

UC Irvine

UC Irvine Previously Published Works

Title

Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting

Permalink

<https://escholarship.org/uc/item/4s8540ds>

Journal

Atmospheric Environment, 35(3)

ISSN

1352-2310

Authors

Karl, Thomas
Guenther, Alex
Jordan, Alfons
[et al.](#)

Publication Date

2001

DOI

10.1016/s1352-2310(00)00405-2

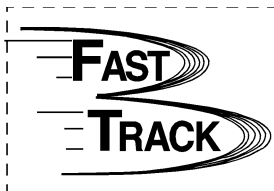
Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed



PERGAMON



Atmospheric Environment 35 (2001) 491–495

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting

Thomas Karl^a, Alex Guenther^a, Alfons Jordan^b, Ray Fall^c, Werner Lindinger^{b,*}

^aAtmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80307, USA

^bInstitut für Ionenphysik, Universität Innsbruck, Technikerstrasse 25, 6020 Innsbruck, Austria

^cDepartment of Chemistry and Biochemistry, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-0215, USA

Received 15 June 2000; accepted 18 August 2000

Abstract

Biogenic oxygenated volatile organic compound (VOC) fluxes have been directly measured by eddy covariance using the combination of a fast response, real-time VOC sensor and an acoustic anemometer. VOC detection is based on proton-transfer reaction mass spectrometry which has currently a response time of ca. 0.8 s and the system is suitable for making nearly unattended, long-term and continuous measurements of VOC fluxes. The eddy covariance system has a detection limit, for most VOCs, of less than $0.1 \text{ mg m}^{-2} \text{ h}^{-1}$. The system was field tested above a hayfield near St. Johann, Austria where cut and drying grasses released a variety of VOCs. High fluxes were observed for about 2 days after cutting and were dominated by methanol ($1\text{--}8.4 \text{ mg m}^{-2} \text{ h}^{-1}$), acetaldehyde ($0.5\text{--}3 \text{ mg m}^{-2} \text{ h}^{-1}$), hexenals ($0.1\text{--}1.5 \text{ mg m}^{-2} \text{ h}^{-1}$) and acetone ($0.1\text{--}1.5 \text{ mg m}^{-2} \text{ h}^{-1}$). The eddy covariance measurements generally agreed with flux estimates based on enclosure measurements and surface layer gradients. The sensitivity and selectivity of the system make it suitable for quantifying the fluxes of the dominant biogenic VOCs from a variety of landscapes and sources. © 2000 Published by Elsevier Science Ltd.

Keywords: Biogenic; Volatile organic compounds; Eddy covariance; PTR-MS; Hay

1. Introduction

Volatile organic compounds (VOCs) play an important role in determining the chemical composition of the atmosphere (Fehsenfeld et al., 1992). These compounds are emitted from diverse sources but are primarily of biogenic origin. The processes controlling these emissions must be understood in order to accurately describe their impact on the earth system. Past investigations of biogenic VOC emissions have focused on emissions of isoprene and monoterpenes but it has been suggested that about half of the global total are oxygenated VOCs including alcohols, aldehydes and ketones (Guenther et al., 1995). A major limitation in

the investigation of these oxygenated VOCs has been the difficulty in measuring these compounds and, in particular, vertical fluxes in the turbulent boundary layer above a source. Methods that have been used to measure vertical turbulent fluxes, e.g., relaxed eddy accumulation and surface layer gradients, rely on assumptions that are reasonable in some cases but can result in large errors in estimated fluxes (Dabberdt et al., 1993). These methods are typically labor intensive, limiting the number of measurements that can be made, and face technical challenges that often limit the number of compounds that can be quantified (especially oxygenated VOCs). Eddy covariance flux measurements are directly determined by measuring the covariance of chemical concentration with vertical wind speed. It is the most direct flux measurement method but has only been used for a selected number of compounds because it imposes two critical constraints on a chemical measurement system: a fast-response time and specificity for the compound

* Corresponding author. Tel.: +43-512-507-6242; fax: +43-512-507-2932.

E-mail address: werner.lindinger@uibk.ac.at (W. Lindinger).

whose flux is being determined. The response time required for this study (with a measurement height of about 4.5 m and unstable conditions with Monin–Obukhov lengths between -3 and -15 m) is less than 1 s. These two constraints have limited the application of eddy covariance to about a dozen trace gases in total and only a few non-methane VOCs, isoprene (Guenther and Hills, 1998), acetone and formic acid (Shaw et al., 1998).

The application of a fast-response, proton-transfer reaction mass spectrometry (PTR-MS) system greatly expands the range of compounds that can be investigated using eddy covariance flux measurements. In this paper we describe the capabilities of this system including limitations, and then compare eddy covariance field measurements with flux estimates based on enclosure measurements extrapolation and estimated from surface layer gradients. The field test is an investigation of emissions from grass hay harvesting which is a potentially important source of oxygenated VOCs in the atmosphere (Kirstine et al., 1998; Fall et al., 1999; de Gouw et al., 1999, 2000).

2. Methods

2.1. PTR-MS

The measurements were performed using a PTR-MS system which allows for real-time monitoring of the concentrations of VOCs. The system and measuring procedure have been described earlier (Lindinger et al., 1998). The air to be investigated was sampled with a pumping speed of 0.5 l min^{-1} through a Teflon line of 1 mm inner diameter, from which a small fraction of ca. $20 \text{ STP cm}^3 \text{ min}^{-1}$ was led into the PTR-MS system. The response time of the system is ca. 0.8 s.

2.2. Micrometeorological measurements

Eddy covariance and surface layer gradient systems were deployed near the center of a managed hay pasture near St. Johann (latitude 47.5°N , longitude 12.4°E), in Tyrol, Austria. The pasture grasses were dominated by *Dactylis glomerata*, *Poa pratensis*, *Phleum pratense*, *Trifolium pratense* and *Poa trivialis*. The sampling site was located near the center of the approximately 3 ha pasture and the upwind fetch was typically about 150 m. The footprint for typical measurement conditions (wind speeds between 1 and 3 m s^{-1} and unstable conditions with Monin–Obukhov lengths between -3 and -15 m) suggest an underestimate of not more than 20% due to the contribution of the field further upwind, which was not mowed. The field was mowed in the morning of August 21, 1999 and flux measurements were made from August 21 to 22. Daytime temperatures ranged from

about 20°C on the first day to about 24°C on the second day. Gradient measurements were made at heights of 0.7 and 4.5 m above ground level and the eddy covariance system was at a height of 4.5 m. Estimates of eddy diffusivity used for gradient flux estimates were based on the measured temperature gradient, sensible heat flux and an iterative calculation procedure similar to that described by Fuentes et al. (1996).

2.3. Enclosure measurements

A dynamic (flow-through) enclosure system was used to characterize two of the dominant grasses in the hayfield, *Dactylis glomerata* and *Poa pratensis*. The grasses were cut and immediately placed in the enclosure. A constant flow rate of $135 \text{ STP cm}^3 \text{ min}^{-1}$ was maintained through the 350 ml enclosure and VOC concentrations were monitored over the whole period of drying. Measurements were repeated for drying temperatures of 25, 30 and 35°C .

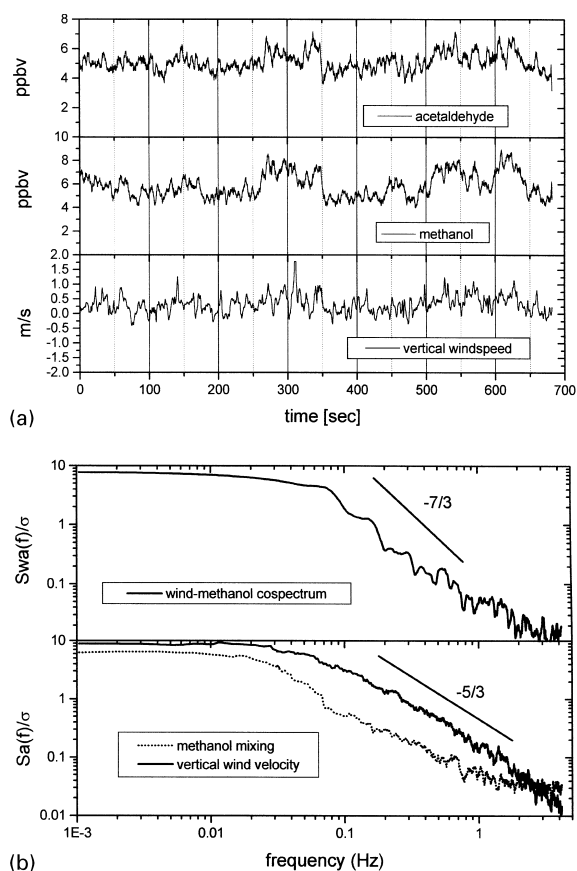


Fig. 1. (a) Time traces (200 s) of methanol and acetaldehyde mixing ratios and the vertical wind speed measured at 4.5 m above a hayfield in Austria and demonstrating the strong correlation between these variables. (b) Normalized methanol and vertical wind velocity (w) spectra and cospectra.

3. Results and discussion

3.1. Eddy covariance system

3.1.1. Sensitivity

The PTR-MS instrument noise is primarily high frequency, random noise, and is relatively independent of concentration. At a sampling rate of 10 Hz and average concentrations of 0.5 ppbv, the relative noise level is equivalent to about 40%. This is reduced to 4% at 0.1 Hz (equivalent to a 10 s time period). The high-frequency noise does not significantly influence the eddy covariance flux measurements, which were averaged over 15 min periods.

3.1.2. Response time

The response time was estimated by adding short pulses of air containing acetone to the system inlet and monitoring the respective ion signal in the PTR-MS. The time elapsed during the increase of the ion signal to 95% and the decline to 0% of the maximum ion signal during application of the acetone pulse was measured to be ca. 0.8 s. As it is notoriously difficult to generate a true step change in concentration in laboratory flows, we assume that the actual response time of the system is less than 0.8 s. Acetone is a typical non-sticky compound and thus can be taken as a representative of the VOCs investigated in this research, which are non-sticky as well. This would not apply for most of the volatile acids. The response time estimates indicate that this system should be ca-

pable of resolving VOC fluctuations at rates as high as 1–2 Hz. Spectra and cospectra of vertical wind velocity and methanol mixing ratios are shown in Fig. 1b; the slopes of the wind–methanol cospectrum and the individual spectra are close to the theoretical slopes, $-7/3$ and $-5/3$, respectively. The attenuation due to passing through the sample tubing limits the response time of the system to approximately 8 Hz using a flow rate of 0.5 l min^{-1} in 450 cm of 0.1 cm diameter tubing. This value was calculated according to Massman (1991).

3.1.3. Selectivity

The compounds measured here appear at the following masses: methanol (M33), acetaldehyde (M45), acetone (M59), pentenols plus 2-methylbutanal (M69), hexenals (M57, M81 and M99), hexenols plus hexanal (M83), and butanone (M73). Details of these assignments are discussed by Fall et al. (1999) and confirmation was also achieved by recent gas-chromatography–PTR-MS measurements (Karl, 2000). Characterizing and limiting interferences is a significant challenge for a VOC eddy covariance system. An important component of the application of this system is the use of other tools, e.g. gas chromatography, for identifying the compound mix present at a given field site. In some cases, the flux measured by this system will represent the sum of several compounds, for example the total monoterpene emission or the deposition of both methyl vinyl ketone and methacrolein. The resulting information will be useful as long as

Table 1
Comparison of VOC fluxes obtained with enclosures, surface gradient and eddy correlation. The total VOC release per gram dryweight during the drying period in a cuvette is also given

	Methanol	Acetaldehyde	Acetone	Butanone	Pentenols plus 2-methylbutanal	Hexenals	Hexenols plus hexanal
Cuvette							
VOC release drying ($\mu\text{g gdw}^{-1}$)	160	20–80	20–40	11–80	15	100–240	30–60
Chamber							
Fluxes cutting transient ($\text{mg m}^{-2} \text{h}^{-1}$)	0.3–1.1	0.4–0.7	0.1–0.2	0.05–0.01	0.1–0.9	40–50	1–3
Fluxes drying ($\text{mg m}^{-2} \text{h}^{-1}$)	0.6–1.44	0.3–0.8	0.1–0.2	0.06	0.07–0.1	0.2–0.4	0.1–0.3
Gradient							
Fluxes drying 1st day ($\text{mg m}^{-2} \text{h}^{-1}$)	1.3–8.4	1.0–3.0	0.6–1.5	—	0.1–0.3	0.1–1.5	0.1–0.3
Fluxes drying 2nd day ($\text{mg m}^{-2} \text{h}^{-1}$)	1.0–2.0	0.7–1.0	0.2–0.33	0.02	0.4	0.16	0.3
Eddy correlation							
Fluxes drying 2nd day ($\text{mg m}^{-2} \text{h}^{-1}$)	1.4–2.0	0.5–1.5	(0.1)–0.5	—	0.7	0.5	0.2

both deposition and emission fluxes of compounds do not occur with the same resulting mass ion.

3.1.4. Linearity and stability

The linearity of the system in the range of the VOC concentrations measured during the present work has been proven in several earlier investigations (Lindinger et al., 1998). The drift can be eliminated by standardizing the VOC concentrations by the H_3O^+ primary ions. Lack of significant drift indicates that long-term unattended operation of the system is feasible.

3.2. VOC fluxes from hay harvesting

As illustrated in Fig. 1a, a positive correlation between vertical wind speed and VOC concentrations was observed above the hayfield after mowing. The spectra and cospectra (Fig. 1b) demonstrate the expected frequency distribution for the vertical wind speed (w) in an unstable surface layer.

Table 1 compares the fluxes measured by eddy covariance with estimates based on enclosure measurements and surface layer gradients obtained by using the Monin–Obukhov similarity approach (Fuentes et al., 1996). The eddy covariance measurements generally agreed with flux estimates based on enclosure measurements and surface layer gradients. For example, cuvette measurements of the methanol yielded $160 \mu\text{g gdw}^{-1}$. This corresponds to an estimated flux of $3 \text{ mg m}^{-2} \text{ h}^{-1}$; this flux compares to fluxes from chamber, surface gradient and eddy correlation ranging from 0.6 to $8.4 \text{ mg m}^{-2} \text{ h}^{-1}$. Summing individual VOC fluxes at midday gives $7\text{--}15 \text{ mg C m}^{-2} \text{ h}^{-1}$. The largest contributions to the total flux were made by methanol (40%) and acetaldehyde (25%); smaller, but significant, fluxes of C5 and C6 leaf wound VOCs were also detected. The highest, transient VOC releases occurred during hay cutting (Table 1) and when the hay was turned as part of the drying process (not shown).

4. Conclusions

Above-canopy VOC fluxes can be measured using the eddy covariance method with VOC detection based on PTR-MS. The resulting eddy covariance system provides a direct measurement of VOC fluxes and is suitable for long-term, nearly unattended, operation. The lower detection limit ($< 0.1 \text{ mg C m}^{-2} \text{ h}^{-1}$) makes the system useful for measuring fluxes from a wide range of locations. Care must be taken at locations where there may be downward and upward fluxes of VOCs yielding the same protonated ions by PTR-MS.

Field tests at a mowed hayfield site demonstrate that the system is capable of accurately estimating VOC fluxes of methanol, acetaldehyde, acetone, pentenols plus

2-methylbutanal, hexenals and hexanal plus hexenols; these are typical VOCs released from wounded vegetation (Fall et al., 1999; de Gouw et al., 1999, 2000). Although the mean temperatures were rather low, around 20°C , the total VOC flux for the entire drying period is estimated to be about $100\text{--}300 \text{ mg C m}^{-2}$. These results indicate that hay mowing can be a significant source of VOC emission into the atmosphere, and should be included in VOC emission inventories.

Acknowledgements

This work was supported by the Austrian ‘Fonds zur Förderung der wissenschaftlichen Forschung’, project P14130, and NSF grant ATM-9805191 and University of Colorado Faculty Fellowship (to RF). The National Center for Atmospheric Research is sponsored by The National Science Foundation.

References

- Dabberdt, W.F., Lenschow, D.H., Horst, T.W., Zimmerman, P.R., Oncley, S.P., Delany, A.C., 1993. Atmosphere–surface exchange measurements. *Science* 260, 1472–1482.
- de Gouw, J.A., Howard, C.J., Custer, T., Baker, B.M., Fall, R., 2000. Proton-transfer chemical-ionization mass spectrometry allows real-time analysis of volatile organic compounds released from cutting and drying of crops. *Environmental Science and Technology* 34, 2640–2648.
- de Gouw, J.A., Howard, C.J., Custer, T., Fall, R., 1999. Emissions of volatile organic compounds from cut grass and clover are enhanced during the drying process. *Geophysical Research Letters* 26, 811–814.
- Fall, R., Karl, T., Hansel, A., Jordan, A., Lindinger, W., 1999. Volatile organic compounds emitted after leaf wounding: on-line analysis by proton-transfer reaction mass spectrometry. *Journal of Geophysical Research* 104, 15963–15974.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A., Hewitt, C., Lamb, B., Liu, S., Trainer, M., Westberg, H., Zimmerman, P., 1992. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Global Biogeochemical Cycles* 6, 389–430.
- Fuentes, J.D., Wang, D., Neumann, H.H., Gillespie, T.J., Den Hartog, G., Dann, T.F., 1996. Ambient biogenic hydrocarbons and isoprene emissions from a mixed deciduous forest. *Journal of Atmospheric Chemistry* 25, 67–95.
- Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McZKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. *Journal of Geophysical Research* 100, 8873–8892.
- Guenther, A., Hills, A.J., 1998. Eddy covariance measurement of isoprene fluxes. *Journal of Geophysical Research* 103, 13145–13152.
- Karl, T., 2000. Time resolved investigations on biogenic trace gas exchanges using proton-transfer-reaction mass spectrometry. Ph.D. Thesis, University of Innsbruck.

- Kirstine, W., Galbally, I., Ye, Y., Hooper, M., 1998. Emissions of volatile organic compounds (primarily oxygenated species) from pasture. *Journal of Geophysical Research* 103, 10605–10619.
- Lindinger, W., Hansel, A., Jordan, A., 1998. On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS). Medical applications, food control and environmental research. *International Journal of Mass Spectrometry and Ion Processing* 173, 191–241.
- Massman, W.J., 1991. The attenuation of concentration fluctuations in turbulent flow through a tube. *Journal of Geophysical Research* 96 D8, 15269–15273.
- Shaw, W.J., Spicer, C.W., Kenny, D., 1998. Eddy correlation fluxes of trace gases using a tandem mass spectrometer. *Atmospheric Environment* 32, 2887–2898.