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Determination of Carbonyl Compounds in and above the Canopy of a Norway Spruce Forest

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Motivation

Carbonyl compounds can be emitted directly from vegetation (e.g. trees, corn and grassland) and from anthropogenic sources (e.g. traffic, disinfectants and solvents). A further important source is the secondary formation from biogenic and anthropogenic hydrocarbons and alcohols in the atmosphere.

In combination with other sub-projects the conditions for the emission of carbonyl compounds and precursors of carbonyl compounds by a *Norway Spruce* forest should be identified.

For the determination of fluxes over complex terrain the REA is the unique working technique. The measurement of carbonyl compound concentrations at two different heights and the first tests of a REA system at the Waldstein tower were directed to study the source-sink behaviour of the *Norway Spruce* forest.

Experimental

After the successful development of the new designed sampling unit for carbonyl compounds with the DNPH method two of these have been applied during the summer campaign at the Waldstein. At a height of 12m (within the treetop) and at 24 m (above the treetop) the 90-minutes-samples were taken over the whole experiment period, simultaneously.

The stability of the DNPH-derivatives is higher in an acetonitrile solution. So, the tubes were eluted immediately after the collection period.

Up to the ternary gradient (water – acetonitrile – tetrahydrofurane) HPLC analysis samples were stored at –21°C.

About 850 samples were analysed from the 2001 field campaign by HPLC with UV detection at 360 nm and 380 nm.

Tube elution was improved for small volume analysis:

• elution of non-derivatized DNPH by 3 ml H_2O

• elution of Carbonyl-DNPH by 3 ml acetonitrile

• evaporation of acetonitrile at 45°C by clean N_2 stream to 500µl

During the 2002 field campaign the LABVIEW-controlled REA system was tested.

Results

The concentration profile of carbonyl compounds measured during the 2001 campaign refer to deposition in most cases.

The estimation of secondary formation above the canopy will be possible from the data of this year flux estimations and precursor data.

Primary emissions were detected for acetaldehyde, propionaldehyde and methyl ethyl ketone during the morning hours of the warm days at the end of the campaign, especially.

Highest carbonyl compound concentrations were observed for acetone.

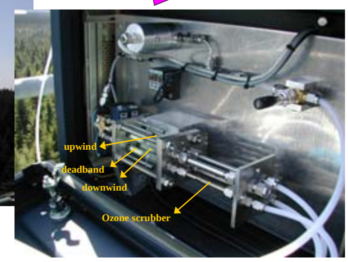
In night samples Pinonaldehyde concentrations up to 200 ppt were observed.

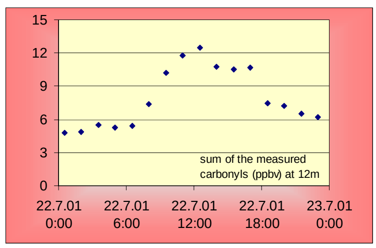
Further important carbonyl compounds are formaldehyde, trans-2-hexenal and butyraldehyde. Traces of other carbonyl species have been detected as well. Benzaldehyde and crotonaldehyde are well known for their anthropogenic origin (maximum was observed at westerly wind direction).

The Relaxed eddy accumulation system

Ultrasonic anemometer and sampling inlet

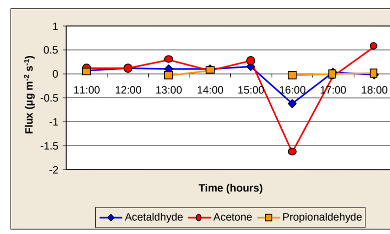
Sampling tubes and fast valves at the backside of the control-PC



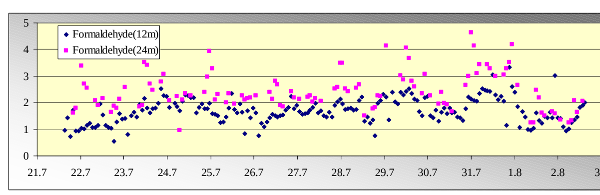


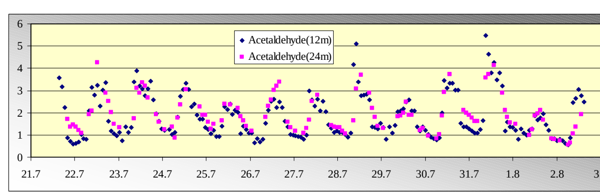
Typical diurnal variation of carbonyl compound concentration during a dry and warm summer day

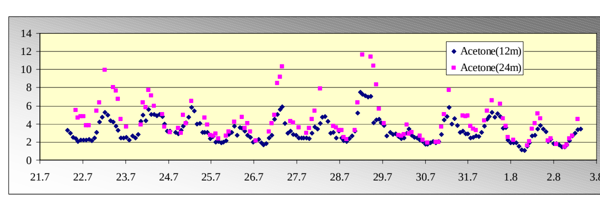
Result of first flux measurements:
positive flux values → emission
negative flux values → deposition

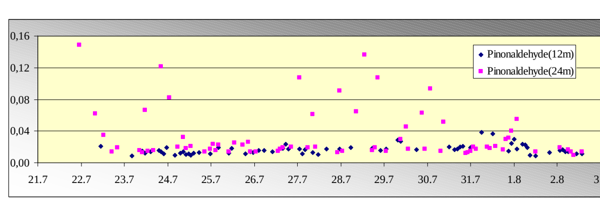


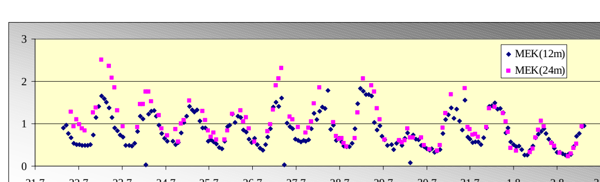
Main Carbonyl Compounds during „Golden Days“











Outlook

- Complete the measurements of the second field campaign.
- Comparison of data from both campaigns with data from cuvette measurements and flux measurements.
- Investigation of meteorological influences on the carbonyl compound concentrations.
- Delivery of a data set for the modelling group.

Acknowledgements

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