Relaxed eddy accumulation flux measurements of wound-induced oxygenated VOCs from a cut hay field in Austria

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Abstract

The study of oxygenated volatile organic compounds (OVOCs) is critical to understanding total VOC emission fluxes. OVOC emissions play an important role in regional tropospheric chemistry, especially as precursors for the formation of photochemical smog and tropospheric ozone (O₃). Past studies have focused mainly on forest canopy fluxes of VOCs. Current emission model parameters include forest sources, but do not take into account the possible area source of OVOCs emitted during wounding episodes such as hay harvesting. I analyzed 10 gas cartridge samples taken above a harvested hay field in Austria using the relaxed eddy accumulation (REA) technique. The REA technique involves separating air samples by updrafts and downdrafts. The general theory behind REA is that if an emission flux is present above an area, the concentration of compounds in the updraft samples should be greater than the concentration of compounds in the downdraft sample. Using gas chromatography coupled with a flame ionization detector, I found the compounds acetaldehyde, methanol, acetone, and hexenal in the samples, but I was not able to determine if there was a significant flux of these compounds. Preliminary results indicated that our method of analyzing OVOCs is not sensitive enough yet to successfully employ the REA technique for measuring OVOC fluxes. In particular, the role of humidity in both sample collection and analysis, and the effects of long-term storage need to be further investigated.

1. Introduction

There are both anthropogenic and biogenic sources of trace gases, but human activities are believed to be one of the main sources that affect the atmosphere, especially by influencing regional and global pollutant levels. In order to better understand the contributions of both sources, the type, quantity, and controlling mechanisms of trace gas emissions must be characterized.

One large class of gas emissions are volatile organic compounds (VOCs), which include hydrocarbons. VOC emissions are known to play an important role in
tropospheric chemistry, especially as precursors for the formation of photochemical smog and tropospheric ozone ($O_3$). Over the past few decades, scientists have been aware of and studied trace emissions from vegetation. Most of the research focus has been on the emissions of two VOCs, isoprene and monoterpenes from forest systems and individual tree species. Scientists have yet to fully characterize other sources of VOCs.

The study of oxygenated volatile organic compounds (OVOCs) is critical to understanding total VOC emission fluxes because there is evidence that the most abundant VOC at some sites are OVOCs (Baker, 1999). Oxygenated volatile organic compounds are different from VOCs because they have at least one added oxygen atom bonded to the molecule. In most cases, the added oxygen atom(s) make the compounds polar, causing the compounds to be 'stickier' or have a greater affinity to various surfaces. Accurately measuring OVOCs is difficult due to its greater affinity for surfaces. There are no known direct impacts of OVOCs, but there are significant indirect impacts that involve pollution formation. This study involves the use of relaxed eddy accumulation to measure fluxes of OVOCs emitted during harvesting of grasslands / agricultural areas.

Many of the compounds emitted above cut grasslands / agricultural areas are key elements in the production of photochemical smog. For example, acetaldehyde is an important precursor for the formation of ozone and $CH_3C(O)O_2NO_2$ or peroxyacetal nitrate (PAN). Detectable levels of PAN over farmland in Indiana, as reported during the 1995 Southern Oxidants Study (Williams et al., 1997) may be a result of the release of acetaldehyde and other wound compounds from harvested hay crops (de Gouw et al., 1999).

Given that approximately one quarter of the Earth's land surface is covered with grasslands and pastures (Graedel & Crutzen, 1993), the potential for large seasonal OVOC emissions to the troposphere is great. The impacts of human activities such as crop and timber harvesting, lawn mowing, and rangeland management practices are significant when considering the effects of OVOCs on tropospheric chemistry. Guenther et al. (2000) expressed the need to characterize these emissions in order to accurately simulate biogenic emissions through models. Accurate models can help predict future pollution episodes or evaluate how effective pollution abatement programs will be.
Most plants naturally produce and emit VOCs under normal conditions, but when the plant is subjected to stress or wounding, there is often a very large increase in VOC emissions and a change in emission composition. Fall (1999) has reported that wounding exposes stored pools of VOCs within the plant to evaporation and may induce the formation of new VOCs. Kirstine et al. (1998) observed that emissions from cut grass clippings were 180 times the maximum emission rate for undamaged grass under similar conditions. Further drying of the grass causes greater cell damage within the plant. There was a secondary increase in VOC emissions from cut and drying grass that was dominated by (z)-3-hexenal and acetaldehyde (de Gouw et al., 1999). Karl (2000) also found that large fluxes of the OVOCs methanol, acetaldehyde, hexenals, and acetone could be detected up to two days after cutting. Production of the hexenal family compounds is linked to physical wounding of leaves and is easily sensed in the odor of newly mown grass.

The relaxed eddy accumulation technique was used to measure emission fluxes of OVOCs and to test its ability to characterize the flux of oxygenated compounds in the field. The method has been compared to the eddy covariance method and shown to be in reasonable agreement for measurements of isoprene (Bowling et al., 1998). Eddy covariance is the preferred technique when fast sensors are available and field conditions are suitable, otherwise REA may prove to be more practical for field deployment. The main difference between the two methods is that REA allows for the use of sensors that have a slower response time, like gas chromatography. This is an advantage for researchers interested in gathering field samples because they may bring them back to the lab for analysis. REA is a micrometeorological technique that avoids the possible complications, such as physical damage to the vegetation or introduction of artificial environmental conditions, that are associated with enclosure methods (Bowling, 1998). Measurements may also be taken on a larger scale or land area than with enclosure techniques.
2. Experiment

2.1 Sampling Site

Measurements of wound-induced emission fluxes were taken between May 24th and 25th, 2000 from a cut hay field located near St. Johann (latitude 47.5 N, longitude 12.4 E) in Tyrol, Austria. The field was approximately 4 ha in size and consisted of the dominant grass species *Dactylis glomerata*, *Poa pratensis*, *Phleum pratense*, *Poa trivialis*, and one clover species *Trifolium pratense*. The relaxed eddy accumulation system was positioned at the south end of the field.

2.2 Sample Collection

Emission flux samples were collected using the relaxed eddy accumulation (REA) technique. The system consisted of a sonic anemometer ( Applied Technologies Inc., Boulder, Colorado) that measured vertical wind speed, a portable computer that controlled the separation of emission fluxes, fast-switching valves that facilitated separation, and a set of Teflon bags (reservoirs) in which the emission samples were stored (Figure 1). The general theory guiding REA is that if an emission flux is present above a certain area, the concentration of compounds in the updraft samples will be greater than the concentration of compounds in the downdraft samples. Two air samples were collected over approximately 30 minutes, one consisting of updraft air and the other consisting of downdraft air. A minimum vertical wind threshold velocity differentiated the updraft and downdraft air samples. The optimal value for the threshold velocity is 0.6 $\sigma_w$, which stands for the standard deviation of the wind velocity (Oncley et al. 1993), to maximize the concentration difference between updrafts and downdrafts and decrease analytical uncertainties of the flux measurements. The samples taken from each reservoir were loaded onto material solid absorbent cartridges. There were a total of 28 cartridges, i.e. 14 pairs, sampled at the site. The cartridges were stored at freezing temperatures ($\sim$ -30°C) for a period of two months.
2.3 Sample Analysis

The updraft and downdraft cartridge samples were analyzed using gas chromatography (GC) coupled with a flame ionization detector (FID). The analysis was focused on qualitative results rather than quantitative results. The GC and FID system was calibrated extensively in order to achieve good separation of peaks on the chromatograms and to accurately identify compounds within the samples.

Calibration of the system consisted of running a series of 1) cartridge desorption (heating) times, 2) standard gas concentrations (quantification and identification), 3) dilution tests for detection limits and ability of the system to measure concentrations, and 4) humidity tests for determining the effects of humidity on detection and concentrations of compounds.

In order to remove the gas compounds from the absorbent material in the cartridges, the cartridge was heated to ~ 325°C. The heating volatilizes the trapped compounds so that they can be picked up by the helium carrier gas and travel through the column of the GC. If there is not enough time for the compounds to volatilize and transfer off the cartridge, the resulting chromatogram is inaccurate in both composition and concentration. A transfer time of 15 minutes was determined to be sufficient to desorb the compounds from the cartridges.
The series of standard runs consisted of a multi-VOC standard, an alkane standard \((C_2 - C_{10})\), and tubes of expected wound compounds. The multi-VOC standard was used to achieve good peak separation of the chromatogram and to match the known compounds to the appropriate peak and retention time. Once good separation was achieved, an alkane standard was injected along with the multi-VOC standard. The alkane standard provided a baseline for retention times and more importantly, retention indices. Retention indices are stable values used for identification. The retention indices for the multi-VOC standard compounds were calculated as follows:

\[
R_{ix} = \frac{[Rt(x) - Rt(C_n)]}{[Rt(C_{n+1}) - Rt(C_n)] \times 100 + (100 \times n)}
\]  

(1)

Where \(R_i\) represents the retention index, \(R_t\) represents the retention time for a certain compound \((x)\), and \(C_n\) stands for the alkane made up of ‘n’ carbon atoms. Retention indices for the compounds of interest are provided in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>415</td>
</tr>
<tr>
<td>Methanol</td>
<td>430</td>
</tr>
<tr>
<td>Acetone</td>
<td>528</td>
</tr>
<tr>
<td>Hexenal</td>
<td>836</td>
</tr>
</tbody>
</table>

Table 1. Retention indices for four compounds of interest

Tubes of expected wound compounds contained an array of hexenal family compounds. Their purpose was to establish a range of retention times to survey for and to test the GC system’s ability to detect lighter compounds than were in the multi-VOC standard. Retention indices were figured for these compounds, but identification is still problematic since there is no definite reference library for most oxygenated VOCs.

Dilution tests were conducted by diluting a constant concentration of multi-VOC standard with zero (clean) air. The resulting dilution curves needed to have a linear relationship in order to infer that the system was in fact detecting the compounds of interest and that the peak areas were proportional to the concentration of each compound. The dilution curves were considered satisfactory once higher input flows (20-30) were
employed (Figure 2). Lower input flows reached the control limits of the flow meter, resulting in poor dilution curves.

![Graph showing dilution curves for major compounds](image)

Figure 2. Dilution curves for major compounds.

It was previously believed that water in the samples must be removed in order to attain good chromatography. The purpose of adding water to samples and then trying to remove it was to test if any compounds would be lost in the water. Refer to Baker 2000 for a further explanation of humidity removal effects. Humidity tests were conducted by passing the sample air through a bubbler (humidifier) before it was run through the GC column. The humidity in the test samples was the worse case scenario for the actual samples. In many instances, the attempted removal of water from samples has at least partially removed water-soluble (mainly polar) compounds as well (Baker, 1999). In this study when humid samples were compared to dry samples, there was no significant loss or gain of concentrations except for the compounds methanol and ethanol (Figure 3). Methanol and ethanol were 75% and 70% relative to dry sample concentrations.
Figure 3. Comparison of humid samples to dry samples, expressed as a percentage of the dry samples.

All attempts to remove humidity from the test samples did not improve the percentage of methanol or ethanol recovered. Because of this result and the fact that the actual samples were taken under fairly dry conditions, no attempt was made to remove water from the cartridge samples.

2.4 Flux Calculations

Concentrations of each compound were determined by peak area with respect to system calibration dilutions and flows. As follows with the REA technique, emission fluxes were calculated with the following equation:

\[ \text{Flux} \left( \mu g \ m^{-2} \ s^{-1} \right) = \beta \sigma_w (C_u - C_d) \]  \hspace{1cm} (2)

The value $\beta$ is a dimensionless proportionality constant that under stable conditions is $\sim 0.6$. The value $\sigma_w$ is the standard deviation of the vertical wind velocity and $C_u$ and $C_d$ are the concentrations of the updraft and downdraft samples, respectively. Preliminary flux calculations greater than 0.1 $\mu g \ m^{-2} \ s^{-1}$ were considered significant fluxes.

3. Results

Due to time and technical constraints, only 10 of the 28 cartridge samples have been analyzed. The final chromatograms exhibited multiple compounds in the sample, but previous calibration only allowed for the positive identification of four main
compounds: acetaldehyde, methanol, acetone, and hexenal. Appendix ‘A’ contains example chromatograms of an updraft and downdraft sample.

Preliminary flux calculations have shown no discernable trend in emissions. Both positive and negative fluxes were detected for all compounds except methanol (Figure 5).

![Variation in REA sample cartridge fluxes](image)

Figure 5. Flux calculations of the five sample pairs analyzed.

4. Discussion

In order to estimate a true flux, accurate updraft and downdraft samples need to be taken. These samples should have a difference that is greater than the precision of the analytical method used to determine them. It has previously been shown that relaxed eddy accumulation is sensitive enough to accurately measure the VOCs isoprene and MBO, but it seems that measuring fluxes of oxygenated VOCs requires greater sensitivity during the collection, storage, and analysis components of the technique. There are many possible reasons for the irregularity of the flux measurements; the most likely cause(s) deal with humidity, storage, and outside contamination of the samples.

Humidity testing was conducted on a worst-case basis only, so only worst-case results were considered. It was more likely that the samples contained relatively low humidity levels, but the effects on composition and concentration of compounds are unknown for such low humidity levels.
The storage of the compounds for a long period of time brings into question the ability of the storage cartridges, the temperature at which the sample can be successfully stored, and the absolute time period of storage before compounds are lost. Previous studies (Baker, 2000) have shown that cartridges can be stored for a long period of time as long as they are kept at freezing temperatures.

Another factor that researchers must always consider when sampling under field conditions is the uncertainty introduced by uncontrollable environmental conditions. For example, samples taken when the wind direction was coming from behind the REA sampling system represents a measurement of a neighboring un-cut field instead of the harvest site. Instances like these may account for some of the negative flux values obtained. A possible solution to inaccurate sampling is to place the REA system in the center of the field.

5. Conclusion

There is no conclusive evidence yet that relaxed eddy accumulation sampling and analysis are sensitive enough to detect fluxes of oxygenated volatile organic compounds. The general theory behind REA is sound, but the implementation of the technique has yet to be fine-tuned. As mentioned in the discussion, there are many further tests that need to be performed before the REA technique is able to take accurate measurements of OVOC flux emissions.

Even though OVOC flux emissions were not accurately calculated in this study, the initial steps to accurate measurements have been taken in the course of gas chromatography calibrations. Calibration efforts have shown that water removal from small samples is not necessary in most cases. The actual calibration of the GC is nearly complete and ready to run future samples.

Currently, there is a field study being conducted in Fort Morgan, Colorado on flux emissions of OVOCs from two harvested alfalfa fields. The REA technique is being deployed to take additional emission samples. Later analysis will hopefully prove more conclusive as to flux emission composition and concentration, as the samples will be stored for a shorter period of time before actual analysis.
References


Cart A 00122 down

File=C:\CF\DATA1\O-VOC05.SBR Sample name=oxygenates Date printed= 07-31-1980 Time= 16:16:19
0.00 to 20.00 min. Low Y = 4.46149 mv High Y = 64.46149 mv Span = 60.00000 mv

\text{formaldehyde}
\text{methanol}
\text{aceton}
\text{heptanal}
\text{C9}
\text{C10}