

Reply to comments from Referee #2

This study evaluates deuterated surrogates (α -pinene-d₃ and β -caryophyllene-d₂) for tracing adsorptive and reactive losses of monoterpenes (MTs) and sesquiterpenes (SQTs) in dynamic chambers. Using standard gas mixtures, it examines the effects of concentration, temperature, humidity, and O₃. Adsorptive losses varied with concentration and temperature, while O₃-induced losses were species-specific. The surrogates effectively corrected losses, but additional deuterated compounds are recommended for broader coverage. A strong correlation between adsorption and O₃ reactivity underscores the need for careful loss correction, particularly for highly reactive SQTs, which should be measured with O₃-free air when correction is unavailable. Overall, the manuscript is well written, and the results are valuable to the literature. I have some minor comments:

Lines 82-83: Please briefly mention the size and dimensions of the chamber, as they affect VOC losses via surface adsorption.

Reply: Following your suggestion, we have included the chamber's dimensions in the revised manuscript "*It has a diameter of 25 cm and a height of 28 cm, yielding a volume of 13.7 L.*" (L90)

Section 3.1: Is there an adsorption model that can be used to quantify VOC loss? The authors may refer to He et al. (AMT, 2024) for relevant methods. (Reference: He, L., Liu, W., Li, Y., Wang, J., Kuwata, M., and Liu, Y.: Wall loss of semi-volatile organic compounds in a Teflon bag chamber for the temperature range of 262–298 K: mechanistic insight on temperature dependence, Atmos. Meas. Tech., 17, 755–764, <https://doi.org/10.5194/amt-17-755-2024>, 2024).

Reply: Thank you very much for providing the reference of He et al. (2024) on adsorption modelling. Indeed, previous studies, such as Ghirardo et al. (2020), have proposed whole chamber system calibration to correct for VOC losses, and we also proposed a correction method based on laboratory evaluations (Zeng et al., 2022a). While these methods are useful in ideal laboratory conditions, they seem impractical for field measurements due to: 1) differences in chamber materials and designs; 2) variations in plant leaves and their surfaces; and 3) fluctuating environmental parameters like temperature, light, humidity, and ozone concentrations. Therefore, instead of relying on modelling, we introduce deuterated surrogates to avoid these complexities. In the revised manuscript, we have clarified this in the "Introduction" section with the following addition: "*While previous laboratory studies have evaluated adsorptive losses in empty chambers (Kolari et al., 2012; Hohaus et al., 2016; Helin et al., 2020; Ghirardo et al., 2020; Zeng et al., 2022a; He et al., 2024) and proposed correction methods for simplified chamber systems (Ghirardo et al., 2020; Zeng et al., 2022a; He et al., 2024), variations in chamber design, plant species and environmental conditions introduce additional complexities for field measurements. To address these challenges, internal surrogates are recommended for evaluating and correcting such losses in dynamic chambers (Ortega et al., 2008; Zeng et al., 2022a).*" (L 68-74)

Related references:

Ortega, J., Helmig, D., Daly, R. W., Tanner, D. M., Guenther, A. B., and Herrick, J. D.: Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part B: Applications, Chemosphere, 72, 365-380, <https://doi.org/10.1016/j.chemosphere.2008.02.054>, 2008.

- Kolari, P., Back, J., Taipale, R., Ruuskanen, T. M., Kajos, M. K., Rinne, J., Kulmala, M., and Hari, P.: Evaluation of accuracy in measurements of VOC emissions with dynamic chamber system, *Atmos. Environ.*, 62, 344-351, <https://doi.org/10.1016/j.atmosenv.2012.08.054>, 2012.
- Hohaus, T., Kuhn, U., Andres, S., Kaminski, M., Rohrer, F., Tillmann, R., Wahner, A., Wegener, R., Yu, Z., and Kiendler-Scharr, A.: A new plant chamber facility, PLUS, coupled to the atmosphere simulation chamber SAPHIR, *Atmos. Meas. Tech.*, 9, 1247-1259, <https://doi.org/10.5194/amt-9-1247-2016>, 2016.
- Ghirardo, A., Lindstein, F., Koch, K., Buegger, F., Schloter, M., Albert, A., Michelsen, A., Winkler, J. B., Schnitzler, J. P., and Rinnan, R.: Origin of volatile organic compound emissions from subarctic tundra under global warming, *Glob. Chang. Biol.*, 26, 1908-1925, <https://doi.org/10.1111/gcb.14935>, 2020.
- Helin, A., Hakola, H., and Hellén, H.: Optimisation of a thermal desorption–gas chromatography–mass spectrometry method for the analysis of monoterpenes, sesquiterpenes and diterpenes, *Atmos. Meas. Tech.*, 13, 3543-3560, <https://doi.org/10.5194/amt-13-3543-2020>, 2020.
- Zeng, J., Zhang, Y., Zhang, H., Song, W., Wu, Z., and Wang, X.: Design and characterization of a semi-open dynamic chamber for measuring biogenic volatile organic compound (BVOC) emissions from plants, *Atmos. Meas. Tech.*, 15, 79-93, <https://doi.org/10.5194/amt-15-79-2022>, 2022a.
- He, L., Liu, W., Li, Y., Wang, J., Kuwata, M., and Liu, Y.: Wall loss of semi-volatile organic compounds in a Teflon bag chamber for the temperature range of 262-298 K: mechanistic insight on temperature dependence, *Atmos. Meas. Tech.*, 17, 755-764, [10.5194/amt-17-755-2024](https://doi.org/10.5194/amt-17-755-2024), 2024.

Lines 136-137: Please add references to this sentence.

Reply: We have added two related references in the revised manuscript (L146).

- Ortega, J., Helmig, D., Daly, R. W., Tanner, D. M., Guenther, A. B., and Herrick, J. D.: Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part B: Applications, *Chemosphere*, 72, 365-380, <https://doi.org/10.1016/j.chemosphere.2008.02.054>, 2008.
- Niinemets, U., Kuhn, U., Harley, P. C., Staudt, M., Arneth, A., Cescatti, A., Ciccioli, P., Copolovici, L., Geron, C., Guenther, A., Kesselmeier, J., Lerdau, M. T., Monson, R. K., and Peñuelas, J.: Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols, *Biogeosciences*, 8, 2209-2246, <https://doi.org/10.5194/bg-8-2209-2011>, 2011.

Lines 142-148: Why do reactive VOCs exhibit greater adsorption loss? Any explanation?

Reply: Based on our observations, monoterpenes or sesquiterpenes that are more reactive with ozone tend to exhibit greater adsorption losses. While we cannot definitely explain this phenomenon, it may be related to the molecular structure of these compounds. Terpenes, with one or more unsaturated bonds and varying structural configurations (cyclic, bicyclic, or acyclic), show

enhanced reactivity with ozone due to their higher π -electron cloud density. This increased electron density may also facilitate stronger van der Waals interactions with non-polar surfaces, such as chamber walls, thereby increasing their adsorption capacity. We believe it is an interesting observation that warrants further exploration and may inspire future studies. Therefore, we just report our observation results although we do not have a solid explanation at present.

Line 181: Why not use α -pinene or β -caryophyllene directly instead of their isotopes for calibrating losses?

Reply: α -Pinene and β -caryophyllene are both monoterpene and sesquiterpene emitted from plants and thus cannot serve as internal surrogates for calibrating losses, as they are directly relevant to plant emissions. Internal surrogates need to meet two criterions: 1) they should not be present in the plant emissions profile or the circulating air, and 2) they should exhibit similar adsorptive behaviors as the target compounds under varying environmental conditions. By using deuterated surrogates, such as α -pinene-d₃ and β -caryophyllene-d₂, which are plant-irrelevant, we can better mimic the behavior of plant-derived volatiles while avoiding the complexities associated with plant-emitted compounds.

Lines 191-193: Any suggestions for green leaf volatiles such as aldehydes and alcohols? How does humidity impact their losses? Please discuss.

Reply: Green leaf volatiles, including aldehydes and alcohols, are indeed emitted by plants and are water soluble, meaning their adsorption may be influenced more by humidity. The impact of humidity on adsorptive loss is complex, as it involves competition for adsorption sites between water molecules and volatiles, as well as potential changes in the energy spectrum of the adsorption sites due to the presence of condensed water. In our previous study (Zeng et al., 2022a), we have evaluated the effects of humidity (RH=0-100%) on the adsorptive loss of some water-soluble compounds, such as acetonitrile, acrylonitrile, acrolein, and acetone, in dynamic chambers. While the humidity effects varied slightly across compounds, we found that the absolute effects were negligible in dynamic chambers. This aligns with findings from other studies (Kolari et al., 2012; Hohaus et al., 2016). Since this study attempted to use deuterated surrogates to calibrate more important monoterpenes and sesquiterpenes, we did not extend our discussion to oxygenated volatiles.

Kolari, P., Back, J., Taipale, R., Ruuskanen, T. M., Kajos, M. K., Rinne, J., Kulmala, M., and Hari, P.: Evaluation of accuracy in measurements of VOC emissions with dynamic chamber system, *Atmos. Environ.*, 62, 344-351, <https://doi.org/10.1016/j.atmosenv.2012.08.054>, 2012.

Hohaus, T., Kuhn, U., Andres, S., Kaminski, M., Rohrer, F., Tillmann, R., Wahner, A., Wegener, R., Yu, Z., and Kiendler-Scharr, A.: A new plant chamber facility, PLUS, coupled to the atmosphere simulation chamber SAPHIR, *Atmos. Meas. Tech.*, 9, 1247-1259, <https://doi.org/10.5194/amt-9-1247-2016>, 2016.

Zeng, J., Zhang, Y., Zhang, H., Song, W., Wu, Z., and Wang, X.: Design and characterization of a semi-open dynamic chamber for measuring biogenic volatile organic compound (BVOC) emissions from plants, *Atmos. Meas. Tech.*, 15, 79-93, <https://doi.org/10.5194/amt-15-79-2022>,

2022a.

Line 197: Were O₃ scrubbers or denuders applied before cartridge sampling?

Reply: Yes, ozone scrubbers were used to scavenge ozone before cartridge sampling when conducting the experiments for the ozone effect.

Lines 245-249: Sesquiterpene emissions from plants may be more sensitive to O₃ stress as reported by the literature. Using O₃-free air may not reflect real-world conditions. Why not apply a correction factor for sesquiterpene loss due to O₃ instead?

Reply: While it is true that sesquiterpene emissions may be more sensitive to O₃, calculating the reactive loss of sesquiterpenes due to O₃ in a controlled environment is straightforward, as it relies on reaction rate constants and O₃ concentrations. However, field measurements introduce significant uncertainties due to: 1) diurnal temperature fluctuations that affect temperature-dependent reaction kinetics; 2) operational complexity of continuous O₃ monitoring; 3) large uncertainties in reported rate constants (Table S3); and 4) challenges in distinguishing between stomatal O₃ uptake and chemical reactions. These factors make it difficult to accurately quantify reactive losses in the field.

To address these challenges, we used deuterated surrogates, which allow for simultaneous quantification of adsorptive and reactive losses under real-world conditions. Our findings demonstrate that highly reactive sesquiterpenes like caryophyllene and α -humulene are subject to substantial O₃-driven degradation (Fig. 5). While long-term O₃ fumigation can affect sesquiterpene emissions, short-term O₃ scavenging during sampling is less likely to impact plant physiology or sesquiterpene emissions, as suggested by Niinemets et al. (2011) and supported by other studies (Helmig et al., 2007, 2013; Ortega et al., 2008).

Related references:

Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., and Sakulyanontvittaya, T.: Sesquiterpene emissions from pine trees - Identifications, emission rates and flux estimates for the contiguous United States, *Environ. Sci. Technol.*, 41, 1545-1553, <https://doi.org/10.1021/es0618907>, 2007.

Helmig, D., Daly, R. W., Milford, J., and Guenther, A.: Seasonal trends of biogenic terpene emissions, *Chemosphere*, 93, 35-46, <https://doi.org/10.1016/j.chemosphere.2013.04.058>, 2013.

Ortega, J., Helmig, D., Daly, R. W., Tanner, D. M., Guenther, A. B., and Herrick, J. D.: Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part B: Applications, *Chemosphere*, 72, 365-380, <https://doi.org/10.1016/j.chemosphere.2008.02.054>, 2008.

Niinemets, U., Kuhn, U., Harley, P. C., Staudt, M., Arneth, A., Cescatti, A., Ciccioli, P., Copolovici, L., Geron, C., Guenther, A., Kesselmeier, J., Lerdau, M. T., Monson, R. K., and Peñuelas, J.: Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols, *Biogeosciences*, 8, 2209-2246, <https://doi.org/10.5194/bg-8-2209-2011>, 2011.

Table 1: It would be useful to include literature-reported reaction rates for compounds in both groups 1 and 2, which helps readers understand the extent of reaction rate differences.

Reply: Following your suggestion, we have included literature-reported reaction rates for all tested monoterpenes and sesquiterpenes in Table S3 in the Supplement.

Table S3. Rate constants (k , $\times 10^{-16}$ cm³ molecule⁻¹ s⁻¹) of MTs and SQTs with ozone.

Compounds	k ($\times 10^{-16}$ cm ³ molecule ⁻¹ s ⁻¹)
α -Pinene-d3	
α -Pinene	0.866 ² ; 0.866 ³ ; 0.96 ⁵
β -Pinene	0.15 ² ; 0.15 ³ ; 0.19 ⁵
β -Myrcene	5.93 \pm 0.17 ¹ ; 4.7 ²
α -Phellandrene	28.15 \pm 1.11 ¹ ; 29.8 ² ; 29 ⁵
3-Carene	0.37 ² ; 0.371 ³ ; 0.49 ⁵
Limonene	3.06 \pm 0.14 ¹ ; 2 ² ; 2 ³ ; 2.2 ⁵
1,8-Cineole	0.15 ⁵
γ -Terpinene	1.4 ² ; 1.6 ⁵
Terpinolene	19.21 \pm 1.20 ¹ ; 16 ⁵
Linalool	4.3 ³
α -Longipinene	20.17 \pm 0.98 ¹ ; 2.9 ⁴
Longicyclene	0.114 ⁷
α -Copaene	1.6 ² ; 2.9 ⁴ ; 1.5 ⁵
α -Gurjunene	14.56 \pm 0.15 ¹
β -Caryophyllene	115.33 \pm 3.83 ¹ ; 116 ² ; 116 ³ ; 110 ⁴ ; 120 ⁵
β -Caryophyllene-d2	129.14 \pm 4.42 ¹
Thujopsene	8.64 \pm 0.16 ¹
Aromadendrene	65 ⁴
α -Humulene	147.04 \pm 3.87 ¹ ; 117 ² ; 140 ⁴ ; 120 ⁵
Alloaromadendrene	0.12 ⁶
β -Chamigrene	15.14 \pm 0.16 ¹

1. this study; 2. Atkinson, 1997; 3. Hoffmann et al., 1997; 4. Pollmann et al., 2005; 5. IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (<http://iupac.pole-ether.fr>); 6. Yee et al., 2016; 7. Frazier et al., 2022

Lines 273-274: Again, would chamber-specific correction factors for different VOCs be more effective?

Reply: As stated above, chamber- and compound-specific correction factors are typical more applicable to simple, empty chamber systems (Zeng et al., 2022a; He et al., 2024). However, in the field, the complex and variable nature of plant surfaces, physiological processes, and environmental conditions makes such correction factors impractical.

Zeng, J., Zhang, Y., Zhang, H., Song, W., Wu, Z., and Wang, X.: Design and characterization of a semi-open dynamic chamber for measuring biogenic volatile organic compound (BVOC) emissions from plants, *Atmos. Meas. Tech.*, 15, 79-93, <https://doi.org/10.5194/amt-15-79-2022>,

2022a.

He, L., Liu, W., Li, Y., Wang, J., Kuwata, M., and Liu, Y.: Wall loss of semi-volatile organic compounds in a Teflon bag chamber for the temperature range of 262-298 K: mechanistic insight on temperature dependence, *Atmos. Meas. Tech.*, 17, 755-764, [10.5194/amt-17-755-2024](https://doi.org/10.5194/amt-17-755-2024), 2024.