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Evaluation of semi-static enclosure technique for rapid surveys of biogenic volatile organic compounds (BVOCs) emission measurements

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Abstract

Biogenic volatile organic compounds (BVOCs) are important drivers of atmospheric chemical composition and accurate model simulations require characterization of the emissions associated with specific vegetation types which is typically determined using enclosure measurements. Static enclosure techniques were used for past BVOC emission measurement studies, especially in the 1960s to 1980s, but are no longer widely used because of concerns that the resulting emission rates are not representative. The main advantages of the static approach are the capability for rapid measurements and a lower detection limit that enables the use of less sensitive analytical techniques. We evaluate a version of the static approach which we call the semi-static approach. In order to evaluate the performance of the semi-static approach for BVOCs emission measurements, multiple replicate measurements for different plants were conducted in a laboratory growth chamber using both semi-static and dynamic enclosure techniques. Variability of replicate measurements was calculated

and the results from the two techniques were compared. The semi-static technique provided consistent measurements for isoprene but not for α-pinene, β-pinene and other compounds that are stored in leaves. The measured isoprene emission factors were much higher than dynamic measurements. There were a large number of compounds to be detected by dynamic technique that could not be detected by the semi-static technique. But the semi-static technique could still provide qualitative information on categorization of non, low and high emitters for some compounds.

Keywords: BVOC emission; semi-static enclosure technique; dynamic enclosure technique; emission factor

1. Introduction

Biogenic volatile organic compounds (BVOCs) play important roles in formation of ozone (O_3) and secondary organic aerosol (SOA) (Nozière et al., 2011; Sartelet et al., 2012). It is essential to accurately estimate BVOC emissions to support air quality evaluations and effective decision-making regarding air pollution control. BVOC emission factor measurements are the primary basis for emission inventory development (Guenther et al., 2006; 2012). Both static and dynamic enclosure techniques have been employed in the past to measure branch and leaf-level emission factors but the dynamic approach is now recommended for accurate measurements (Niinemets et al., 2011). A static system does not have air circulation and environmental control (Tsui et al., 2009; Prendez et al., 2013), while a dynamic system has air circulation and can have full environmental control (Ortega et al., 2008; Helmig et al., 2013). In the simple static enclosure system, no air is purged in, thus, the temperature inside the chamber will rise dramatically due to the greenhouse effect, if the chamber is exposed to sunlight, while photosynthesis and transpiration by the plant will lead to unrealistically low CO_2 and high H_2O concentrations which can perturb the BVOC emission rates (Ortega and Helmig, 2008). As a result, static systems are expected to yield unrealistic estimates of BVOC emission rates (Niinemets et al., 2011). The dynamic system can provide an enclosure environment that is more representative of natural conditions through keeping a large amount of purged air in and

out of the chamber continually. The dynamic system is often run for a long period of time (one or more days) to ensure that BVOC emissions are not perturbed by any disturbance while enclosing the vegetation. While more representative emission rates can be obtained with a dynamic enclosure, the concentration dilution from the high flow rate of purge air results in measurements by the dynamic enclosure technique that are generally limited by the minimum detectable trace gas concentration difference between incoming and outgoing air, especially for the compounds with lower emission potential.

Semi-static enclosure technique, a derivative of the static enclosure technique, was used for some of the earliest measurements of BVOC emissions (Rasmussen 1972, Zimmerman, 1979, Lamb et al., 1985) and continues to be used in some regions (Li, 2015). The semi-static system introduces a large amount of zero air into the enclosure but without outflow. This system is relatively simple to operate and is rapid (~10 min or less) which means that environmental variations within the sampling chamber are minimized because of the short enclosure time and purged zero air.

BVOC emission measurements are still needed to characterize dominant vegetation in many regions of the world including China, where some whole-canopy flux studies and branch and leaf-level enclosure (static, semi-static and dynamic) studies have been conducted (e.g., Bai et al., 1994; Bai et al., 2012, 2015; Bao et al., 2014; Chang et al., 2012; Klinger et al., 2002; Guo, 2012; Tsui et al., 2009; Zhao et al., 1996; Zhao et al., 2004; Li, 2015) but there are still important ecosystems and plant species that have not been sufficiently characterized. It is currently difficult to determine whether the available database of semi-static enclosure measurements are useful for incorporating into BVOC emission databases in order to establish local emission rate datasets. Since a shorter time is needed for each experiment using semi-static technique, the semi-static approach could also be useful for plant emission screening studies. Thus, we have evaluated the performance of semi-static BVOC emission measurements to determine whether it can be applied to obtain useful emission rate data. Therefore, in this study, we conducted multiple replicate measurements with different individuals of two plant species in an environmental controlled plant growth chamber using both semi-static and

dynamic enclosure techniques. First, repeatability was examined to characterize the reliability of measurements by the semi-static system. Then, the results from the semi-static enclosure were compared with those from a dynamic enclosure to demonstrate the capability of the semi-static system.

2. Methodology

2.1 Plant material

Replicate measurements were conducted on three individuals of *Populus trichocarpa* and three individuals of *Liquidambar styraciflua*. Both are widely distributed tree species in the US. They were all potted plants of 1−2 years of age purchased from the Forest Farm nursery (www.forestfarm.com). The heights of individuals were about 40 cm for *Populus trichocarpa* and 88–108 cm for *Liquidambar styraciflua*. They were repotted in plastic pots filled with a blend of 85−95% Canadian Sphagnum peat moss, perlite, dolomite lime, and wetting agent. The plants were grown in a plant growth chamber (2.5 m length × 2.5 m width ×2.5 m height) with ~1000 μmol m^{-2} s^{-1} of photosynthetically active radiation (PAR) at the top leaves for a daylength of 12 hours. The relative humidity was maintained around 60% and the temperature was 23 during day and night. All trees were irrigated every other day.

2.2 Enclosure measurements

For each plant species, replicate emissions from three individuals were collected under the same laboratory conditions using both semi-static and dynamic enclosure techniques. The experiments were performed in the Biosphere Atmosphere Interactions Laboratory at University of California, Irvine, USA in summer 2017. Teflon bags (Welch Fluorocarbon, Inc., USA) were used to enclose the whole plant for each individual, which were almost 100% transparent to PAR as determined by direct measurement. The volume of bags used for *Populus trichocarpa* and *Liquidambar styraciflua* were 18 L (24"×20") and 110 L (44"×32"), respectively. For dynamic enclosure system, the zero air stream leading to the enclosure was supplied by a high capacity vacuum pump (Gast Manufacturing, Inc., USA). The zero air was scrubbed of VOC using a charcoal filter before pumping into the bag. For

semi-static enclosure system, the zero air was supplied by a zero air generator (Aadco Instruments, USA). For both enclosure systems, zero air was delivered to the bag enclosure through 0.25 inch o.d. Teflon tubing.

For the semi-static enclosure, there was only inflow of zero air but no outflow. A Teflon sample line extended from the enclosure to Silonite™ coated 1-L bottle canisters (Bottle-Vac Samplers, Entech Instruments, USA) for instantaneous sample collection. To sample BVOCs using the semi-static enclosure system, a background sample of air outside the bag was collected immediately after enclosing the plant. Then, the 110-L bag was purged with zero air at a larger flow rate of 8 L min^{-1} for ~6 min (2.5 L min^{-1} for ~3 min for 18-L bag). Next, the air flow rate was decreased to 3 L min^{-1} and the purge was continued for an additional ~2 min (1 L min^{-1} for ~1 min for 18-L bag), which was expected to allow the air in the bag to be well mixed. Finally, a grab sample of air in the bag was collected into an evacuated bottle. We assumed that the air in the bag had been mixed well in the enclosure so that the collected sample could be expected to be representative for the average concentration inside the enclosure, and that the volume and VOC concentration were constant during the emission sample collection. After the experiments, we confirmed that the enclosure had been relatively airtight, and the total volume of the residual air in the bag at the beginning of enclosure and the purged zero air was not large enough to cause gas to leak from the bag. In this study, we assumed that plants emitted no Freon113 and so the mass of Freon113 in the background and emission sample could be used as a tracer to calculate the BVOC emission factors measured by semi-static enclosure technique.

The dynamic enclosure was equipped with inlet and outlet air flow. Zero air was continuously pumped into the enclosure. After enclosing, enclosures were allowed to equilibrate for 2–3 hours prior to sampling. BVOC samples were collected onto solid adsorbent cartridges, filled with preconditioned Tenax TA and Carbotrap, by pumping air from the enclosure at a constant flow of 200 mL min^{-1} using a mass flow controlled air sampling pump (GilAir Plus Air Sampling Pump, Sensidyne, USA). The sample time was 30 min and sample volumes were 6 L. Before enclosing each plant, blank samples

were taken from the empty enclosure with the same equipment inside the plant enclosure, such as Teflon lines and temperature sensor. The BVOC emission factors were calculated based on the difference in the BVOC concentration in outflow and inflow air and the flow rate of inflow air.

The collected samples, both bottle and cartridge samples, were analyzed with a TD-GC-TOF-MS system (Markes International, USA). The VOCs were cryofocused at -10 onto a cold trap and then desorbed at 285 and transferred to a 30-m Agilent DB-5 column for separation at a flow rate of 1.20 mL/min with Helium as carrier gas. The column was programmed at the initial temperature of -30 and the highest temperature of 260 and the running time was 35 min. The measured compounds included isoprene, monoterpene and sesquiterpene species, some alkanes and alkenes, aromatics, and Freon compounds.

2.3 Calculation of Emission factor

For each semi-static enclosure experiment, after determining the background and emission sample VOC concentrations, the emission factor was calculated with Equation (1):

$$EF = \frac{C\times(V+V_0)-C_0\times V_0}{\Delta t\times A} \quad (1)$$

where EF is the emission factor (μg m^{-2} h^{-1}) of the VOC species; C and C_0 are the VOC species concentrations (μg m^{-3}) in the emission and background samples, respectively; V is the total volume (m^3) of zero air purged into the enclosure bag; V_0 is the volume, m^3, of residual air in the bag after enclosing but before purging zero air. It was estimated based on the mass of Freon113 before and after enclosing. In our study, the V_0 values were estimated as 7 L for the 18-L chamber and 35 L for the 110-L chamber averagely; Δt is the total enclosure time (h); and A is the leaf area (m^2) of the leaves on the enclosed branch.

Dynamic enclosure measured emission factors were calculated based on Equation (2):

$$EF = \frac{F\times(C_{emission}-C_{blank})}{A} \quad (2)$$

Where F is the flow rate of zero air into the enclosure (L min^{-1}); $C_{emission}$ and C_{blank} are VOCs concentrations (μg m^{-3}) of outflow air sample with plant and no plant enclosed, respectively.

After obtaining the emission results for each emission sample measured by semi-static and dynamic enclosure, the emission factors of each individual plant were calculated by averaging all its replicated measurements for each enclosure technique. The emission factors for each plant species, *Populus trichocarpa* and *Liquidambar styraciflua*, could be calculated by averaging the results of three individuals of each plant species.

3. Results and discussion

3.1 Uncertainties of semi-static measurements

The emission results of replicate measurements for *Populus trichocarpa* and *Liquidambar styraciflua* trees are shown in Table 1. The variabilities of emission measurements for all the BVOCs are listed in Table S1 and S2. The variability of isoprene emissions from the replicate measurements using the semi-static system for each individual plant were 10.2%–14.0%, while the differences of α-pinene and β-pinene emissions were 25.4%–134.2%. For *Populus trichocarpa*, the differences of isoprene, α-pinene, and β-pinene emissions between different individuals of the same plant species were 22.7%, 9.0%, and 37.3%, respectively. For *Liquidambar styraciflua*, their variability was 31.4%, 82.8%, and 51.2% for semi-static, but only 15.2%, 26.0%, and 6.8% when using the dynamic system.

Table 1. The variability (standard deviation % of mean) of isoprene, α-pinene, and β-pinene emission factor (μg m^{-2} h^{-1}) observed for replicate semi-static and dynamic enclosure measurements. ND indicates the emission factor was below the detection limit.

Trees [a]	Semi-static enclosure				Dynamic enclosure			
	Replicates	isoprene	α-pinene	β-pinene	Replicates	isoprene	α-pinene	β-pinene
P1	14	10.2	73.0	52.9	10	9.1	ND	ND
P2	12	12.2	74.1	85.2	9	2.7	ND	ND
P3	10	13.9	54.1	72.6	10	4.1	ND	ND
individual differences		22.7	9.0	37.3		1.4	-	-
L1	6		40.6	25.4	7	10.7	22.1	9.8

L2	6	14.0	85.8	68.8	8	14.3	8.6	2.9
L3	6	10.3	128.9	134.2	7	2.0	27.0	11.4
individual differences		31.4	82.8	51.2		15.2	26.0	6.8

[a] P1–P3 indicates the three individuals of *Populus trichocarpa*; L1–L3 indicates the three individuals of *Liquidambar styraciflua*.

For α-pinene and β-pinene emissions, semi-static enclosure measurements had much higher variability than dynamic measurements, not only within the same individuals but also among different plants. The variability for monoterpene emissions determined with the semi-static technique was much higher than the variability for isoprene emission. α-Pinene and β-pinene are released from specialized storage structures in leaves of these plants, which were disturbed during enclosure. In the semi-static system, the chamber was not equilibrated to steady state for enclosed plants after enclosing and before sampling. The observed burst of monoterpene emission was expected due to disturbance when enclosing (Niinemets et al., 2011). This disturbance results in emission rate errors, especially for plant species with specialized storage tissues for these compounds. So for these compounds, the measurement results using a semi-static system would tend to overestimate emissions and have much larger uncertainty. This demonstrates the difficulty in obtaining quantitative monoterpene emission measurements using the semi-static enclosure technique. However, despite the large uncertainties of α-pinene and β-pinene emission measurements using semi-static method, they could still provide qualitative information on which plants have the capacity to emit monoterpenes and which compounds dominate the total emission. It could detect low levels of monoterpene emissions from *Populus trichocarpa* whereas the dynamic system would have characterized this species as a non-emitter for monoterpenes. *Populus trichocarpa* had the lower emission potential of α-pinene and β-pinene in steady state under the detection limit of dynamic method. While they had a burst of emissions due to disturbance and concentration accumulation during the semi-static enclosure so that they could be detected but not quantified accurately. In the case of *Liquidambar styraciflua*, the

semi-static approach correctly identified this species as a high monoterpene emitter with emissions dominated by a-pinene. The observations shown in Table 1 also demonstrate that the semi-static technique has better performance for isoprene emission measurement than α-pinene and β-pinene, which are compounds stored in leaves. In addition, semi-static enclosure measurements had much higher variability than dynamic measurements because BVOCs emissions could be disturbed much during enclosure and influenced by the CO_2 deficiency in the zero air when using the semi-static technique. Notably, the large variability of measurements by semi-static approach might also partially result from estimation of V_0. When calculating the emission factors using Equation (1), the accuracy of Freon113 was the key to the accurate calculation. The precision of Freon113 measurements in our study was 5.6% which still might introduce errors to the calculation.

3.2 Comparison of semi-static and dynamic system measurements

The average emission factors measured by using semi-static and dynamic enclosure were also compared for the same plant (Table 2). Isoprene emissions measured using the semi-static method were 1.4–2.4 times higher than those by the dynamic method. One possible cause for this is because there was no CO_2 in the zero air which flushed into the chamber during semi-static enclosure which is known to increase the emission of isoprene (Possell et al., 2005; Wilkinson et al., 2009). This could be corrected for the semi-static system measurement of isoprene emission by including CO_2 in the zero air. There were even larger differences for the mean values of α-pinene and β-pinene for the dynamic and semi-static systems with emissions measured using the semi-static method that were about 10 to 24 times higher than by the dynamic method. In addition, the variability was higher for monoterpene compounds emissions measured by semi-static system than for the dynamic system.

Table 2. Comparison between the emission results measured by semi-static and dynamic system. ND indicates the emission factor was below the detection limit

Emission factor ($\mu g\ m^{-2}\ h^{-1}$)	*Populus trichocarpa*			*Liquidambar styraciflua*		
	isoprene	α-pinene	β-pinene	isoprene	α-pinene	β-pinene

semi-static enclosure	2776±631	0.8±0.1	0.2±0.1	1152±362	72±60	173±89
dynamic enclosure	1981±29	ND	ND	487±74	3±1	18±1
difference (%)	40.1	-	-	136.8	2293.3	879.1

Table 3. The number of each VOC categories observed with semi-static and dynamic system

Number of observed compounds	*Populus trichocarpa*		*Liquidambar styraciflua*	
	semi-static system	dynamic system	semi-static system	dynamic system
monoterpenes	8	2	10	14
sesquiterpenes	2	4	2	6
alkanes	7	18	1	11
alkenes	1	4	0	3
aromatics	1	1	4	2

In addition to the emission factors of the compounds shown in Table 2, we also compared the semi-static and dynamic method measurements of other monoterpenes and sesquiterpenes, and other VOCs including alkanes, alkenes, and aromatics. Table 3 shows the number of monoterpenes, sesquiterpenes, alkanes, alkenes, and aromatics observed with each system for each tree species. The dynamic approach suggested that these plants emitted a large number of compounds that could not be detected using the semi-static approach. The semi-static measurements observed some other VOCs that have not previously been reported as emissions from plants. This estimated emission with the semi-static system could be a result of the ambient air that remained in the chamber after enclosing. However, some of these compounds were also observed with the dynamic branch enclosure system. For the dynamic enclosures, this means that the compounds were observed at higher levels in the plant enclosure than in the blank (without plant) chamber. This included some alkanes and aromatics. Monoterpene compounds, including α-pinene, β-pinene, α-thujene, camphene, 3-carene, D-limonene, E-β-ocimene, and γ-terpinene, were detected from the emissions of *Populus trichocarpa* using

semi-static enclosure technique, while only α-pinene, β-pinene, 3-carene, and E-β-ocimene were detected by the dynamic enclosure technique. However, the dynamic enclosure detected more sesquiterpene compounds, such as aromadendrene, humulene, and delta-cadinene. This may be because these compounds are lost on chamber walls during the short sampling period of the semi-static system but the enclosure surfaces eventually reach an equilibrium for the dynamic enclosure system. In addition, the less purged zero air into the enclosure and large uncertainty of semi-static technique in emission measurements may partially contribute to their wall loss. More researches should be conducted to investigate the wall loss effect for these compounds if conducting rapid surveys of BVOCs using semi-static technique in the future. For *Liquidambar styraciflua* trees, both monoterpene and sesquiterpene had more compounds detected when using dynamic enclosure technique. For both plant species, more alkanes and alkenes compounds could be detected by dynamic approach. Generally, semi-static enclosure technique could detect fewer compounds than dynamic one. But there were still some observed compounds with semi-static system that could not be detected by the dynamic approach.

4. Conclusions

The semi-static technique is useful for characterizing plants as emitters or non-emitters for compounds such as α-pinene and β-pinene, which are stored in leaves of the investigated plants and may be useful for semi-quantitative measurements to characterize plants as high, low and non-emitters for isoprene emission. The measured isoprene emission factors had a larger variability than those measured by dynamic technique, and their mean was higher than that determined for the dynamic measurements. We conclude that semi-static enclosure technique can be used as a screening tool to characterize emitters and non-emitters of compounds such as monoterpenes that are stored in specialized storage tissues. The performance for isoprene is better and enables categorization of non, low and high emitters.

For accurate quantitative measurements of BVOCs emissions, dynamic enclosure technique is required as recommended by Niinemets et al. 2011. Also, dynamic enclosure technique tended to

work at least as well as the semi-static technique for the number of compounds detected and should be used to explore more BVOC species from plants.

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