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Jingle bells, what are those smells? Indoor VOC emissions from a live Christmas tree

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ABSTRACT

Every year in the United States conifers are purchased to serve as Christmas trees in homes where they emit volatile organic compounds (VOCs) to the indoor environment. Although many studies have measured the ecosystem-level emissions of VOCs from conifers outdoors (characterizing monoterpene, isoprene, and aldehyde emissions), little is known about VOC emission rates once a conifer is brought indoors. Using a proton transfer reaction-mass spectrometer we characterized the VOCs emitted from a freshly cut Douglas Fir for 17 days in an environmentally controlled chamber. Ozone injections were also performed to analyze indoor chemistry that may occur. Introduction of the tree into the chamber increased the response of 52 mass spectra signals detected by the PTR-MS by at least 500 counts per second (cps) compared to background levels, with concentrations sharply decreasing after the first two days. Monoterpenes were emitted from the tree at a rate of 12.4 mg h^{-1} the first day and fell to 1 mg h^{-1} by day three. Overall, monoterpene emissions from this Douglas fir were initially comparable to other strong indoor monoterpene sources (fragranced products and air fresheners) but decayed quickly and, within days, were smaller than other common indoor sources. Addition of ozone to the chamber resulted in decreased monoterpene concentrations that coincided with modest increases in formaldehyde. Four other emitted VOCs were tentatively identified due to their large increase within the first few hours of the tree placed in the chamber, behavior during ozonation, or pattern of accumulation over time.

1. Introduction

Between 25 and 30 million live Christmas trees are sold in the U.S every year [1]. Despite their widespread use, volatile organic compound (VOC) emissions from live trees in indoor environments have not, to the best of our knowledge, been studied.

1.1. Conifers emit monoterpenes outdoors

A major gap in knowledge is how VOC emissions change when a typical Christmas tree is cut down and placed indoors. It is well-known that outdoors, conifers emit monoterpenes that are responsible for their distinct pine aroma. Monoterpenes in forested environments play a major role in regulating air quality. Although monoterpenes themselves are not climate forcers, they can react to form secondary organic aerosols (SOA) [2]. A review of 37 different studies by Geron [3] demonstrated that monoterpene emissions from Douglas firs are comprised mainly of α-pinene and β-pinene. While the emissions from softwoods like conifers are dominated by monoterpenes, emissions of isoprene [4], aldehydes [5], and estragole [6] have been reported as well.

1.2. Consumer products also emit monoterpenes

Monoterpenes are emitted from building materials and consumer goods used indoors such as air fresheners, candles, and personal care products—to name a few. They are known for their fragrance: typically pine, citrus, or other “nature” smells. A study by Singer et al. [7] found that during the use of a scented oil plug-in air freshener (a constant source), terpenes such as limonene and linalool were emitted at 1.6 mg h^{-1} and 6.2 mg h^{-1} respectively over three days. Similar to a wall-plugin air freshener source, building materials are another constant source of monoterpenes in the indoor environment. Poppendieck et al. [8] measured a whole-house monoterpene emission rate ranging from 4.0 mg h^{-1} to 6.2 mg h^{-1} in the first 15 months after a house was constructed with building materials that were specified to be low emitting (including wooden floors and cabinetry).

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Other indoor sources can be transient in duration and dependent on occupant use. Data from Singer et al. [7] can be used to show that when mopping a 15 m^2 floor at a rate of 6 g product m^{-2}, limonene can be emitted at a rate of 6 mg h^{-1} to 14 mg h^{-1} (averaged value over 24 h). In a study by Uhde and Schulz [9], limonene was found in 10 out of 14 different room scent-enhancing products. The maximum emission rate for limonene was in a scented spray, releasing 9.1 mg h^{-1}. However, a large range of chemicals, including other monoterpenes, were also emitted after spraying. Salthammer et al. [10] reported up to 1.18 mg h^{-1} of limonene coming from a "fresh" scent candle while burning, as well as 0.36 mg h^{-1} of formaldehyde. Personal care products that are used daily such as shampoo and antiperspirants can be a significant emitter of VOCs indoors. Yeoman et al. [11] found that the limonene emission rate from products used during a shower is 7.27 mg h^{-1}. Coggon et al. [12] estimated the total monoterpene emission rates from fragranced consumer products to be 9.2 mg h^{-1} per person.

1.3. Ozone reacts with monoterpenes indoors forming byproducts

Indoor monoterpenes emitted from consumer products or conifers could react with O_3 to form by-products. O_3 is an oxidant that is generally formed outdoors and transported indoors via ventilation and infiltration. Many studies have examined the formation of secondary reaction products of O_3 reactions indoors. In particular, O_3–terpenoid reactions produce secondary products that include aldehydes such as formaldehyde and acetaldehyde, organic acids, hydrogen peroxide, SOAs, and hydroxyl radicals (OH) [13–17]. Destaillats et. al. [15] demonstrated formaldehyde is a major byproduct from consumer good emissions, with yields of 20 % to 30 % with respect to O_3 consumed. Weschler and Shields [18] demonstrated that terpene ozonolysis can be a significant source of sub-micrometer particles, an important pollutant in indoor settings.

1.4. Potential health effects of ozonolysis byproducts

Building inhabitants inhale O_3 as well as airborne byproducts derived from reactions that consume O_3. Some of these O_3 reaction byproducts (e.g., formaldehyde and organic peroxides) are known to be toxic or irritating [19]. The formation of unidentified strong upper airway irritants in reaction mixtures of terpenes and O_3 was confirmed by Wilkins et al. [20]. Literature reviews by Rohr [21] and Wolkoff [22] concluded in that O_3 terpene reaction byproducts induce adverse respiratory effects at high concentrations, but the effect is less clear at typical indoor levels. Both authors noted the long-term health impacts of ultrafine particle byproducts is uncertain. If the initial terpene emissions from a from Christmas tree is high enough the ozone reaction chemistry may be relevant to impact indoor air quality. The odor thresholds of some aldehydes and terpenes are low enough to affect the perceived indoor environmental quality [5]. For example, d-limonene has an odor threshold range of 1.8 ppb_v to 310 ppb_v (10 μg m^{-3} to 1800 μg m^{-3}) [23]. Note that many papers in the field use non-International System of Units (non-SI); this paper will present air concentrations on a volume basis with conversions to SI mass concentrations assuming 25 °C and 101.3 kPa. Hence, terpene emissions from Christmas trees, especially in the presence of O_3, could potentially degrade perceived indoor environmental quality.

2. Material and methods

To understand how indoor air quality changes when a live Christmas tree is brought indoors, we placed a freshly cut Douglas fir tree in an environmental chamber for 17 days and measured the monoterpene emissions. Although Christmas trees may be indoors a longer duration, this time frame allowed the characterization of the initial emission decay. We compared the emission rates from the Christmas tree to other indoor monoterpene sources discussed above. The tree was exposed to O_3 for approximately twelve hours a day to examine potential secondary reaction product formation from cyclical outdoor O_3 penetration to indoor spaces. Additionally, we identified other VOCs that were emitted outside of the terpene chemical class.

Fig. 1. The tested Douglas fir in the stainless-steel chamber.

The tree was retrieved from a cut-your-own tree lot in Maryland, United States, on December 18th, 2022. The outdoor temperature was 1 °C. The tree was cut down during the winter to represent the typical biological state of Christmas trees when cut.

The 12.0 kg (wet mass), 1.76 m tall tree was placed in 4.5 L of water in a 31.5 m^3, stainless steel chamber 2.5 h after it was cut (Fig. 1). The tree stand was placed in the middle of the chamber on a 60 cm tall stainless-steel table. The tree was watered daily by a researcher adding a measured amount of tap water in the base of the stand up to a fill line. Watering the tree was the only time each day the chamber door was opened. Daily water consumption decreased during the 17-day experiment (Figure S-1). After the experiment we removed the tree and measured a 0.14 L d^{-1} water loss from the tree stand due to evaporation. Accounting for this evaporation loss, water consumption on the last day of the experiment was 0.46 L d^{-1}, indicating the tree was still biologically active.

The Douglas fir was transformed into a Christmas tree by aiming four 1 600 lumen, 5 000 K, 13.5 W LED lights at the tree (15 cm to 75 cm away from needles) and wrapping it with three LED decorative light strings. The combined wattage of the lights was 52 W. The lights were on roughly 12 h every day throughout the experiment.

The chamber temperature was regulated to 22.0 °C +/- 0.1 °C and a relative humidity of 49.4 % +/- 0.6 %. The chamber had an unfiltered recirculation rate through the HVAC system of 192 m^3 h^{-1}, measured with a bolometer. The outdoor air change rate (0.57 h^{-1}, Figure S-2) was measured once during the experiment via the decay of sulfur hexafluoride. This 15 m^3 h^{-1} outdoor airflow represented 8 % of the total flow through the HVAC system. Outdoor air was filtered with HEPA (High Efficiency Particulate Air) and activated carbon filters prior to the conditioning system. A metal mixing fan (300 m^3 h^{-1}) was aimed at the tree to enhance internal chamber mixing to ensure uniform

concentrations. The enhanced air movement over the tree may have increased the emission rates of chemicals with air phase mass transfer limitations (typically less volatile chemicals) and increase the migration of ozone to the tree surface enhancing ozone surface loss reactions.

2.1. Simulation of outdoor-to-indoor transport of ozone

O_3 was injected intermittently to the chamber to mimic maximum outdoor levels that may penetrate indoors during December. Specifically, a worst-case North America indoor O_3 estimate of 10 ppb_v (20 $\mu g\,m^{-3}$) to 15 ppb_v (30 $\mu g\,m^{-3}$) was determined assuming 25 % of the typical outdoor levels in the winter in Southern California (40 ppb_v, 80 $\mu g\,m^{-3}$) would be observed indoors [24]. We recognize most areas in the North America will have lower indoor ozone concentrations in December. O_3 was generated using 1 000 mL min^{-1} of ultra-high purity oxygen feeding an O_3 generator located outside of the chamber. During the twelve-hour O_3 injection periods the generator was turned on for 22 s every 6 min to 18 min and the supply lines were flushed with oxygen for an additional 15 s. Injection intervals were varied to maintain roughly 15 ppb_v (30 $\mu g\,m^{-3}$) of O_3. Chamber O_3 concentrations were monitored using a dual-cell, UV photometric monitor with a sampling line that terminated within 1 m of the tree. O_3 measurements were recorded as one minute average values.

2.2. VOC measurements

VOCs were measured using a proton transfer reaction time-of-flight mass spectrometer (PTR-MS) [25]. PTR-MS data were collected at a 1 s time resolution and data were averaged to 10 s. The chamber air was sampled using 6 mm (¼") perfluoroalkoxy (PFA) tubing at a flowrate of 1 L min^{-1} and the PTR-MS subsampled that flow at 120 mL min^{-1}. The instrument was operated with a mass resolution of approximately 10,000 (m/Δm) for m/Q 59.049 (acetone). Calibrations and background measurements were performed hourly using a multi-component standard VOC cylinder diluted with ultra-zero air. Non-calibrated chemicals were reported as count per second (cps). The instrument is unable to differentiate between isomers and so we quantify the sum of monoterpene isomer concentrations from the $C_{10}H_{17^+}$ signal. Several samples were analyzed with a thermal desorption (TD) gas-chromatography (GC) pre-separation step after measurement with the PTR-MS to assist in identification of some species.

Liquid injections of neat chemicals were used after the experiment to calibrate the retention times of four monoterpenes in order to characterize the monoterpene population observed from the Christmas tree chromatogram at the end of the experiment. We use the measured sensitivity for limonene (2 653 cps ppb_v^{-1}) to convert between $C_{10}H_{17}^+$ ion counts per second (cps) and ppb_v. PTR-MS data was collected every second and averaged to 10 s. While Christmas trees may be treated with pesticides, this PTR-MS analysis was not optimized to detect these chemicals.

Formaldehyde was measured separately using a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS). Formaldehyde data was collected with one second resolution and averaged to 10 s in post-processing.

2.3. Emission rate calculation

Emission rates for identified VOCs were estimated using a mass balance approach.

$$V\frac{dC}{dt} = QC_o - QC + E(t) \quad (1)$$

where V is the volume of the chamber (m^3), Q is the outside air flow rate ($m^3\ h^{-1}$), C is the chamber concentration (mg m^{-3}), C_o is the outside air concentration entering the chamber (mg m^{-3}), and $E(t)$ is the emission rate (mg h^{-1}). The emission rate in this mass balance does not differentiate between primary emissions from the tree and any secondary byproduct production for that chemical. While monoterpenes likely are predominantly a primary emission, formaldehyde may have contributions from both primary and secondary production. As the tree's biological activity was decreasing with time it was assumed the emission rate changed with time. Since the outdoor air went through an activated carbon and particle filter it was assumed that C_o was equal to zero. Chemical loss was not considered in the emission rate calculation, so only data when O_3 was not present in the chamber was used to calculate emission rates.

Eq. 1 can be rearranged:

$$\frac{dC}{dt} = -\frac{Q}{V}C + \frac{E(t)}{V} = -\lambda C + \frac{E(t)}{V} \quad (2)$$

where λ is the air change rate (h^{-1}). This equation then can be solved numerically using a forward Euler method for E(t).

$$E(t_{n+1}) \cong V\left(\frac{(C_{t_{n+1}} - C_{t_n})}{t_{n+1} - t_n} + \lambda C_{t_n}\right) \quad (3)$$

The timestep used was ten seconds. Emission rates were only calculated for time periods starting 4 h after the tree was placed in the chamber and time periods when no ozone was present in the chamber (data from six hours after ozone injection stopped to the start of the next ozone injection).

3. Results and discussion

3.1. VOCs detected

The PTR-MS data indicates that the tree-emitted VOCs are not limited just to monoterpenes, but also included a population of oxidized VOCs. There were 52 distinct ions detected to have risen by at least 500 cps (Figure S-3) from background after the tree had been in the chamber for four hours, though some of the ions may be fragments of larger VOCs [26,27]. For instance, in these four hours we observed an increase in $C_6H_9^+$, the primary fragment ion from monoterpenes. Below we highlight measurements of several ions that were notable because their signal increased during the measurement period or showed variability in response to ozonation.

Concentrations of monoterpenes exceeded 100 ppb_v (550 $\mu g\,m^{-3}$) on the first day of placement into the chamber (Fig. 2). Within 3.5 days of being in the chamber monoterpene concentrations fell below 10 ppb_v (55 $\mu g\,m^{-3}$), and by the end of the experiment, we measured concentrations around 3.5 ppb_v (19 $\mu g\,m^{-3}$). During the experiment we quantified the monoterpene concentration through measurement of $C_{10}H_{17}^+$ on the PTR-MS. Through pre-separation of the chamber air using a GC we found that the $C_{10}H_{17}^+$ signal at the end of the experiment (Day 17) had contributions from multiple terpenes, but a majority of the signal was limonene (~63 %). This is in contrast to the findings of a review of 37 studies by Geron [3] which found live Douglas fir emissions were over 85 % α- and β-pinene. This contrast may be due to varying attenuation of monoterpene emission rates as the tree becomes stressed in the process of perishing. Stressed trees can change chemical composition of xylem and phylum fluids. Lodgepole pine trees stressed by mountain pine beetles have been shown to increase monoterpene concentrations in bark [28].

Assuming a significant portion of the signal was in fact limonene, the concentrations detected were in the range of limonene's odor thresholds (1.8 ppb_v to 310 ppb_v, or 10 $\mu g\,m^{-3}$ to 1 800 $\mu g\,m^{-3}$) [23], but far below sensory irritation or workplace limitation values. Short-term critical exposure limits (CELs) for α-pinene and d-limonene were developed within the EPHECT project (Emissions, Exposure Patterns and Health Effects of Consumer Products in the EU), based on sensory irritation as the critical effect. The values for d-limonene were 16 180 ppb_v (90 000 $\mu g\,m^{-3}$) for α-pinene and 8 090 ppb_v (45

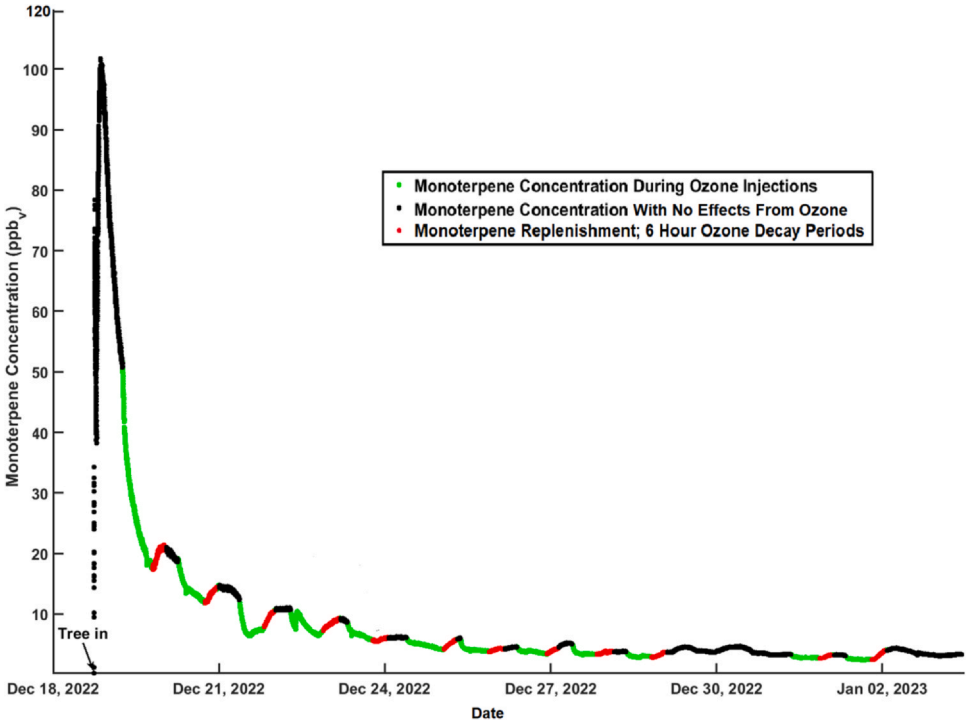

Fig. 2. Monoterpene concentrations measured in the chamber during the tree experiment. Green data represents ozonation periods, red data the following six hours as ozone concentrations decay (time it takes the chamber to reach 95 % of steady state), and black data was used to calculate the monoterpene emission rates.

000 μg m^{-3}) [29]. Neither OSHA (Occupational Safety and Health Administration) and NIOSH (National Institute for Occupational Safety and Health) have developed inhalation standards for α-pinene or limonene [30,31]. While AIHA (American Industrial Hygiene Association) has set a time-weighted average occupational exposure limit for d-limonene of 30 000 ppb$_v$ (167 000 μg m^{-3})[23], these values are set for healthy working adults. These values do not consider vulnerable populations, such as pregnant women, young children, and elderly people.

Table 1 is a summary of detected ions elevated in signal from background and possibly related to conifers. The ion ratio gives an indication of whether the chamber concentration of the chemical increased (> 1) or decreased (< 1) over the course of the experiment. $C_{10}H_{17}^+$ is the ion from monoterpene ionization in the PTR-MS.

Several ions detected by the PTR-MS in elevated levels were not able to have their exact identities verified by the GC including several notable ions, $C_4H_7O_4^+$, $C_6H_7O_2^+$, $C_6H_{11}O_3^+$, and $C_6H_9O_2^+$. We suspect (but cannot confirm) these ions are succinic acid, catechol, ethyl acetoacetate, and sorbic acid respectively based on their occurrence in vegetation. Catechol has been shown to react with O_3 and produce hydroxyl radicals at the air-water interface [32]. Succinic acid has been identified by the US Department of Energy as a chemical that could be derived from biomass [33], and has been found in samples of atmospheric aerosol particles [34]. Sorbic acid is a chemical found in several different types of plants and pine needles [35].

In contrast to monoterpenes, the signals for $C_4H_7O_4^+$ (Figure S-4), $C_6H_7O_2^+$ (Figure S-5), and $C_6H_{11}O_3^+$ accumulated in the chamber over time. Given the constant air change rate, increasing concentration requires either that the emission rate of these VOCs increased throughout the experiment, or sorption into an dynamic surface film on the chamber walls with a changing gas-to-surface partitioning over the course of the experiment. The composition of the surface film on the chamber walls may have changed as it initially likely included rapidly emitting chemicals that then desorbed over time. Since these VOCs were not positively identified we could not quantify an emission rate. The signal increase of $C_4H_7O_4^+$ correlates with a decrease in daily water uptake by the tree, possibly indicating a biological connection between the tree dying and increased emission of these species. Additionally, these ions have been identified in previous literature from biomass burning [36] and oxidation of VOCs [37].

Overall, this data demonstrates that the tree is emitting more of the measured VOCs than it is removing from process such as sorption. This finding is consistent with studies that have demonstrated that plant VOC removal rates are too small to matter in buildings [38].

Table 1
Compounds detected during the tree experiment, and their fraction change over the course of the experiment as detected by the PTR-MS.

Ion	Fraction change in Ion Signal (Day 17/Day 1)
$C_{10}H_{17}^+$	0.033
$C_6H_7O_2^+$	5.5
$C_6H_{11}O_3^+$	1.49
$C_4H_7O_4^+$	1.60
$C_6H_9O_2^+$	0.75

3.2. Concentration decay and emission rates

The monoterpene concentration decreased by over 65 % in the first 24 h (Fig. 2). Time dependent emission rates were determined by solving a chamber mass balance numerically over time (Eq. 3) when ozone was not being injected. In other words, emission rates were determined from the black data presented in Fig. 2, starting at the peak.

The maximum emission rate for monoterpenes was 12.4 mg h^{-1} (Fig. 3). By the third day, the monoterpene emission rate decreased to 1 mg h^{-1}. Copeland and Cape et al. [6] compiled emission rates from outdoor Douglas firs in Europe and North America based on dry weight from both branch enclosure methods and above-canopy flux data. The monoterpene emissions rate was within the range of 0.44 ug g^{-1} dry weight h^{-1} to 6.8 ug g^{-1} dry weight h^{-1}. To find a comparable value, the dry weight of the tree used in this experiment (assumed moisture content of 109 % dry weight [39]) was estimated, and peak emission rate for the evening our tree was cut is 1.2 ug g^{-1} dry weight h^{-1}.

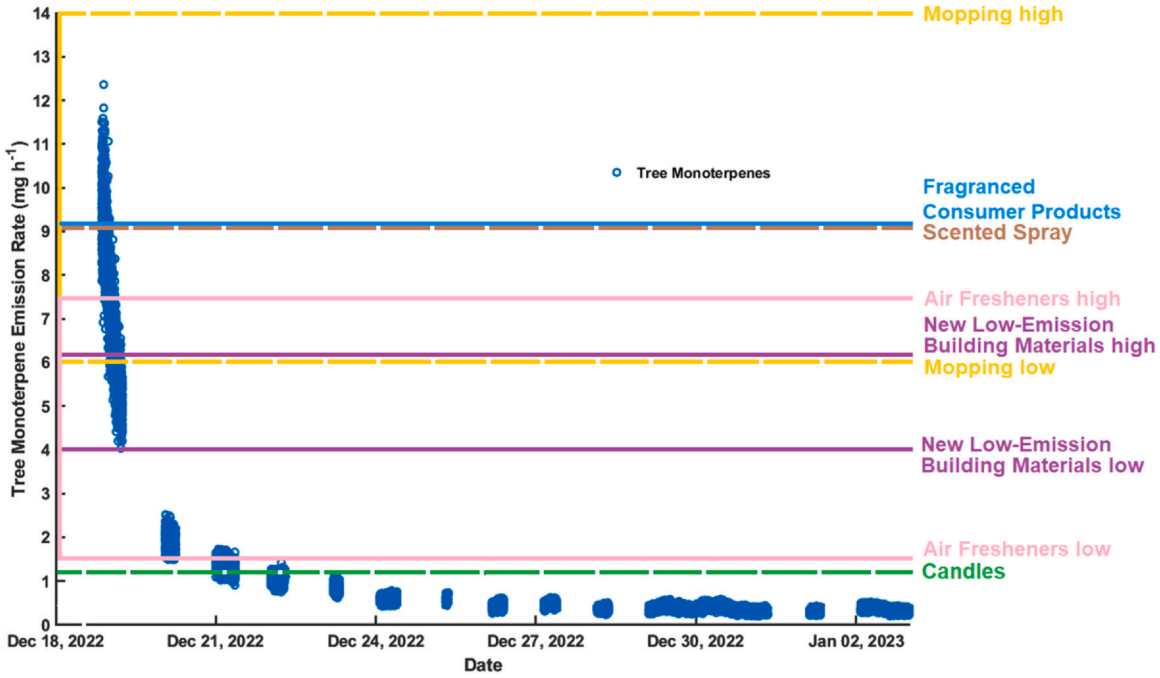

Fig. 3. Monoterpene emission rate from the live Douglas fir compared with other indoor sources. Solid lines represent constant indoor sources. Fragranced consumer products are estimated on a daily basis and normalize to a per h basis here for comparison [12]. Air fresheners emit with a large range of rates depending on the product used [7]. Monoterpene emissions from new building materials in a residential building represent average emission values from the first 15 months after construction [8]. Mopping, scented sprays, candles are considered an intermittent source, represented by a dashed line [7,9,10,41].

The monoterpene emission rate after three days is less than the emission rates of other constant indoor emission sources described earlier such as air fresheners (1.5 mg h^{-1} to 7.5 mg h^{-1}) [40]) and new building materials (4.0 mg h^{-1} to 6.2 mg h^{-1}) [8]. The monoterpene emission rate on day three is about the same as intermittent indoor sources like candles (1.2 mg h^{-1}) [10], but much less than other intermittent sources like scented sprays (9.1 mg h^{-1}) [9] and mopping [7]. However, total exposure to continuous emissions from a tree would be greater than exposure to occasional intermittent sources like a single candle. Overall, monoterpene emissions from this Douglas fir were initially comparable to other strong indoor monoterpene sources (scented sprays and air fresheners) but decayed quickly and, within days, were much smaller than sources that are often present indoors.

3.3. Ozone chemistry

The ozone concentration in the chamber before injection varied from 2 ppb_v to 3 ppb_v (Fig. 4). In the presence of injected ozone, several VOC concentrations were reduced. For instance, the monoterpene concentration when O_3 is injected decreases (green data, Fig. 2). This is consistent with the ozone-terpenoid reactions summarized in Singer et al. [40]. Monoterpene concentrations in the 6-hour periods following ozonation are replenished as seen by the data in red in Fig. 2. This phenomenon agrees with the 5.3 h it theoretically takes a non-reactive or sorbing chemical in the chamber to reach 95 % of a steady state value after a perturbation based on the measured chamber air change rate (3/air change rate).

In contrast to the monoterpenes, the signal for $C_6H_9O_2^+$ (tentatively identified as sorbic acid) increased during times of ozonation (Figure S-6). This could be due to terpene reactions with oxidants that can produce weak organic acids [42], such as sorbic acid.

Formaldehyde is an end product of ozonolysis of terpenes [43]. The concentration of formaldehyde increased during ozone injections. When ozone concentrations increased (blue trace, Fig. 4), the concentration of formaldehyde (orange trace) went up as well. The increase in formaldehyde concentration was between 1 ppb_v (1.2 μg m^{-3}) and 1.5 ppb_v (1.9 μg m^{-3}) for days with ozone injections. This increase is an indication that reactions between ozone and precursors (e.g., monoterpenes) are occurring and eventually resulting in formaldehyde formation. To see specific times of ozonation, refer to Figure S-7.

On Day 2, the formaldehyde concentration increased 1.2 ppb_v (1.5 μg m^{-3}) over the time frame ozone was injected. At the end of the ozone injection the monoterpene concentration was 4.2 ppb_v (5.2 μg m^{-3}) below the projected concentration if no ozone was present. This projected concentration was determined by fitting a line for the data with no impact from ozone (black lines) shown for December 20th and December 21st in Fig. 2 and subtracting the actual concentration at the end of the ozone injection (where red and green lines meet) from fit value at the same point in time. This results in a 28 % formaldehyde molar yield assuming all the formaldehyde increase when ozone is injected is from ozonolysis of the mixture of monoterpenes. Lee et al. [43] determined molar formaldehyde ozonolysis yields for individual terpenes in a Teflon chamber ranged from 3.5 % to 76 %, with 28 % for α-pinene.

Data from the Day 2 ozone injection can also be used to estimate a formaldehyde production rate from ozonolysis of tree emissions. During this time period the average ozone concentration was 14 ppb_v (28 μg m^{-3}) and the monoterpene concentrations decreased from 15 ppb_v to 12 ppb_v (84 μg m^{-3} to 66 μg m^{-3}). Assuming the entire increase in formaldehyde concentration on Day 2 (1.2 ppb_v, 1.5 μg m^{-3}, over the time frame of ozone injection) is due to ozonolysis, the production rate for formaldehyde is 27 μg h^{-1}. Since formaldehyde concentrations in the ventilation air were not measured, primary emissions of formaldehyde cannot be directly determined. However, the formaldehyde concentration in the chamber increased from 0.5 ppb_v (0.6 μg m^{-3}) the day before the tree was placed in the chamber to 3.1 ppb_v (3.9 μg m^{-3}) when the tree was present prior to the ozone being injected on Day 2. This 2.6 ppb_v (3.2 μg m^{-3}) increase in formaldehyde concentration when the tree was placed in the chamber is the maximum concentration increase due to initial primary emissions for this tree (the researcher setting up the tree in the stand could have contributed to this value). For context, typical indoor formaldehyde concentrations in 105 new

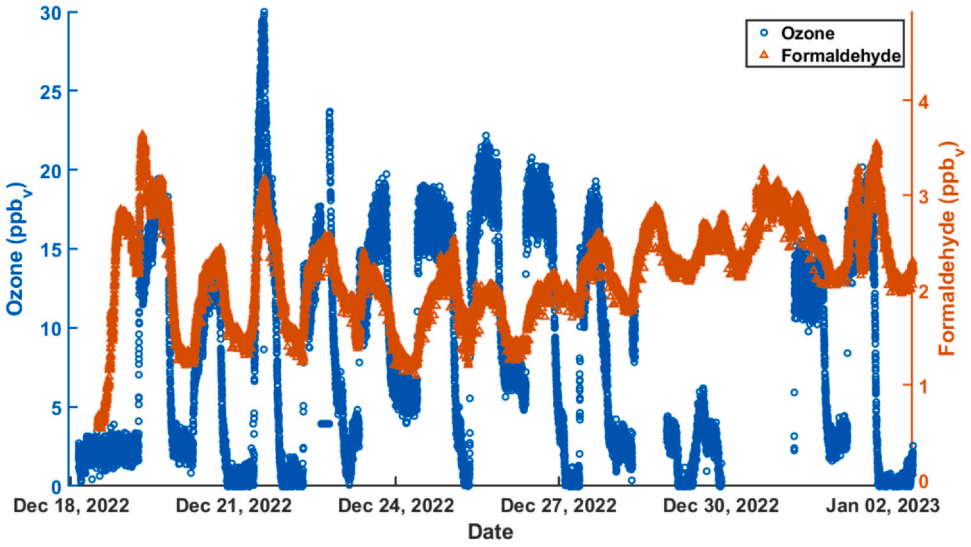

Fig. 4. Ozone (left, blue) and formaldehyde concentrations during the experiment. (1 ppb_v ozone = 1.98 mg m^{-3}, 1 ppb_v formaldehyde = 1.2 µg m^{-3}). The data missing on the 31st of December is due to an unexpected error with the monitor.

homes which on average had air change rates of one half of this study (0.26 h^{-1} compared to 0.57 h^{-1} here) is 29 ppb_v (36 µg m^{-3}) [44].

3.4. Future work

To the best of the authors' knowledge, this research is the first to quantify emissions from an indoor Christmas tree. The quantification of monoterpene emission rates and ozone chemistry allow readers to relatively place Christmas tree emissions among other indoor sources influencing indoor chemistry. However, this experiment was exploratory in nature and future investigations could address questions resulting from this research.

The sample size of one tree helped us understand emissions from conifers, but it is not holistic. Future work should investigate a greater number of trees, species or trees in different life-stages. Forthcoming studies should be designed to quantify tree ozone loss independent of ventilation and chamber wall losses. Future efforts could confirm the presence of specific chemicals with neat standards and link emissions from dying Christmas trees to outdoor trees in stressed environments. In addition, different analytical techniques could target chemicals like pesticides and chemicals that are not captured in the sorbent trap or do not make it through the GC column used in this study. Future efforts should take more frequent GC measurements to determine how the composition of emission profiles of common ions (e.g., $C_{10}H_{17}^+$) change over time. Finally, this novel experimental approach of placing of plants in a large chamber could be used to investigate emissions of other plants indoors.

4. Conclusions

A freshly cut Christmas tree can release comparable amounts of monoterpenes as personal care products, air fresheners, or other household goods over the first two to three days after being cut. Although the emission rate from monoterpenes reached over 12 mg h^{-1}, the monoterpene concentration observed at the beginning of the experiment decayed quickly, dropping to one third of the peak value within 24 h. We observed, and tentatively identified, four other chemicals that were likely either co-emitted with monoterpenes or oxidation products of terpene ozonolysis. Monoterpene concentrations were reduced in the presence of ozone, while formaldehyde concentrations increased, indicating indoor chemistry occurs in the presence of ozone and a Christmas tree. Overall, we conclude that when a live Christmas tree is placed indoors it will emit monoterpenes at levels similar to other common indoor sources and likely have modest impacts on indoor chemistry that diminish with time.

CRediT authorship contribution statement

Poppendieck Dustin: Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. **Robertson Rileigh:** Data curation, Writing – original draft, Writing – review & editing. **Link Michael F:** Data curation, Formal analysis, Methodology, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indenv.2023.100002.

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