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Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting

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[1] There is interest in and significant uncertainty about the emissions of oxygenated volatile organic compounds (oxVOCs) from vegetation to the atmosphere. Here, we measured the fluxes of selected oxVOCs from an alfalfa field, before, during, and after cutting, using a combination of disjunct eddy covariance and proton-transfer-reaction mass spectrometry. Over the course of 1 day a significant methanol flux of $4 \text{ mg m}^{-2} \text{ h}^{-1}$ was observed from undisturbed alfalfa with a maximum at 0800 LT, possibly caused by the evaporation of dew. A smaller release of hexenals during this day ($0.04 \text{ mg m}^{-2} \text{ h}^{-1}$) demonstrated the sensitivity of the method. Other results suggested that acetaldehyde and acetone were released in the afternoon but were lost by dry deposition in the evening and morning; deposition velocities were estimated to be 0.2 cm s^{-1} (acetaldehyde) and 0.09 cm s^{-1} (acetone). After the alfalfa was cut the emissions of methanol, acetaldehyde, acetone, and hexenals were significantly enhanced and remained high for three days during which the alfalfa was drying. After a rainstorm the oxVOC emissions from the cut, wet alfalfa increased even more. Nighttime measurements yielded low oxVOC fluxes in general, but the high variability of the concentrations during the night and the high degree of correlation between different oxVOCs suggest that the nighttime releases of oxVOCs from alfalfa were nonzero. This work suggests that the global source of oxVOCs due to the production of hay is of minor importance. The emission flux of methanol from vegetation during the growing season may be very large on a global basis. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** biogenic hydrocarbons, volatile organic compounds, flux measurements, eddy covariance

1. Introduction

[2] It has long been recognized that the volatile organic compounds (VOCs) released by vegetation can contribute significantly to, and in many cases, dominate, the pool of reactive hydrocarbons in the atmosphere. These so-called biogenic hydrocarbons play an important role in the chemistry of tropospheric ozone and aerosols and have therefore been investigated for many years [Fehsenfeld *et al.*, 1992]. Research has focused mostly on emissions of isoprene and monoterpenes, and considerable progress has been made toward a systematic quantification of their sources [Guenther *et al.*, 1995]. Recent work has indicated the high atmospheric abundance of oxygenated VOCs (oxVOCs) from biogenic sources. For example, Goldan *et al.* [1995] detected high levels of methanol and acetone at a pine forest site in the United States, and Kirstine *et al.* [1998] and Fukui and Doskey [1998] studied the VOC emissions from pasture and grassland and found these to be dominated by oxygenated compounds. In general, however, the magnitude of the oxVOC release from vegetation and the controlling factors are poorly

understood, and there is a clear need for further research [Kesselmeier and Staudt, 1999; Guenther *et al.*, 2000].

[3] The wounding of leaves is one of the mechanisms that lead to the release of VOCs from vegetation to the atmosphere. Most plants are known to respond to wounding by emitting a number of C_6 aldehydes and alcohols and ester derivatives of the alcohols. These wound compounds are assumed to be released for their antibiotic properties, and the biochemistry involved in their production has been described by Hatanaka [1993]. Arey *et al.* [1991] examined the release of VOCs from 29 agricultural plants in California's Central Valley and found the C_6 wound compounds to be among the dominant species, which suggests that wounding may be a significant mechanism for VOCs to escape from a leaf. More recently, Kirstine *et al.* [1998] measured the VOC release from slashed pasture grasses and found strongly increased emissions soon after wounding of not only the C_6 wound compounds but also of smaller oxVOCs such as methanol, ethanol, acetaldehyde, acetone, and butanone. Comparable observations were made by Fukui and Doskey [1998] and König *et al.* [1995] when vegetation was disturbed, for instance, by the sampling enclosure. Fall *et al.* [1999] studied the wound-induced VOC release from aspen leaves in the laboratory, which allowed the emissions to be quantified and the mechanism of Hatanaka [1993] to be investigated. Subsequent experiments by de Gouw *et al.* [1999] demonstrated that the VOC emissions from cut-off grass and clover leaves increase even more during the drying process, possibly caused by the larger extent of the damage as cellular structures collapse.

[4] Enclosures were used in most of the studies on the release of wound compounds from plants, which presumably influenced the measurements as indicated by several authors [Arey *et al.*, 1991; König *et al.*, 1995; Fukui and Doskey, 1998]. Micrometeorological

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techniques such as eddy covariance provide direct methods to measure the surface-atmosphere exchange of trace constituents, without the disturbing influence of enclosures [Dabberdt *et al.*, 1993]. In eddy covariance the turbulent mixing of trace gases released at the surface is studied by measuring both the concentration and the three-dimensional (3-D) wind velocity vector with fast response sensors. The emission (or deposition) flux is then determined from the covariance between the concentration and vertical wind speed. Eddy covariance can be used only if a sufficiently fast chemical sensor is available. Its use for studying biogenic emissions has therefore been limited to measuring isoprene fluxes [Guenther and Hills, 1998]. The prospects of using mass spectrometric techniques for eddy covariance measurements of oxVOCs were recently explored by Shaw *et al.* [1998] and Karl *et al.* [2001a, 2001b].

[5] In this work, we use the recently developed disjunct eddy covariance method in combination with mass spectrometry to measure the VOC fluxes from a field of alfalfa (one of the main hay crops in the United States) before, during, and after cutting the field. The experiment was designed to decide if the results of the laboratory experiments by Fall *et al.* [1999] and de Gouw *et al.* [1999, 2000] on wounded and drying vegetation can be extrapolated to oxVOC releases from croplands to the atmosphere. The disjunct eddy sampling (DES) method, recently introduced by Rinne *et al.* [2000], is an eddy flux technique, in which the sampling of air is discontinuous. Grab samples are collected at regular intervals by evacuating a sample container and briefly opening (0.2 s) a fast-acting valve. The time between sampling (10–30 s) is subsequently used to analyze the samples off line. The traditional approach to eddy covariance has been to sample air continuously. In DES a subset of the whole time series is obtained, which can be shown to give the same flux. DES relaxes the requirement for fast chemical sensors and allows true eddy covariance flux measurements using relatively slow sensors.

[6] In this experiment the grab samples are analyzed using proton-transfer-reaction mass spectrometry (PTR-MS). PTR-MS is a recent method to measure VOCs in ambient air with a high sensitivity and fast response time [Lindinger *et al.*, 1998]. The technique has proved to be a useful tool in laboratory measurements of the VOCs released from wounded and dead plant matter [Fall *et al.*, 1999; Warneke *et al.*, 1999] and has been used for atmospheric measurements from aircraft and ships [e.g., Crutzen *et al.*, 2000]. The response time of the PTR-MS used for this study is more than 1 s, which may not be sufficiently fast for continuous eddy covariance without additional corrections due to a loss of correlation in small-scale eddies [Guenther and Hills, 1998]. By combining PTR-MS with DES the response time of the chemical sensor is determined by the 0.2-s fill time of the sample containers rather than by the >1-s response time of the VOC analysis, and the method may be sufficiently fast for eddy covariance without significant corrections. Moreover, several VOC concentrations, and hence fluxes, can be determined simultaneously from the grab samples.

[7] In this paper we present the results of a field experiment conducted near Fort Morgan, Colorado, in August 2000. Over a period of 5 days we monitored the fluxes of several oxVOCs from a field of alfalfa. On the second day the field was cut, and the remaining 3 days the cut alfalfa was drying in the field. Technical details of the flux measurement system are described elsewhere [Rinne *et al.*, 2001]. Here, the results of the alfalfa experiment are presented and discussed in detail, along with the implications of the results for the chemistry of the atmosphere.

2. Experimental Design

2.1. Disjunct Eddy Covariance

[8] In disjunct eddy covariance [Rinne *et al.*, 2000, 2001], grab samples are alternately collected in two sample containers by

Table 1. Organic Compounds Detected With Proton-Transfer-Reaction Mass Spectrometry in the Present Experiment

Compound	Product Ion Mass, amu	Calibration Factor, ncps ppbv ⁻¹
Methanol	33	32
Acetaldehyde	45	41
Acetone	59	80
(Z)-3-hexenal	81 (30%), 99 (70%)	50
(E)-2-hexenal	81 (3%), 99 (97%)	50
(Z)-3-hexenol	83 (78%), 101 (22%)	50
(Z)-3-hexenyl acetate	83 (82%), 143 (18%)	50

evacuating them and by briefly opening a fast-acting valve for about 0.2 s. At the same time, the 3-D wind velocity vector is recorded with a sonic anemometer. After sampling, the containers are analyzed off line during 20–25 s. Two sample containers are used in parallel in order to optimize the collected amount of data: one is analyzed while the other is being pumped down and vice versa. Rinne *et al.* [2000] used disjunct eddy sampling (DES) in combination with true eddy accumulation to determine monoterpene fluxes at a forested, high-altitude site in Colorado. Here, we use DES in combination with PTR-MS to measure true eddy covariance fluxes from an alfalfa field. The 1-L sample containers are made of Teflon to minimize memory effects of VOCs in the sampling system. Rinne *et al.* [2001] give a more detailed description of the flux measurement setup.

2.2. Proton-Transfer-Reaction Mass Spectrometry

[9] Mixing ratios of several VOCs in the two sample containers were measured using proton-transfer-reaction mass spectrometry (PTR-MS). PTR-MS has been developed by Lindinger *et al.* [1998] and provides a method for measuring VOCs in ambient air with a high sensitivity and fast response time. In PTR-MS, primarily organic trace gases in air are ionized by proton-transfer reactions with H₃O⁺ ions in a drift-tube reactor. The reagent and product ions are mass analyzed and detected with a quadrupole mass spectrometer (Balzers 422). The PTR-MS instrument was connected with the sample containers of the disjunct eddy sampling system by 2 m × 0.32 cm OD perfluoroalkoxy (PFA) tubing. Teflon-bodied three-way valves were used to alternate between the two sample containers.

[10] The samples were analyzed for the presence of methanol, acetaldehyde, acetone, and the C₆ wound compounds (Z)-3-hexenal, (E)-2-hexenal, (Z)-3-hexenol, and (Z)-3-hexenyl acetate. Laboratory and field studies had indicated that these are the dominant VOCs released from wounded vegetation [Kirstine *et al.*, 1998; Fall *et al.*, 1999; de Gouw *et al.*, 1999, 2000]. In Table 1 these VOCs are given along with the mass of the ions that are produced in reaction with H₃O⁺ ions, and the calibration factors used in the analysis. Methanol, acetaldehyde, and acetone are detected at their respective masses plus one (due to the proton) [Lindinger *et al.*, 1998], whereas the ions produced from the C₆ wound VOCs were determined experimentally using mixtures of the pure compounds (Aldrich Chemicals, Bedoukian Research) in synthetic air. Owing to the higher operating pressure in our PTR-MS instrument (2.5 mbar), the kinetic energy and thus the fragmentation of the product ions is reduced in comparison with previous work by Fall *et al.* [1999]. The ions produced from the four C₆ wound compounds in Table 1 do not have unique masses. In addition to the masses pertaining to methanol, acetaldehyde, and acetone, we measured therefore at all five masses corresponding to the C₆ wound compounds and tried to interpret the observations at those five masses in terms of the contribution from the four C₆ wound VOCs. As discussed below, this worked well for (Z)-3-hexenal and (E)-2-hexenal at masses 81 and 99 amu but was problematic for (Z)-3-hexenol and (Z)-3-hexenyl acetate at masses 83, 101, and 143 amu, in which case there was likely interference from other, unidentified VOCs.

Figure 1. Time series of the measured methanol mixing ratio in the grab samples and the vertical wind velocity at the time the samples were collected during a half-hour interval of the experiment in Fort Morgan.

[11] The calibration factors are defined as the ion signal produced at a VOC mixing ratio of 1 parts per billion by volume (ppbv) and are normalized to an H_3O^+ signal of 10^6 counts s^{-1} (cps). They are given in units of normalized counts per second per ppbv (ncps ppbv $^{-1}$). The calibration factors for methanol, acetaldehyde, and acetone were measured using a standard mixture of these gases in nitrogen [Warneke *et al.*, 2001], and the accuracy is estimated to be 20%. The calibration factors for the C_6 wound compounds were estimated and the accuracy is estimated to be 40%. Background signals, owing to gaseous impurities in the instrument, can vary between zero and a few hundred parts per trillion by volume (pptv) and need to be accounted for. This is done by removing the VOCs from the sample flow with a catalytic converter (Pt-coated quartz wool at 350°C), which is found to be more than 99% effective. In the present experiment a proper determination of background impurity levels is of lesser importance, as the ambient concentrations were in most cases far higher than the background. Moreover, the background levels are not correlated with the vertical wind velocity and therefore do not contribute to the eddy covariance flux.

[12] In PTR-MS, only the mass of the product ions is determined, and the possibility of interference from other compounds needs to be considered. No VOCs are known that give a significant contribution at the product ion masses pertaining to methanol (33 amu) and acetaldehyde (45 amu). The signal observed at 45 amu is very weakly dependent on the CO_2 mixing ratio in the sampled air, probably caused by formation of CO_2H^+ ions in the differentially pumped chamber between the drift tube and the quadrupole mass spectrometer in the PTR-MS [Warneke *et al.*, 2001]. In the experiments described here, CO_2 contributes to a slight offset for acetaldehyde but does not influence the eddy covariance fluxes for this compound, even when there is a downward flux of CO_2 . Propanal is detected at the same mass as acetone (59 amu). In this work, the signal observed at 59 amu is attributed entirely to acetone: alternative measurements using gas chromatography with mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) have shown that acetone is more abundant than propanal after leaf wounding [Kirstine *et al.*, 1998; de Gouw *et al.*, 2000]. There are a number of alternative possibilities for some of the product ion masses corresponding to the C_6 wound compounds. Monoterpenes, for example, are detected at masses 137 and 81 amu. These interfering compounds are not expected to respond similarly to leaf wounding, and also we can verify the consistency between the distributions of fragment ions determined in the laboratory (Table 1) with the field measurements at these masses.

2.3. Field Experiment

[13] A field experiment was performed at an alfalfa field in August 2000 near Fort Morgan, in the eastern plains of Colorado. Alfalfa (*Medicago sativa*) is one of the main hay crops in the United States and is usually harvested 4 times a year in Colorado. The DES/PTR-MS measurement setup was placed at the center of

a circular, irrigated alfalfa field. The field was flat and had a radius of ~ 390 m. The DES was installed at a height of 2.6 m above the surface, 0.6 m below the sonic anemometer. As discussed by Kristensen *et al.* [1997] and Rinne *et al.* [2001], this separation between the gas inlet and the anemometer causes less than 5% underestimation to the flux results due to a loss of correlation in small-scale eddies. The alfalfa plants reached an average height of ~ 0.5 m before they were cut. Before and after the harvest, the distance between the DES/PTR-MS setup and the emitting plants was therefore slightly different. The flow of air toward the instrument was obstructed in the wind sector between 210° and 240°, i.e., for southwestern wind, by a measurement trailer, the field's irrigation system, and the setup itself, but the wind rarely came from this direction. Weather conditions were sunny and dry, except in the night of 15–16 August when there was light rain for a number of hours. Daytime temperatures varied between 29° and 34°C. Typical night- and daytime horizontal wind velocities were 2–3 m s^{-1} and 4–6 m s^{-1} , respectively, except in the afternoon of 15 August, when the wind speed increased before a thunderstorm.

3. Results

3.1. Fluxes of Methanol, Acetaldehyde, and Acetone

[14] Figure 1 gives an example of the vertical wind velocities measured over a half-hour period and the simultaneously observed methanol concentrations. The different data points are separated by 25 s, i.e., the time needed for the PTR-MS analyses of the sample containers. It is clear from Figure 1 that the correlation between the vertical wind speed and methanol concentration is very good: the linear correlation coefficient is 0.71 for this particular half-hour interval.

[15] From the covariance between the vertical wind velocities in Figure 2a and the VOC mixing ratios in Figure 2b, the VOC fluxes were determined for half-hour intervals as described by Rinne *et al.* [2001], and the results are presented in Figure 2c for methanol, acetaldehyde, and acetone. The data of 12 August were obtained in undisturbed conditions. On 13 August the cutting of the alfalfa field started around 0900 LT, and it was finished in the morning of 14 August. The shaded areas in Figures 2b and 2c indicate when the cutting machine drove in circles of increasing radius around the instrumental setup. During the first few hours the measured concentrations showed a maximum when the cutting machine passed upwind from the measurement setup. The measured covariances during this period are not very representative of the surface emission, since in this case the emissions cannot be considered homogeneous. After the initial few hours the cutting machine was sufficiently far away from the measurement setup to assume that it no longer influenced the measurements. The data obtained after that reflect, therefore, what happened when the cut alfalfa was drying on the field.

Figure 2. Results of the field experiment conducted near Fort Morgan, Colorado: (a) the measured vertical wind velocity, (b) the volatile organic compound (VOC) mixing ratios determined from the grab samples, and (c) the eddy covariance fluxes of VOCs. The hatched areas indicate when the field was cut.

[16] It is clear from Figure 2c that the VOC emissions were significantly enhanced after the field was cut. Acetaldehyde and acetone, in particular, show almost no emissions from undisturbed alfalfa, but high emissions in the 3 days after the cutting. Figure 2c also shows distinct diurnal variations in the fluxes of methanol, acetaldehyde, and acetone. This is explained by the much more efficient drying during the day due to intense radiation and higher ambient temperatures. It should also be noted that it was difficult to estimate the nighttime flux using eddy covariance, because of the low vertical wind speeds and hence the inefficient vertical mixing.

[17] In this experiment the measured variability and mixing ratios of methanol were very high, indicating a strong emission. Indeed, the maximum daytime methanol flux ($4\text{--}10\text{ mg m}^{-2}\text{ h}^{-1}$) is similar to the maximum isoprene fluxes from oak forests and other landscapes with high biogenic VOC emissions [Guenther and Hills, 1998]. It is remarkable that the methanol flux from undisturbed alfalfa was the highest at 0800 LT rather than midday. This observation may be due to the evaporation of the dew, and all

the compounds dissolved in it, which formed on the alfalfa plants during the night. More detailed analyses, including measurements of the heat and water vapor flux, are needed to corroborate these conclusions. A strikingly similar feature was observed in the laboratory by Nemecek-Marshall *et al.* [1995], who observed bursts of methanol from bean plants in a leaf cuvette shortly after bringing the plants into the light. The transient peaks were attributed by these authors to the volatilization of methanol condensed on the leaf surface, but leaf damage caused by the cuvette could not be ruled out.

3.2. Fluxes of Wound Compounds

[18] Figure 3b shows the signals measured at masses 81 and 99 amu from the grab sample analyses. Both signals can be produced from (Z)-3-hexenal and (E)-2-hexenal, which are the first VOCs formed after wounding a leaf [Hatanaka, 1993]. It is easily seen from Figure 3b that the signals at 81 and 99 amu increased instantly when the cutting started and remained highly variable

Figure 3. Further results of the field experiment near Fort Morgan: (a) the measured vertical wind velocity, (b) the normalized ion count rates observed at masses 81 and 99, and (c) the combined eddy covariance flux of (Z)-3-hexenal and (E)-2-hexenal. The hatched areas indicate when the field was cut.

during 13 August. Furthermore, the signals at masses 81 and 99 amu were very well correlated as can be seen from Figure 4. The ratio between the signals was found to be 0.373, which is somewhat smaller than the ratio of 0.43 expected for (Z)-3-hexenal (Table 1) but much higher than the ratio of 0.03 for (E)-2-hexenal. From this we conclude that the signals observed at 81 and 99 amu correspond mostly to (Z)-3-hexenal, with a smaller contribution (15%) from (E)-2-hexenal. This observation agrees well with previous work from Kirstine *et al.* [1998] and Fall *et al.* [1999], who also found that the wound-induced emissions of (Z)-3-hexenal are higher than those of (E)-2-hexenal.

[19] The normalized count rates observed at masses 81 and 99 amu were added and the fragment ratios and calibration factors from Table 1 used to obtain the volume mixing ratio of the sum of (Z)-3-hexenal and (E)-2-hexenal. The combined flux of these compounds was determined using eddy covariance, and the result is shown in Figure 3c. During the first few hours after the cutting started, the flux was high (up to $7 \text{ mg m}^{-2} \text{ h}^{-1}$) but difficult to quantify owing to the fact that a strong peak was observed whenever the harvesting machine passed upwind from the measurement setup. The measurements of the C_6 wound compounds suffered more from this effect than the measurements of methanol, acetaldehyde, and acetone, because hexenal is mostly emitted from freshly cut vegetation, whereas these other VOCs are more efficiently emitted from drying vegetation [de Gouw *et al.*, 2000]. The highest observed hexenal fluxes are off-scale in Figure 3c; instead, we focus on the smaller flux values, which were obtained later in the day on 13 August, and on the other days. It can be seen from Figure 3c that the combined flux of hexenals was, for most of the time, much smaller than the flux of methanol. Interestingly, there is a weak indication of a nonzero flux of hexenal on the day before the cutting started. This may have been an artifact, the wounding of the alfalfa around the setup by the researchers themselves, but a footprint analysis

shows that the VOCs released in the immediate vicinity of the setup are not effectively sampled by the instruments [Schuepp *et al.*, 1990]. It seems more likely therefore that the observed hexenal release was due to natural wounding, possibly caused by feeding insects, the wind or other stress. It is interesting to note that grasshoppers were abundant in the alfalfa field before the cutting. Of course, these observations are only based on the

Figure 4. The correlation between the normalized ion count rates observed at masses 99 and 81 from the grab samples.

Figure 5. Measured VOC fluxes after rainfall in the night of 15–16 August.

results of 1 day and more decisive conclusions await further confirmation by other studies.

[20] An attempt was made to determine (Z)-3-hexenol and (Z)-3-hexenyl acetate from the grab samples, by measuring the ion signals at 83, 101, and 143 amu (Table 1). These would compounds are also expected to be released from damaged and drying vegetation [Kirstine *et al.*, 1998]. The signals at these masses clearly responded to the cutting of the alfalfa, similarly to (Z)-3-hexenal and (E)-2-hexenal (Figure 3b), which indicates that these compounds were indeed present. It is difficult, however, to interpret the observed signals at masses 83, 101, and 143 amu in terms of (Z)-3-hexenol and (Z)-3-hexenyl acetate only. Other compounds must have been present during the experiment, and we have therefore not used these results. From the observed mixing ratios the contribution of (Z)-3-hexenol and (Z)-3-hexenyl acetate to the total oxVOC flux is estimated to be smaller than that of (Z)-3-hexenal.

3.3. Increased Emission After Rainfall

[21] During the night of 15–16 August a number of thunderstorms developed in eastern Colorado, followed by rainfall for a number of hours on the measurement location. This interrupted the measurements. The next day, when the sun came out and the wet alfalfa was drying, the measured fluxes were significantly enhanced and the results are shown in Figure 5. The fluxes of acetaldehyde and methanol, in particular, were strongly increased compared with the fluxes observed during the four earlier days. These findings agree qualitatively with the work of Warneke *et al.* [1999], who observed significantly higher oxVOC emissions from wetted plant material in the laboratory.

3.4. Cumulative Fluxes

[22] Figure 6 shows the cumulative oxVOC fluxes measured before the cutting started. These results are obtained by integrating the data shown in Figures 2c and 3c. By integrating the flux, small but systematic fluxes can be seen more clearly, and indeed

Figure 6 shows several interesting features. The methanol emissions started shortly after 0600 LT on 12 August and lasted until late in the afternoon. On 13 August the methanol emission started around the same time. This was still before the cutting started around 0900 LT, indicated in Figure 6 by the shaded area and shows that the morning release of methanol on 12 August was not an isolated event. The cumulative flux of hexenal steadily increased between noon and 1800 LT on 12 August, demonstrating that there was indeed some release of hexenal from the undisturbed vegetation as concluded above from Figure 3c. From Figure 6 the average flux of hexenal between 1200 and 1800 LT is estimated to be $0.04 \text{ mg m}^{-2} \text{ h}^{-1}$.

[23] The cumulative fluxes of acetaldehyde and acetone decreased before noon on 12 August, increased in the afternoon, and decreased again in the night of 12–13 August, before they were enhanced dramatically on 13 August owing to the cutting. Evidently, the exchange of acetaldehyde and acetone between plants and the atmosphere can be bidirectional; a conclusion also drawn by Kesselmeier and Staudt [1999] and Kesselmeier [2001] for formaldehyde, acetaldehyde, and organic acids. Kesselmeier [2001] demonstrated that the flux of acetaldehyde can be linearly dependent on the ambient mixing ratio, with emission below and deposition above a so-called compensation point of 0.5–1.5 ppbv. The present data set contains a weak indication for the existence of a similar compensation point at 1.4 ppbv for acetaldehyde and 2.2 ppbv for acetone.

[24] From Figure 6 the deposition fluxes of acetaldehyde and acetone before noon were both estimated to be around $0.02 \text{ mg m}^{-2} \text{ h}^{-1}$, which is similar to the downward flux observed by Kesselmeier [2001] for two different oak species. Combined with the average mixing ratios of acetaldehyde (1.9 ppbv) and acetone (3.2 ppbv) over this interval, the corresponding deposition velocities are 0.2 cm s^{-1} for acetaldehyde and 0.09 cm s^{-1} for acetone. These are entirely realistic values: somewhat higher than the continental deposition velocity of CO (0.03 cm s^{-1}), for instance, and lower than that for ozone (0.4 cm s^{-1}) [Hauglus-

Figure 6. Cumulative VOC fluxes during the period before the cutting. The hatched areas indicate when the cutting started.

taine *et al.*, 1994]. The higher deposition velocity of acetaldehyde with respect to acetone cannot be explained by the difference in solubility: the Henry's law constant is $27 \text{ mol kg}^{-1} \text{ bar}^{-1}$ for acetone and $13 \text{ mol kg}^{-1} \text{ bar}^{-1}$ for acetaldehyde [Benkelberg *et al.*, 1995]. The difference in deposition velocities, however, is in accord with Jayne *et al.* [1992], who found that the uptake of acetaldehyde by water surfaces is higher than expected based on its solubility only. In the afternoon of 12 August the undisturbed alfalfa apparently released some acetaldehyde and acetone, possibly the same molecules that were deposited earlier. From Figure 6 the emission fluxes in the afternoon are estimated to be around $0.02 \text{ mg m}^{-2} \text{ h}^{-1}$. More research is obviously needed to confirm the findings on the flux of hexenal and the bidirectional exchange of acetone and acetaldehyde, as these observations are solely based on the results of 1 day.

3.5. Nighttime Measurements

[25] It can be expected that the drying alfalfa also released some VOCs during the night, even though the lower temperature and radiation and the increased humidity slow the drying process. Figures 2c and 3c, however, show that the nighttime eddy covariance fluxes were in general close to zero. The question arises whether the nighttime emissions were indeed small or that the eddy covariance technique did not give reliable results due to the increased stability of the surface layer. The friction velocity (the square root of the absolute value of the covariance between vertical and horizontal wind velocities) decreased during most of the nights below 0.1 m s^{-1} , which is low for eddy covariance measurements. Also, the footprint of the measurement, i.e., the area from which the emissions are effectively sampled [Schuepp *et al.*, 1990], became very large at night and in many cases exceeded the size of the alfalfa field. It can therefore no longer be assumed that the emissions were homogeneous.

[26] A number of observations indicate that the nighttime release of VOCs may not have been zero in this experiment. It is seen in Figure 2b that the VOC concentrations and the variability were high during the three nights after the field was cut, whereas the concentrations were relatively low and constant during the night before the cutting. Also, during part of the night of 14–15 August the mixing ratios of methanol, acetaldehyde and acetone in the grab samples were not only highly variable but also extremely well correlated as shown in Figure 7. These observations suggest that the drying alfalfa also released VOCs at night: the nighttime concentrations built up higher because of the inefficient vertical mixing. Moreover, we know from the daytime measurements that acetaldehyde and acetone were not significantly emitted from undisturbed alfalfa and are therefore not likely to come from neighboring fields, which were not being harvested at the time of our experiment. According to Wesely [1988], both the variability and the good correlation indicate the presence of a flux of methanol, acetone, and acetaldehyde in either the downward or the upward direction. Again, the high acetone and acetaldehyde values strongly suggest that it was an upward flux. We conclude that the nighttime release of VOCs from the drying alfalfa was not zero, but quantification remains difficult.

4. Discussion

4.1. VOC Emissions Due to Crop Harvesting

[27] From the measured fluxes in Figures 2c, 3c, and 5 the total emissions of the measured VOCs were estimated for each day and the results are given in Table 2. For 12–14 August the data set is almost complete, and the few missing data points were determined by interpolation to obtain the integrated amounts. On 15 August the measurements were interrupted at 2130 LT, but the missing data are not expected to make a noticeable difference to the integrated fluxes, as nighttime emissions were low. On 16 August we only obtained data between 0800 and 1500 LT and thus integrated over

Figure 7. Mixing ratios of methanol, acetaldehyde, and acetone during the night of 14–15 August.

this period. These integrated emissions may therefore be only lower estimates and are placed in parentheses in Table 2.

[28] From Table 2 the influence of the cutting and drying alfalfa can be clearly seen. Methanol emissions increased by a factor 2 to 3, and then slowly decreased in the subsequent days. Acetaldehyde and acetone emissions increased from virtually zero and seemingly reached a maximum on the day after the cutting. Hexenal was strongly emitted on the day of the cutting, but much smaller amounts were released from the drying alfalfa. Qualitatively, these findings are in accord with the laboratory experiment of de Gouw *et al.* [2000] on alfalfa, who found strong emissions of methanol and hexenal immediately after cutting and mostly acetone, methanol, and acetaldehyde from the drying leaves. In the laboratory work, however, the relative contribution of acetaldehyde and acetone was higher than observed here during the drying phase. Possible explanations are that the drying alfalfa in the field remained relatively wet in comparison with the laboratory experiment or that the plants were grown under different conditions. Also, oxVOC releases can vary significantly in different cultivars as illustrated by Fall *et al.* [2001].

[29] The amounts released on 13–15 August were added to obtain an idea of the total VOC emissions due to the harvest of alfalfa. In Table 2 these totals are shown and converted to a fraction of the dry weight, using an alfalfa yield of 0.40 kg m^{-2} determined for this field. Also shown in Table 2 are the results of previous studies on wounded and drying vegetation. It is seen in Table 2 that the results of the present experiment agree reasonably well with the literature values. The value for the hexenal flux inferred from our data is lower than the range of values reported in the literature, but these fluxes are difficult to quantify using eddy covariance, owing to the transient nature of the emissions. The amount of acetaldehyde observed in the previous work of de Gouw *et al.* [2000] for cut clover is smaller than the range of values shown in Table 2, but these values were obtained

Table 2. Daily Integrated Volatile Organic Compound Emissions Observed During the Alfalfa Experiment^a

Date	Methanol, mg m ⁻²	Acetaldehyde, mg m ⁻²	Acetone, mg m ⁻²	Hexenal, mg m ⁻²
12 Aug.	12.9	-0.05	-0.09	0.3
13 Aug.	35.2	2.5	1.3	6.4
14 Aug.	32.7	3.4	3.4	0.5
15 Aug.	25.5	2.9	2.5	0.6
16 Aug.	(55.4)	(4.7)	(1.0)	(0.4)
Total 13–15 Aug.	93.4	8.9	7.2	7.5
Total Release	Methanol, μg gdw ⁻¹	Acetaldehyde, μg gdw ⁻¹	Acetone, μg gdw ⁻¹	Hexenal, μg gdw ⁻¹
This work	230	22	18	19
Cut clover ^b	510	80	90	120
Cut grass ^b	150	40	15	160
Cut clover ^c	240	3	16	80
Drying grass ^d	160	20–80	20–40	100–240

^a The data on 12–14 August were integrated from midnight to midnight, the data on 15 August from midnight until 2130 LT, and the data on 16 August from 0800 until 1500 LT. The total amounts are converted to units of μg gdw⁻¹ (μg per gram dry weight) using an alfalfa yield of 0.4 kg m⁻² and compared with literature values.

^b Enclosure measurement by *Kirstine et al.* [1998]; using a total VOC release of 600 μg gdw⁻¹ from their Figure 5, and the speciation of VOCs according to their Table 5.

^c Laboratory experiment by *de Gouw et al.* [2000].

^d Laboratory experiment by *Karl et al.* [2001a].

immediately after cutting, whereas acetaldehyde seems to increase more strongly during the drying phase.

[30] The global production of hay is estimated by *Karl et al.* [2001b] as 1000 Tg yr⁻¹. From this number and the VOC emissions per dry weight (Table 2), the total VOC emissions due to hay production are expected to be lower than 1 Tg yr⁻¹, i.e., a small amount compared with other biogenic sources of oxVOCs [*Guenther et al.*, 2000]. Our current estimate is lower than the previously published estimate, which was based on laboratory data only [*de Gouw et al.*, 1999]. As mentioned above, the difference may be due to the fact that the drying was less complete in the field, or that oxVOC releases can vary significantly between different cultivars [*Fall et al.*, 2001].

[31] The current findings imply that the emissions of methanol and acetone caused by crop harvesting may not be important for the global atmosphere. It has been suggested that acetone and methanol contribute to the concentration of odd hydrogen radicals in the upper troposphere [*Singh et al.*, 1995], but other sources of these compounds are far higher than the source from crop harvesting [*Singh et al.*, 2000]. Methanol and acetone are relatively inert in the lower atmosphere and the effects on local air chemistry are therefore minor. Contrary to this, acetaldehyde and hexenal are much more reactive in the lower atmosphere and their release due to crop harvesting may play a role in the chemistry of rural atmospheres.

4.2. VOC Emissions From Undisturbed Alfalfa

[32] In the case of methanol the most notable finding of the present experiment is the fact that it is released in significant amounts from undisturbed alfalfa. It is true that the methanol emission is increased after cutting the field, but the increase is not dramatic, and it can also be expected that the emissions will be low after the hay is removed from the field. The experiment suggests therefore that methanol emissions from alfalfa may not be significantly enhanced by the harvest. The presently observed peak methanol flux of 4 mg m⁻² h⁻¹ from undisturbed alfalfa (or 10 μg gdw⁻¹ h⁻¹ using the alfalfa yield of 0.4 kg m⁻²) is comparable in magnitude to the release observed from other plants. Laboratory work by *MacDonald and Fall* [1993] showed emissions ranging from 1.5 to 45.7 μg gdw⁻¹ h⁻¹ from a variety of plants, including tree species and a number of agricultural crops. *Kirstine et al.* [1998] measured midday methanol fluxes of 0.9–1.3 mg m⁻² h⁻¹ from grass and up to 9–20 mg m⁻² h⁻¹ from clover. *Fukui and Doskey* [1998] reported a 2-year average noontime emission of 0.46 ± 0.07 mg m⁻² h⁻¹ at a grassland site during the growing

season. *Schade and Goldstein* [2001] presented a 2-month averaged methanol flux from ponderosa pine with a daily maximum around 4.0 mg m⁻² h⁻¹. Recently, *Baker et al.* [2001] observed daytime methanol fluxes of ~1 mg m⁻² h⁻¹ from a subalpine conifer forest.

[33] In the model of *Guenther et al.* [1995] a global source of OVOCs (other VOCs) of 260 Tg yr⁻¹ was estimated assuming an emission factor ϵ of 1.5 μg gdw⁻¹ h⁻¹ for all different ecosystems. In this paper and in most of the work summarized above the measured emission factor even exceeds the value of 1.5 μg gdw⁻¹ h⁻¹, indicating that the biogenic source of methanol in the atmosphere is large. Significant uncertainties do remain, however, for instance, owing to the unknown contribution of tropical forests. The global budget of methanol was recently reviewed by *Singh et al.* [2000], who estimated the total source to be 122 (75–210) Tg yr⁻¹, with a biogenic contribution of 75 (50–125) Tg yr⁻¹. Both values are higher than the estimated total sink of 40–50 Tg yr⁻¹. The present work gives further support to the biogenic source estimate of *Singh et al.* [2000] and thus for the existence of a deficit in the budget.

[34] The measured release of hexenal from undisturbed alfalfa was small (0.04 mg m⁻² h⁻¹ or 0.1 μg gdw⁻¹ h⁻¹), but owing to its high reactivity, it was the dominant reactive VOC observed here, in accordance with the findings of *Arey et al.* [1991] for other crop species. This suggests that hexenal may play a role in the chemistry of rural atmospheres, most likely by sequestering NO_x through the formation of organic nitrates [*Arey et al.*, 1991]. Furthermore, this work proves that the overall emission of hexenal can be significantly enhanced by the harvesting of crops. It is noteworthy that C₆ wound compounds have been shown to play a role in attracting herbivorous and carnivorous insects to their food sources [e.g., *Turlings et al.*, 1990], which shows that wound-induced emissions are common. Nevertheless, a release of hexenal of 0.1 μg gdw⁻¹ h⁻¹ is small compared with isoprene and monoterpene emissions from certain tree species [*Guenther et al.*, 1995], and it is expected to have a minor impact on the chemistry of the global atmosphere.

5. Conclusions and Future Outlook

[35] The atmospheric fluxes of methanol, acetaldehyde, acetone, and hexenal from an alfalfa field before, during, and after cutting were measured using a combination of disjunct eddy

covariance and PTR-MS. Over the course of 1 day a strong emission of methanol and a weak release of hexenal were found from the undisturbed alfalfa. After the cutting, these emissions were significantly enhanced, and also a strong release of acetaldehyde and acetone was observed. The integrated oxVOC emissions inferred from the measurements agree reasonably well with the results of laboratory experiments on wounded and drying vegetation. This suggests that laboratory screening may be sufficient to estimate the oxVOC fluxes from other agricultural crops.

[36] The experiments suggest that the oxVOC emissions caused by the production of hay are of minor importance on a global scale. The release of the more reactive wound compounds (Z)-3-hexenal, (E)-2-hexenal and acetaldehyde may locally impact the chemistry of the rural troposphere during the harvest. Other leaf wounding and drying processes such as natural senescence and droughts may lead to a larger VOC release than crop harvesting, but not much is known about this at present.

[37] An important outcome of the present work is the observation of a strong release of methanol from undisturbed alfalfa. This finding provides further support that the biogenic source of this compound is large and probably significantly larger than the estimated total sink. Closing the atmospheric methanol budget is important, as it may give detailed insight into the mechanisms involved in the release and removal of oxVOCs. Moreover, methanol is commonly suggested as an alternative fuel in combustion engines and in fuel cells. It is therefore necessary to understand its atmospheric chemistry in detail and to account properly for the present sources and sinks.

[38] A small emission of hexenal was observed from the undisturbed alfalfa, possibly owing to the wind, feeding insects, or other stresses. If confirmed by future measurements, these results suggest that emissions of wound compounds may be present in many different ecosystems under varying conditions (independent of light and temperature for example). Finally, the results suggest that acetaldehyde and acetone can be lost to alfalfa by dry deposition. The deposition velocities inferred from the data indicate that dry deposition may be a significant loss process for oxVOCs in the atmosphere, which warrants more research.

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