**Atmospheric
Chemistry
and Physics
Discussions**

Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF

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Abstract

Eddy covariance (EC) is the preferable technique for flux measurements since it is the only direct flux determination method. It requires a continuum of high time resolution measurements (e.g. 5–20 Hz). For volatile organic compounds (VOC) soft ionization via proton transfer reaction has proven to be a quantitative method for real time mass spectrometry; here we use a proton transfer reaction time of flight mass spectrometer (PTR-TOF) for 10 Hz EC measurements of full mass spectra up to m/z 315. The mass resolution of the PTR-TOF enabled the identification of chemical formulas and separation of oxygenated and hydrocarbon species exhibiting the same nominal mass. We determined 481 ion mass peaks from ambient air concentration above a managed, temperate mountain grassland in Neustift, Stubai Valley, Austria. During harvesting we found significant fluxes of 18 compounds distributed over 43 ions, including protonated parent compounds, as well as their isotopes and fragments and VOC-H$^+$-water clusters. The dominant BVOC fluxes were methanol, acetaldehyde, ethanol, hexenal and other C_6 leaf wound compounds, acetone, acetic acid, monoterpenes and sequiterpenes.

The smallest reliable fluxes we determined were less than 0.1 nmol m^{-2} s^{-1}, as in the case of sesquiterpene emissions from freshly cut grass. Terpenoids, including mono- and sesquiterpenes, were also deposited to the grassland before and after the harvesting. During cutting, total VOC emission fluxes up to 200 nmol C m^{-2} s^{-1} were measured. Methanol emissions accounted for half of the emissions of oxygenated VOCs and a third of the carbon of all measured VOC emissions during harvesting.

1 Introduction

Traditional flux measurement techniques of volatile organic compounds (VOCs) using proton-transfer-reaction – mass-spectrometry (PTR-MS) enable either eddy covariance (EC) measurement of one compound or disjunct eddy covariance (DEC) of

several selected volatile organic compounds (e.g., Karl et al., 2001). Conventional PTR-MS uses a quadrupole mass filter which allows measuring one mass at a time with a mass separation capability of one atomic mass unit. The newly developed PTR – time-of-flight (PTR-TOF) (Graus et al., 2010, Jordan et al., 2010) can measure
5 10 Hz time series of full mass spectra with a mass accuracy sufficient to determine chemical formulas (i.e. separate oxygen containing VOCs from pure hydrocarbons). Data processing methods of continuous high-time and high-mass resolution PTR-TOF data has previously been described by Graus et al. (2010). It was demonstrated that a mass resolution of 4400 m/Δm and a mass accuracy of 2.5 ppm can be achieved if
10 internal calibrations of the temperature dependent mass scale are continuously performed. Unlike in the PTRMS where transmission decreases drastically after 100 m/z, the PTR-TOF sensitivity increases towards heavier compounds providing enhanced detection capacity of semi-volatile organic compounds. The 10 Hz measurement of full mass spectra and gain in sensitivity at high masses is in particular important when
15 determining simultaneous emissions of heavier compounds (for example protonated sesquiterpenes at 205.1945 m/z) and the deposition of oxidation products of emitted VOCs. The features of the PTR-TOF enable simultaneous measurement of EC fluxes of all protonated VOCs, no longer constraining the flux measurements to a preselected set of a limited number of compounds. Müller et al. (2010) described how 10 Hz TOF
20 datasets can be binned to infer compound specific count rates for spectra that contain up to 150 000 time-of-flight bins. We show how to widen the VOC flux measurements from a hand full of species measurable by the PTR-MS combined with DEC to the measurement of simultaneous EC fluxes of all species detectable by the PTR-method with the PTR-TOF. Determining the simultaneous EC fluxes opens up a new possibility to
25 screen fluxes for a wide range of organic compounds and allows determining their fate in the atmosphere (e.g. deposition fluxes) ultimately improving the understanding of VOC biosphere-atmosphere-interactions. Due to the rapid mass scanning ability of the PTR-TOF, the sum of emissions of all detectable VOCs can be measured to decrease the uncertainty in the amount of carbon released as VOCs (Chapin et al., 2006), to

investigate the role of VOCs in the missing reactivity observed in OH-reactivity measurements (e.g., Sinha et al., 2010), and explore the argument that the current emission inventories may miss up to half of the reactive carbon as a VOC flux entering the atmosphere (Goldstein and Galbally, 2007; di Carlo et al., 2004).

Current estimates of the annual production rate of secondary organic aerosols (SOA) lie between 12 and 200 Tg/yr (Kanakidou et al., 2005; Hallquist et al., 2009), mainly due to gaps of knowledge in aerosol formation processes and to the uncertainty of emissions of biogenic and anthropogenic SOA precursors. Secondary aerosol formation has been related to growth from BVOCs that are oxidized in the atmosphere (e.g., Claeys et al., 2004; Tunved et al., 2006; Laaksonen et al., 2008). Mono- and sesquiterpenes have been identified to take part in SOA formation; due to large uncertainties in the primary emissions of VOCs more SOA precursors are expected to be found (Kanakidou et al., 2005). Recent findings suggest that organic compounds can take part in the nucleation itself (Metzger et al., 2010) and that the composition of the available BVOCs is important while Kiendler-Scharr et al. (2009) found that in certain conditions isoprene can also reduce organic aerosol formation. Therefore it is no surprise, that SOA is currently poorly constrained in regional air quality models as well as in global climate models. The lack of understanding SOA formation also presents a significant uncertainty for radiative forcing calculations used to assess climate change (IPCC, 2007).

BVOC emissions depend on the plant species and are affected by plant development, acclimation and various stresses (e.g., Ninemets et al., 2010). In addition to the seasonal and annual variation in plant BVOC emissions, changes in land use and grown crop species may affect the atmospheric VOC composition. Ambitious expansion of the biofuel industry receives growing interest for offsetting carbon emissions. This could have consequences for air quality mitigation strategies if selected biofuel crops emit significant amounts of reactive VOCs that in return increase tropospheric ozone production. Lawn mowing activities have also been identified as a source of reactive VOCs (Karl et al., 2001b) in urban areas, where ozone production tends to be

limited by the availability of VOCs.

In this paper, we revisit the question of reactive VOC emissions from harvesting and grass cutting activities using a PTR-TOF and simultaneously survey fluxes of all compounds detectable with the PTR-method. We expand the analysis procedures described by Müller et al. (2010) and present PTR-TOF data processing methods for flux calculations of a wide range of compounds with different properties. In particular we evaluate basic quality control procedures necessary for finding correct lag-times in PTR-TOF datasets to determine which ions (m/z) in the mass spectra are emitted or deposited. We list factors that must be taken into account when identifying emitted and deposited compounds using PTR-TOF measurements. We also discuss the reliability of the obtained fluxes and the confidence of absolute flux values using results from 10 Hz VOC measurements over grassland during periods characterized by growing, drying of cut grass and grass after harvesting.

2 Methods

2.1 Field site and instrumentation

VOC fluxes were measured at a field site above temperate mountain grassland, in the Stubai valley, Austria, close to the village of Neustift (47° 07′ N, 11° 19′ E) at 970 m a.s.l.. The measurement location is in the middle of the flat valley bottom and the flux footprint consists mainly of two patches with similar vegetation that are intensively managed by two different farmers. Graminoids make up on average 20–40% of the total above-ground biomass, the rest being forbs (Wohlfahrt et al., 2010). A detailed description of the field site, including a description of vegetation, soil and climate, is given by Wohlfahrt et al. (2008). Bamberger et al. (2010) have described diurnal patterns of methanol, acetaldehyde, and leaf wound compound fluxes during harvesting at the field site from disjunct eddy covariance measurements of 15 masses using a PTR-MS.

Here we present fluxes for three sunny periods from August 2009: intact fully grown

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grassland with a green area index (GAI) of 6.5 m^2 m^{-2} (intact grass, 1–2 August), cut and drying grass (cut grass; 5–6 August) and the field after the grass had been removed, with a GAI of 1.7 m^2 m^{-2} (after harvesting; 7–8 August). During the period of intact grass 1–2 August, daytime temperature maximum was 29 °C and nighttime minimum 8 °C. The 3 August was a cool, cloudy and rainy day, with daytime maxima of 17 °C and 28 mm of rain. The edges of the field patch were cut on the evening of the 4 August and the patch itself was cut at 9 a.m. (all times in Central European Time) and left to dry on 5 August. The cut grass was turned on 5 August and in the morning on 6 August; it was removed between 02:30 and 05:00 p.m. on 6 August. After the grass cutting the days were sunny and the temperatures varied between 10 °C (nighttime) and 25 °C (daytime).

The three wind components and the speed of sounds were measured using a three-dimensional sonic anemometer (R3IA, Gill Instruments, Lymington, UK) at 20 Hz acquisition frequency. The VOC inlet was mounted 2.5 m above ground, and 0.1 below and laterally 0.1 m from the center of the 3-D sonic anemometer. Sample air was drawn through a temperature stabilized (35 °C), 12 m long ¼″ Teflon® tube (ID 3.9 mm) to the PTR-TOF with a constant flow of 9 standard liter per minute (SLPM). We heated the PTR-TOF drift tube to 50 °C and operated at 600 V drift voltage and 2.3 mbar drift tube pressure, corresponding to an E/N ratio of about 130 Td (E being the electric field strength and N the gas number density; 1 Td=10^{-17} V cm^2). We measured instrumental background (zero calibration) 2–4 times per day (each time for 25 min) at ambient humidity levels from VOC-free air from a continuously flushed, home-built catalytic converter at 350 °C. Sensitivity calibrations were performed by dynamic dilution of VOCs using a multi-component gas standard (Apel Riemer Environmental Inc., USA) on 31 July and 8 August. The calibration gas contained acetone, acetonitrile, acrolein, benzene, 2-butanone, ethanol, formaldehyde, hexanone, isoprene, methanol, monoterpenes (α-pinene), nonanone, octanone, toluene, o- and p-xylene. The instrument performance was stable and signal intensities were good. For example, methanol sensitivity was 33 cps/ppbv and acetone 70 cps/ppbv and the

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sensitivities varied only 2.2% between the calibrations. The oxygen containing compounds (acetone, acrolein, hexanone, octanone and nonanone) had a higher average normalized sensitivity of 26.6 ncps/ppbv (between 22.5 and 31.1 ncps/ppbv) than the pure hydrocarbons (isoprene, toluene and xylene) that had an average normalized sensitivity of 15.0 ncps/ppbv (between 12.6 and 18.1 ncps/ppbv). For the compounds that were not calibrated, we used the average normalized sensitivities for oxygen containing compounds and for pure hydrocarbons, respectively. The time-of-flight path length is sensitive to temperature variation and therefore mass scale calibration was done continuously by adding dichlorobenzene (protonated $m/z = 146.9763$) and trichlorobenzene (protonated $m/z = 180.9373$) to the PTR-TOF inlet. A thorough description and characterization of the PTR-TOF instrument is given by Graus et al. (2010). Müller et al. (2010) describe the data acquisition and processing methods used for flux measurements in detail which will be described only shortly below.

The PTR-TOF determines the arrival times of all ions with a 0.2 ns time resolution resulting in 150 000 "bins" per spectrum with a multi channel plate and a time to digital converter (TDC). By storing 3333 co-added extractions per spectra we measured a 10 Hz time series of full PTR-TOF spectra. The data was acquired in 6 min segments (hdf5 file format (http://www.hdfgroup.org/)) using the TOF-DAQ v1.72 software (Tofwerk AG, Switzerland). Each of the 6 min PTR-TOF spectra was mass scale corrected using Matlab (Mathworks, USA) based functions by M. Müller that have been described by Müller et al. (2010). We obtained one mass scale spectrum each 0.1 s between m/z 20 and m/z 315. The ion counts were inferred from peak fitting of the six minute sum spectra. The measured mass resolving power (m/Δm) and mass accuracy – determined from the calibration data – were 4800 and better than 10 ppm, respectively. The mass accuracy was sufficient to determine chemical formulas; for example to separate pure hydrocarbons from oxygen containing VOCs.

2.2 VOC flux calculations and quality assurance

We calculated eddy covariance fluxes for 481 mass peaks from the 10 Hz PTR-TOF signal and the 20 Hz sonic anemometer data. The used Matlab-routine was based on a method described by Karl et al. (2002). We re-sampled the 20 Hz wind data to match the 10 Hz VOC data, applied a three-axis coordinate rotation of the wind data according to Wilczak et al. (2001) and determined the maximum covariance between smoothed, de-trended VOC concentrations and the vertical wind velocity in a lag-time window. If a maximum (or minimum) was not found within a time window between -2 s and 2 s seconds we used a lag-time of 2 s or – when available – chose the previously found lag-time. With this routine we calculated half-hour mean flux values for all 481 ion mass peaks determined from a 6 min average spectrum using peak fitting routines described by Müller et al. (2010). As a first quality control criterion we searched for fluxes that were either higher than 0.05 nmol m^{-2} s^{-1} or lower than -0.05 nmol m^{-2} s^{-1} for at least 5% of the entire sampling period. This filtering resulted in 107 remaining ion mass peaks that were visually inspected for their fluxes. Chemical formulas were assigned to the remaining mass peaks which are listed in Table 1.

We selected half hour periods that fulfilled the quality criteria for reliable flux measurements (turbulence, stationary test, footprint) based on Bamberger et al. (2010). The half-hour flux uncertainty was calculated for each compound using a visual inspection for rating: fluxes that exhibited a distinct and well defined maximum (or minimum) of the covariance were rated as class-A fluxes; fluxes with poorly defined maxima (or minima) (e.g. broad peaks with no sharp maximum or minimum around the lag-time) were rated as class-B fluxes; other calculated flux values were considered as noise. We removed half-hour periods with clear anthropogenic influence indicated by benzene and toluene volume mixing ratios above 2 ppbv (in total 2.5 h).

The flux uncertainty was determined from the noise of the covariance function in the manner proposed by Wienhold et al. (1994) and adapted by Spirig et al. (2005). The idea is to determine the general noise of the covariance by calculating the standard

deviation of the covariance for time shifts between vertical wind velocity and concentration that are well beyond the integral time scale (true lag-time). Spirig et al. (2005) determined the noise of two 20 s lag windows; here we opened the noise window to 40 s. Our true lag was around 0 s and we calculated the noise between lag-time ranges of -190 s to -150 s and 150 s to 190 s and multiplied it by 1.96 to get a 95% confidence interval for each flux measurement (Rinne et al., 2007).

3 Results and discussion

3.1 Influence of water flux on VOC fluxes

When determining the compounds that are emitted or deposited, it is important to take into account the possibility of water flux induced protonated mass peak fluxes. Changes in relative humidity of the sample air can affect the primary ion and water cluster distribution in the drift tube, especially under conditions of low to moderate collision energies in the drift tube. The simultaneous flux of water can influence fluxes observed for VOCs with humidity influenced detection. The fluxes of compounds that have a proton affinity high enough to enable a direct proton transfer from water clusters (mainly $H_2OH_3O^+$ and $(H_2O)_2H_3O^+$), in addition to the proton transfer from the primary ion (H_3O^+), are influenced very little if at all. However, the flux of water will have a contribution if the compound is protonated by ligand switching: a flux artifact can result when the compound forms a ligand with the water cluster (that has a real flux), breaks down in the drift tube and is detected as a protonated compound. In addition, the compound-water-cluster flux is a combination of the flux of the compound and water. In the following section we will describe how to identify and take into account humidity influences on VOC fluxes.

3.2 Identification of emitted and deposited compounds

The PTR-TOF was used to detect emitted and deposited compounds and to identify their chemical formula, after the PTR-TOF flux datasets was interpreted with caution and observation of one compound at several ions was taken into account. From the visual inspection we found 37 out of the 107 ion mass peaks that had a well defined covariance (referred to class- A fluxes), 12 ion mass peaks had only a poorly defined covariance (referred to class-B fluxes), and the rest (58) of the ion mass peak covariance functions did not show a local maximum or minimum and were associated with random covariance (noise). Class-B fluxes were typically observed for ion mass peaks with low signal intensities e.g. for isotopes of prototaned compounds and for compounds that had been ionized by charge transfer or had humidity dependent ion mass peak signals. Humidity dependent class-B fluxes were observed for several ions including protonated di- and trichlorobenzene that were added to the inlet in high amounts for accurate and continuous mass scale calibration. Fluxes due to ionization by charge transfer of ions produced in the instrument (such as O_2^+, NO^+, N_2H^+, CO_2H^+) and humidity dependency were considered as measurement artifacts. Here we define a physically meaningful flux: 1) the flux was not a measurement artifact 2) the ion mass peak did not correspond to an isotope or VOC-water cluster or a fragment of a protonated compound exhibiting a flux. We consider that ion mass peaks with a physically meaningful flux corresponded to a compound that was truly emitted from or deposited to the grassland. We also excluded cases where the ion abundance was strongly humidity dependent, because in these cases the flux is masked by the latent heat flux. Large changes in latent heat fluxes during the drying of grass resulted in detectable changes of water cluster containing ions related to specific VOCs (e.g. methanol-water clusters). In the case of isobaric ions (i.e. multiple peaks at one nominal mass), we discarded small mass peaks sitting on the shoulder of large mass peaks in the continuous mass spectrum, if the large mass peak exhibited a significant flux (Müller et al., 2010).

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Based on the previous criteria we determined that 17 compounds that were either deposited to or emitted from the grassland were responsible for fluxes of 43 ions (Table 1). In addition to the ions listed in Table 1 fluxes were observed for ions that were associated with measurement artifacts due to ion chemistry related to VOC and water changes. The ions with an measurement artifact flux were: 1) oxygen (at m/z 31.98899), 2) neighboring mass peaks including a background impurity (at m/z 33.01852) affected by the neighboring methanol signal (described by Müller et al., 2010) as well as other neighboring mass peaks at 71.0860 and 83.0815 and 87.0810 and 97.0653 (see Table 1 for corresponding parent ions), 3) a nitrogen containing ion (at m/z 35.0371) and 4) protonated di- and trichlorobenzene and their isotopes. We also observed class-B fluxes for a fragment of several compounds on m/z 41.0385 as well as on m/z 63.027135, 63.0444, and 129.1284. The identification of chemical formulas of the given compound classes ($C_xH_yO_z^+$) based on the measured mass of molecular ions worked unambiguously within the limits determined by the instruments mass accuracy and precision similar to the performance shown in Graus et al. (2010). While this information identifies the atomic composition of VOCs, the PTR-TOF can not identify the chemical structure itself. We therefore assigned compound classes to these isobaric formulas. A single VOC may give several ions: 1) the protonated parent compound which is the most abundant ion in most cases; 2) an ion formed by charge transfer from O_2^+ and/or NO^+, the sum of these primary ion impurities was always lower than 2% of the H_3O^+ ions, 3) protonated isotopes of the parent compound, 4) fragments of a protonated parent compound and 5) protonated VOC-water clusters (VOC–H^+–$(H_2O)_n$, $n=1,2$). Masses were sorted according to their likely protonated parent compound (see Table 1). When possible, fragments were assigned to their parent ion (protonated compound) based on known fragmentation patterns and flux ratios; e.g. over intact grass the fragment at m/z 81.0705 (C_6H_8–H^+) was clearly a monoterpene fragment and followed exactly the protonated monoterpene ($C_{10}H_{16}$–H^+, m/z 137.1330) flux behaviour (Table 2). However, when the grass was cut the C_6H_8–H^+-fragment at m/z 81.0705 was the sum of protonated fragments from C_6 leaf

wound compounds (e.g. hexanal, hexenols) as well as monoterpenes. In cases when fragments could not be assigned to a single protonated parent compound, according to the emission intensities and patterns of the parent ions, they were lumped as a separate class of compounds (Tables 3 and 4).

In summary, correct identification of the emitted and deposited VOCs or their sum formulas requires, in addition to the high mass resolving power (m/Δm) and mass accuracy of the PTR-TOF, careful interpretation of the observed ions. For example, methanol emission from drying grass gives rise to a positive flux of the protonated parent compound ($CH_3OH–H^+$, m/z 33.034), the ^{13}C, ^{17}O or deuterium isotope ($^{13}CH_3OH–H^+$, $CH_3^{17}OH–H^+$ and $CH_3OH–H^+$ where one H is a D, m/z 34.038), the ^{18}O or ^{13}C and D isotope ($CH_3^{18}OH–H^+$, m/z 35.038) and the protonated methanol-water cluster ($CH_3OH–H–H_2O^+$, m/z 51.045).

3.3 Flux detection and confidence limits

The smallest fluxes that we reliably calculated were less than $0.1\,\mathrm{nmol\,m^{-2}\,s^{-1}}$, as in the case of sesquiterpene emissions from freshly cut grass on 5 August from 11:00–11:30 CET (Fig. 1). The flux detection limit depends on vertical wind speed and the VOC signal, especially at low concentrations significant noise arises from the counting statistics of the detector (Lenschow and Kristensen, 1985). In addition, the flux at the true lag-time needs to exceed the general noise of the covariance function (Wienhold et al., 1994). The class-A and class-B flux values always passed the 95%confidence interval. The sign of the class-A fluxes calculated with the automated routine were consistent with the visually determined values, however this was not the case for some of the class-B. Due to the lack of a general detection limit, each half-hour flux value was inspected separately and only fluxes rated class-A were considered reliable and were used for further analysis. Class-A fluxes always passed the 95%-confidence interval criterion (Fig. 2).

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3.4 Compounds emitted from and deposited to the grassland

Unexpectedly, the dominant VOC fluxes over intact grass were, in addition to methanol emission fluxes, deposition fluxes of acetic acid and terpenoids (Table 2). The sign of acetic acid fluxes is known to depend on the ambient concentration (Kesselmeier and Staudt, 1999). As the ambient air concentration increases above the leaf-internal compensation point, the release from vegetation changes to deposition. However, the deposition of terpenoids comes as a surprise, since terpenoids are typically associated with emission only (Kesselmeier and Staudt, 1999). Our field site is surrounded by coniferous forests dominating the valley slopes. We expect that terpenes are transported to the grassland site from these forests following the thermal slope and valley wind circulation and then deposited. Harvesting changed the terpenoid flux pattern from deposition to emission (Fig. 2) the cut induced release indicated that mono- and sesquiterpenes are stored inside the vegetation and were released due to the mechanical damage.

VOC fluxes over grassland changed dramatically during harvesting (Figs. 3 and 4). In total we found 17 compounds which were emitted during the grass cutting (Table 3) and observed emissions of single-oxygenated C_4 and C_5 VOCs and $C_5H_8O_2$ as well as mono- and sesquiterpene from grassland for the first time. Laboratory PTR-TOF and adsorbent sample GC-MS measurements confirmed that these compound groups are emitted during drying of some of the grass species growing at the field site (Brilli et al., submitted). We propose that the flux of C_4H_6O-compound is due to direct emission and not a flux of methyl-vinyl-ketone (MVK) and/or methacrolein from isoprene oxidation. Direct emission of MVK from birch have been observed by Folkers et al. (2002) in laboratory measurements oxidation from isoprene was excluded by isotopic labeling of primary emissions (Wildt et al., personal communication, 2010). The C_5-compound containing two oxygen atoms was likely furfural, which can be emitted from fruits (Stensmyr et al., 2001), soil bacteria (Leff and Fierer, 2008) and degeneration of cellulose (Łojewski et al., 2010). Furfural was emitted up to $4.5\,\mathrm{nmol\,m^{-2}\,s^{-1}}$ during the drying

of grass and was not emitted after grass removal indicating that for this site the drying grass was the more important source than soil activity (Tables 3 and 4). Ethanol emissions during grass drying were substantial, between 2.4 and 8.2 nmol m^{-2} s^{-1}, but not observed before or after harvesting. Ethanol emissions due to stress and aerobic metabolism (Davies, 1980) likely also occur outside the harvesting period; due to poor sensitivity for ethanol we could not observe the ethanol emissions before harvesting. All emissions declined rapidly during the drying of cut grass. Out of the 17 species emitted from the freshly cut grass only 8 were emitted after the dried grass had been removed (Table 4). In addition the terpenoid fluxes had changed back to deposition.

Methanol dominated the VOC emissions all the time and emission of methanol from vegetation in general (e.g., Ninemets et al., 2004; Fall et al., 1999) and from grassland is well known (e.g., Brunner et al., 2007; Bamberger et al., 2010). The major biogenic source of methanol is the demethylation of the pectin matrix during the decay or expansion of plant cell walls (Galbally and Kirstine, 2002; Fall, 2003) and methanol emissions have been shown to correlate with plant growth rates (Hüve et al., 2007). Other major driving factors for methanol emissions from leaves appear to be temperature and stomatal conductance (Harley et al., 2007). The latter can be explained by the high solubility of methanol (Niinemets et al., 2004). The magnitude of methanol emissions before cutting agreed extremely well (Table 5) with the results of Bamberger et al. (2010) obtained with a PTRMS for the same site during the previous vegetation period. Observed methanol emissions before cutting were somewhat higher than those reported by Brunner et al. (2007) for an intensively and extensively managed grassland during maturation. Higher methanol emissions were reported by Warneke et al. (2002) for an alfalfa field (Table 5). These differences may be reflective of differences in environmental conditions (e.g. temperature), as well as different plant species composition. Highest methanol emissions were consistently observed on the day of cutting and during drying of plants and the peak emissions were typically in the 70–110 nmol m^{-2} s^{-1} range (Table 5). Smallest cutting induced emissions were less than one third of these values (Brunner et al., 2010), while on the other hand the largest emissions (Karl et al.,

2001a) were over $400 \, \text{nmol} \, \text{m}^{-2} \, \text{s}^{-1}$. During cutting and drying the VOCs stored inside plants in the gas or liquid phase (Niinemets et al., 2004) escape to the atmosphere through the severed plant cells. The similarity in peak methanol fluxes is striking given the abovementioned likely differences in environmental conditions and plant species composition between studies. In addition, Brilli et al. (submitted) have shown that the magnitude of VOC emission after wounding scales with the severed plant area and studies may thus be expected to differ depending on the vertical plant area distribution with respect to the cutting height. Emissions were usually at least 50% lower during periods when the cut vegetation was left to dry at the field (possibly turned periodically by agricultural machinery; Table 5). This is thought to reflect the depletion of VOC pools within the severed plant material. Finally, after the cut plant material was removed methanol emissions further declined (Table 5) and approached typical growing season background values within several days (Bamberger et al., 2010).

In addition to methanol, the release of C_6 leaf wound compounds, acetone and acetaldehyde from cut grass has been observed in several studies (Karl et al., 2001a,c; Warneke et al., 2002; Oloffson et al., 2003; Davison et al., 2008; Bamberger et al., 2010) and counted for the majority of the emitted VOCs. Similar to methanol, emissions of these compounds were highest during the cutting event (acetaldehyde: 3–$35 \, \text{nmol} \, \text{m}^{-2} \, \text{s}^{-1}$; acetone: $1–13 \, \text{nmol} \, \text{m}^{-2} \, \text{s}^{-1}$) as compared to the periods thereafter. Due to differences between studies in how the C_6 leaf wound compounds are reported, it is difficult to compare their flux magnitudes (Table 5).

3.5 Reactive VOC carbon budget

We calculated time integrated carbon fluxes (Fig. 4) for three groups: 1) pure hydrocarbons and 2) one and 3) two oxygen containing VOCs. Methanol emissions are an order of magnitude higher than any other VOC. On a carbon basis it accounts for half of the oxygen containing VOC emissions and less than a third of the total VOC flux (Fig. 5). Longer chained VOCs, especially C_{10}–C_{15} terpenoids, account for a significant fraction

of the carbon emissions during grass cutting. We also observed deposition fluxes of monoterpenes and sesquiterpenes before and after the harvesting period (Tables 2–4). These deposition fluxes result in a decrease of the cumulative VOC flux shown in Fig. 4 after the grass was removed. Regionally these VOC emissions could play a role for local air quality during periods of intense harvesting activities, especially in areas with some anthropogenic influence where NO_x is not limiting ozone formation. Future plans to drastically increase the production of biomass as feedstock for the bioenergy and bioproducts industry could increase the atmospheric input of these reactive VOCs.

4 Summary and conclusion

We used PTR-TOF to measure VOC eddy covariance fluxes over grassland with a flux detection limit on the order of $0.1\,\mathrm{nmol\,m^{-2}\,s^{-1}}$. PTR-TOF allowed scanning a wide range of VOCs. A total VOC emission flux up to $200\,\mathrm{nmol\,C\,m^{-2}\,s^{-1}}$ was measured during harvesting activities. These flux measurements also indicated significant deposition of mono- and sesquiterpenes to intact grassland. The deposition as well as release of unexpected VOCs, including MVK, furfural, mono- and sesquiterpenes, from the drying grass demonstrated the usefulness of expanding VOC flux measurements to a wide range of compounds whose exchange patterns have previously been poorly characterized. Harvesting practices could become an important source of reactive VOC if biofuel crops are grown on large scales and should be considered in emission inventories used for air quality modeling.

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Table 1. Volatile organic compounds with emission or deposition flux above the grassland before, during or after harvesting, exact measured *m/z* of well defined class-A fluxes (bold) or only less reliable class-B fluxes, exact mass of parent ion mass peak, isotopes, VOC-water clusters and fragments of the protonated parent compound.

Molecular formula	Likely compound			
	Parent ion	Isotope	Water cluster	Fragment
$CH_3OH–H^+$	Methanol			
		34.0376	*51.0445*	
	33.0336	*35.0383*		
$C_2H_3OH–H^+$	Acetaldehyde			
	45.0340	*46.0375*		
$C_2H_5OH–H^+$	Ethanol			
	47.0493			
$C_6H_8–H^+$	e.g. fragment of C_6-compounds (e.g. hexanal, hexenols) and terpenoids			
	81.0705	*82.0738*		
$C_6H_{10}O–H^+$	Green leaf volatiles (e.g. hexenals)			
				43.0183
	99.0811	*100.0780*		*57.0340*
$C_2H_4O_2–H^+$	Acetic acid			
	61.0291			*43.0183*
$C_6H_{10}–H^+$	e.g. fragment of C_6-compounds (e.g. hexanal, hexenols)			
	83.0861			
$C_5H_4O_2–H^+$	e.g. furfural			
	97.0287	*62.0334*		
$C_3H_6O–H^+$	Acetone (and propanol)			
	59.0496	*60.0530*	*77.0595*	
$C_5H_8–H^+$	Fragment of methylbutanals or pentenols (and isoprene)			
	69.0705	*70.0743*		
$C_4H_8O–H^+$	e.g. butanone, butanal			
	73.0653	*74.0655*		
$C_4H_6O–H^+$	Methyl-vinyl-ketone (and methacrolein)			
	71.0497	*72.0534*		
$C_5H_8O–H^+$	e.g. pentanal			
	85.0653			
$C_5H_{10}O–H^+$	e.g. methylbutanals, pentenols			
	87.0810			43.01833
$C_{10}H_{16}–H^+$	Monoterpenes (and sesquiterpene fragment)			
				95.0862
	137.1330	*138.1365*		see $C_6H_8–H^+$
$C_{10}OH_{16}–H^+$	Terpenoid e.g. camphor			
	153.1278			
$C_{15}H_{24}–H^+$	Sesquiterpenes			
	205.1945			

Table 2. VOC fluxes over intact grass during a sunny day 24 h between 11:00 CET on 1 August and 11:00 CET on 2 August in 2009 in Neustift, Stubai valley. Fluxes were calculated from the half-hour concentration and wind covariance and only class-A fluxes, with a well defined maximum or minimum in the covariance, were taken into account. The 95% flux confidence is calculated from the mean noise of class-A fluxes. The Nr of 30-min fluxes shows how many class-A fluxes (emission or deposition) were observed.

Exact m/z measured	Molecular formula	Likely compound	Mean flux (min/max) ($nmol\,m^{-2}\,s^{-1}$)	Mean 95% confidence ($nmol\,m^{-2}\,s^{-1}$)	30-min fluxes (Nr)
33.0336	$CH_3OH–H^+$	Methanol	5.89 (1.14/9.31)	1.04	14
205.1945	$C_{15}H_{24}–H^+$	Sesquiterpenes	−0.03 (−0.07/−0.01)	0.01	6
61.0291	$C_2H_4O_2–H^+$	Acetic acid	−0.18 (−0.19/−0.16)	0.10	2
153.1278	$C_{10}OH_{16}–H^+$	Terpenoid e.g. camphor	−0.19 (−0.41/−0.05)	0.01	11
137.1330	$C_{10}H_{16}–H^+$	Monoterpenes (and sesquiterpene fragment)	−3.39 (−8.21/−0.21)	0.90	11

Table 3. VOC fluxes over drying cut grass during a sunny day for 24 h between 11:00 CET on 5 August and 11:00 CET 6 August in 2009 in Neustift, Stubai valley. Fluxes were calculated from the half-hour concentration and wind covariance and only class-A fluxes, with a well defined maximum or minimum in the covariance, were taken into account. The 95% flux confidence is calculated from the mean noise of class-A fluxes. The Nr of 30-min fluxes shows how many class-A fluxes (emission or deposition) were observed, for mono- and sesquiterpenes we give Nr of emission+deposition fluxes, separately.

Exact m/z measured	Molecular formula	Likely compound	Mean flux (min/max) (nmol m^{-2} s^{-1})	Mean 95% confidence (nmol m^{-2} s^{-1})	30-min fluxes (Nr)
33.0336	$CH_3OH{-}H^+$	Methanol	44.55 (16.68/98.05)	6.65	15
45.0340	$C_2H_3OH{-}H^+$	Acetaldehyde	6.66 (0.83/10.68)	1.12	16
47.0493	$C_2H_5OH{-}H^+$	Ethanol	4.80 (2.42/8.21)	1.03	12
81.0705	$C_6H_8{-}H^+$	e.g. fragment of C_6-compounds (e.g. hexanal, hexenols) and terpenoids	2.31 (0.43/7.55)	0.51	10
99.0811	$C_6H_{10}O{-}H^+$	green leaf volatiles (e.g. hexenals)	2.19 (0.48/7.92)	0.41	15
61.0291	$C_2H_4O_2{-}H^+$	Acetic acid	1.21 (0.53/1.96)	0.39	6
83.0861	$C_6H_{10}{-}H^+$	e.g. fragment of C_6-compounds (e.g. hexanal, hexenols)	1.14 (0.15/4.80)	0.23	14
97.0287	$C_5H_4O_2{-}H^+$	e.g. furfural	1.12 (0.05/4.49)	0.18	13
59.0496	$C_3H_6O{-}H^+$	Acetone (and propanol)	1.10 (0.54/2.17)	0.39	13
69.0705	$C_5H_8{-}H^+$	Fragment of methylbutanals or pentenols (and isoprene)	0.77 (0.25/1.55)	0.20	8
73.0653	$C_4H_8O{-}H^+$	e.g. butanone, butanal	0.56 (0.44/0.68)	0.18	2
71.0497	$C_4H_6O{-}H^+$	Methyl-vinyl-ketone and methacrolein	0.37 (0.32/0.39)	0.07	5
85.0653	$C_5H_8O{-}H^+$	e.g. pentanal	0.27 (0.10/0.62)	0.06	13
87.0810	$C_5H_{10}O{-}H^+$	e.g. methylbutanals, pentenols	0.27 (0.07/0.71)	0.06	13
137.1330	$C_{10}H_{16}{-}H^+$	Monoterpenes (and sesquiterpene fragment)	0.13 (−1.85/2.21)	0.03	5+4
153.1278	$C_{10}OH_{16}{-}H^+$	Terpenoid e.g. camphor	0.10 (0.09/0.11)	0.06	2
205.1945	$C_{15}H_{24}{-}H^+$	Sesquiterpenes	0.09 (−0.01/0.23)	0.02	9+1

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Table 4. VOC fluxes after removal of cut grass during a sunny day between 08:00 CET on 7 August and 08:00 CET on 8 August in 2009 in Neustift, Stubai valley. Fluxes were calculated from the 30-min concentration and wind covariance and only class-A fluxes, with a well defined maximum or minimum in the covariance, were taken into account. The 95% flux confidence is calculated from the mean noise of class-A fluxes. The Nr of 30-min fluxes shows how many class-A fluxes (emission or deposition) were observed, for and sesquiterpenes we give Nr of emission+deposition fluxes, separately.

Exact m/z measured	Molecular formula	Likely compound	Mean flux (min/max) (nmol m^{-2} s^{-1})	Mean 95% confidence (nmol m^{-2} s^{-1})	30-min fluxes (Nr)
33.0336	CH_3OH–H^+	Methanol	6.71 (1.12/16.85)	1.27	26
61.0291	$C_2H_4O_2$–H^+	Acetic acid	1.02 (0.54/1.34)	0.32	7
59.0496	C_3H_6O–H^+	Acetone (and propanol)	0.80 (0.13/1.80)	0.71	5
71.0497	C_4H_6O–H^+	Methyl-vinyl-ketone and methacrolein	0.24 (0.14/0.32)	0.06	5
83.0861	C_6H_{10}–H^+	e.g. fragment of C_6-compounds (e.g. hexanal, hexenols)	0.10 (0.07/0.12)	0.03	5
99.0811	$C_6H_{10}O$–H^+	Green leaf volatiles (e.g. hexenals)	0.08 (0.06/0.11)	0.02	5
85.0653	C_5H_8O–H^+	e.g. pentanal	0.07	0.03	1
87.0810	$C_5H_{10}O$–H^+	e.g. methylbutanals, pentenols	0.08 (0.07/0.09)	0.02	2
205.1945	$C_{15}H_{24}$–H^+	Sesquiterpenes	−0.01 (−0.03/0.003)	0.01	1+7
153.1278	$C_{10}OH_{16}$–H^+	Terpenoid e.g. camphor	−0.08 (−0.11/−0.05)	0.03	3
81.0705	C_6H_8–H^+	e.g. fragment of C_6-compounds and terpenoids	−0.51 (−0.76/−0.38)	0.14	4
137.1330	$C_{10}H_{16}$–H^+	Monoterpenes (and sesquiterpene fragment)	−1.14 (−2.88/−0.20)	0.27	16

Table 5. Literature survey of VOC flux studies before, during and after cutting of herbaceous vegetation. The selection of studies was based on the availability of quantitative in-situ VOC flux measurements reported on a ground area basis. Here we list maximum flux rates in $\mathrm{nmol\,m^{-2}\,s^{-1}}$.

	Study site	Method	Date	Management	Days after cut	methanol	acetaldehyde	acetone	butanone	Methylbutanals, pentenals (and isoprene)	C₆ compounds
this study	agricultural grassland, intensive	EC, PTR-TOF	08/2009	undisturbed	−4	9.3	m	m	m	m	m [a,b,c]
				cutting	0	98.1	10.7	2.2	0.7	1.6	20.3 [a,b,c]
				grass removed	2	16.9	m	1.8	m	m	0.2 [a,b,c]
Bamberger et al., 2010	agricultural grassland, intensive	EC, PTR-MS	08/2008	undisturbed	−1	9.6	1.2	m	−	m	1.4 [c]
				cutting	0	78.4	11	m	−	m	8.3 [c]
				drying	1	26.4	9.5	m	−	m	2.0 [c]
Davison et al., 2008	agricultural grassland, extensive	EC, GC-FID-PTR-MS	06/2005	cutting	0	91.5	19.4	12.7	5.6	−	20.6 [d], 8.9 [e]
				drying	1	26.6	10.5	3	1.2	−	1.5 [d], 1.8 [e]
Brunner et al., 2007	agricultural grassland, intensive	EC, PTR-MS	06/2004	undisturbed [1]	−	4	−	−	−	−	−
				cutting	0	30	−	−	−	−	−
				grass removed	1	6.9	−	−	−	−	−
	agricultural grassland, extensive		06/2004	undisturbed [1]	−	10	−	−	−	−	−
				cutting	0	110.9	−	−	−	−	−
				drying	1	20	−	−	−	−	−
				grass removed	1	19	−	−	−	−	−
Oloffson et al., 2003	golf course	REA, GC/MS	09/2000	cutting	0	−	−	−	−	−	3.6 [h], 1.4 [g], 0.0 [e]
				hay removed	1	−	−	−	−	−	0.005 [h], 0.0 [g], 0.0 [e]
			07/2001	cutting	0	−	−	−	−	−	2.7 [h], 0.2 [g], 4.1 [e]
				hay removed	1	−	−	−	−	−	0.1 [h], 0.0 [g], 0.0 [e]
Warneke et al., 2002	alfalfa field	EC, PTR-MS	08/2000	undisturbed	−1	32.9	0.4	0.2	−	−	m [e,f,g,h]
				cutting	0	69.4	2.9	1.2	−	−	m [e,f,g,h]
				drying [2]	1	44.2	m	m	−	−	m [e,f,g,h]
Karl et al., 2001c	agricultural grassland	EC, PTR-MS	08/1999	drying	1	17.3	9.5	2.4	−	2.9	m [c], 0.7 [d]
		gradient	08/1999	cutting	0	72.8	18.9	7.2	m	1.2	m [c], 1 [d]
		gradient		drying	1	17.3	6.3	1.6	0.1	1.6	m [c], 1 [d]
Karl et al., 2001a	agricultural grassland	EC, PTR-MS	05/2000	cutting	0	309	34.1	0.3	0.6	2.9 [3]	m [a,b,c]
				drying	1	106.1	10	m	m	m [3]	m [a,b,c,4]
		gradient	05/2000	cutting	0	436.9	20.4	1.2	1.1	5.9 [3]	m [a,b,c]

cutting: during the day of cutting with grass drying on the field;
drying: at least one day after cut with grass drying on the field;
− flux not measured;
m flux measured, but not reported;
[1] during mature phase, [2] small patch was cut in the morning, [3] no isoprene, [4] fluxes generally lower by a factor of 3 than on day of cut,
[a] hexanal, [b] hexenols, [c] hexenals, [d] hexenols plus hexanal, [e] (Z)-3-hexenal, [f] (E)-2-hexenal, [g] (Z)-3-hexenol, [h] (Z)-3-hexenyl acetate
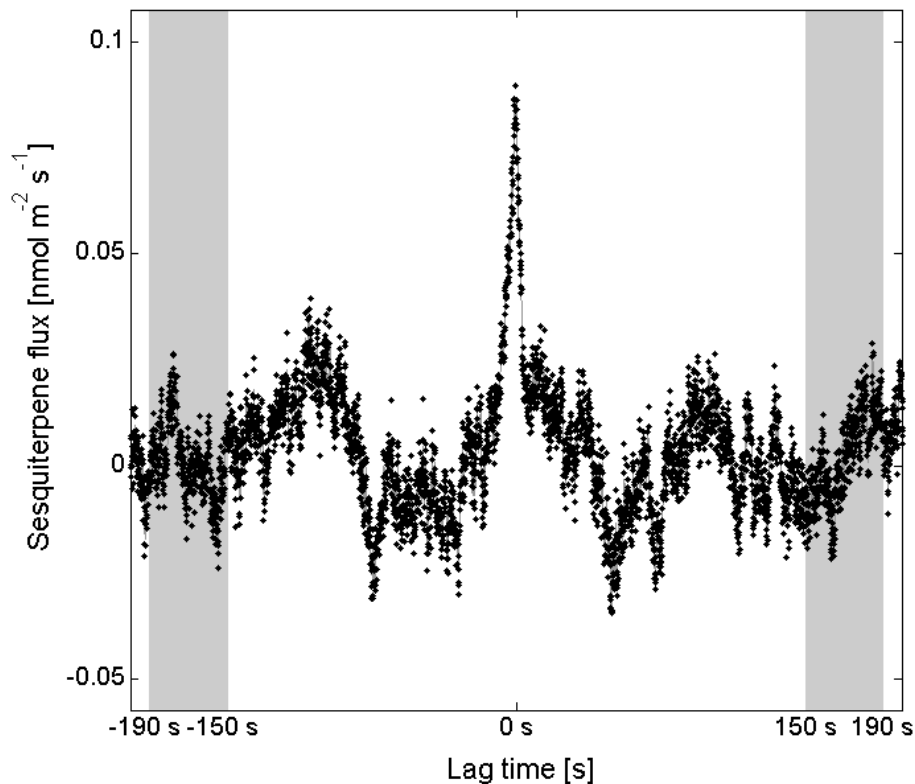
Fig. 1. Example of an eddy covariance flux of sesquiterpenes (at protonated compound mass peak 205.1945 *m/z*) visually rated as a class-A flux (5 August 2009 at 12:00–12:30 CET). The flux was determined as the maximum covariance. The standard deviation of covariance in the shaded area was considered as the noise of the flux and used to calculate the flux confidence.

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Fig. 2. Monoterpenes flux (137.1330 *m/z*) during the morning of grass cutting on 5 August. The clear deposition to the intact grassland **(A)**, changes during the grass cutting between 09:00 and 10:30 CET (**B** and **C**) into an emission **(D)** from some of the cut grass species that were left to dry on the field. The uncertainty of the flux is calculated by multiplying the standard deviation of the shaded areas with 1.96 to get the 95% confidence intervals indicated with bars.
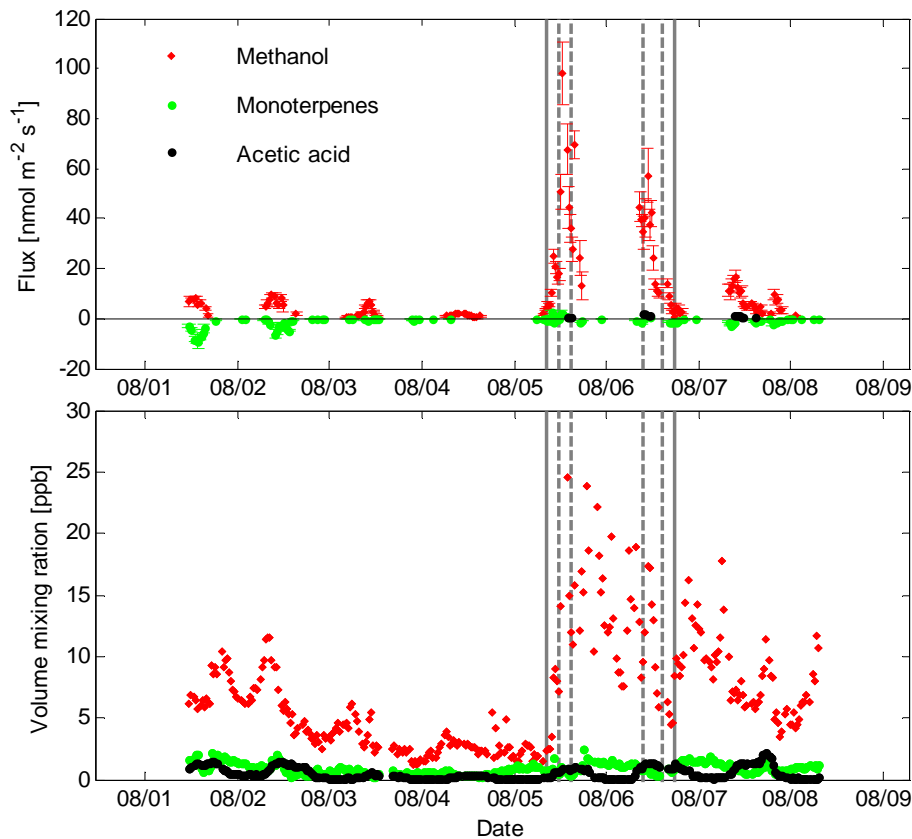
Fig. 3. The temporal behavior of methanol, acetic acid and monoterpenes fluxes (upper panel) 95% confidence levels are indicated with bars, and volume mixing ratios (lower panel). Cutting of grass on 5 August morning and removal on evening of 6 August is indicated with a solid line and the turnings of the drying grass by dashed lines.

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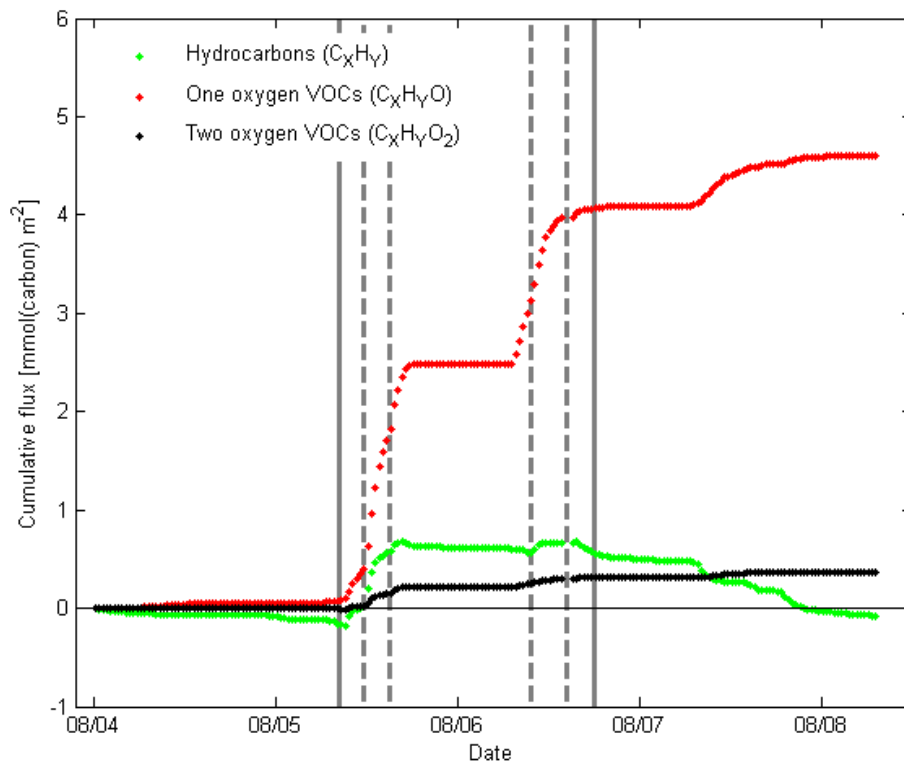Printer-friendly Version

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Fig. 4. The cumulative sum of the VOC fluxes of pure hydrocarbons, one oxygen containing VOCs and two oxygen containing VOCs from 1 to 8 August 2009. Linearly interpolated values were used to fill gaps in data that were an hour or less. Cut and remove of grass are indicated with continuous gray line, turnings of drying grass with dashed lines.

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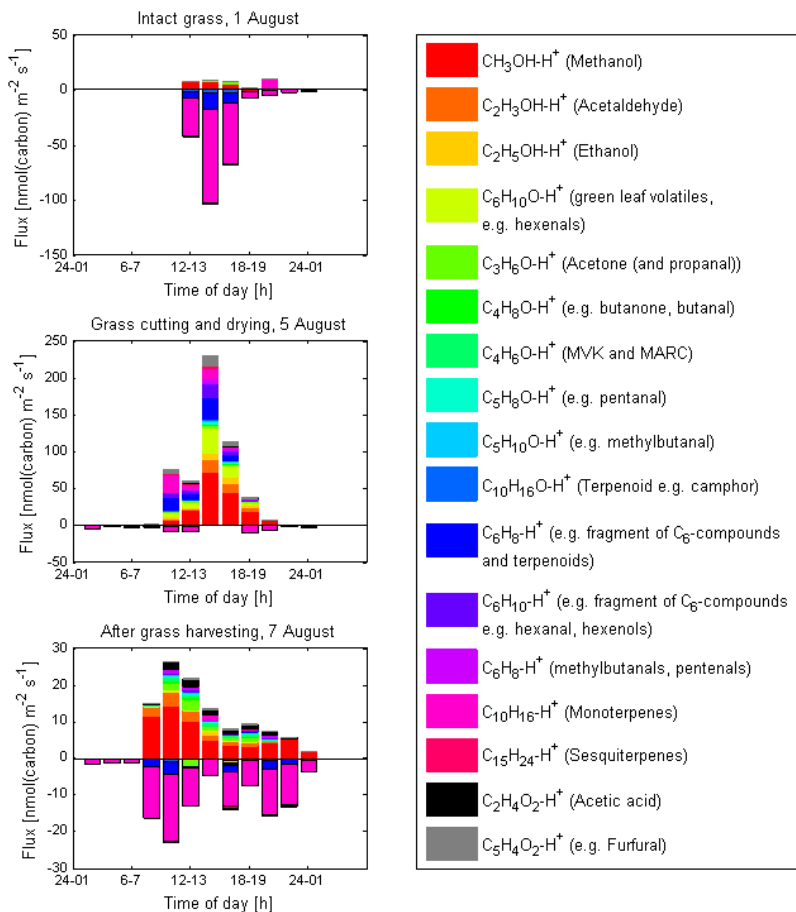◄ | ►

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Fig. 5. The diurnal pattern of VOC carbon fluxes from intact grass (2 August), cut drying grass (5 August) and after grass harvesting (7 August) in two hour means of class-A fluxes.