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Eddy covariance measurements of oxygenated volatile organic compound fluxes from crop harvesting using a redesigned proton-transfer-reaction mass spectrometer

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Abstract. A redesigned proton-transfer-reaction mass spectrometer was deployed in the field to measure atmospheric fluxes of volatile organic compounds (VOCs) released following the cutting and drying of hay. The instrument has a fast response, around 0.1 s, allowing use of the eddy covariance technique. Measurements were done over a 3-day period in a hay field in the eastern part of Tirol, Austria, in the early growing season and are compared to earlier results obtained using a slower-response instrument in the late growing season [*Karl et al.*, 2000]. Peak upward fluxes of the order of 9.9×10^{-6} g m^{-2} s^{-1} for methanol, 1.5×10^{-6} g m^{-2} s^{-1} for acetaldehyde, and 1.5×10^{-6} g m^{-2} s^{-1} for the sum of hexenals, hexenols, hexanal, pentenols, 3-methylbutanal, and butanone were observed during and after harvesting. Time-integrated values for the first day were of the order of 65 ± 20 mg m^{-2} (130 ± 40 µg per gram dry weight(gdw)$^{-1}$) for methanol and 13 ± 4 mg m^{-2} (26 ± 8 µg gdw^{-1}) for acetaldehyde. VOC fluxes measured in this study were generally higher than in August 1999, which can be explained by higher temperatures and higher photosynthetic productivity. Good agreement with another means for estimating VOC fluxes, the surface gradient method, was achieved. This paper presents measurements of eddy covariance for a wide variety of oxygenated VOCs and shows that hay harvesting can influence the local air quality in many regions in the Alps on a short-term basis.

1. Introduction

Measuring turbulent transfer of trace gases is one of the fundamental problems in studing atmospheric chemical exchange processes near the Earth's surface. In the past, several approaches have been used to measure fluxes near the surface, such as the surface layer gradient, the mixed layer gradient (e.g., with tethered balloons, *Greenberg et al.*, 1999), relaxed eddy accumulation (REA) [*Guenther et al.*, 1996], and most recently the disjunct eddy covariance system (DEC) [*Rinne et al.*, 2001]. All these methods, except DEC, do not require fast chemical sensors and are therefore suitable for cartridge sampling with subsequent gas chromatographic(GC) analysis. The assumptions made are often reasonable but can result in large errors in some cases [*Dabberdt et al.*, 1993]. Assuming the ergodic hypothesis, the most direct way to measure atmospheric fluxes is eddy covariance, which requires sampling rates of ≥ 8 Hz. Eddy covariance has been used for

momentum and temperature flux measurements since the late 1960s [*Kaimal and Businger*, 1970]. In contrast, only recently have the first volatile organic compound (VOC) sensors been introduced for monitoring fast VOC fluctuations, as in the case of isoprene using a chemiluminescence system [*Guenther and Hills*, 1998], and for acetone, ammonia, nitric acid, and formic acid, using an atmospheric-pressure-ionization mass spectrometer [*Shaw et al.*, 1998]. Nevertheless, these sensors are limited to a few volatile species, and a system that is able to measure a broader range of compounds (e.g., terpenes, aldehydes, and alcohols) is desired. Proton-transfer-reaction mass spectrometry (PTR-MS) has proven to be a valuable tool in quantifying atmospheric trace gases [*Crutzen et al.*, 2000]. A first test of the use of PTR-MS for eddy covariance analysis of VOC fluxes involved an instrument with a conventionally designed drift tube, allowing a response time of around 0.8 (~1 Hz); these experiments, performed in August 1999, were promising [*Karl et al.*, 2000]. Here we extend the capability of the PTR-MS instrument by redesigning the drift-tube segment in order to shorten the response time to ~0.12 s and by increasing the sensitivity by a factor of 3. We present eddy covariance measurements of a variety of oxygenated VOCs released after hay cutting and provide an assessment of the redesigned PTR-MS instrument's capability for estimating atmospheric fluxes of trace gases.

The role of natural and man-made VOCs in shaping the chemistry of the atmosphere is an important area of research [*Singh et al.*, 1995]. Living vegetation releases a large number of VOCs [*Helas et al.*, 1995; *Fall et al.*, 1999], and many of these compounds are reactive and can significantly alter the

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chemistry of the atmosphere [*Fehsenfeld et al.*, 1992; *Guenther et al.*, 1995]. The impact of VOCs on formation of atmospheric oxidants, such as ozone, is not limited to the Earth's remote forested areas. For example, forests surrounding metropolitan areas may release more reactive VOCs than man-made sources [*Chameides et al.*, 1992]. It is also well known that disturbed or wounded plants release a mixture of C_6 hexyl and hexenyl compounds that are derived from major leaf fatty acids; these VOCs are primarily responsible for the odor of cut grass [*Hatanaka*, 1993]. *Kirstine et al.* [1998] have shown that in addition to C_6 compounds, cutting grass or clover releases significant amounts of other oxygenated VOCs, ~0.25% of net primary productivity. Recently, PTR-MS was used to quantify VOC release from wounded plants, including grasses, in extensive laboratory experiments [*Fall et al.*,1999; *De Gouw et al.*, 2000]. It was also shown that significant amounts of VOCs can be released by freeze damaged and senescing vegetation in the late season [*Karl et al.*, 2000; *Fall et al.*, 2001b]; these VOCs included C_6 and C_5 compounds such as (E)-2-hexenal, (Z)-3-hexenal, hexenols, pentenols, and 3-methylbutanal. Many of these wound-induced compounds have reactivities with OH similar to that of isoprene [*Orlando et al.*, 2001] and may therefore play an important role in the atmosphere's oxidative capacity and in formation of secondary products. Recent observations of unusually high peroxypropionyl nitrate in air at North American field sites [*Williams et al.*, 1997; *Roberts et al.*, 1998] may be related to hexenyl compound emission during cutting and drying of crops and subsequent photochemical reactions.

We have been interested in assessing the fluxes of oxygenated VOCs resulting from intensive agriculture. Currently, there are continuing efforts to develop regional, North American, and global VOC emission inventories [*Lamb et al.*, 1993; *Guenther et al.*, 1995, 2000], but these inventories generally do not have well established emission factors for VOCs released from cropping. The work presented here is a first step in establishing crop VOC emission factors.

2. Experimental Methods

2.1. Instrumentation

The PTR-MS instrument design has been described in detail by *Lindinger et al.* [1998]. Here we just briefly discuss the basic underlying principles of this instrument. H_3O^+ ions, which are produced in a hollow cathode discharge, are injected into a conventional drift tube. The air to be analyzed itself acts as the buffer gas and is introduced at the front end of the drift tube segment at a pressure of 2.4 mbar. H_3O^+ ions will only react with trace components in the air having higher proton affinities (PA) than H_2O (165.2 kcal mol^{-1}); thus reactions with all major air constituents, such as N_2, O_2, CO_2, CH_4, and noble gases are excluded. This leads to

$$H_3O^+ + R \xrightarrow{\ k\ } RH^+ + H_2O \qquad (1)$$
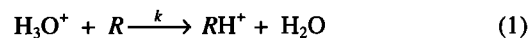
The density [R] of a neutral impurity R is calculated from the count rates per second (cps)(RH^+) and cps(H_3O^+) obtained in the downstream quadrupole mass spectrometer according to (1),

$$cps(RH^+) = cps(H_3O^+) \, (1 - e^{-k[R]t}) \cong cps(H_3O^+) \, [R] \, k \, t \qquad (2)$$

where t is the transit time of the H_3O^+ ions through the drift tube. The value of t is calculated from known mobility values of H_3O^+ in air [*Viehland and Mason*, 1995] or measured directly by pulsing ion signals and looking at the arrival time spectrum. The reaction rate coefficient k, related to the components studied in the present investigation, lies in the range 1.0×10^{-9} cm^3 s^{-1} $< k < 3 \times 10^{-9}$ cm^3 s^{-1}, close to their collisional limiting values.

Commercially available PTR-MS instruments (www.ptr-ms.com) usually show a response time between 0.8 and 1.5 s, thus limiting the sampling capability beyond 2 Hz. In principle, for flux experiments above a surface emission source, the lower response time can be compensated for by increasing the sampling height. However, this also leads to an increased flux detection limit because concentrations decrease
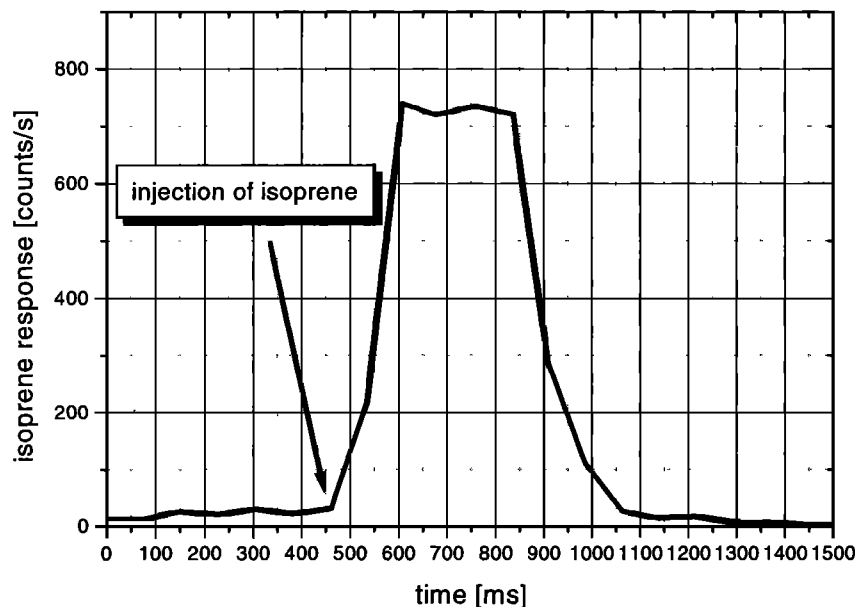

Figure 1. Injection of an isoprene standard showing the response time of the redesigned PTR-MS instrument.

Table 1. Summary of Breakup Patterns at 125 Townsend (Td) for C_6 and C_5 Compounds Released From Wounded Vegetation Major Fragments.

VOC	Protonated Parent	Ionized Mass Fragments, %
C₆ compounds		
(E)-2-hexenal	99	99 (33), 81 (13), **57 (54)**[a]
(Z)-3-hexenal	99	99 (27), **81 (69)**[a], 57 (4)
(Z)-3-hexenol	101	101 (1), **83 (74)**[a], 59 (5), 55 (22)
(E)-3-hexenol	101	101 (2), **83 (70)**[a], 59 (20), 55 (8)
(E)-2-hexenol	101	101 (0.2), **83 (76)**[a], 69 (0.8), 55 (23)
(Z)-3-hexenyl acetate	143	143 (2), **83 (61)**[a], 57 (3), 55 (34)
(E)-2-hexenyl acetate	143	143 (2), 99 (1), **83 (66)**[a], 55 (28), 39 (3)
hexanal	101	101 (5), **83 (95)**[a]
hexanol	103	**85 (29)**[a], 57 (17), 43 (40), 41 (14)
hexyl acetate	145	145 (3), 85 (8), **61 (53)**[a], 57 (5), 43 (27), 41 (4)
C₅ compounds		
2-methylbutanal	87	**87 (80)**[a], 69 (20)
3-methylbutanal	87	87 (25), **69 (75)**[a]
1-penten-3-ol	87	87 (<5), **69 (>95)**[a]
(Z)-2-penten-1-ol	87	87 (<5), **69 (>95)**[a]
(E)-2-penten-1-ol	87	87 (<5), **69 (>95)**[a]

[a] major fragments

with increasing sampling height. In order to increase the PTR-MS response time, we redesigned the original drift tube segment and minimized the exchange time of the buffer gas down to ~0.12 s, which makes this new instrument suitable for eddy covariance sampling at frequencies up to 8 Hz. Viton gaskets in the hollow cathode discharge and the drift-tube segment were changed to perfluoroalkoxy(PFA)-Teflon. This helped to reduce the instrument's background down below 10 pptv. Figure 1 shows the response time characteristics after injecting a short pulse of isoprene; half-maximal response occurred ~65 ms after injection. The sensitivity of the PTR-MS instrument was also improved by a factor of 3, resulting in count rates of the order of 180 Hz ppbv^{-1} (counts per second per parts per billion by volume) for acetone and 100 Hz ppbv^{-1} for methanol at 2.4 mbar buffer gas pressure with a reaction time of 110 µs and 5-6 MHz H_3O^+ ions, and thus infers a detection limit of ~100 pptv for a 0.1-s integration time. Using the relation $\delta F = \rho r \sigma_w \delta C$ for the purpose of error analysis, with ρ being the air density, r the correlation coefficient typically between 0.3 and 0.5, and the variance for vertical wind velocity $\sigma_w = 0.5$ m s^{-1}, provides a detection limit δF of ~2 x 10^{-8} g C m^{-2} s^{-1}.

In many cases the proton-transfer reactions are nondissociative [*Lindinger et al.*, 1998]; however, in the present case, where emissions of various pentenol, hexenal, and hexenol family compounds were investigated, dissociation can occur during

the proton transfer. Using standard compounds that were available commercially, we examined the fragmentation patterns of each under PTR-MS conditions that were identical to that used in field VOC flux analyses. The compounds measured appeared at the following masses: methanol (M33$^+$), acetaldehyde (M45$^+$), acetone (M59$^+$), pentenols plus 3-methylbutanal (M69$^+$), hexenals (M57$^+$, M81$^+$, and M99$^+$), hexanal plus hexenols (M83$^+$), and butanone (M73$^+$). The results for C_6 and C_5 wound compounds are summarized in Table 1. Confirmation was also achieved by a recently described GC-PTR-MS measurement method [*Fall et al.*, 2001b] as shown in Figure 2; these results suggest that for drying bluegrass (*Poa pratensis*) the main VOCs on masses M59$^+$, M69$^+$, and M83$^+$ are acetone, 1-penten-3-ol, and hexanal plus (E)-2-hexenol, respectively.

2.2. Site and Measurement Description

The field experiment was conducted on a 4 ha hay field in St. Johann in Tirol, Austria (latitude 47.5°N, longitude 12.4°E), from May 23 to 26 2000. The pasture grasses were dominated by *Dactylis glomerata*, *Poa pratensis*, *Phleum pratense*, *Trifolium pratense*, and *Poa trivialis*, which is the typical composition of alpine annual grasses used for hay production in this region. A map of the site including the dominant wind directions on May 24 and 25 is shown in Figure 3. The
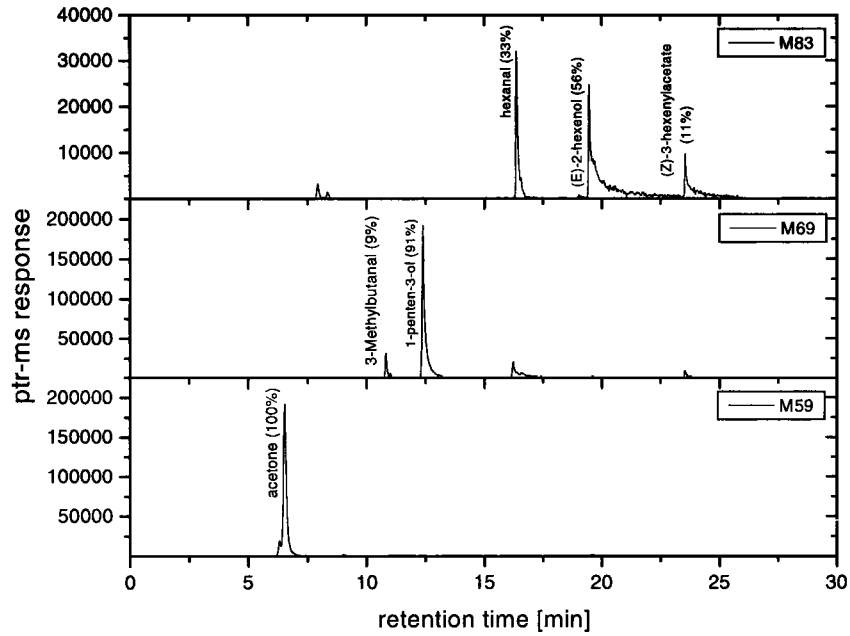
Figure 2. Gas chromatographic identification of protonated masses M83+, M69+, and M59+ using the PTR-MS instrument as detector. Chromatogram shown for VOCs released during the drying of bluegrass (*Poa pratensis*).

calculated footprint [*Horst and Weil*, 1992] for a measurement height of 4 m (Obukhov length L = -20 m) is also shown in Figure 3. The footprint for a measurement height of 4 m (upper inlet for surface gradient measurements) indicated that 90% of the cumulative footprint occurred within 200 m at an Obukhov length L of –20 m.

The experiments were situated at the south end of the field and included the redesigned fast response PTR-MS instrument for eddy covariance measurements and one commercially available PTR-MS instrument (response time of ~1.5 s) for surface layer gradient analysis. In addition, one REA system was applied [*Guenther et al.*, 1996]. At certain occasions,,
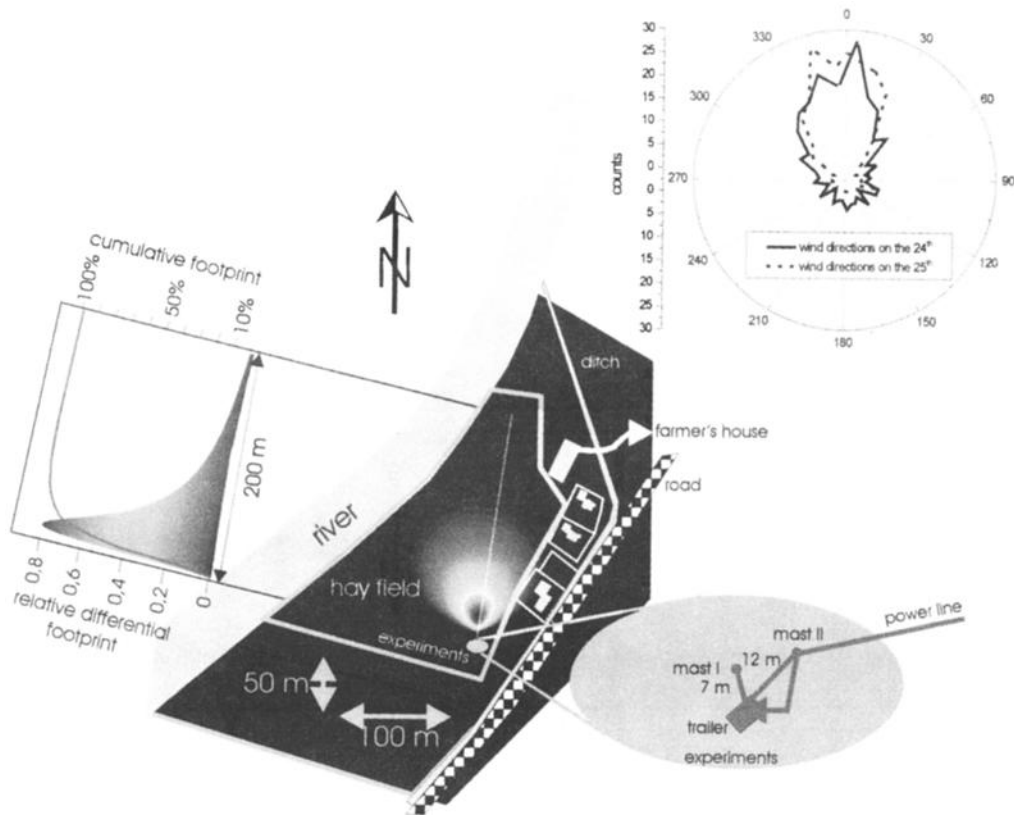

Figure 3. Description of the field site including wind directions on May 24 and 25. The experiments were situated at the south end of the field and are zoomed out. The footprint is indicated by the gray scale ranging from white to black. A transect shows the differential and cumulative footprint.

Teflon bags were connected for intercomparison and analyzed by the second PTR-MS instrument. Only measurements with the optimal fetch between 150 and 200 m were sorted out in order to calculate fluxes.

Eddy covariance measurements were performed at a height of 1 m above the ground. A 15 m tube (ID. ¼ inch) was pumped by a diaphragm pump (Pfeiffer, MD4) at a pumping speed of 15 L min^{-1}. A bypass with a 20-μm medium polar deactivated glass capillary (Supelco) led 15 cm^3 min^{-1} STP of this air stream into the PTR-MS instrument. This setup assured a fast response and caused a delay time of <1.7 s. The attenuation through the sample tubing was calculated according to *Massman* (1991) and could be neglected as significant high-pass filtering only occurred beyond 15 Hz.

The second PTR-MS instrument, which was used for surface layer gradients, measured the VOC compositions at heights of 1 and 4 m. Turbulence data were obtained from a USA-1 T sonic anemometer with a built in turbulence kit. The REA system sampled at a height of 1 m above ground. All three inlets at 1 m were placed within a distance of 1.5 m. The horizontal displacement between the eddy covariance sampling inlet and the averaging path of the sonic anemometer was ~30 cm. According to *Kristensen* et al. [1997], the resulting "flux loss" due to this horizontal displacement is estimated to be ~15%. A second three-dimensional (3-D) sonic anemometer (ATI) provided 10 Hz wind data for both the REA and the eddy covariance systems. Both sample inlets were placed near the sonic array. Two 10-m masts provided wind, temperature, and humidity (UMS, Umweltanalytische Meßsysteme) gradients at heights of 5 and 10 m. The intensive mast (mast I) also provided data for global radiation (Starpyranometer 8101) at a height of 3 m and pressure (UMS-Model276) at 1.5 m. Power was obtained from a nearby house via a 500-m-long cable, so that no diesel generator had to be used, avoiding unwanted interferences with some chemical species.

2.3. Data Acquisition and Data Treatment

Ten hertz wind and concentration data were recorded on two separate laptop computers which were synchronized in time every hour. In order to perform the Fourier analysis with subsequent calculation of spectra and cospectra the data sets were conditioned according to general aspects as discussed by *Stull* [1988]: (1) spike removal, (2) detrending, (3) substraction of the mean, and (4) removal of sharp edges with the bell taper function (multiplication of sine squared terms near the beginning and ending of each dataset)

In contrast to conventional atmospheric-pressure-ionization mass spectrometers, the PTR-MS strictly describes a system which is characterized by a first-order differential equation (1), so the time constant is dependent only on the delay time in the sample tubing. In order to get the delay time and to synchronize the corresponding wind and concentration data sets a correlation routine was applied similar to that discussed by *McMillen* [1988]. The maximal correlation within ±5 s was defined to be equal to the delay time plus uncertainties due to possible desynchronized time series. Two other powerful procedures for getting delay constants shall just briefly be mentioned. *Beier and Weber* [1992] modified the correlation optimization in the following way. The cospectrum around $1/t_d$ will show a significant change if the delay time (t_d) is varied. Wrong delay times act like a low bass and show a significant gap in the cospectrum. Another tool to assess delay times is to look at the quadratur spectrum Q_{wa} [*Stull*, 1988].

High correlation will cause a quadratur spectrum which is close to zero. If there is a phase shift, Q_{wa} will show a significant deviation around $1/t_d$ in direction of the time delay. In that way, not only t_d but also its sign can be calculated.

3. Results

Figures 4a and 4b show a 100-and 23-s trace of vertical wind (w), methanol, and acetaldehyde fluctuations, respectively, on May 24. Several features in these graphs show that there is a positive correlation between VOC mixing ratios and vertical wind speed. As indicated by the arrow in Figure 4a, a passage of a turbulent plume by the measurement mast with its characteristic ramp structure (similar to that observed by *Shaw et al.* [1998]) caused increasing VOC concentrations and a strong fall off afterward. Figure 4b shows that all major vertical wind fluctuations are positively correlated with methanol and acetaldehyde mixing ratios. Spectra and cospectra of methanol, acetaldehyde, and vertical wind velocities are shown in Figure 5 and were obtained after applying the data procedure described above. The methanol and acetaldehyde spectra follow the slope of -5/3 between 0.1 and 1 Hz, indicative for the inertial subrange. Above 1 Hz the spectrum for acetaldehyde rolls off earlier than that for methanol due to possible memory effects and apparent noise. Nevertheless, comparing with the covariance of vertical wind speed and temperature (wTcovariance), the resulting error is <5 % and thus can be neglected because natural high-frequency fluctuations are small. Looking at the wind-acetaldehyde cospectrum, high-frequency noise seems to be uncorrelated. Thus the flux lost due to a sampling rate of 8 Hz is much smaller than losses (~15%) caused by the sampling height (1 m) and the horizontal displacement between sampling inlet and sonic anemometer.

Diurnal variations of measured fluxes for methanol and acetaldehyde on May 24 and 25 are plotted in Figures 6a and 6b. The hay field was cut on May 24 between 0800 and 1000LT (local standard time). The local meteorological patterns resulted in northerly winds (optimal fetch) during most hours (see Figure 3). Thus only fluxes obtained with the optimal footprint are presented. To assure sampling rates of 10 Hz, only a few masses were monitored at a time. As indicated in Figures 6a(bottom) and 6b(bottom), eddy covariance measurements of methanol and acetaldehyde were interrupted at certain occasions. During these times, other compounds (indicated by their protonated masses) were monitored. Methanol and acetaldehyde were highest around 1430LT with maximal fluxes of 9.9 x 10^{-6} and 1.5 x 10^{-6} g m^{-2} s^{-1}, respectively, on May 24. During the second day, fluxes were generally lower by a factor of 3, yielding 3.4 x 10^{-6} g m^{-2} s^{-1} for methanol and 4.4 x 10^{-7} g m^{-2} s^{-1} for acetaldehyde. On both days a sharp decline of surface fluxes after 1500LT was observed. This decline is mainly correlated to falling latent and sensible heat fluxes, which are drawn together with acetaldehyde fluxes in Figure 6 (top). In addition, the farmer started collecting the hay at 1545LT on May 25. By 1630LT no hay remained on the field, and therefore VOC fluxes rapidly decreased below the detection limit. Lower VOC fluxes around midday on May 25 follow closely latent and sensible heat flux and indicate the passage of some convective clouds. Maximal temperatures (24°C on May 24 and 26°C on May 25) occurred in the early afternoon around 1400LT on both days. VOC fluxes seem to be driven by temperature (Figure 6b); a small lag period between the highest VOC
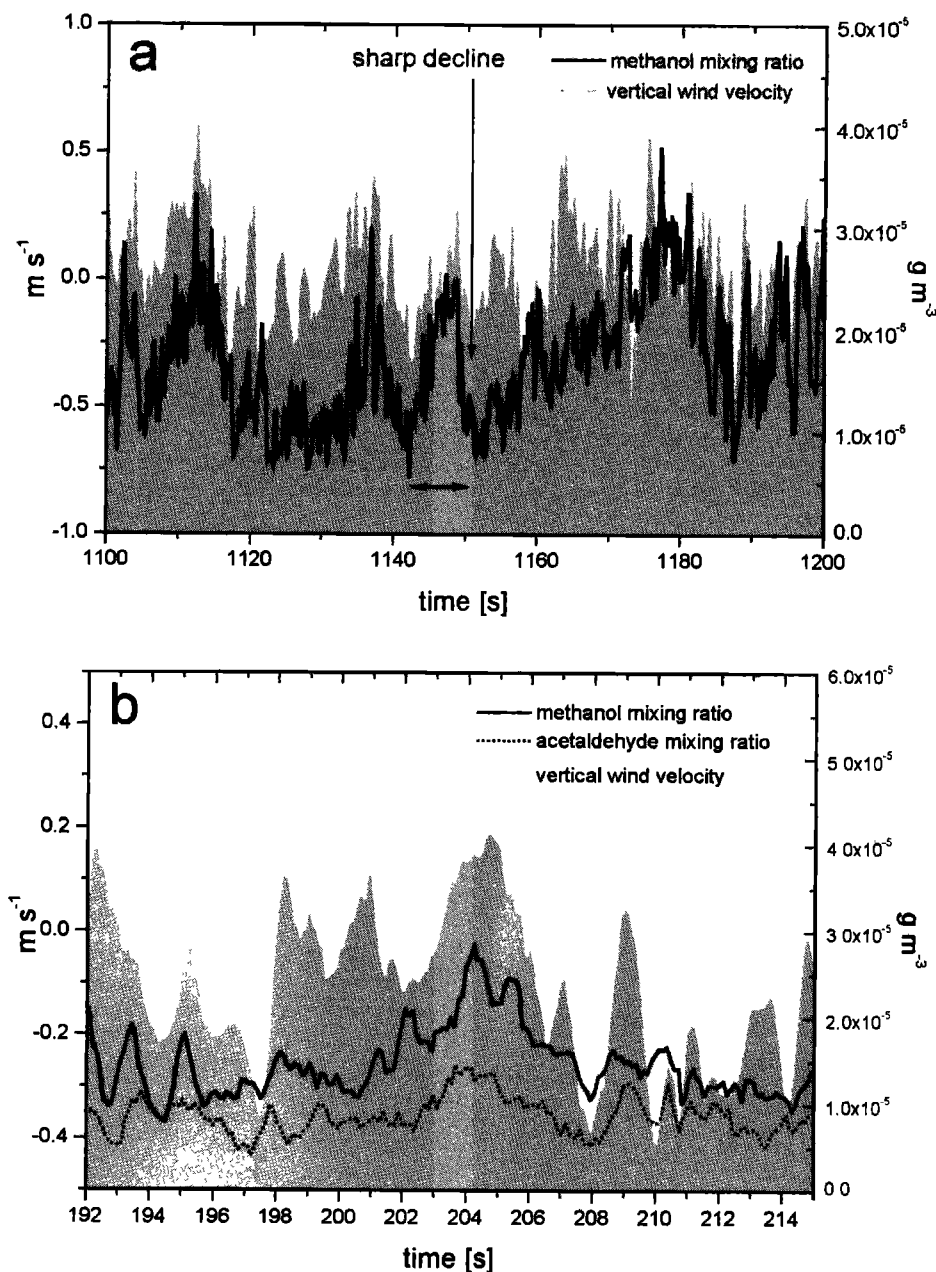
Figure 4. (a) A 100-s trace of methanol mixing ratios plotted together with vertical wind speed, and (b) a 23-s trace of methanol and acetaldehyde mixing ratios plotted together with vertical wind speed. The arrow in Figure 4a indicates a sharp decline of mixing ratios along with negative vertical wind speed showing the positive correlation between these quantities.

fluxes and the maximum ambient temperature can be rationalized by the expected delayed increase of the ground temperature.

Smaller fluxes of compounds associated with leaf wounding [*Kirstine et al.*, 1998; *Fall et al.*, 1999] such as hexanal, hexenals, hexenols, 3-methylbutanal, pentenols, and butanone, were observed on both days. The highest flux amongst these was observed for hexanal plus 2(E)-hexenol which peaked at 6.7×10^{-7} g m^{-2} s^{-1} on May 24. Protonated mass 99$^+$ which represents the sum of hexenal isomers showed upward fluxes in the range of 4-12 x 10^{-7} g m^{-2} s^{-1} on this day. Looking at the distinct fragments for (E)-2-hexenal (M57$^+$) and (Z)-3-hexenal (M81$^+$), measured at 1400 and 1630LT, suggests that the

abundance and thus their contribution to fragment M99$^+$, is ~50%. M69$^+$ (pentenols plus 3-methylbutanal) was observed to be in the range of 1-3.5 x 10^{-7} g m^{-2} s^{-1}. As stated earlier and shown in Figure 2, we think that for bluegrass and the four other species dominating this hay field, mainly 1-penten-3-ol contributes to the observed fragment M69$^+$; nevertheless, one has to be careful when extrapolating to all grass species present in the field. We clearly can exclude other interferences on M69$^+$ such as isoprene because no isoprene-emitting species were present in the hay field, and the general abundance of isoprene-emitting plants throughout the Alps is rather low [*Simpson et al.*, 1999]. Again, fluxes for the above mentioned compounds were generally lower by a factor of 3
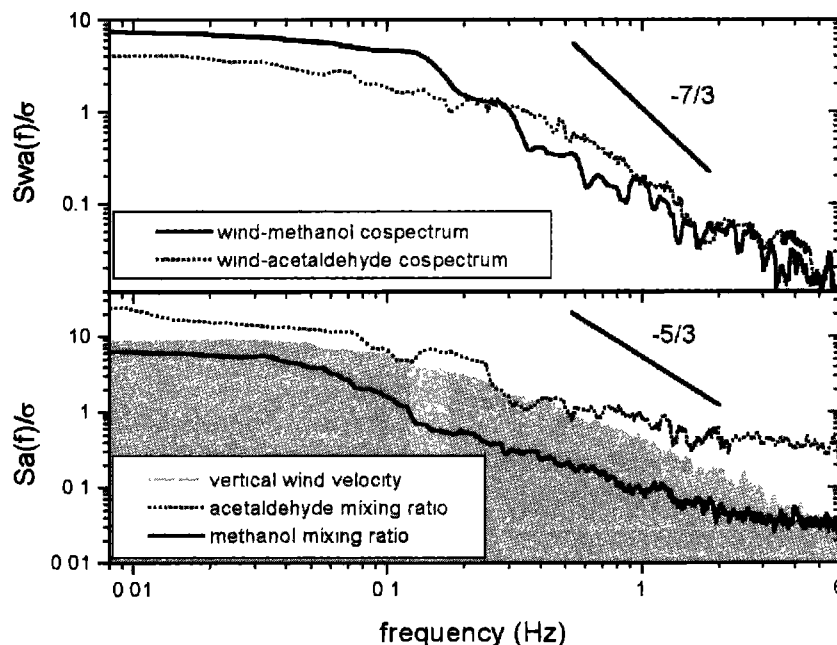
Figure 5. (a) Cospectra of methanol-wind and acetaldehyde-wind demonstrating that high-frequency noise is mainly random and independent of mixing ratio.(b)Spectra for methanol, acetaldehyde mixing ratios and vertical wind speed. The −5/3 slope indicates the theoretical slope of the inertial subrange.

on May 25. With only one exception, fluxes obtained in this early growing season (May 2000) study were higher than fluxes measured in the late growing season in August 1999 (Table 2). Higher fluxes can be rationalized by the fact that the net photosynthetic productivity (NPP) in spring is ~3 times higher than in fall and temperatures in fall are typically 3-5°C lower. In contrast to the experiment performed in August 1999 [*Karl et al.*, 2000], no significant fluxes for acetone were

found. One of the explanations for this discrepancy could be that acetone has many sources including photochemical production. These additional sources for acetone can also result in deposition. Significant downward fluxes for acetone, above grassland, for example, were observed by *Shaw et al.* [1998]. Acetone concentrations during this field study were in the range of 1-5 ppbv, and friction velocities (u^*) were of the order of 0.25 to 0.45 m s^{-1}. Thus small acetone fluxes cannot
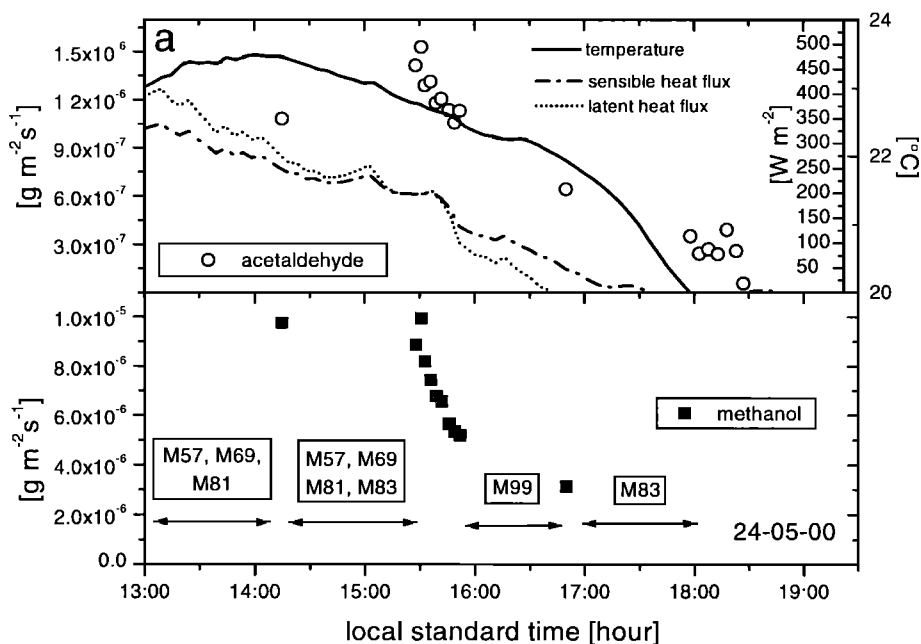

Figure 6a. Fluxes of methanol and acetaldehyde on May 24, 2000. (top) temperature and latent and sensible heat fluxes. VOC fluxes followed mainly sensible and latent heat fluxes. (bottom) indicating times where eddy covariance was done for different compounds.

Figure 6b. Fluxes of methanol and acetaldehyde on May 25, 2000. (top) temperature and latent and sensible heat fluxes. VOC fluxes followed mainly sensible and latent heat fluxes. (bottom) indicating times where eddy covariance was done for different compounds.
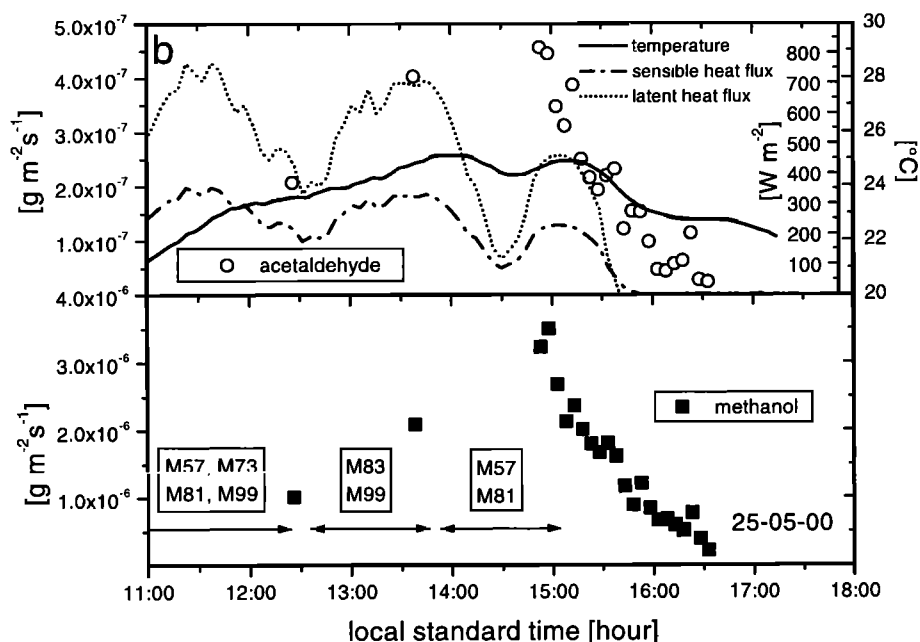
be explained by small mixing ratios or insufficient turbulence but are due to compensating downward (deposition) and upward (emission) fluxes in the surface layer (correlation coefficient r_{cw} close to zero). For this reason, observed net fluxes for acetone may not reflect the upward flux of acetone from drying hay. Generally higher emission rates for acetone from chamber experiments [De Gouw et al., 1999; Karl, 2000] could be explained by this effect. Small downward fluxes of acetone measured by the gradient technique before cutting and after the hay had been collected also seem to support this idea. Compared to hexenals, fluxes for butanone were observed to be lower by a factor of 10 yielding values of ~8 x 10^{-8} g m^{-2}s^{-1} on May 24 and ~4 x 10^{-8} g m^{-2}s^{-1} on May 25. This agrees well with emissions for butanone obtained from chamber experiments [Karl, 2000] which yielded 10-80 μg per gram dry

weight (gdw^{-1}) compared with 100-240 μg gdw^{-1} for hexenal emissions [Karl et al., 2000].

The range for the above mentioned emissions probably reflects the variability between different species. It also shows that the variability of hexenyl-type compounds seems to be less than that for butanone. Part of this variability can be attributed to a different biochemical origin for butanone and acetone. The production mechanisms for the latter compounds, which are probably linked to cyanogenic glycoside metabolism [Fall et al., 2001a], seems to be more variable among plants than the C_6 wound mechanism [Hatanaka, 1993]. De Gouw et al. [1999] reported total emissions of 800 μg gdw^{-1} (acetone) and 700 μg gdw^{-1} (butanone) for clover. These values are 10 times higher than the above mentioned emissions for five natural perennial grasses investigated here. This demonstrates

Table 2. Comparison of Measured Fluxes by Various Methods and at Two Sites in Western Austria.[a]

Compound	Fluxes obtained in May 2000, g m^{-2}s^{-1}		Fluxes Obtained in August 1999, g m^{-2}s^{-1}
	EC	Method Gradient	Gradient Method
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}
Pentenols plus 3-Methylbutanal	2.0 x 10^{-7}	4 x 10^{-7}	8 x 10^{-8}
Hexanal plus (E)-2-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}

[a]The data represent the highest fluxes observed on the first day after cutting.
EC; eddy covariance.

that owing to the variability of acetone and butanone emissions from different hay crops, extrapolation to global scale has to be done with extreme caution.

Table 2 lists the major VOC fluxes we measured and compares results obtained from eddy covariance, the surface gradients, and a flux experiment which we performed in August 1999 [Karl et al., 2000]. Fluxes obtained with these different methods generally agree well. In each case, methanol and acetaldehyde showed the highest fluxes. Measured values obtained in August 1999 are lower for the reasons discussed above. We did not observe a significantly different VOC emission pattern between the 1999 study and the present one, which suggests that there is no large seasonal trend.

Integrated emissions for methanol and acetaldehyde are 65 ± 20 and 13 ± 4 mg m^{-2}, respectively, on May 24 and were approximately lower by a factor of 3 on May 25. The average biomass density was measured to be 500 gdw m^{-2}, thus yielding 130 ± 40 µg methanol gdw^{-1} and 26 ± 8 µg acetaldehyde gdw^{-1}. These numbers are in reasonable agreement with results obtained previously from chamber enclosures (160 µg methanol gdw^{-1}, 20-80 µg acetaldehyde gdw^{-1}) [Karl, 2000]. These values were integrated over the measurement period, assuming that emissions in the morning and during the night were significantly lower. Although the decreased turbulence (friction velocities < 0.2 m s^{-1}) during the stable nocturnal boundary layer did not allow us to measure nighttime fluxes accurately enough, we can justify decreased emission rates by significantly lower mean concentrations (methanol and acetaldehyde concentrations were lower by a factor of 8 and 5, respectively). If emissions during the night were similar to those during the day, the stable nocturnal boundary layer would cause enhanced concentrations during the night because pollutants would be trapped in a smaller reservoir layer.

4. Discussion

This paper presents results that show that the redesigned, fast-response PTR-MS instrument can be used to measure fluxes of various VOCs including oxygenates using eddy covariance. A response time of 0.12 s 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 1 m, displacement between sampling line and averaging path of the sonic anemometer, and a response time of 0.12 s) of the measured fluxes presented in this paper 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 is perennial grasses used for livestock farming. We demonstrated 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 [De Gouw et al., 1999, 2000; Karl, 2000]. These phases can be explained by release from cellular pools (e.g., methanol), by rapid formation by metabolic disruption (e.g., acetaldehyde), and by well-known leaf wound response (e.g., hexenals) [Fall et al., 1999]. The

continued VOC releases during the drying of cut hay is likely explained by the slow collapse of cellular structures, which results in additional VOC formation.

About 50% of the St. Johann basin area is covered by hay fields which are harvested 3 times (April-May, June-July, August-September) per year. Because of sudden weather changes, harvesting in this area can be limited to a few days in each of these periods, resulting in intensive harvesting periods. If 30% of the farming area around St. Johann is subjected to mowing activities and subsequently covered by drying vegetation, this would give an input of ~6.7 x 10^6 g d^{-1} methanol, 1.3 x 10^6 g d^{-1} acetaldehyde, and a total of 1.3 x 10^6 g d^{-1} for all other reactive compounds investigated in this work. Lifetimes for these compounds are in the range of a few hours for pentenals [Orlando et al., 2001] and hexenals [Atkinson et al, 1995] to 1 day for acetaldehyde and 200 days for methanol. Acetaldehyde also has a significant photolysis rate. Photochemical degradation of the reactive VOCs mentioned would contribute to photochemical oxidant formation including peroxyradical production by well-known mechanisms [Atkinson, 2000]. From our results we estimate the potential area average reactive VOC emission for St. Johann hay fields to be ~1.6 x10^5 g km^{-2} d^{-1}. This is higher than the estimated area average reactive VOC emission (~1 x10^5 g km^{-2} d^{-1}) for the South Coast Air Basin (SOCAB, Los Angeles) [Harley et al., 1992]. Model studies [Lloyd et al., 1989] for the Los Angeles Basin, which is considered to be one of the most polluted urban areas in the United States, have shown that in order to meet the National Ambient Air Quality Standard (NAAQS), the area average reactive VOC emission has to be reduced down to ~1 x10^4 g km^{-2} d^{-1} to meet the U.S. standard for ozone (assuming that NO$_x$ emissions are at ~1 x10^4 g km^{-2} d^{-1}). The St. Johann basin faces increasing transit traffic and thus high NO$_x$ levels resulting from car exhaust. A traffic census on the B312 highway, which is one of the major east-west transit routes in Austria crossing the St. Johann basin, yielded a mean of ~4600 cars and ~900 trucks per working day in May 2000 (http://www.bmv.gv.at). Peroxyradicals under high NO$_x$ conditions react to give peroxyacetyl nitrate (PAN)-type compounds. These secondary products are important species in photochemical smog and sequester NO$_x$ into longer lived species. Therefore PAN-type compounds make NO$_x$ available for long range transport. Whereas acetaldehyde mainly reacts to form PAN, hexenals give rise to peroxypropionyl nitrate (PPN) [Atkinson et al., 1995]. Interestingly enough, high values of PPN were observed at field sites near areas subjected to intensive agriculture [Williams et al., 1997; Roberts et al., 1998]. Thus, together with anthropogenic NO$_x$ emissions, reactive VOCs such as acetaldehyde, hexanal, pentenols, hexenols, and hexenals will influence the local air quality in many regions in the Alps on a short term basis and might have an impact on the increasing ozone levels that have been measured in the Alps [Prévôt et al., 2000].

Biogenic sources are estimated to produce more than 90% of the annual global VOC emission of ~1150 Tg yr^{-1} [Guenther et al., 1995]. Recent studies have considered the contributions of cut grass to this annual total. Kirstine et al. [1998] estimated a global oxygenated VOC flux of 35 Tg yr^{-1} from grasslands and suggest that about half of this total would be associated with wounding if cutting or grazing occur about every 7 weeks. Their estimates do not include emissions from drying grass. De Gouw et al. [1999] calculate a global annual acetone flux

of 1.6 Tg yr^{-1} from drying hay. This flux is based on a global hay production of 2×10^4 Tg yr^{-1} which is ~20 times greater than the estimate of 1999 hay production given by the Food and Agricultural Organization (FAO) of the United Nations agricultural statistics database (*http://apps.fao.org*). Using the FAO 1999 hay production estimate and the emission rates obtained from this study, we estimate that the annual global sum of all oxygenated VOCs from hay drying is of the order of 1 Tg (~0.1% of the global total). This result indicates that annual global emissions of oxygenated VOC from drying hay are a very small component of VOC emissions from all sources. However, it does not rule out the possibility that hay drying could be a significant source of specific compounds especially given the apparent large variability in emission rates for compounds such acetone and butanone. Additional work is needed to determine if drying hay makes a significant contribution to global annual emissions of these compounds.

Here we have quantified VOC fluxes during hay harvesting in the field in the early growing season. Our results support the idea that hay cropping and harvesting under certain circumstances can have a significant influence on local air chemistry. Wounded vegetation resulting from man's activities or natural processes (e.g., senescing vegetation [*Karl et al.*, 2001]) can lead to a substantial input of VOCs in the troposphere and thus should be taken into account in regional photochemistry models. The fast-response PTR-MS instrument described here will be useful in quantifying these fluxes.

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