

1 **A High Frequency Response**
2 **Relaxed Eddy Accumulation Flux Measurement System for Sampling Short-Lived**
3 **Biogenic Volatile Organic Compounds**

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Abstract

A second generation relaxed eddy accumulation system was built and tested with the capability to measure vertical biogenic volatile organic compound (VOC) fluxes at levels as low as $10 \mu\text{g m}^{-2} \text{ hr}^{-1}$. The system features a continuous, integrated gas phase ozone removal procedure to allow for the measurement of highly reactive species such as β -caryophyllene and polar terpenoids such as linalool. A two component internal standard continuously added to the accumulators was used to correct for switching induced volumetric errors and as a check on VOC losses exceeding accumulator tube adsorption limits. In addition the internal standards were used to demonstrate that accumulators quickly return to target flow rates at segregation valve switching frequencies up to at least 0.8 Hz. The system was able to measure daytime hourly fluxes of individual biogenic VOC including oxygenated terpenoids, monoterpenes and sesquiterpenes.

1. Background

Relaxed eddy accumulation (REA) or conditional sampling theory has provided an important avenue to the measurement of trace gas area source atmosphere-biosphere exchange. While eddy correlation methods are the preferred technique when fast (~ 10 Hz) chemical sensors are available (usually for a single component), REA can utilize slower sensors to measure single or multi-component fluxes [Businger, 1991]. With REA, updrafts and downdrafts are sorted into collection reservoirs over an integration period (typically 30-60 minutes) sufficient to sample a representative range of eddy sizes. If the target analyte(s) are not sufficiently stable or easily contaminated, on-site analysis may be performed. When the analytes are stable in the reservoirs, analysis may be performed in the laboratory where stable environmental conditions permit application of sophisticated separation and detection methods.

REA theory [Businger and Oncley, 1990], derived from eddy correlation theory, states that the vertical flux F , can be determined by the product of a constant, β , times the standard deviation of the vertical wind velocity Φ_w (where the mean vertical wind velocity is zero), and the difference between the mean updraft concentration and the mean downdraft concentration ($\bar{C}_{up} - \bar{C}_{down}$):

$F = \beta \sigma_w (\bar{C}_{up} - \bar{C}_{down})$ (1). Furthermore, the sorting of up and downdraft samples shall be performed at constant flow rate. While the vertical wind speed component can be easily measured using commercial sonic anemometers, the determination of the concentration differential poses three significant challenges. First, the sorting of updrafts and downdraft samples into their respective accumulators should be performed without cross-contamination from the other direction. Since the decision to direct the sample to one direction or the other requires a finite time period to measure the wind velocity and direction and another time period

to compute and execute a sorting command, sorting errors can arise due to the time lag. The second major challenge is to quickly establish a constant flow rate in each accumulator when switching between accumulators. Without constant sampling, eddies will not be equally sampled and the resulting concentration differential may be biased. A third major challenge in measuring biogenic volatile organic fluxes is the loss of highly reactive compounds in the accumulators due to reaction with co-sampled ambient ozone.

2. Previous Design Approaches

2.1 Directional Sorting.

General guidance for measuring fluxes in the boundary layer specify that eddies should be sampled at 10 Hz to ensure accurate characterization of the scalar gradient. A review of previous REA systems reveals widely differing approaches to achieving this goal through hardware and software design. These stem from consideration of issues of analyte stability/storability, the selection of an appropriate analytical technique and the resulting sample volume required to accurately measure the analyte concentration differential. With systems herein referred to as Type 1 designs, the accumulator samples air from the anemometer measurement zone concurrently with measurement of the vertical wind velocity. Consequently any decisions to start or stop directional routing will be late in implementation and improper binning of the samples will always occur. Whether or not this causes a significant reduction in measured flux is dependent upon the duration of the lag and the number of these events relative to the contribution of the events of longer duration. Numerous examples of Type I design can be found [Valentine *et al.*, 1997; Ciccioli *et al.*, 2003; Darmais *et al.*, 2000; Pryor *et al.*, 2002; Nemitz *et al.*, 2001; Majewski *et al.*, 1993; Baker, *et al.*, 1999; Beverland *et al.*, 1996; Schery *et*

al., 1998; Amman, 1998; Graus *et al.*, 2006; Meyers, *et al.*, 2006; Gaman *et al.*, 2004; Haapanala *et al.*, 2006; Skov *et al.*, 2006]. These are often used where it is critical to avoid analyte losses to inlet tubing and valves i. e. nitric acid, ammonia, reactive gas mercury, particles, etc. [Pryor *et al.*, 2002; Meyers *et al.*, 2006; Skov *et al.*, 2006; Schery *et al.*, 1998; Nemitz *et al.*, 2001; Gaman *et al.*, 2004; Baum and Ham, 2009]. The impact of improper binning on flux accuracy for any set of measurement conditions has been estimated for some of these designs by numerically simulating the effect of a given lag on co-collected sensible heat flux data [Amman, 1998; Beverland *et al.* 1996; Schery *et al.*, 1998; Graus *et al.*, 2006; Majewski *et al.*, 1993; Meyers *et al.*, 2006].

In Type II REA system designs, a constant flow inlet tube(s) prior to the accumulator routing (segregation) valves can be used to create sufficient delay to synchronize directional transitions with accumulator routing. There are several examples of such systems using plastic bags to collect sample [Oncley *et al.*, 1993; Pattey *et al.*, 1993; B. Baker *et al.*, 1999; Haapanala *et al.*, 2006; Delon *et al.*, 2000; Brut *et al.*, 2004], extractive type (adsorbent tubes) systems [Nie *et al.*, 1995; Olofsson *et al.*, 2005] and on-line analysis [J. Baker *et al.*, 1992; Cobos *et al.*, 2002; Valverde-Canossa *et al.*, 2006; Bash and Miller, 2008; Schade and Goldstein, 2001].

2.2 Achieving the constant flow rate sampling requirement

Since all REA system designs require valves to start and stop sampling to implement sorting of up and downdraft samples, it is essential that the pressure differential across the valve inlet(s) and exit be equivalent regardless of their position. If the two valve states (sampling and not sampling or zero gas) pressure differentials are not equal then each valve transition will cause

flow surges or back surges to stabilize pressures thus violating the constant flow requirement. This issue can be most severe in systems where no neutral (below threshold) channel is used and the flow is completely stopped and started through the segregation valves. Systems using whole air accumulators, such as Summa cans or polymer bags where it is not desirable to dilute the sample with zero air, are more susceptible to this issue. REA systems using extractive type accumulators which pass the bulk air components, such as adsorbent tubes, coated denuders or filter packs, allow system designs of continuous flow of sample and analyte-free zero gas. Thus, constant flow can be more easily achieved through judicious placement of three way valves, flow controllers and pumps with extractive type accumulators..

2.3 Valve Switching Transients

Common to all REA design types are accumulator volumetric errors introduced by flow interruption caused by valve switching. Depending on the valve design, flow may be completely or partially restricted as the actuating mechanism moves from one state to the other [Nie *et al.*, 1995]. Typically, upon activation, the actuator held in place by spring tension, is moved by application of a magnetic field supplied by a coil. The turn-on response time, as defined by the valve industry, is the time between the application of the coil energizing voltage until the downstream pressure reaches 90% of the applied pressure. This time may be further decomposed to 1) an initial lag between the start of the applied coil voltage and the start of the valve plunger movement (start of flow disturbance) and 2) the completion of the movement of the plunger to its energized state. If the duration of the initial lag is known, this can be accounted for in synchronizing the arrival of eddy samples to the segregation valves. The lag and duration of the second part may be reduced through application of programmed voltage switching signals (high

triggering voltages followed by lower holding voltages). The valve response to switching off the coil voltage is usually not the symmetrical with the on response. The return of the plunger is governed by the collapse of the coil magnetic field and the spring tension on the plunger. This can lead to two (or three in three valve systems) being open for part of the cycle. While designers of other REAs sometimes note a valve response time and perhaps a synchronization delay to offset the electronic-flow delay, the disturbance to flow constancy and volumetric accuracy impact of the unavoidable flow transient are not explicitly discussed.

2.4 Analyte Losses

The adsorptivity and reactivity of the target analytes help determine the choice of materials that will contact the sample flow path. Fluorinated polymers such as Teflon are often selected due to their low adsorptivity and freedom from out gassing of volatile organic compounds. As a consequence, ambient ozone which is often present at levels of 20-100 ppbv is also efficiently conducted through the REA plumbing. Since ozone is quite reactive toward many olefinic hydrocarbons, especially many mono and sesquiterpenoids, losses can result in the plumbing and accumulators. These losses can be severe, particularly when the accumulators are of the extractive type, such as a porous polymer adsorbent, e.g. Tenax-TA. In this case, the surface buildup of a reactive compound on an adsorbent, continuously bathed in co-sampled ozone, creates more opportunity for loss than in the gas phase. One remedy is to insert an ozone-removing filter upstream of the accumulator such as several plies of manganese dioxide-coated copper screens [Ciccioli *et al.*, 1999; Christensen *et al.*, 2000; Darmais *et al.*, 2000; Graus *et al.*, 2006; Haapanala *et al.*, 2006], KI [Park *et al.*, 2010] or sodium bisulfite coated filter paper

[Helmig, 1997; Pollmann *et al.*, 2005]. However, with less volatile or polar compounds, these filters may also remove the target analytes [Hoffman, 1995].

Our second generation REA described herein, incorporates: 1) synchronous routing of 100 ms eddy capture samples to extractive-type accumulators using continuous flow from either sample or zero gas, 2) internal standard gases added to the sample stream to allow for volumetric corrections made necessary by valve switching transients, 3) an integrated gas-phase ozone removal system that reduces VOC ozone loss to negligible levels and 4) continuous data logging of REA operations and micrometeorological sensor array signals.

3. Design criteria

3.1 Matching Flux Detection with Sample Volume and Analytical Method

To design an appropriate flux measurement system, we must first answer the following questions: What compounds do we want to measure? At what rates do we expect these compounds to be emitted to the atmosphere? Global estimates of biogenic non-methane volatile organic compound emissions have identified isoprene as the single largest (~35-50%) contributor to the budget [Guenther *et al.* 1995; 2006]. Uncertainty of those estimates have been significantly reduced as a result much research over the past 20 years. However, the balance of the VOC budget is comprised of contributions from many compounds, especially those broadly classified as mono and sesquiterpenoids and which are recognized significant contributors to formation of secondary organic aerosol. These estimates, largely derived from branch enclosure measurements, are assigned large errors due in part to foliage disturbance issues surrounding these measurements. Hence, our objectives here are to focus on those compounds which would

benefit from non-disturbing micrometeorological-based measurements. A survey of reported flux estimates for major compounds within these classes finds fluxes in the range of 10-10000 $\mu\text{g m}^{-2} \text{ hr}^{-1}$ over forests and croplands [Guenther *et al.*, 1995; Rinne *et al.*, 2000; Helmig *et al.*, 1998; Gallagher *et al.*, 2000; Valentini *et al.*, 1997; Plaza *et al.*, 2005; Ciccioli *et al.*, 1999].

To measure fluxes as low as $10 \mu\text{g m}^{-2} \text{ hr}^{-1}$, the sampling and analytical technique employed must accurately measure the mean concentration differential of these compounds between the up and down accumulators. Businger and Delany [1990] found that the sensor resolution, R , necessary for a flux measurement accurate to $\pm 10\%$, can be determined from the equation, $R = 0.1|Fc|AP$ (2), where F_c is the flux and AP is the atmospheric parameter. AP is defined as $(\beta\sigma_w)^{-1}$ which ranges from 2 to 6 s m^{-1} when $\beta=0.58$. To facilitate easier measurement, the mean concentration differential may be increased by rejecting vertical velocities below $0.6\sigma_w$ (small eddies) and using a reduced β of 0.39 (computed according to Baker, 2000]. Thus a new AP range of ~ 3 to 9 s m^{-1} is computed. Figure 1 illustrates the estimated chemical resolution needed to measure fluxes during optimum daytime mixing conditions. Gray areas to the right of the solid squares at a resolution of $\sim 1 \text{ pptC}$ (0.5 NgC m^{-3}) indicate fluxes ranging from about 2 to 6 $\mu\text{g m}^{-2} \text{ hr}^{-1}$ should be measurable depending on mixing conditions.

To resolve 1 pptC, sufficient sample volume must be collected to deliver target analytes to the analytical detector within the range of accurate quantitation. Typically, this is defined as the Limit of Quantitation (LOQ) where the signal must be greater than ten times the noise level of the detector. For our gas chromatographic system (model 5890 Hewlett-Packard gas

chromatograph with flame ionization detection), approximately 15 L of sample are required to align the chemical resolution requirement with the LOQ of the chromatographic detector.

3.2 Accumulator sizing

Candidate accumulator designs must be able to deliver the analytes to the chromatographic system while preserving analyte integrity. Extractive-type accumulators offer the best approach to achieve flow constancy and retain target analytes from large sample volumes. Accumulator tubes packed with solid adsorbent media can be designed to meet these requirements. In choosing the proper adsorbent or adsorbent combination, it is important to consider the factors which govern retention of analytes on adsorbents. Adsorbents typically possess uniform, high specific surface areas (area/mass) and are chosen by their attractive properties to the analytes and their lack of retention of the bulk air components e. g. O₂, N₂, CO₂, H₂O. In addition, they must be capable of releasing these compounds without alteration when the adsorbent bed is heated in the laboratory.

Passage of an air stream containing a mixture of analytes of differing volatility and polarity through an adsorbent bed creates a competition for the available surface area of the adsorbent. Compounds most attracted to the adsorbent surface are deposited first while less attracted compounds move further into the adsorbent bed. As sampling continues, more surface attractive compounds displace less attractive compounds. If the sampling temperatures rise above laboratory conditions, the rate of migration for any adsorbed compound will increase at approximately twice the rate for every 10°C rise in temperature. In addition all adsorbed compounds will slowly migrate in the direction of the gas flow in proportion to the flow rate.

229 Thus sufficient adsorbent must be used to account for the total sample volume (sample + zero
230 gas) and any temperature excursions, both field and laboratory, that would cause deeper
231 penetration of the analytes into the adsorbent bed. Our system was set up to operate for a 55
232 minute flux integration period at 1.00 L min^{-1} or 55 liters total (sample + zero gas). With a $0.6\sigma_w$
233 velocity filter, each accumulator will collect sample 30% of the time ($55 \text{ L}/0.3 = 16.5 \text{ liters}$).
234 Thus, the adsorbent tube was sized to retain 55 L plus additional adsorbent to ensure against a
235 10°C elevation (35°C) – for a total of 110 liters.

236 Extensive evaluations of Tenax and graphitized carbon adsorbents were carried out to evaluate
237 suitability for capture and recovery of biogenic compounds [Arnts 2010]. The popular
238 graphitized carbons were found to be unsuitable because of a tendency to catalyze
239 transformations of olefins and alcohols. Tenax-TA, however, was found to retain and thermally
240 release these compounds without the artifacts of the graphitic materials. To determine sufficient
241 VOC breakthrough characteristics of Tenax-TA, multi-component mixtures of terpenes,
242 sesquiterpenes, aromatics and alkanes were sampled by small adsorbent tubes at various sample
243 volumes. The tubes were then thermally desorbed and analyzed to determine VOC recoveries.
244 The least well retained biogenic compound was α -pinene. The maximum volume without
245 breakthrough of the α -pinene was used to scale up from the small (5.33 mm ID) to the larger
246 REA tubes (12.7 mm ID) using the same linear sampling rate (13.2 cm s^{-1}). The Tenax-TA bed
247 depth was increased by a factor of 1.5 (5 grams) and thus up to 119 L (@ 25°C) could be sampled
248 with the REA tubes. The Tenax-TA bed was held in place by 2 micron pore size stainless steel
249 wire mesh disks that have been passivated using the Sulfinert process. A second adsorbent bed
250 of Carbotrap (see following discussion) which tends to crumble to fine particles, was retained by

a compressed wafer of stainless steel wool. Glass and silica wool bed retainers, which are usually used in adsorbent tubes, were found to take up unacceptable quantities of water.

3.3 Controlling VOC Losses from Ozone

Canopy level flux measurements are representative of the actual biogenic emission to the atmosphere only if there are no sources or sinks occurring during transport to the point of measurement. With transport time scales on the order of 30 to 90 seconds, most of the biogenic terpenoids will be diluted but not significantly reacted. However some compounds such as γ -terpinene and β -caryophyllene can be drastically oxidized in the presence of ambient ozone. In addition, the un-reacted portion of those compounds, surviving the transport to the flux measurement point of collection, can be further lost if ambient ozone is allowed to contact the VOC adsorbed on the surface of the accumulator substrate, i. e. Tenax-TA. Since the probability of ozone-VOC contact increases as the VOC is accumulated on the adsorbent surface, the rate of loss increases [Arnts, 2008] offsetting the advantage of larger sample volumes. Transport losses due to ozone can be estimated through modeling if ambient ozone concentrations and accompanying turbulence measurements are available. Residual VOC sampled by the REA inlet can be preserved by immediately blending in another VOC to scavenge the co-sampled ozone. To do this, trans-2-butene (10% in nitrogen @ $\sim 100 \text{ cm}^3 \text{ min}^{-1}$) was continuously added to reduce competition of terpenoid for ozone to a negligible level. To allow sufficient time for the scavenging process to occur, the sample passes through heated (40°C) inert Sulfinert coils (5 second residence time). The trans-2-butene is not efficiently retained by the accumulator adsorbents (Tenax-TA/Carbotrap) and thus passes through the accumulator tubes.

3.4 Volumetric Corrections for Switching Transients.

Despite a design which facilitates rapid switching of sample-zero gas and minimal flow disruptions, there remains an unavoidable switching transient associated with the time required to change valve states. We tested a Teflon-body 3-way solenoid valve (model 225T031, 12 VDC, Neptune Research, Caldwell, NJ) using a fast hot wire anemometer (Series 50, Thermo Systems Inc., St. Paul, MN) and an oscilloscope. These tests indicated that actuator movement started about 6 ms after start of the triggering voltage and completed about 3 ms later. Upon cessation of the applied voltage, the valve returns to its ground state driven solely by the tensioning spring on the actuator. This return is not as crisp as the coil driven opening. The impact of these transients on volumetric accuracy and hence on flux accuracy, is not constant since the duration of the sampling periods will vary. At high switching frequencies (≤ 10 Hz) the relative contribution of the disturbance is larger than longer periods of sampling where stasis is undisturbed until the next switch.

In the actual field system, the switching transients are not observed by the mass flow controllers due to the dampening effect of the reaction coil, tubing and accumulator volumes coupled with the inability of the flow controllers to respond to short term fluctuations (manufacturer specification: < 2 sec to within 2% of set point for MKS model 1100 mass flow controllers). Thus the volume obtained by the summation of the products of the instantaneous flow rates and the 100 ms sampling periods for each accumulator may not be accurate. To remedy this, we used the approach of adding a known quantity of internal standard to the sample and assaying the resulting concentration to calculate the volume of the sample. To implement this, we continuously introduced a stable, relatively inert internal standard gas to the main sampling

stream. We selected two saturated hydrocarbons (methylcyclohexane and 2-methylheptane) which are not present in the zero gas. They were also selected because they are not present above 1 ppbC in ambient rural air and they can be easily separated by high resolution capillary gas chromatography. Note: the Tenax-TA in the accumulator tubes will retain most of the methylcyclohexane and 2-methylheptane but some breakthrough will occur. To remedy this we added 1.5 grams of Carbotrap adsorbent to the rear of the REA tubes to capture any residual internal standard. Both compounds are easily captured and recovered by thermal desorption. To obtain the corrected REA sample volume we compare the resulting internal standard quantity in switched sample (flux measurement) with that of the result of a non-switched measurement (continuous, constant flow rate sampling) of known volume. Since we also know the concentration of the internal standard cylinder and the flow rates of introduction and inlet flow rates, we have a second check on the volume of the switched (flux) samples.

4. System Design and Operation

4.1 Gas Handling System

Figure 2 illustrates the key components of the gas management system. Air is sampled at 13.5 L min⁻¹ from the plane of the vertical wind velocity measurement zone (about 20 cm behind and about 6 cm above the sonic sensor measurement zone) through an open face, 47 mm, Teflon membrane (20-30 micron) particle filter (Savillex Inc., Eden Prairie, MN). Flow rates and tubing diameter were selected so as to maintain turbulent conditions (Reynolds number ~5000) and promote minimum axial mixing. The sample flow is immediately mixed with internal standard and ozone scavenger to produce approximately 25 ppbC each of methylcyclohexane, 2-methylheptane and about 600 ppm of trans-2-butene in the sample stream. The segregator

(module) consists of three sample valves where 1.0 L min^{-1} is shunted off for selection by one of the three valves. During the 400 ms required to reach the segregator valves, the data system determines which path is appropriate for each arriving 100 ms segment. The segregated samples then pass through a heated (40°C) passivated coil ($1/4''$ OD X $0.21''$ ID Sulfinert treated stainless steel) to allow sufficient time (5 s) for ozone scavenging by the trans-2-butene. The ozone-depleted sample then passes through a six port Teflon manifold valve (model 18-132-900 General Valve, Fairfield, NJ or model 225T091 Neptune Research, West Caldwell, NJ) which routes the sample to the current adsorbent tube accumulator. The sample path is heated (40°C) from the particle filter inlet through the upstream manifold valves. The tubes are clamped into an aluminum manifold which is cooled by a battery of Peltier-type thermoelectric coolers. Cooling is generally regulated to about 25°C (or higher if necessary to avoid water vapor condensation).

The three sample valves are also supplied with (VOC free) nitrogen at 2 L min^{-1} so that the two valves currently not sampling, will maintain gas flow to the neutral and idle tube. Pressure sensors up and downstream of the valves allow the operator to observe and remove pressure differentials which would cause over or under sampling following a switching event. The mass flow controllers are housed in a separate, insulated temperature controlled stainless steel box to minimize drift. To reduce mass flow dependency on humidity, the sample passes through silica gel desiccant trap before entering the flow controllers [Lee, 2000]. Fluorocarbon polymers used in mass flow controllers were found to be swelled by contact with trans-2-butene so capillaries and metal frits were used to govern flow. Ten percent trans-2-butene in nitrogen

was prepared from 99+% grade (Sigma-Aldrich) by dilution in a high pressure aluminum cylinder.

4.2 Electronic Systems

The enabling electronics for the REA measurements and the ancillary hardware necessary for energy balance and atmospheric stability measurements are outlined in Figure 3. While much of the system was under computer control, several systems operated autonomously. These are the individual temperature regulation of the inlet line, segregator and manifold valves, and reaction coils which were set to 40°C using PID-type controllers (Watlow, Richmond, VA). In addition the mass flow controllers were controlled by power supply/readout units (model 247C, MKS Instruments).

In order to affect uninterrupted segregation valve decision making, i. e. avoiding computer operating system interrupts, a specialized printed circuit board was developed by Hampton Technologies to generate sonic triggering commands using a precision on-board clock. The sonic anemometer (model SAT-3V, Applied Technologies Inc., Longmont, CO, USA) was operated at 10 Hz and set to external triggering. The sonic performed 100 ms averaging in the first time frame after triggering, computed the results of all three directions and temperature in the next 100 ms and then reported it out in the third time frame to Data Packer 1 (DP1). During this same time frame, Data Packer 1 received analog data from the H₂O/CO₂ analyzer and performed parallel 100 ms averaging. The DP1 reported the resulting data back to the Controller computer. Simultaneously, DP2 performed 10 second averaging of voltages from a pyranometer (solar radiation), net radiometer (net radiation), a photosynthetically active radiation sensor

(PAR), a vertical array of precision thermocouples, segregator valve zone pressure sensors, and accumulator tube manifold temperature. DP3, at ground level, also performed 10 second averaging of voltages from soil heat flux sensors and thermocouples and DP4 performed 10 second averaging of mass flow controller outputs and from an atmospheric pressure sensor. The data packers avoided analog voltage drops associated with long field cables via use of digital communication by either serial binary or ASCII code. DP data packets were received by the Controller computer which correlated the various averages with the proper time stamp before writing the data to a file.

4.3 Data Acquisition and Control System

The integrated data acquisition and control system was built by Applied Technologies Inc. (Longmont, CO) with the primary sonic monitoring and valve control architecture evolved from a system initially developed by one of us (Hampton) at the National Center for Atmospheric Research (NCAR) and further revised by Hampton Technologies Inc. (Longmont, CO). The system used two personal computers: 1) a primary controller (MS-DOS based) which interacted directly with the sonic anemometer and segregation valves and 2) a supervisory computer which recorded the data stream from the controller. The controller coordinated both the sonic data stream and all of the Data Packer communications, sorted them to their proper files and coordinated assignment of proper time stamps. Separate fast (10 Hz) and slow (0.1 Hz) files were created and passed to the supervisor PC where calibration factors were applied to the raw data and then converted to appropriate units for recording to files and real-time graphical displays.

The supervisory PC REA interface program allowed the operator to perform a variety of functions including entry of sensor calibration factors, real-time graphical display of all current sensor outputs, internal pressure balancing tests and alignments, entry of site conditions, accumulator tube leak checking, entry of sonic-valve synchronization delay time, entry of time base for rolling vertical velocity statistics, entry of accumulator tube tracking numbers, flux measurement duration and percent of σ_w to exclude from sampling. The various real-time displays of radiation, wind direction-wind speed and vertical temperature allowed the operator to judge whether conditions were conducive to flux measurements. Accumulator tube manifold temperature set points could be entered while observing current dew points to avoid condensation.

To address the previously stated issue of the need to achieve equivalent pressures across the two upstream ports of the segregator valves, the mass flow controllers were calibrated so that the zero gas was supplied at twice the sample flow rate. Thus during flux measurements only one segregator would be drawing sample while the other two were drawing zero gas. To check this and make any fine tuning adjustments to the zero gas flow, the supervisory PC allowed the operator to perform a dynamic switching test to observe the equivalency of pressures across the zero gas and sample side ports of the segregator valves. The operator may select any switching interval from 100 ms to 10s of seconds. By observing the pressures on both sides of the valves during a switching cycle, the operator may fine tune the mass flow controllers to achieve pressure equivalence.

After completion of calibrations and system QA checks, fresh accumulator tubes were loaded into the manifold (up to six sets). A leak checking routine was available to verify all tubes were securely installed. Finally, the operator entered tracking numbers for each tube and their associated manifold port position (left or right side and port number), the duration of the measurement (usually 55 minutes for a flux measurement), the type of measurement (flux, system balance or contamination), for flux runs the % of σ_w to exclude from sampling and the delay (if any) between measurements. Upon starting the loaded work assignment, the system created data files with names that include the start time. Simultaneously, it began triggering of the sonic and receiving data until the specified buffer (usually 5 minutes) had filled and the starting mean vertical velocity and standard deviation had been established. The first set of tubes was automatically selected and randomly assigned as up or down for the length of the measurement period (a check on channel bias). Sorting of up and down draft samples began using the % exclusion of the rolling σ_w and valve actions were lagged according to entered synchronization delays. During this period the operator could observe all mass flow rates, radiation profiles and wind direction/velocity distributions as well as view the rolling vertical velocity with imposed velocity exclusion thresholds. At the conclusion of each flux measurement, the associated files were closed and the next run is started.

4.4 Field measurement conditions

The REA system was set up on a walk-up tower located at the Duke University Blackwood Division FACE (Free Atmosphere Carbon Exchange) site near Chapel Hill, NC. The surrounding vegetation consisted of a primary canopy of planted Loblolly pine with some sweetgum, tulip poplar and red maple understory. The tower was part of the control (non-CO₂ fumigated) ring group. An temperature controlled instrument shed on the edge of the ring was

used to house the DAC system and mass flow controller electronics. The REA system was operated on days selected for optimum predicted meteorological conditions throughout 2007 over temperatures which ranged from 0 to 37°C. A full discussion of those results and their value in estimating emission model accuracy will be the subject of a companion paper. Measurements were set up to integrate fluxes over a 55 minute period with up to six consecutive runs made before re-loading the system with fresh sample tubes. The inlet sample line and total flow rate were selected to match the 400 ms system delay (plus another 6 ms to account for the valve response time delay) in processing the directional data stream from the sonic anemometer. The accumulator flow rates were set to 1.00 L min⁻¹ and the sampling vertical velocity-based threshold was set to 0.6 σ_w based on a rolling 300 second buffer of mean vertical velocity and its standard deviation.

In addition to the flux measurements, one hour (60 L) continuous samples were periodically drawn for gas chromatographic-mass spectroscopic analysis to aid in identification of emissions. The larger volume was necessary to compensate for the lower full scan mass spectrometer sensitivity compared to the flame ionization detector. Also, a parallel emission study of the loblolly pine foliage using Teflon bag enclosures without the presence of ozone was conducted and used to help link ambient measurements to their source (Geron and Arnts, 2010).

4.5 Analysis of Accumulator Tubes

After sampling, tubes are capped and returned to the laboratory for analysis. A custom built thermal desorption apparatus was constructed to process the non-standard large size tubes [Arnts, 2010 supplementary materials therein]. In brief, the system allowed up to 16 tubes to be

thermally desorbed, cryogenically focused and injected into one of two gas chromatographs for quantification (flame ionization detection) and identification (mass spectral matching with the NIST/EPA data base). The sample path through the system was passivated with Restek's Sulfinert process and heated to prevent sorptive losses. The processing of the tubes includes steps to remove residual water vapor and trans-2-butene before high temperature thermal desorption. Also, an n-alkane internal standard was added to aid in retention time adjustment and peak identification. The flame ionization detector was calibrated with a Scott prepared mixture of isooctane and 2,5-dimethylhexane in nitrogen which was calibrated against a NIST-certified propane in nitrogen standard. Based on mass spectral analysis of field samples, pure samples of the tentatively identified compounds were obtained and used to prepare dilute mixtures in the laboratory. These mixtures were then sampled and analyzed to compare with the field samples. Retention time matches provided additional confidence in peak identification of field samples. For compounds for which no commercial sources were available, retention time indices were compared with published values in the NIST data base to help with identification (<http://webbook.nist.gov/chemistry/cas-ser.html>).

4.6 Data Analysis

Text data files (10 Hz and 0.1 Hz) from the REA and the tube analytical files were read into a custom Matlab data reduction program. Time signatures were compared with time intervals and running frequency to check system consistency and missing or excess data. Sonic wind speed and temperature data were cleaned of electronic spikes and replaced when data points exceeded six standard deviations from the average. Raw and de-spiked energy data were plotted. The biogenic fluxes were calculated using Equation 1. The standard deviations of the vertical

velocity, σ_w , were calculated using the planar-fit method [Lee, et al. 2004]. The β coefficient was calculated using Baker's method [2000] using sonic temperatures filtered with the $0.6 \sigma_w$ threshold [Pattey et al., 1993]. Un-rotated data were used to calculate the effective β coefficient [Baker, 2000] using sonic temperatures filtered with the $0.6\sigma_w$ threshold [Pattey et al., 1993]. Internal standard results of un-switched runs of known volume were then compared with flux run tube results to calculate the corrected sample volume and re-computed VOC concentration. The up-down concentration differentials were then computed and the fluxes calculated using the associated β and the run σ_w .

5.0 Results

Our first step in reducing the data to fluxes was to examine the ratio of the two internal standard compounds introduced during sampling. The carbon ratio of the 2-methylheptane (2MH) to the methylcyclohexane (MCX) in the original gas was 1.2:1. If collection and recovery are complete from the accumulator tubes, the ratio should not change. If the adsorption capacity of the adsorbent is exceeded (i.e. due to excessive hydrocarbon loading) or the temperature of the tube during sampling is excessive, then the least well retained component will preferentially be lost. In our case the MCX will be lost first, resulting in an increase in the 2MH/MCX ratio. In Figure 4 we plotted the ratio of MCX/2MH vs. the temperature of the tube manifold during collection. The data indicated that when temperatures exceeded $\sim 27^\circ\text{C}$, in some runs the MCX decreased relative to the 2MH demonstrating some loss of MCX. Therefore, in instances where the ratio exceeded 1.4 we used the 2-methylheptane alone to compute volumetric corrections for the associated flux measurements. Typically, the tube manifold temperature control should have

prevented the tubes from exceeding 25°C. However, there were a few periods when the dew point was so high that the coolers used a higher set point to avoid condensing water in the tubes.

Next we examined whether there was any evidence that the sample volumes collected was greatly modified by the pressure transients during switching and thus a need for a correction factor. Such a correction would be most important at high switching frequencies where the flow disruption would be a significant portion of the sampling period. There are two independent ways to calculate the sample volumes: by summing the volume of samples flowing through the sample tubes and by measuring the volumes using the two internal standard gases. Hence we plotted the ratio of volumes determined by these two methods. The volume using the flow method was calculated by summing of the product of the number of up and down 100 ms time intervals and the average flow rate. The volume using the internal standard method was calculated from the volume of each internal standard using the GC-FID. The ratio of the two methods versus the number of 100 ms valve transitions during sample period are plotted in Figure 5. The mean ratio was 1.04 ± 0.14 indicating that on average the volume determined by use of the internal standards was about 4% lower than a strict time X flow rate computational result. No frequency dependent response is evident from this data - even at the highest switching frequency around 2800 (corresponding to mean sampling durations of about 1.2 seconds or 0.8 Hz). Clearly, the system design is quite adequate for sampling above forest canopies where the eddies tend to be large with very little contribution from the high frequencies. Data above and below the optimum 1/1 ratio probably indicates some accumulator mass flow controller drift from optimum flow rates. Regression analysis of the separate up and down ratios indicated no significant correlation with switching frequency. Furthermore, frequency analysis of the sonic

data indicated that there was very little contribution from eddies shorter than 1 second over our forest canopy.

Flux measurements over smoother surfaces such as agricultural crops, may require better sampling accuracy than forest canopies. To evaluate if our system would still be accurate at a switching frequency of 10 Hz, a supplementary test was devised to test whether sample durations of 100 ms would still be accurately sampled. For this test, a square wave switching function was supplied to the segregation valves for a 21 minute period and molecular sieve packed accumulator tubes were used to collect water vapor for the left sample, right sample and neutral (below threshold) channels. A continuous sample from the main line was also sampled to obtain a measurement of the water vapor without a switching transient disturbance. With alternating switching intervals of 100 ms (neutral to right, right to neutral, neutral to left, left to neutral, etc.), the three channels were within 1% of their expected water accumulation and the total accumulation of the summation of the switched channels was within 5% of the continuously collected channel. This demonstrated that sample/zero switching transitions were followed by immediate resumption of stable flow after the valve switching transient has passed. Thus pressure surges or back streaming appears to have been minimized through system pressure balancing.

Two sets of two day daytime flux measurements profiles were collected in winter and summer and are presented to illustrate system performance (Figure 6). To simplify plotting, the sum of the 24 biogenic VOCs measured are combined into common groups: monoterpenes (α -pinene, β -pinene, limonene, β -phellandrene, myrcene, camphene, p-cymene, sabinene, α -phellandrene),

oxygenated monoterpenes (linalool, camphor, α -terpineol, terpin-4-ol, nopinone, verbenone), sesquiterpenes (β -caryophyllene, cis- α -bergamotene, δ -cadinene, copaene, β -cedrene, α -muurolene, α -humulene, trans- α -bergamotene). The 2-methyl-3-buten-2-ol is shown in isolation since it constitutes a fairly large component of the summer flux. In general the observed monoterpene fluxes behaved as predicted by the generally used emission-temperature algorithms [Guenther *et al.*, 1993] with higher emissions on warmer days and higher emissions in the summer compared with winter. However, compound class relative contributions changed seasonally. Most of the winter emissions were monoterpenes with little contribution from the oxygenated terpenoids and sesquiterpenes. The 2-methyl-3-buten-2-ol was absent in the winter emissions while constituting the single largest emission in the summer. Note: It is likely that some accumulator tube breakthrough of 2-methyl-3-buten-2-ol occurred in July. These fluxes should therefore be viewed as probably low. The sesquiterpenes make significant contributions to the flux in the summer during the warmest part of the day. Most of this is composed of β -caryophyllene which is largely removed in transport by reaction with ambient ozone. Thus only a portion of the β -caryophyllene was sampled by the REA. As predicted from the *Businger and Delaney* [1990], the fluxes below about $10 \mu\text{g m}^{-2}\text{-hr}^{-1}$ appear quite noisy with negative excursions observed as the limit of detection is approached.

In summary we have demonstrated a flux measurement system that is capable of tracking the eddy movements of highly reactive biogenic VOCs over forest atmospheres. Unlike previous systems limited by solid surface ozone scrubbers (i. e. manganese dioxide, potassium iodide, sodium thiosulfate), its unique gas phase ozone management system along with a heated path permits the accurate measurement of reactive semi-volatiles like β -caryophyllene and adsorptive

polar terpenoids such as linalool. Use of internal standards demonstrated that high speed sorting of samples was performed without significant flow back streaming across segregation valves causing sample volumetric errors. Furthermore, the use of the dual internal standard which are more volatile than the target analytes, was useful in verifying that accumulator adsorptive limits where not exceeded.

Acknowledgment

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References

- Amman, C. (1998), On the applicability of relaxed eddy accumulation and common methods for measuring trace gas surface fluxes, Ph. D. thesis, Swiss Federal Institute of Technology Zurich, Zurich, Switzerland.
- Arnts, R. R. (2008), Reduction of biogenic VOC sampling losses from ozone via trans-2-butene addition, *Environ. Sci. Technol.*, 42(20), 7663-7669, DOI: 10.1021/es050440w.
- Arnts, R. R. (2010), Evaluation of adsorbent sampling tube materials and adsorbents for analysis of volatile biogenic organic compounds, *Atmos. Environ.*, 44(12), 1579-1584, doi:10.1016/j.atmosenv.2010.01.004.
- Baker, B., A. Guenther, J. Greenberg, A. Goldstein, and R. Fall (1999), Canopy fluxes of 2-methyl-3-buten-2-ol over a ponderosa pine forest by relaxed eddy accumulation: field data and model comparison, *J. Geophys. Res.*, 104(D21), 26107-26114.
- Baker, J. M. (2000), Conditional sampling revisited, *Agric. For. Meteorol.*, 104, 59-65.
- Baker, J. M., J. M. Norman and W. L. Bland (1992), Field-scale application of flux measurement by conditional sampling, *Agric. For. Meteorol.*, 62, 31-52.

603 Bash, J. O., and Miller, D. (2008), A relaxed eddy accumulation system for measuring surface
 604 fluxes of total gaseous mercury, *J. Atmos. Oceanic Technol.*, 25, 244-257,
 605 doi:10.1175/2007JTECHA908.1.
 606
 607 Baum, K. A. and J. M. Ham (2010) Adaptation of a speciation sampling cartridge for measuring
 608 ammonia from cattle feedlots using relaxed eddy accumulation, *Atmos. Environ.*, 43, 1753-1759,
 609 doi: 10.1016/j.atmosenv.2008.12.021.
 610
 611 Beverland, I. J., D. H. Ónéil, S. L. Scott, and J. B. Moncrieff (1996), Design, construction and
 612 operation of flux measurement systems using the conditional sampling technique, *Atmos.*
 613 *Environ.*, 30(18), 3209-3220.
 614
 615 Brut, A., D. Legain, P. Durand, and P. Laville (2004), A relaxed eddy accumulator for surface
 616 flux measurements on ground-based platforms and aboard research vessels, *J. Atmos. Oceanic*
 617 *Technol*, 21, 411-427, doi:10.1175/1520-0426(2004) 021.
 618
 619 Businger, J. A. (1991), Conditional sampling technique for flux measurement, U. S. Patent
 620 #526959.
 621
 622 Businger, J. A and A. C. Delany (1990), Chemical sensor resolution required for measuring
 623 surface fluxes by three common micrometeorological techniques, *J. Atmos. Chem.*, 10, 399-410.
 624

625 Businger, J. A. and S. P. Oncley (1990), Flux measurement with conditional sampling, J. Atmos.
 626 Oceanic Technol., 7, 349-352.
 627
 628 Christensen, C. S., P. Hummelshøj, N. O. Jensen, B. Larsen, C. Lohse, K. Pilegaard, H. Skov
 629 (2000), Determination of the terpene flux from orange species and Norway spruce by relaxed
 630 eddy accumulation, Atmos. Environ. 34, 3057-3067.
 631
 632 Ciccioli, P., E. Brancaleoni, M. Frattoni, V. Di Palo, R. Valentini, G. Tirone, G. Seufert, N.
 633 Bertin, U. Hansen, O. Csiky, R. Lenz, and M. Sharma (1999), Emission of reactive terpene
 634 compounds from orange orchards and their removal by within-canopy processes, J. Geophys.
 635 Res., 104(D7), 8077-8094.
 636
 637 Ciccioli, P., E. Brancaleoni, M. Frattoni, S. Marta, A. Brachetti, M. Vitullo, G. Tirone, and E.
 638 Valentini (2003), Relaxed eddy accumulation, a new technique for measuring emission and
 639 deposition fluxes of volatile organic compounds by capillary gas chromatography and mass
 640 spectrometry, J. Chromatog. A, 985, 283-296.
 641
 642 Cobos, D. R., J. M. Baker, and E. A. Nater (2002), Conditional sampling for measuring mercury
 643 vapor fluxes, Atmos. Environ., 36, 4309-4321.
 644
 645 Darmais, S., L. Dutaur, B. Larsen, S. Cieslik, L. Luchetta, V. Simon, and L. Torres (2000),
 646 Emission fluxes of VOC by orange trees determined by both relaxed eddy accumulation and
 647 vertical gradient approaches, Chemosphere, 2, 47-56.

648

649 Delon, C., A. Druilhet, and R. Delmas (2000), Aircraft assessment of trace compound fluxes in
650 atmosphere with relaxed eddy accumulation: sensitivity to the conditions of selection, J.
651 Geophys. Res., 105(D16), 20461-20472.

652

653 Gallagher, M. W., R. Clayborough, K. M. Beswick, C. N. Hewitt, S. Owen, J. Moncrieff and K.
654 Pilegaard (2000), Assessment of a relaxed eddy accumulation for measurements of fluxes of
655 biogenic volatile organic compounds: study over arable crops and a mature beech forest, Atmos.
656 Environ., 34, 2887-2899.

657

658 Gaman, A., Ü. Rannik, P. Aalto, T. Pohja, E. Siivola, M. Kumala and T. Vesala (2004), Relaxed
659 eddy accumulation system for size-resolved aerosol particle flux measurements, J. Atmos.
660 Oceanic Technol., 21, 933-943.

661

662 Geron, C. D, and R. R. Arnts (2010), Seasonal monoterpene and sesquiterpene emissions from
663 *Pinus taeda* and *Pinus virginiana*, Atmos. Environ., 44(34), 4240-4251.

664

665 Graus, M., A. Hansel, A. Wishaler, C. Lindinger, R. Forkel, K. Hauff, M. Klauer, A. Pfichner, B.
666 Rappenglück, D. Steigner, and R. Steinbrecher (2006), A relaxed eddy accumulation method for
667 the measurement of isoprenoid canopy-fluxes using an online gas-chromatographic technique
668 and PTR-MS simultaneously, Atmos. Environ., 40, S43-S54,
669 doi:10.1016/j.atmosenv.2005.09.094.

670

671 Guenther, A., C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M.
 672 Lerdau, W. A. MacKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P.
 673 Zimmerman (1995), A global model of natural volatile organic compound emissions, J.
 674 Geophys. Res., 100(D5), 8873-8892.
 675
 676 Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P. Palmer, and C. Geron (2006), Estimates of
 677 global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols
 678 from Nature), Atmos. Chem. Phys., 6, 3181-3210.
 679
 680 Guenther, A., P. Zimmerman, P. Harley, R. Monson, and R. Fall (1993), Isoprene and
 681 monoterpene emission rate variability: model evaluation and sensitivity analysis, J. Geophys.
 682 Res., 98, 12609-12617.
 683
 684 Haapanala, S., J. Rinne, K.-H. Pystynen, H. Hellén, H. Hakola, and T. Riutta (2006),
 685 Measurement of hydrocarbon emissions from a boreal fen using the REA technique,
 686 Biogeosciences, 3, 103-112.
 687
 688 Helmig, D. (1997), Ozone removal techniques in the sampling of atmospheric volatile organic
 689 trace gases, Atmos. Environ., 31(21), 3635-3651.
 690
 691 Helmig, D., B. Balsey, K. Davis, L. R. Kuck, M. Jensen, J. Bognar, T. Smith, Jr., R. V. Arrieta,
 692 R. Rodríguez, and J. W. Birks (1998), Vertical profiling and determination of landscape fluxes of

biogenic nonmethane hydrocarbons within the planetary boundary layer in the Peruvian Amazon,
J. Geophys. Res., 103(D19), 25519-25532.

Hoffman, T.(1995), Adsorptive preconcentration technique including oxidant scavenging for
the measurement of reactive natural hydrocarbons in ambient air. *Fresenius J. Anal. Chem.*,
1995, 351, 41.

Lee, X. (2000), Water vapor density effect on measurements of trace gas mixing ratio and flux
with a mass flow controller, J. Geophys. Res., 105(D14), 17807-17810.

Lee, X., J. Finnigan, and K. T. Paw U (2004), Coordinate systems and flux bias error, In:
Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis (Lee, X.,
W. Massman, and B. Law, eds) Kluwer Academic Publishers, Dordrecht, Netherlands, 33-66.

Majewski, M., R. Desjardins, P. Rochette, E. Pattey, J. Selber, and D. Glotfelty 1993, Field
comparison of an eddy accumulation and aerodynamic-gradient system for measuring pesticide
volatilization fluxes, Environ. Sci. Technol., 27, 121-128.

Meyers, T. P., W. T. Luke, and J. J. Meisinger (2006), Fluxes of ammonia and sulfate over maize
using relaxed eddy accumulation, Agric. For. Meteor., 136, 203-213, doi:
10.1016/j.agrformet.2004.10.005.

Nemitz, E., M. Flynn, P. I. Williams, C. Milford, M. R. Theobald, A. Blatter, M. W. Gallagher,
 and M. A. Sutton (2001), A relaxed eddy accumulation system for the automated measurement
 of atmospheric ammonia fluxes, *Water Air & Soil Pollution: Focus*, 1, 189-202.

Nie, D., T. E. Kleindienst, R. R. Arnts and J. E. Sickles II (1995), The design and testing of a
 relaxed eddy accumulation system, *J. Geophys. Res.*, 100(D6), 11414-11423.

Olofsson, M., B. Ek-Olausson, N. O. Jensen, S. Langer, and E. Ljungström (2005), The flux of
 isoprene from a willow coppice plantation and the effect on air quality, *Atmos. Environ.*, 39,
 2061-2070, doi:10.1016/j.atmosenv.2004.12.015.

Oncley, S. P., A. C. Delany, T. W. Horst and P. P. Tans (1993), Verification of flux
 measurement using relaxed eddy accumulation, *Atmos. Environ.*, 27A(15), 2417-2426.

Park, C., G. W. Schade, and I. Boedeker (2010), Flux measurements of volatile organic
 compounds by the relaxed eddy accumulation method combined with a GC-FID system in urban
 Houston, Texas, *Atmos. Environ.*, 44, 2605-2614, doi:10.1016/j.atmosenv.2010.04.016.

Pattey, E., R. L. Desjardins, and P. Rochette (1993), Accuracy of the relaxed eddy-accumulation
 technique, evaluated using CO₂ flux measurements, *Boundary-Layer Meteor.*, 66, 341-355.

Plaza, J., L. Núñez, M. Pujadas, R. Pérez-Pastor, V. Bermejo, S. Garcia-Alonso and S. Elvira
 (2005), Field monoterpene emission of Mediterranean oak (*Quercus ilex*) in the central Iberian

738 Peninsula measured by enclosure and micrometeorological techniques: observation of drought
739 stress effect, *J. Geophys. Res.*, 110, D03303, doi:10.1029/2004JD005168.
740

741 Pollmann, J., J. Ortega, and D. Helmig (2005), Analysis of atmospheric sesquiterpenes: sampling
742 losses and mitigation of ozone interferences, *Environ. Sci. Technol.*, 39, 9620-9629,
743 doi:10.1021/es050440w.
744

745 Pryor, S. C., R. J. Barthelmie, B. Jensen, N. O. Jensen, and L. L. Sørensen (2002), HNO₃ fluxes
746 to a deciduous forest derived using gradient and REA methods, *Atmos. Environ.*, 36, 5993-
747 5999.
748

749 Rinne, J., H. Hakola, T. Laurila, and Ü. Rannik (2000), Canopy scale monoterpene emissions of
750 *Pinus sylvestris* dominated forests, *Atmos. Environ.*, 34, 1099-1107.
751

752 Schade, G. W., and A. H. Goldstein (2001), Fluxes of oxygenated volatile organic compounds
753 from a Ponderosa pine plantation, *J. Geophys. Res.*, 106(D3), 3111-3123.
754

755 Schery, S. D., P. T. Wasiolek, B. M. Nemetz, and F. D. Yarger (1998), Relaxed eddy
756 accumulator for flux measurement of nanometer-size particles, *Aerosol Sci. Technol.*, 28, 159-
757 172.
758

759 Skov, H., S. B. Brooks, M. E. Goodsite, S. E. Lindberg, T. P. Myers, M. S. Landis, M. R. B.
760 Larsen, B. Jensen, G. McConville, and J. Christensen (2006), Fluxes of reactive gaseous mercury

measured with a newly developed method using relaxed eddy accumulation, *Atmos. Environ.*,
40, 5452-5463, doi:10.1016/j.atmosenv.2006.04.0461.

Valentini, R., S. Greco, G. Seufert, N. Bertin, P. Ciccioli, A. Cecinato, E. Brancaleoni, and M.
Frattoni (1997), Fluxes of biogenic VOC from Mediterranean vegetation by trap enrichment
relaxed eddy accumulation, *Atmos. Environ.*, 31(S1), 229-238.

Valverde-Canossa, J., L. Ganzeveld, B. Rappenglück, R. Steinbrecher, O. Klemm, G. Schuster,
and G. K. Moorgat (2006), First measurements of H₂O₂ and organic peroxides surface fluxes by
the relaxed eddy-accumulation technique, *Atmos. Environ.* 40, S55-S67,
doi:10.1016/j.atmosenv.2006.03.038.

Zhu, T., D. Wang, R. L. Desjardins, and J. I Macpherson (1999), Aircraft-based volatile organic
compounds flux measurements with relaxed eddy accumulation, *Atmos. Environ.*, 33, 1969-
1979.

Zhu, T., D. Wang, R. L. Desjardins, J. I Macpherson, E. Pattey, and G. St. Amour (1998),
Aircraft measurements of the concentration and flux of agrochemicals, *Environ. Sci. Technol.*,
32, 1032-1038.

Figure Captions

Figure 1. Relationship between atmospheric parameter, **AP**, and surface flux with chemical resolution. Desired daytime conditions for the atmospheric parameters for REA measurements will range from ~ 3 to 9 s m^{-1} using a β of 0.39 for a vertical velocity threshold of $0.6\sigma_w$. With a 15 L sample, our gas chromatographic system will detect approximately 0.29 pptC (signal/noise ratio of 3/1) shown as the open squares. However for quantitation a signal/noise ratio of 10/1 (limit of quantitation- LOQ) is desired (defined above by the solid squares). The dark area defines the expected operational range of a system with samples at or above the LOQ. Open circles and closed circles define limits with lesser sample sizes, 1.5 L and 0.15 L respectively.

Figure 2. Gas flow schematic of relaxed eddy accumulator. Key components: sonic anemometer (**SA**), open face particle filter holder with Teflon membrane (**PF**), a heated path (**HP**) consisting of a PFA (perfluoro alkoxy) Teflon tube and a heated valve plate (**HVP**) where flow is routed to one of three fast acting 3-way Teflon solenoid valves (sampling valve left, neutral and right – **SVL**, **SVN**, **SVR**) open to direct flow to up, down or neutral accumulators. Pressure is monitored by four pressure sensors (**PSM** and three black squares). Internal standards and trans-2-butene are added behind **PF**. Zero gas (**ZG**) is filtered by a molecular sieve/activated alumina trap (**HCT**) which supply segregator valves normally open ports (left and right supply lines omitted for clarity). Common ports of left and right segregator valves connect to coils of Sulfinert tubing (**RCL** and **RCR**) which in turn pass to two sets of 6-port Teflon manifold (**MV**) valves which index to adsorbent tube accumulators (ST) in cooled manifold (**CM**)

Figure 3. Key electronic components of REA system and data acquisition and control system with independent subsystems. Canopy level components were located on walk-up tower and the remaining components were placed in temperature controlled instrument shed nearby. Solid connecting lines indicate analog signals and dotted lines are digital signals. Data Packer 1 (**DP1**) operated at 10 Hz and Data Packers 2-4 operated at 0.1 Hz. Legend: mass flow controllers (**MFC**), carbon dioxide & water vapor infra-red gas analyzer (**IRGA**), sonic anemometer (**SA**), solid state relay (**SSR**), thermocouple (**TC**), a temperature controlled mass flow controller box (**MFC+AC**), atmospheric pressure sensor (**APS**), soil heat flux sensor (**SHF**). DC power supplies (not shown) also provide power to drive the solid-state relays (**SSR**, 5 VDC), solenoid valves (12 VDC), pressure sensors (18 VDC) and Peltier coolers (12 VDC).

Figure 4. Ratio of 2-methylheptane to methylcyclohexane internal standards in accumulator tubes versus tube manifold temperature for 2007 flux measurements (circles – up, squares- down). The increase in ratio above 25°C for some runs indicates that some methylcyclohexane was lost from the accumulator tubes. The horizontal line at 1.2 indicates mean of 10 volumetric reference samples.

Figure 5. Compilation of 2007 volumetric ratios (uncorrected/corrected) versus the number of valve state changes for the up and down segregators over a 55 minute flux measurement period (circles- up, squares-down).

Figure 6. Measured fluxes on two winter (a) and two summer (b) days over a Loblolly pine (*Pinus taeda*) plantation with a sweetgum (*Liquidambar styraciflua* Liriodendron tulipifera and

830 *Acer rubrum*) understory. Plots were reduced to compound classes for clarity: 1) monoterpenes
831 (open blocks), 2) oxygenated monoterpenes (diagonals), 3) sesquiterpenes (black), and 4) 2-
832 methyl-3-buten-2-ol (verticals, July only). Temperature ranges from morning low to afternoon
833 high: March 6 (6.5-10°C), March 7 (4.8-19.9°C), July 4 (25.9-31.5°C), July 5 (28.7-33.4).

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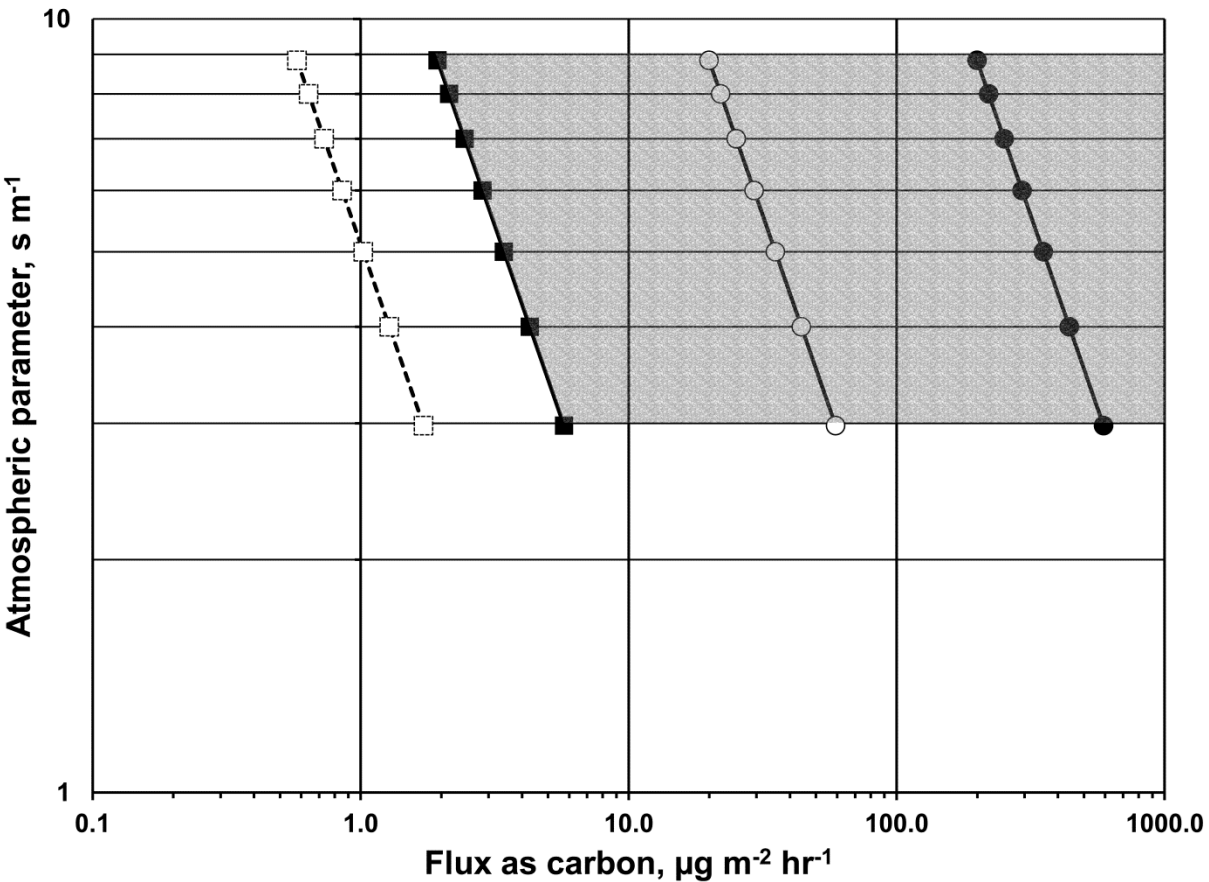
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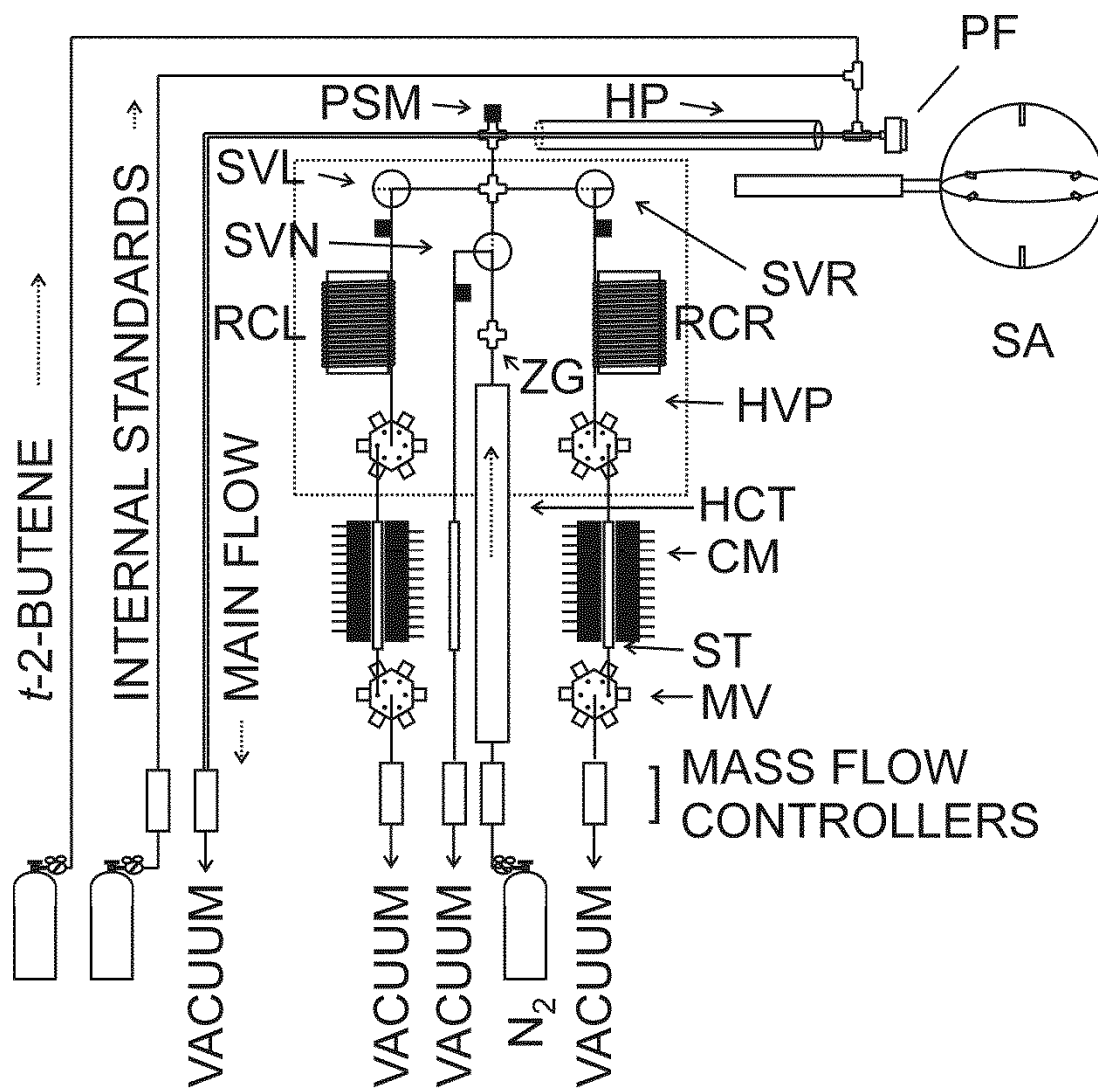
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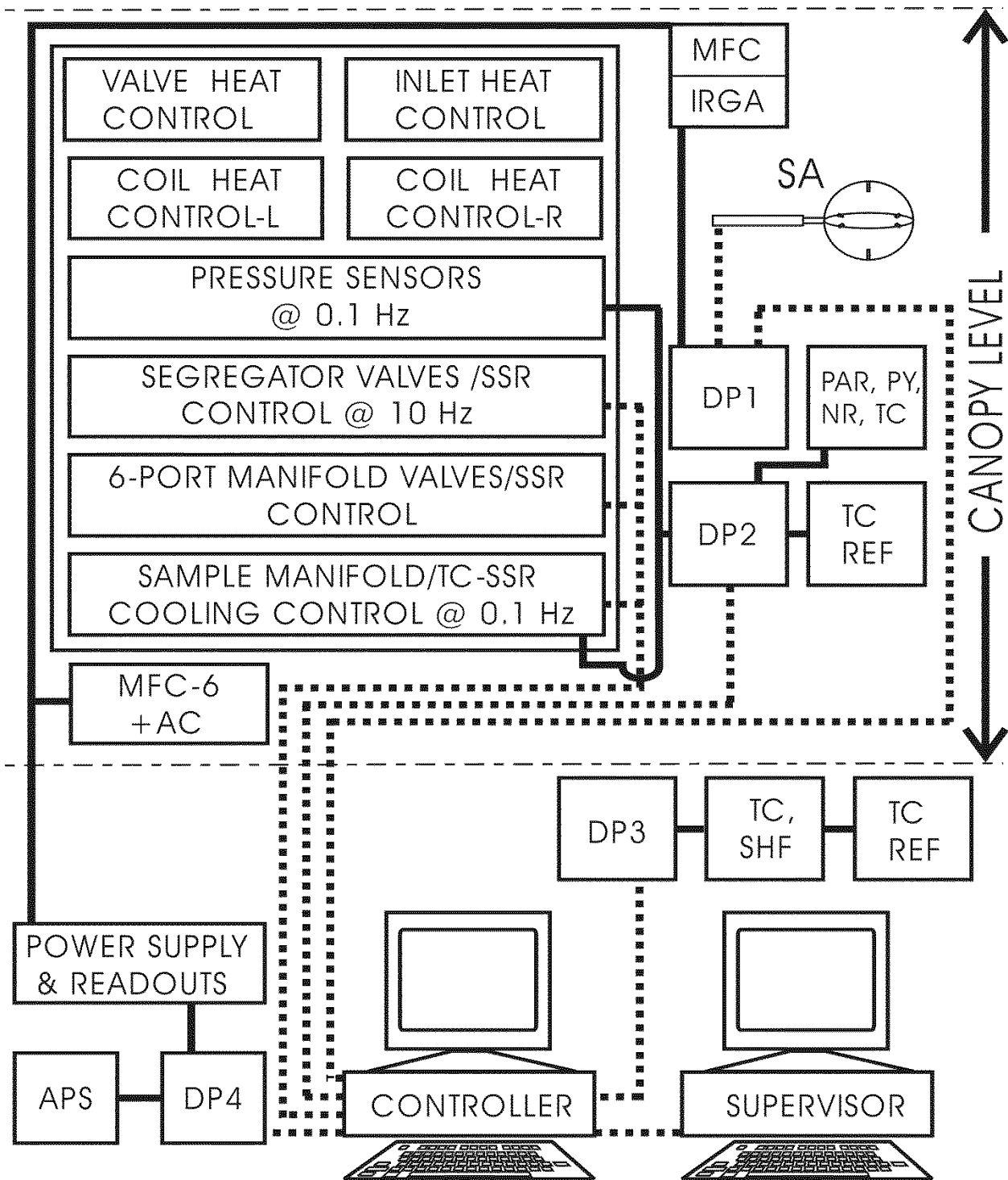
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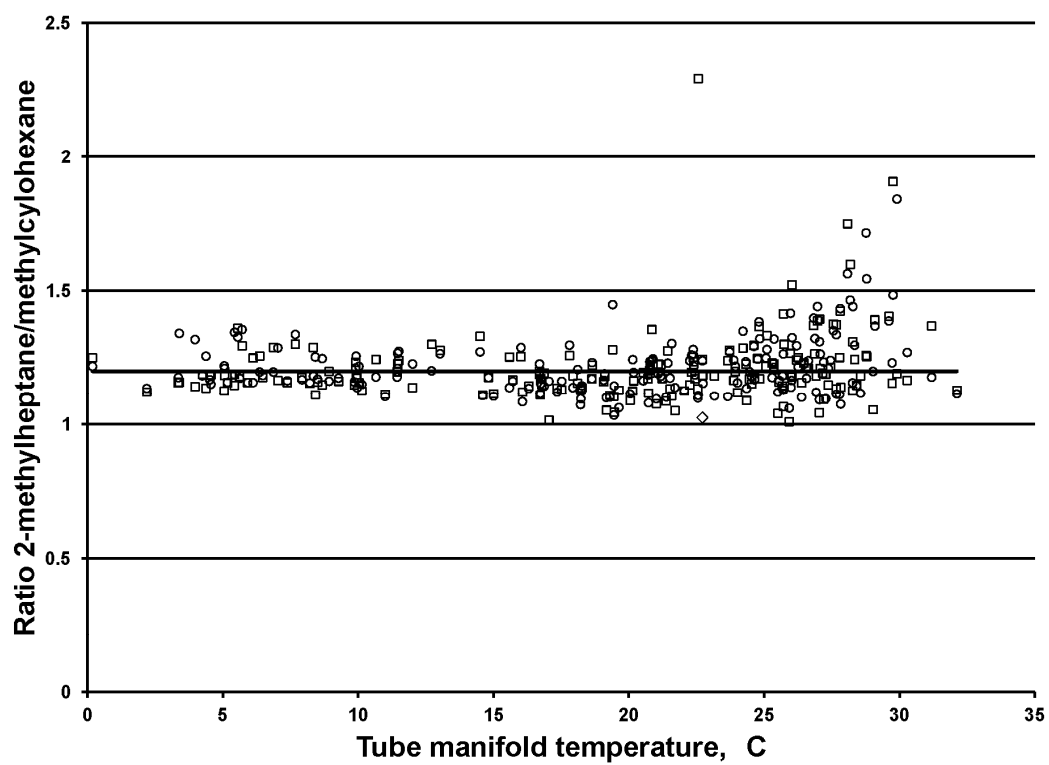
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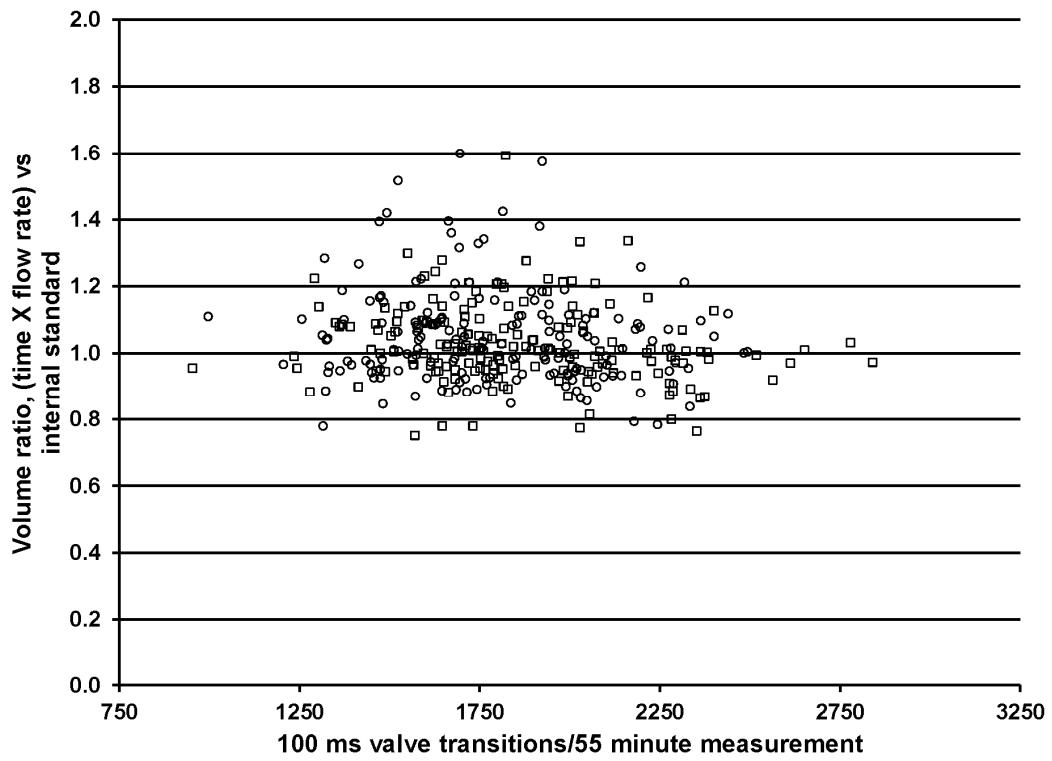


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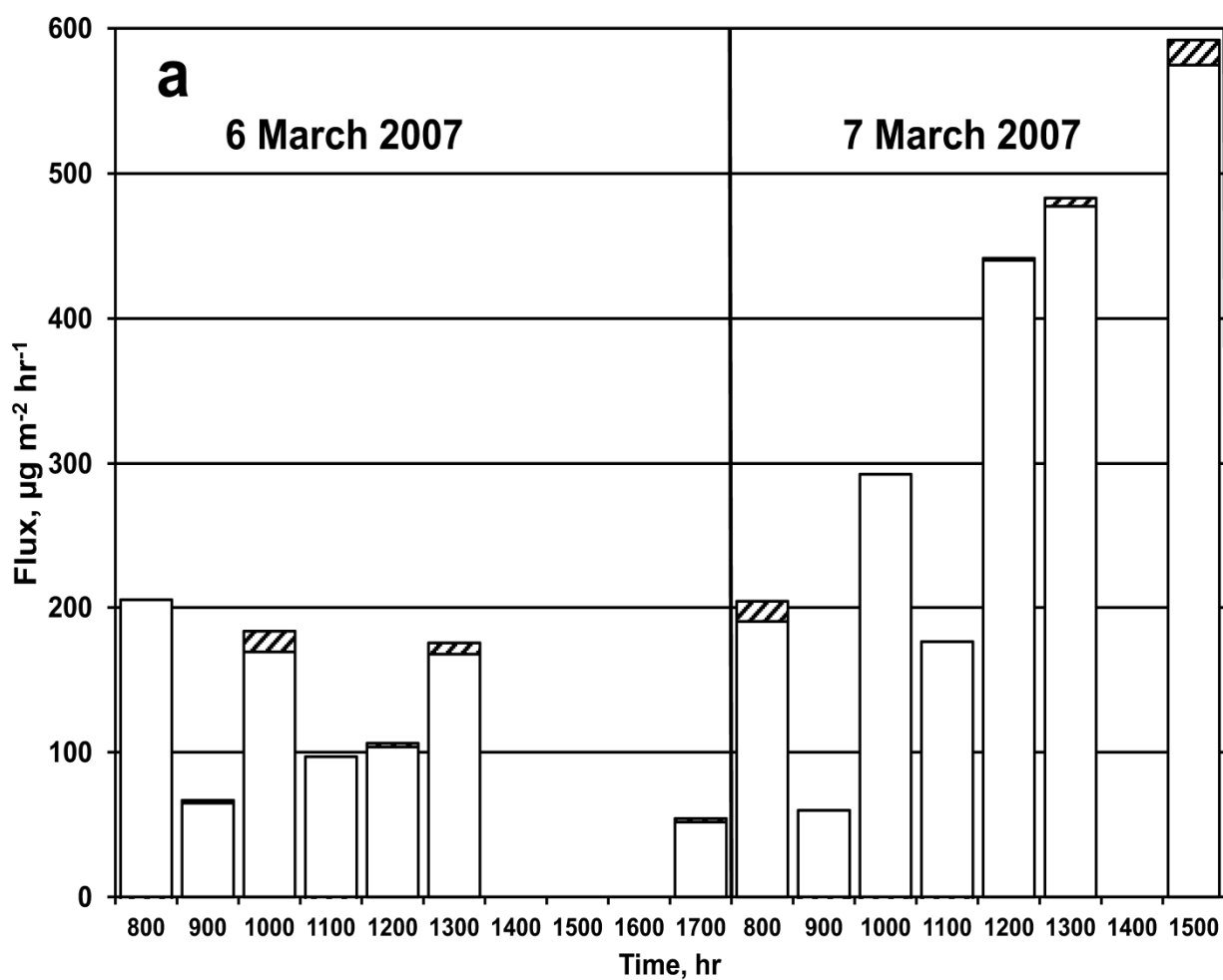
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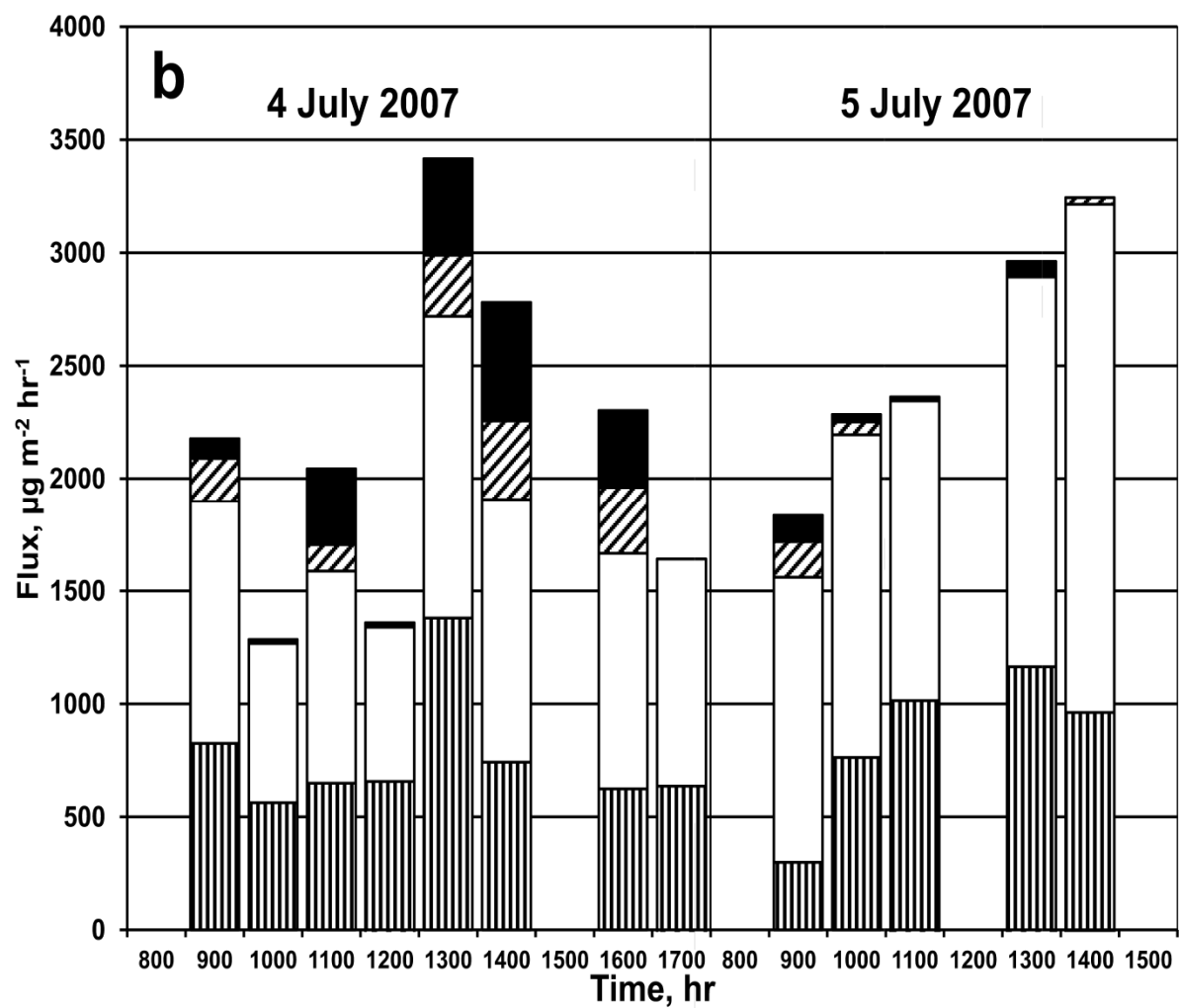
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