

# The VOC-Ozone Connection: a grassland case study

Georg Wohlfahrt (1), Lukas Hörtnagl (1), Ines Bamberger (2), Ralf Schnitzhofer (2), Juergen Dunkl (2), Albin Hammerle (1), Martin Graus (2), Armin Hansel (2)

(1) University of Innsbruck, Institute of Ecology, AUSTRIA, Email: [georg.wohlfahrt@uibk.ac.at](mailto:georg.wohlfahrt@uibk.ac.at)

(2) University of Innsbruck, Institute of Ion Physics and Applied Physics, AUSTRIA

## BACKGROUND

The exchange of biogenic volatile organic compounds (BVOC) between plants and the atmosphere provides an important feedback to the climate system. BVOC are, for example, involved in the generation of tropospheric ozone ( $O_3$ ), which is known to reduce plant photosynthesis and growth, BVOC affect the life time of the greenhouse gas methane ( $CH_4$ ) in the atmosphere, and act as nucleation centres for precipitable water and thus have the potential to change the amount and timing of precipitation.

Methanol ( $CH_3OH$ , abbreviated **MeOH**) is a BVOC that is emitted by plants through a large variety of processes – for example during cell wall elongation and thus more generally speaking during growth and in response to stress, such as hypoxia, low temperatures or high  $O_3$  concentrations.

Here we investigate what has been demonstrated in leaf-level laboratory experiments – that plants respond to **oxidative stress** caused by the stomatal uptake of  $O_3$  by emitting MeOH [1]. To this end we report concurrent MeOH and  $O_3$  flux measurements made above a temperate mountain grassland in Tyrol/Austria during the vegetation period 2008.

## METHODS

Fluxes of MeOH (and several other BVOC) and  $O_3$  were estimated by means of the **eddy covariance method** employing a sonic anemometer for the measurement of the vertical wind speed and a proton-transfer-reaction mass spectrometer (PTR-MS) and a  $O_3$ -analyser for the quantification of the respective scalar concentrations.

As a measure of plant oxidative stress we use the time-integrated  $O_3$  uptake, calculated either on a daily basis (from sunrise) or on a longer-term basis (over the duration of the experiment).

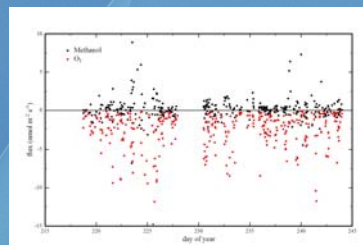


Fig. 1 Half-hourly MeOH and  $O_3$  flux.

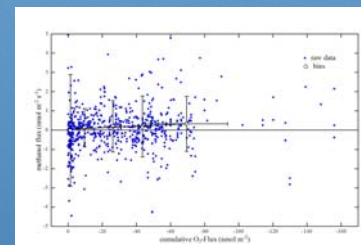


Fig. 2 Half-hourly MeOH-flux versus time-integrated  $O_3$  uptake.  $O_3$  uptake was integrated on a daily basis from sunrise.

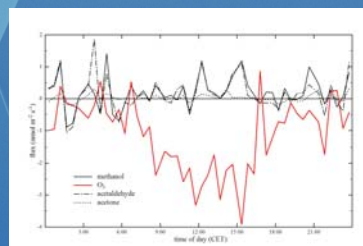


Fig. 3 Bin-average diurnal course of the fluxes of MeOH, Acetaldehyde, Acetone and  $O_3$ .

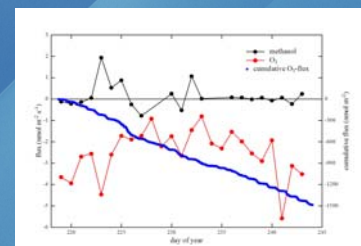


Fig. 4 Midday average MeOH and  $O_3$  flux (symbols) and time-integrated  $O_3$  uptake (integration has been performed over the 25 day duration of the experiment)



The field site:  
Neustift, Stubaal Valley

## RESULTS

Figures 1 and 2 show that, on a daily basis, the flux of MeOH increases with the **time-integrated uptake of  $O_3$**  – MeOH deposition and emission prevailing at low and high time-integrated  $O_3$  uptakes, respectively.

While several other BVOC showed **similar diurnal time** courses as compared to MeOH (Fig. 3) and in fact their fluxes were highly correlated with the flux of MeOH (data not shown), the time-integrated  $O_3$  uptake had little or no effect on their fluxes (data not shown). On longer time scales (25 days), the correlation between oxidative stress and MeOH flux broke down (Fig. 4), indicating that MeOH fluxes at these time scales are driven by other factors (such as the cut of the grass occurring on 10th August or growth) and/or that **detoxification of  $O_3$**  by plants occurs efficiently on a daily basis and that therefore little cumulative effects of  $O_3$  uptake exist beyond one day.

## CONCLUSION

MeOH emission by a temperate mountain grassland was correlated with the time-integrated uptake of  $O_3$  by the ecosystem confirming leaf-level laboratory studies indicating that the oxidative stress induced by  $O_3$  uptake through stomata results in the **emission of MeOH**.

As the reaction with the hydroxyl radical (OH), which is responsible for the destruction of the greenhouse gas  $CH_4$ , is the major sink of atmospheric MeOH, this process provides an **indirect radiative forcing** which should be included by coupled earth-atmosphere models.