2014 and is still in progress.

Ozone fluxes have been continuously measured at an eddy-covariance installation in a Mediterranean Quercus ilex forest in central Italy. Campaigns for field measurements of BVOC exchanges are scheduled in 2014.

Experimental work of partner IRFG was focused on the effect of acute short term ozone treatment on primary and secondary metabolism of *Populus nigra* in a controlled environmental chamber. The changes in BVOC and NO emissions were detected by GC-MS and highly sensitive chemiluminescence NO–NO_2–NO_x analyzer.

The experimental activities of partner Juelich 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.

Further experiments on ozone formation were conducted 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.

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).

4. Results:

We found that isoprene (i) is oxidized to methyl vinyl ketone and methacrolein (i_{ox}) in leaves and that i_{ox}/i emission ratios increase with temperature, possibly due to an increase in ROS production under high temperature and light stress (Jardine et al., 2012). These observations suggest that carbon investment in isoprene production is larger than that inferred from emissions alone and that models of tropospheric chemistry and biota–chemistry–climate interactions should incorporate isoprene oxidation within both the biosphere and the atmosphere with potential implications for better understanding both the oxidizing power of the troposphere and forest response to climate change.

Effect of acute short term ozone treatment on the primary and secondary metabolism was studied in *Populus nigra*. Ozone treatment resulted in decrease of isoprene emission rate and substantial stimulation of NO emission. Upon ozone exposure poplar leaves accumulated higher level of ROS and emitted more lipid-breakdown (LOX) products. At the same time methyl vinyl ketone (MVC) and meyhacrolein (MACR), the two products of isoprene oxidation, were significantly increased. Our data suggest that isoprene could directly react with reactive nitrogen and oxygen species *in planta*.

Impacts of soil moisture on BVOC emissions were investigated for European beech, Norway spruce, Scots pine, and Holm oak. Many experiments with Holm oak were made in collaboration with Silvano Fares (Agricultural Research Council, Research Center for the Soil-Plant System, Roma, Italy) and Giulia Carriero (Instituto Protezione Piante, Consiglio Nazionale Ricerche, Firenze, Italy).

Variations of soil moisture affected pool- and *de-novo* monoterpene emissions from all investigated species. For our purpose of implementing the soil moisture dependence in models we focused on responses of *de-novo* emissions.

Other used reference quantities besides FTSW were the volumetric water content of the soil (MEGAN, Guenther et al., 2012) or the relative water content of the soil (Lavoir et al. 2011). For periods with slowly progressing drought all these quantities were applicable. However, they were non-applicable in case of sudden changes of soil moisture such as irrigation of dry soil. The response of *de-novo* emissions to irrigation was superimposed by recovery of the emissions which took several days.
During early periods of recovery from preceding drought, the fraction of the photosynthetic electron transport used for monoterpene synthesis (Niinemets et al., 2002) was usable as reference quantity. However, already for mild drought an empirical correction factor had to be used to keep the model in accordance to the experimental results and, due to intrinsic problems for conditions of severe drought, the applicability of this reference quantity was uncontrollable for conditions of severe drought.

We therefore focused on a multiplicative approach as used in MEGAN for isoprene. Requirement for using such a multiplicative approach is a negligible interdependency of individual factors used for description. Measurements on temperature dependency of emissions during progressing drought proved the negligibility of interdependence between the factors describing the temperature dependence and the FTSW-dependence. Measurements to control possible negligence of he light intensity dependence on the FTSW dependence are not yet finished.

Using a set of Mediterranean species as BVOC sources the ozone formation potential of the emission mix under NO_X limiting conditions was found to be about 4 ozone molecules produced photochemical from one BVOC emitted (see also Wildt et al. 2014). To allow modelling ozone formation the experiment was repeated using the monoterpene α-pinene as ozone precursor whereby we found about 3.5 ozone molecules formed from one oxidized α-pinene molecule. Using α-pinene as individual BVOC, also measurements on the BVOC dependence of the ozone formation potential were conducted leading to results similar to those of experiments with real plants under drought stress.

The number of O_3 molecules destroyed in BVOC ozonolysis depends on the BVOC mixture. In particular, the average number of double bonds determines the maximum amount of ozone that can be destroyed in absence of photochemical ozone formation.

References:

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. Geosci. Model Dev. 5, 1471 – 1492, 2012.

Lavoir, A.V., Duffet C., Mouillot F., Rambal S., Ratte J.P., Schnitzler J.P., Staudt M. Scaling-up leaf monoterpene emissions from a water limited Quercus ilex woodland. Atmos. Environ., 45, 2888-2897, 2011.

Niinemets, Ü., Seufert, G., Steinbrecher, R., and Tenhunen, J. D.: A model coupling foliar monoterpene emissions to leaf photosynthetic characteristics in Mediterranean evergreen Quercus species. New Phytologist, 153, 257–275, 2002.

5. Milestones achieved:

Milestone 9: Ozone balance for Mediterranean plants

Basic mechanisms of ozone uptake in dependence of the plants' water supply were determined 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 4 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 ~ 4 ozone molecules produced per emitted monoterpene.
Meantime, two review and one research papers were published by partners CNR and IRFG acknowledging the financial support of ECLAIRE. In one of the review papers a concept for modelling the emission of biogenic volatile isoprenoids based on the regulation of physiological mechanisms in the chloroplasts is proposed (Harrison et al. 2013). The other review paper is focused on the importance of volatile isoprenoids in plant protection against environmental constraints in the Mediterranean area (Loreto et al. 2014). The research paper expands current knowledge on the question why plants invest resources in isoprene production (Pollastri et al. 2014).

6. Deviations and reasons:

Data of partner Juelich on the ozone formation potential of constitutive plant emissions is meanwhile published together with the data on the particle formation potential of constitutive plant emissions (Wildt et al., 2014). Results on impacts of heat on BVOC emissions are already published (Kleist et al., 2012) and a manuscript on the impacts of drought on de-novo monoterpene emissions will be submitted mid of 2014.
Due to technical challenges, the experiments on iox compensation point and on BVOC fluxes at a Quercus ilex forest have been postponed to 2014.
Studies in controlled environmental conditions on reactivity of BVOC with NO and ROS are in time according to the Project schedule. Correlation between BVOC emission rate and endogenous induced emission of NO and ROS formation under simulated environmental constrains (high temperature) is scheduled for March 2014 - 2015.

⇨ Some deviations from aims and milestones.

7. Publications:

1.) Jardine KJ, Monson RK, Abrell L, Saleska SR, Arneth A, Jardine A, Ishida FY, Serrano AY, Thomaskarl A, Fares S, Goldstein A, Loreto F, Huxman T 2012, Within-plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein. Global Change Biology. 18: 973–984.

2.) Kleist, E., Mentel, T. F., Andres, S., Bohne, A., Folkers, A., Kiendler-Scharr, A., Rudich, Y., Springer, M., Tillmann, R., and Wildt, J.: Irreversible impacts of heat on the emissions of monoterpenes, sesquiterpenes, phenolic BVOC and green leaf volatiles from several tree species, Biogeosciences, 9, 5111-5123, 10.5194/bg-9-5111-2012, 2012.

3.) 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.

4.) Harrison, S.P., Morfopoulos, C., Srikanta Dani, K.G., Prentice, I. C., Arneth, A., Atwell, B.J., Barkley, M. P., Leishman, M. R., Loreto, F., Medlyn, B. E., Niinemets, Ü., Possell, M., Pecuelas, J., Wright, I.J.: Volatile isoprenoid emissions from plastid to planet, New Phytol. 197: 49-57, 2013.

5.) 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.

6.) Loreto, F., Pollastri, S., Fineschi, S., Velikova, V.: Volatile isoprenoids and their importance for protection against environmental constraints in the Mediterranean area, Environmental and Experimental Botany, 103: 99-106, 2014.

7.) Pollastri, S., Tsonev, T., Loreto, F.: Isoprene improves photochemical efficiency and reduces heat dissipation in plants at physiological temperatures, J. Exp. Bot. 65: 1565–1570, 2014.

8. Meetings:

9. List of Documents/Annexes: