Eddy covariance measurements of isoprene and 232-MBO based on NO+ time-of-flight mass spectrometry

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Abstract:

Isoprene and 2-methyl-3-buten-2-ol (232-MBO) are the dominant biogenic VOCs released throughout the US, thus requiring simultaneous measurements. Recent measurements suggest the presence of isoprene in 232-MBO dominated ecosystems, however analytical difficulties make it problematic to detect both species independently. Based on a new chemical ionization scheme we use eddy covariance measurements to selectively measure fluxes of both species without analytical interference at the Manitou Experimental Forest (MEF) in Colorado. Our measurements show a concentration ratio between isoprene and 232 MBO of 0.24 (ppbv/ppbv), and a flux ratio of 0.10 ([ppbv m/s] / [ppbv m/s]). Daytime average emission factors of isoprene and 232 MBO were 1.4±0.3 and 16.0±3.0 mg/m²/h respectively. Both compounds exhibit light and temperature dependent fluxes. These findings suggest that isoprene is both locally produced and transported to the measurement site dominated by ponderosa pine. This makes it difficult to use MVK and MAC as tracers for estimating the photochemical age of isoprene chemistry at this site. Further our measurements suggest that isoprene can contribute to about 15% of the OH reactivity relative to 232 MBO.
1. Introduction:

Flux measurements of reactive gases play an integral part for biogeochemistry, ecological and atmospheric chemistry research. The most direct way to measure fluxes is achieved by the eddy covariance method [1]. Fast analytical methods capable of measuring at sampling rates up to 10 Hz are required for the eddy covariance method, which poses challenges for conventional analytical methods for volatile organic compounds (VOCs), such as gas chromatography. Sensitive on-line techniques such as chemical ionization mass spectrometry have presented an important breakthrough in recent years. As such real-time eddy covariance measurements of VOCs based on mass spectrometric methods, such as Proton-transfer reaction mass spectrometry, have become tractable tools for quantifying turbulent fluxes in the atmosphere ([2], [3], [4], [5]). New data suggest a wide range of potentially exchanged BVOCs with the atmosphere posing a significant challenge for quantifying natural organic compounds [6]. Chemical ionization methods can sometimes suffer from selectivity and identification issues, especially in complex chemical matrices. While time of flight mass spectrometry has presented a significant step forward in better identification and selectivity ([7], [8]), alternative ionization methods can also aid in tailored applications for environmental real time monitoring.

The selective measurement of isoprene fluxes in a chemical matrix dominated by 232 MBO, as is commonly encountered throughout ecosystems in the Western US ([9], [10]), is still posing a major analytical challenge for on-line (e.g. PTRMS) and off-line techniques (e.g. cartridge sampling coupled to relaxed eddy accumulation; [11]).

For PTR-MS a major interference for the detection of isoprene is the dehydration reaction of 232 MBO, leading to a C_{5}H_{9}^{+} ion. We have recently demonstrated the ability to selectively measure both species based on NO^{+} ionization [12]. Here we extend the analysis to presenting the first flux measurements allowing to selectively distinguish emissions of both species at a coniferous ecosystem in the Rocky Mountains. We use a novel chemical ionization scheme based on NO^{+} ionization coupled to SRI-TOF-MS [12] to measure both isoprene and 232 MBO fluxes. These two biogenic VOCs (BVOC) comprise a major fraction of biogenic emissions in the US; yet isoprene emissions remain poorly quantified in these types of ecosystems (i.e. coniferous ecosystems) due to the lack of appropriate flux measurement techniques in 232 – MBO dominated landscapes.

2. Methods:

2.1. Site

Flux measurements were conducted at the Manitou Experimental Forest (latitude: +39° 6' 2.34", longitude: -105° 6' 8.94"; 2370 m elevation), maintained by the U.S. Forest Service. The site is
representative of the Central Rocky Mountain ponderosa pine zone. The canopy is open and of varying density, with mixed age ponderosa pine up to 100 years old and a surface cover of grasses, sage, crocus, forbs and exposed cryptogrammic soils. The average tree height surrounding the measurement tower was 18.5m. More detail and site information can be found in [10]. Eddy covariance flux measurements were performed for one week in July 2012 (07/14 to 07/19 2012). Measurements were taken from a 30 m tall tower in 2012. Three dimensional winds and temperature were measured using a three dimensional sonic anemometer CSAT-3 (Campbell Scientific) with 10Hz resolution at z = 25.1 m. The SRI-TOF-MS sampled from an ~ 30 m long Teflon line (OD: 3/8”) with the inlet located within 30 cm of the anemometer. Sample air was aspirated at a flow rate of 50 l/min, so that overall delay times were measured between 3 and 5 s. Photosynthetically active radiation (PAR) and air temperature were measured at 27.8m and 25m height using a Li190a quantum sensor (Li-Cor, Lincoln, NE) and an HMP35C-2 (Campbell Scientific, Logan, UT) respectively.

2.2 SRI-TOF-MS

NO⁺ flux measurements were performed using a SRI-TOF-MS 8000 apparatus from Ionicon Analytik GmbH, Innsbruck (Austria) [8]. The ionization conditions in the drift tube were controlled by drift voltage (530V), drift temperature (60 °C) and drift pressure (2.3 mbar) resulting in an E/N of about 115 Townsend (Td). More specific details can be found in [12]. Isoprene and 232 MBO were monitored on m/z 68.0618+ Th and m/z 69.0704+ Th respectively, after correcting for isotopic contributions.

10 Hz mass spectra up to m/z 420+ Th were recorded according to protocols discussed by [4] and [13]. For data acquisition the TOF-DAQ recorder (v. 1.2.91, TOFWERKS, Switzerland) was used and setup such that 10 Hz data were partitioned into individual 6 minute hdf5 files. Online TOF-MS mass scale calibration was achieved by injecting trace amounts of diodomethane (CAS: 75116) at the inlet via a diffusion tube and setting the TOF-DAQ recorder to auto mass scale calibration mode; peaks at m/z 30.996+ Th (NO⁺ isotope), m/z 45.993+ Th (NO₂⁺) and m/z 267.825+ Th (CH₂I₂⁺ diodomethane) were used to calibrate the entire TOF-MS mass scale every 6 minutes. Isoprene and 232 MBO data in counts per second were generated using the TOF-DAQ viewer software (v 1.2.91 TOFWERK AG, Switzerland). The stick spectra were recorded by defining a narrow border integration limit to accurately separate potentially interfering peaks. Individual 10 Hz 6 minute files were exported as net-cdf file. A matlab code (Mathworks, USA) was used to automatically append individual net-cdf files (1304 individual files) into a continuous 10 Hz time series that was used for subsequent flux calculations. Final concentrations were based on a dynamic dilution system, using two ppmv level standards containing isoprene and 232 MBO as described by [10]. The sensitivity for isoprene and 232 MBO was 11 and 13 ncps/ppbv respectively, where ncps represents the normalized count rate with respect to the primary ion NO⁺: ncps = cps_voc / cps_no x 1e6. PTR-MS measurements performed in 2009 are also briefly discussed in this manuscript. A high sensitivity PTR-MS system sampled VOC gradients
alternating between six points (1.5, 5.0, 8.5, 12.0, 17.7 and 25.1 m above ground). Analytical characteristics and instrument performance were presented previously in great detail [10, 12].

2.3 Eddy covariance method

The vertical turbulent flux \( F \) can be expressed as the co-variance between vertical wind velocity \( \langle w' \rangle \) and concentration \( \langle c' \rangle \) fluctuation according to:

\[
F = \langle w'c' \rangle,
\]

where the bracket denotes an appropriate averaging interval, here taken as 30 minutes. We ignore components of advection fluxes, which play a minor role during daytime conditions. Fluxes are calculated after a planar fit rotation of the 3-D wind vectors [14]. We then use the cross covariance to (1) determine lag-times through our sampling setup (here measured to be on the order of 5-6 seconds) and (2) to estimate a flux detection limit by de-correlating the vertical wind speed and the scalar in a cross-correlation analysis [15]. The first method to determine LODs of fluxes is to take the cross covariance function at time shifts of +/- (160-180s) between the vertical wind and concentration dataset and define it as the random noise signal. A second method based on a permutation method of the vertical wind time series similar to [16] is also used to estimate flux detection limits. The average of the cross covariance function at the lag time is then taken as the decorrelated flux noise signal. Based on these methods we calculate typical daytime flux detection limits for isoprene (m/z 68) and 232 MBO (m/z 69) of 0.03±0.01 and 0.08 ±0.04 mg/m²/h respectively. Finally, turbulent fluxes are then calculated using conventional fast fourier transform (FFT) after correction for the tubing transit time.

A stationarity test was performed according to [17]. Here the covariance between vertical wind and concentration is subdivided into 5 periods of 6 minutes. In cases were the covariance function calculated over 30 minutes exceeds the mean of the five 6 minute intervals by more than 30%, non stationary conditions are assumed.

3. Results

Fluxes of 232 MBO and isoprene are shown in figure 1. The sum of 232 MBO and isoprene fluxes (up to 10 mg/m²/h) are in the range of what was reported for this field site previously [10]. Both compounds exhibit a dominant diurnal cycle, where fluxes typically peak during the middle of the day, indicative of light dependent emissions that are linked to photosynthetic processes in plants. Red dots depict periods that failed the stationarity test – these data were subsequently omitted from further analysis; however as can be seen, these periods mostly cluster around nighttime or dawn periods, where fluxes are low. Night time fluxes lie generally below the flux detection limit depicted by the green line and are not further discussed here. Normalized co-spectra for sensible heat, 232 MBO and isoprene (figure 2) (averaged over data that satisfy the flux QA/QC criteria) suggest a maximum flux contribution on time scales between 10 and 100 s. Losses due to high frequency damping can be assessed by comparing VOC fluxes to those of
sensible heat. Here we calculate that the flux contribution above 1 Hz contributed on average 2% to the total flux.

The average ratio between molar isoprene and 232 MBO fluxes is 0.10 ([ppbv m/s]/[ ppbv m/s]). There is a slight diurnal trend (figure 3), where isoprene fluxes tend to be higher during the middle of the day (e.g. up to 0.15) than during dawn. Concentration ratios between these compounds are on average 0.24 ppbv/ppbv, thus about twice as high. These values are close to measurements (0.20 ppbv/ppbv) that were performed at this site a year earlier in 2011 [12] and suggest that a fraction of isoprene is likely also transported to the tower from outside of the flux footprint. Additional support comes from the fact that the concentration ratio of the current dataset tends to decrease during early morning periods (i.e. between 6 - 8 LT). We attribute these periods to the breakup of the nighttime inversion layer. Unfortunately we do not have any gradient measurements for the measurement period in 2012, but we show data from a meteorologically very similar period in August 2009. Figure 4 qualitatively compares the average of 5 diurnal measurements cycles performed in 2009 with diurnal concentration data obtained in 2012. The top panel in figure 4 depicts temperature gradients showing a strong nighttime inversion with ΔT~3.7 °C between 2 m and 43 m. The inversion layer becomes weaker with the onset of turbulent mixing at sunrise (6-8LT), but it typically takes about 3 hours to completely break up at around 9 am. During these morning hours (6-8LT) there is already enough light available to trigger 232-MBO and isoprene emissions, which results in a significant build up of 232 MBO and isoprene concentrations throughout the canopy. The lower panel in figure 4 depicts mixing ratios up to 10 ppbv of the sum of isoprene and 232 MBO. During these hours the inversion layer of the forest canopy weakens which allows some degree of transport of accumulated “canopy air” past the measurement sensor at 25 m, but still prevents significant entrainment of air from above. Concomitantly the concentration ratio tends to drop to about 0.05-0.11 (middle panel in figure 4). This lies close to the ratio that we observe for the molar flux ratios shown in figure 3. Previous work, based on infrequent GC-MS sampling, has assumed that isoprene is mostly transported to the site [18]. Flux and concentration observations presented here suggest that local sources can contribute about half of the isoprene. This is surprising as no obvious local isoprene sources within the footprint of the tower have been identified so far. Consequently the isoprene emission factor used in emission models [19] for this site would normally be set to zero.

The current flux dataset allows for the first time assessing isoprene and 232 MBO emission potentials separately at the canopy scale. Here we use a canopy environment model based on [20], [21], [19]. The model divides the canopy into 5 layers, calculating the energy balance for each layer. Light and temperature dependent BVOC emission parameterizations are described by Guenther et al. [19]. We define an ecosystem exchange potential (EEP) as the weighted emission factor (EF) calculated by inverting the canopy environment model, so that

\[ EEP := f^{-1} \frac{F}{\text{biomass}}. \]
where F/biomass represents the measured flux normalized by biomass density and $r^1$ stands for the model inversion driven by the measured light and temperature environment.

Figure 5 shows the results between 6 and 18 LT. Measurements that lie below the flux detection limit (mostly nighttime) are excluded from the analysis. The red line indicates an average EEP for daytime hours. Overall the EEP stays fairly constant during daytime (e.g. between 9-14 LT). During the measurement period reported here, the site was often dominated by cloudy conditions (14-15 LT on) during afternoons and as a consequence emissions tended to drop rapidly. Deviations during early and late hours, when fluxes are typically much smaller, indicate that common BVOC flux parameterizations don’t capture early and late transitions well. Hewitt et al. [21] observed a similar behavior above a tropical forest and attributed this to the circadian rhythm of plant species. On average the isoprene EEP is 1.4±0.3 mg/m²/h (red line), about 8% of the 232 MBO EEP (16±3 mg/m²/h). Kaser et al. [10] compare emission factors between different BVOC emission model parameterizations and measurements. Their results suggest 21.4 mg/m²/h for the sum of isoprene and 232 MBO, about 19% higher than what we observe here (17.4±3.3 mg/m²/h). These values however lie within the combined uncertainty range of both measurement datasets. Schade et al. [9] reported 232 MBO emissions factors of 2.8 mg/m²/h and Baker et al. [11] about half of this. The uncertainty for upscaled leaf and branch level emission factors and an emission model compilation lies within a range of 5.3 and 23 mg/m²/h [10]; this almost spans half an order of magnitude. These data show a significant site to site variability and suggest that upscaled leaf and branch level, as well as emission model parameterizations, should always be tested against ecosystem scale flux measurements. Current parameterizations for ponderosa pine dominated ecosystems assume no isoprene emissions. Our dataset suggests an EEP of 1.4±0.3 mg/m²/h for this particular ecosystem.

The reaction rate of isoprene with OH is 1.8 times faster than that of 232 MBO. Isoprene emissions can therefore contribute about 15% to the local reactivity relative to 232 MBO. Greenberg et al. [23] concluded that VOC emissions from soils and litter at this site contribute less than 1 % to ecosystem scale fluxes. We hypothesize ponderosa pine as a potential source for isoprene. Gray et al. [24] for example have characterized MBO synthase and found that this enzyme is bifunctional, producing isoprene along with MBO at about 1.1 % (up to about 5% depending on K⁺ availability). Whether isoprene is entirely emitted from ponderosa pine or also other parts of this particular ecosystem however can not be determined conclusively. Future screening of emissions from different plant species within this ecosystem using the presented measurement technique based on NO⁺ ionization are necessary to determine to what extent isoprene emissions can be primarily attributed to ponderosa pine.

4. Conclusion

We have presented the first selective eddy covariance measurements of isoprene and 232-MBO based on NO⁺ time-of-flight mass spectrometry. The measurements confirm 232 MBO as the dominant biogenic VOC emitted from this ecosystem. However, NO⁺ ionization is able to detect
the presence of isoprene fluxes up to 0.8 mg/m$^2$/h comprising about 10 % of the average 232 MBO flux, which has peak fluxes up to 10 mg/m$^2$/h. Our measurements show the importance of using different ion chemistries to clarify atmospheric measurements using on-line mass spectrometric techniques. The presented eddy covariance data show light and temperature dependent emissions for both, isoprene and 232 MBO, which is expected for these compounds. We hypothesize that isoprene is predominantly emitted from ponderosa pine, which is partly supported by biochemical studies of the catalyzing enzyme (MBO synthase) for 232 MBO, but needs to be confirmed by controlled enclosure studies. An ecosystem emission potential (EEP) is calculated using an inverse environment model. Results confirm the magnitude of earlier ecosystem scale measurements of the sum of 232 MBO and isoprene, which are both significantly larger than standard emission factors for this ecosystem. Our measurements demonstrate the necessity to test emission models using aggregated emission factors against ecosystem scale flux measurements in order to reduce inherent uncertainties associated with the upscaling of leaf level measurements. Experimental methods presented here will aid future quantitative assessments of ecosystem scale BVOC flux measurements.

Acknowledgement

This work was supported by the EC Seventh Framework Program (Marie Curie Reintegration Program, “ALP-AIR”, grant no. 334084) to T.K. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship from the National Science Foundation. L.K. is a recipient of a DOC-fFORTE-fellowship of the Austrian Academy of Science.
References:


Figure captions:

Figure 1: Time series of 232 MBO and isoprene fluxes. Red dots indicate periods where flux data are omitted from further analysis due to violation of QA/QC criteria. The green line indicates the flux detection limit.

Figure 2: Averaged cospectra for sensible heat (blue), 232 MBO (red) and isoprene (cyan)

Figure 3: The ratio of the molar isoprene flux to the molar 232 MBO flux

Figure 4: Diurnal cycle of the temperature gradient (top panel), isoprene to 232 MBO concentration ratio, isoprene mixing ratio, 232MBO mixing ratio (at 25.1 m for the 2012 measurements) (middle panel) and 232MBO+isoprene mixing ratio gradients (2009 measurements) (lower panel). Gradient measurements were obtained in a different year (August 2009), for similar meteorological conditions; the concentration ratio and concentrations plotted in the middle panel represent measurements obtained in August 2012.

Figure 5: The distribution of Ecosystem Exchange Potential (EPP) for 232 MBO and isoprene
Figure 1:
Figure 2:

Figure 3:
Figure 4

Figure 5