Oxygenated VOC Fluxes from Crop Harvesting using Proton-Transfer Reaction Mass Spectrometry and Eddy Covariance

Thomas Karl(1), Alex Guenther(1), Christian Lindinger(2), Alfons Jordan(2), Ray Fall(3) And Werner Lindinger(2)†

(1) ACD-NCAR, Boulder, CO, 80303, (2) Institute for Ionphysics, University of Innsbruck, Technikerstr. 25, 6020 Innsbruck, Austria

(3) Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder, CO, 80309 - 0215

We want to dedicate this contribution to the memory of Werner Lindinger, a true friend, an inspiring mentor, and an innovative scientist.

PTR-MS Application - Biogenic Trace Gases

Introduction

Here we demonstrate that the PTR-MS technique can be used to measure fluxes of various VOCs including oxygenates using eddy covariance. A response time of 0.12 sec and a detection limit of < 2 x 10^{-8} g $m^{-2}s^{-1}$ meet important requirements for eddy covariance measurements in many field applications. The total underestimation (sampling height of 1m, displacement between sampling line and averaging path of the sonic anemometer and a response time of 0.12 s) of the measured fluxes presented here is not greater than 20%. We tested the system in St. Johann/Tirol which is situated in a 53 km^2 valley basin in western Tirol. The major crop in this part of Austria are perennial grasses used for livestock farming. We observed that the major VOC emission fluxes included methanol and acetaldehyde as the major volatiles with lesser amounts of C_5 and C_6 leaf wound compounds and traces of acetone and butanone. This suite of VOCs is very similar to that released from slashed pasture grass (Kirstine et al., 1998). Releases of hay crop VOCs occurred in two phases: an initial burst following cutting, and a second larger phase as the hay dried. This behavior is consistent with laboratory studies which have shown similar results (deGouw et al., 2000, Karl 2000, Fall et al., 2001).

Results

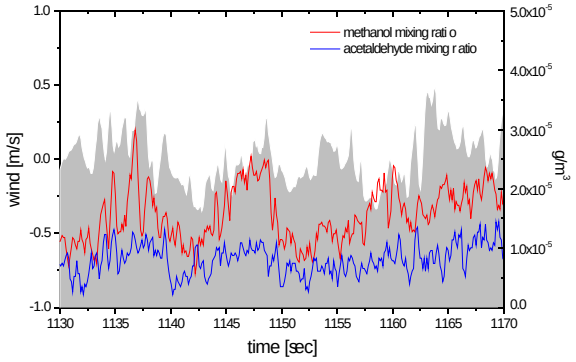

Figure 1 40 sec trace of Methanol and Acetaldehyde mixing ratios plotted together with vertical Windspeed (gray area).

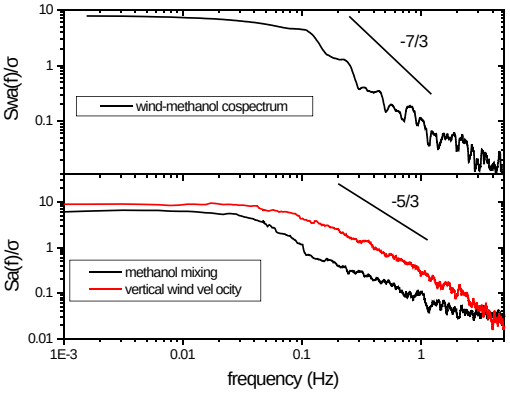

Figure 2 Lower Panel: Spectra for Methanol mixing ratio and vertical wind speed; the -5/3 slope indicates the theoretical slope of the inertial subrange. Upper Panel: cospectrum of methanol-wind demonstrating that high frequency noise is mainly random and independent of mixing ratios.

References

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Site describtion - Footprint

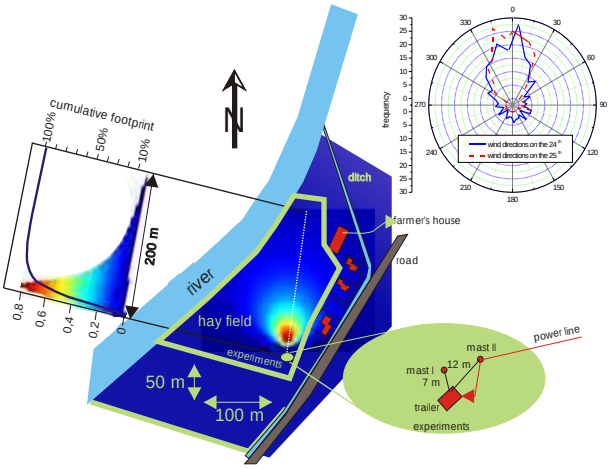


Figure 3 Description of the field site including wind directions on May 24 and 25. The experiments were situated at the south end of the field and are zoomed out. The footprint is indicated by colors ranging from red (highest contribution to total flux) to blue. A transect shows the differential and cumulative footrpint.

Fluxes

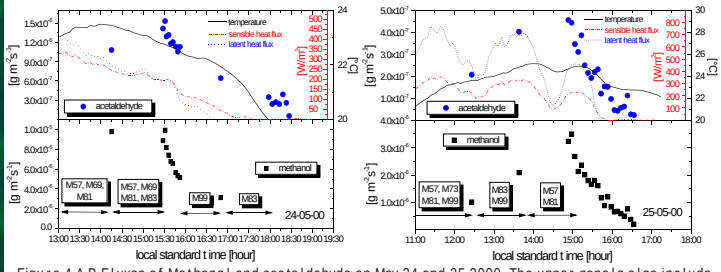


Figure 4 A,B Fluxes of Methanol and acetaldehyde on May 24 and 25 2000. The upper panels also include temperature and latent and sensible heat fluxes. VOC fluxes followed mainly sensible and latent heat fluxes. The arrows indicate times where eddy covariance was done for different compounds.

Table 1 Measured fluxes [$gm^{-2}s^{-1}$]

Fluxes obtained in May 2000			*Fluxes obtained in August 1999*
	Method		*Method*
Compound	*EC*	*Gradient*	*Gradient*
Methanol	9.9 x 10^{-6}	1.4 x 10^{-5}	2 x 10^{-6}
Acetaldehyde	1.5 x 10^{-6}	9.0 x 10^{-7}	8 x 10^{-7}
Hexenals	6 x 10^{-7}	3 x 10^{-7}	4 x 10^{-7}
Pentenals plus 3-Methylbutanal	2.0 x 10^{-7}	4 x 10^{-7}	8 x 10^{-8}
Hexanal plus 2(E)-Hexenol	6.7 x 10^{-7}	5 x 10^{-7}	8 x 10^{-8}
2-Butanone	4 x 10^{-8}	8 x 10^{-8}	<2 x 10^{-8}
Acetone	<2 x 10^{-8}	-5 to 7 x 10^{-8}	4 x 10^{-7}

Instrumentation - PTR-MS

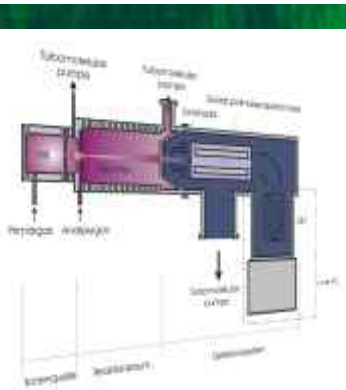
Protontransferreaction

$$H_3O^+ + R \rightarrow RH^+ + H_2O$$

Calculation of the neutral concentration

$$[RH] \quad \frac{1}{k\ t} \quad \frac{cps(RH^+)}{cps(H_3O^+)}$$

Residence Time: 120 ms
Sensitivity: 5-6 MHz H_3O^+ ions equivalent to 80-100 cps/ppbv



Acknowledgments

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