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Analysis of Atmospheric Sesquiterpenes: Sampling Losses and Mitigation of Ozone Interferences

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Atmospheric standards containing parts-per-billion levels of 14 semivolatile hydrocarbon compounds, including eight sesquiterpenes (SQTs) (longipinene, α-copaene, isolongifolene, α-cedrene, *trans*-caryophyllene, aromadendrene, α-humulene, δ-cadinene), two oxidized sesquiterpenoids (*cis*-nerolidol, *trans*-nerolidol), one biogenic ketone (geranylacetone) and three aromatic compounds (1,3,5-triisopropylbenzene, diphenylmethane, nonylbenzene), were collected onto four solid adsorbent materials at increasing ozone mixing ratios (0−100 ppbv O_3) for analysis by thermodesorption−gas chromatography. Substantial sampling losses of up to >90% were found for the most reactive SQT, even at the lowest ozone level investigated of 20 ppbv. Loss rates from the ozone−SQT reaction were used to derive estimates of gas-phase ozone reaction rate constants for longipinene, α-copaene, isolongifolene, geranylacetone, aromadendrene, δ-cadinene, *cis*-nerolidol, and *trans*-nerolidol. Three different ozone mitigation techniques were investigated to prevent these sampling losses. These strategies included (a) placing glass fiber filters impregnated with sodium thiosulfate ($Na_2S_2O_3$) into the sampling line, (b) titration of ozone in the sampling stream with nitric oxide (NO), and (c) catalytically removing ozone with a commercially available manganese dioxide (MnO_2) catalyst. All three techniques reduced ozone-mixing ratios from 100 ppbv to <0.6 ppbv at sampling flow rates of 1 L min^{-1}. When the $Na_2S_2O_3$ filters and the NO-titration techniques were applied, SQT loss rates decreased from 25−60% to 0−5% for most SQT compounds and from >90% to ∼10−50% for the two most reactive compounds at ozone mixing ratios of up to 100 ppbv. The commercial manganese dioxide scrubber, however, caused complete analyte losses (>98%) even at 0 ppbv ozone. These results underline the need and present applicable techniques for removal of ozone in air samples for SQT analysis by solid adsorption techniques.

Introduction

Sesquiterpene (SQT) hydrocarbons ($C_{15}H_{24}$) as well as their oxygenated derivatives, e.g. alcohols, aldehydes, and ketones ($C_{15}H_{22}O$, $C_{15}H_{24}O$, $C_{15}H_{26}O$) have been found in biogenic volatile organic compound (BVOC) emissions from both natural and agricultural vegetation (*1*−*19*). Some studies estimate that SQT may contribute up to 16% of the overall BVOC landscape flux in certain areas (*11*, *13*). However, quantitative SQT flux data are difficult to obtain and remain highly uncertain due to analytical constraints that stem from the low volatility and high reactivity of SQT compounds (*20*−*23*).

Atmospheric oxidation of SQT occurs both by ozonolysis and by reaction with the OH and NO_3 radicals. Reaction rate constants vary widely among different SQT. SQT atmospheric lifetimes from reaction with ambient oxidants are expected to be short. For instance, a reported SQT-ozone lifetime estimate for α-humulene is ∼1 min (*24*). Considering all three oxidation pathways, daytime/nighttime lifetime estimates are ∼1−2 min for *trans*-caryophyllene and α-humulene, ∼2 min/2 h for α-copaene, ∼4 min/2 h for α-cedrene, and 50 min/4 h for longifolene (*22*). Interestingly, one of the most common and most thoroughly investigated SQT, *trans*-caryophyllene, is also one of the most reactive compounds.

The oxidation products of *trans*-caryophyllene were found to reside almost completely in the aerosol phase (*23*), and SQTs are suspected to play an important role in biogenic aerosol formation. Gas-phase oxidation products of *trans*-caryophyllene that have been identified include 3,3-dimethyl-γ-methylene-2-(3-oxobutyl)cyclobutanebutanal, 3,3-dimethyl-γ-oxo-2-(3-oxobutyl)cyclobutanebutanal and formaldehyde (*25*). Reactions of sesquiterpenoid compounds (nerolidol, farnesol) common in epicuticular waxes of Mediterranean plants (*Quercus ilex*, *Citrus sinensis*, *Quercus suber*, *Quercus freinetto*, *Pinus pinea*) at ozone mixing ratios of 50−100 ppbv yielded significant emissions of geranylacetone, 6-methyl-5-hepten-2-one, 4-oxopentanal, and acetone (*26*). Tobacco plants (*Nicotiana tabacum*) show strong SQT-emissions after being exposed to elevated ozone levels (120−170 ppbv) (*27*).

Several studies have addressed the analytical problems arising from interactions between unsaturated terpenoid compounds and ozone during sampling procedures. Calogirou et al. (*28*) found that saturated terpenoid compounds (1,8-cineole, camphor, and bornyl acetate) showed no losses due to ozone, while unsaturated compounds with one double bond (e.g.: camphene, α-pinene, sabinene) showed moderate loss rates (5−35%). Compounds with two or more double bonds (e.g., β-*trans*-ocimene, α-terpinene, *trans*-caryophyllene) showed very strong depletion (80−100%) at ozone mixing ratios of 120 ppbv on Tenax TA cartridges. Larsen et al. (*29*) compared results from 10 European laboratories that analyzed the same monoterpene standard. The sampling was performed at various ozone levels (8, 65, and 125 ppbv). The results were usually accurate and precise at 8 ppbv ozone. However, under elevated ozone conditions (65 and 125 ppbv) significant losses (up to 100% for some compounds) were found. Laboratories utilizing ozone mitigation techniques reported much higher recovery rates and improved accuracy. SQT loss rates reported by Hoffmann (*24*) during solid adsorption sampling without ozone mitigation at 23 ppbv ozone were as follows: longicyclene: ∼0%; γ-muurolene: ∼20%; α-copaene: ∼40%; γ-cadinene: ∼55%; isocaryophyllene: ∼75%; *cis*-α-bergamotene: ∼85%; *trans*-caryophyllene, α-humulene, and α-cubebene: >95%.

The effect of ozone on the integrity of the adsorbent material has to be considered as well. Cao and Hewitt (*30*) investigated degradation of several adsorbent materials (Tenax TA, Tenax GR, Carbotrap, and Chromosorb 106) during passive sampling at 180 ppbv ozone over 1 week. No

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artifact formation was found for Carbotrap and Chromosorb 106, whereas for Tenax TA and Tenax GR oxidation products such as benzaldehyde, phenol, and acetophenone were identified. Similar observations have been made by others (*31*, *32*). In another study on the sampling effects of oxidant-containing air on Tenax TA adsorbent, several degradation products were identified from the reaction with nitrogen dioxide and ozone, but none for reaction with nitric oxide (*33*).

Conclusively, these studies have shown that many BVOC (especially SQTs) are rapidly depleted at elevated ozone concentrations. Consequently, ozone mitigation techniques are required during BVOC sampling. Several techniques for selective ozone removal have previously been applied to reduce these sampling losses. A review of ozone mitigation techniques was presented by Helmig (*34*). Further research, with particular focus on how to minimize sampling losses of biogenic compounds, has been published subsequently (*35*−*37*).

Three promising ozone mitigation methods that have been extensively used in the past were further investigated in this research with emphasis on SQT analysis. These include (a) the application of sodium thiosulfate-impregnated filters, (b) titration of ozone with nitric oxide, and (c) catalytic removal of ozone with manganese dioxide-coated screens. In the first method, the sample flow is directed through a glass-fiber filter impregnated with sodium thiosulfate. Details of this method are discussed by Lehmpuhl and Birks (*38*). This technique has been applied successfully in some studies on light biogenic hydrocarbons such as isoprene and monoterpenes (*39*, *40*). Fick et al. (*36*) showed that 200 mg of crystalline $Na_2S_2O_3$ removed all ozone in 10 L of air at 73−78 ppbv ozone. Helmig et al. (*40*) used $Na_2S_2O_3$-impregnated filters and reported a quantitative ozone removal capacity in 1000 l of air at background ozone mixing ratios (<25 ppbv).

Nitric oxide (NO) is oxidized by ozone with the first-order rate constant of k (298 K, 101.3 hPa) = 1.8×10^{-14} cm^3 molecule^{-1} s^{-1}. Mochida et al. (*41*) analyzed this technique in an extensive modeling study with a regional atmospheric chemistry model (RACM) developed by Stockwell et al. (*42*). According to these calculations, ozone mixing ratios will be reduced by a factor of 100 within ∼1.5 s when the NO concentration is 100 times higher than the ozone concentration. Besides removing ozone, titration with NO can also reduce concentrations of other atmospheric oxidants, such as OH and NO_3. NO titration was utilized by Sirju and Shepson (*43*) in the analysis of aldehydes by the DNPH [(dinitrophenyl)hydrazine] technique. Kuster et al. (*44*) experienced unacceptable chromatographic interferences in non-methane hydrocarbon analysis while applying this technique. Karst et al. (*45*) reported interferences in the determination of aldehyde-DNPH derivatives from nitrogen dioxide, one of the products formed in the NO + ozone reaction. Wedel et al. (*46*) applied this technique to remove ozone prior to the preconcentration step in measurements of volatile organic compounds. The recovery rate for α-cedrene increased from 0% to 72% (at 100 ppbv O_3) when 1 ppmv of NO was added. Komenda et al. (*47*) applied the NO titration technique using a 1 ppmv NO mixing ratio for quantifying isoprene and its oxidation products in ambient air.

MnO_2 destroys ozone catalytically. Hoffmann et al. (*24*, *48*) used MnO_2-coated nets taken from an ozone analyzer to remove ozone prior to monoterpene and SQT trapping on solid adsorbents and found improved recoveries at 23 ppbv ozone. Jüttner (*49*) experienced dramatically higher recoveries for monoterpenes (2−32 times higher) by applying this type of ozone scrubber. Calogirou et al. (*28*) designed and evaluated a scrubber that was made from MnO_2-coated copper screens. Monoterpene losses were prevented for all but the most reactive compounds during sampling at elevated ozone mixing ratios (60 ppbv). Recovery rates for *trans*-caryophyllene under the same conditions improved from 4% to 36%. Janson and Kristenson (*50*) reported monoterpene losses of up to 30% to the scrubber during sampling of ambient air. In all these studies the scrubbers were optimized for ozone removal at very specific face velocities.

Experimental Section

Analytical Techniques. The equipment, procedures, and analytical techniques employed have been described in detail previously (*51*, *52*) and are therefore only summarized here. SQT standards generated with a capillary diffusion system were used for the analytical experiments. The standard contains eight SQTs (longipinene, α-copaene, isolongifolene, α-cedrene, *trans*-caryophyllene, aromadendrene, α-humulene, and δ-cadinene), three aromatic compounds (1,3,5-triisopropylbenzene, diphenylmethane, and nonylbenzene), one biogenic ketone (geranylacetone) and four oxygenated SQTs (*cis*-nerolidol, *trans*-nerolidol, cedrol, and caryophyllene oxide (the later two compounds were not included in the analysis of these experiments)) in nitrogen. The chemical structures of the biogenic analytes can be found in the Supporting Information to this paper and in ref *51*. The aromatic compounds were included because of their low reactivity with ozone. The concurrent analysis of these aromatic compounds was expected to provide ways for monitoring instrument performance and to yield further insight into analyte versus adsorbent effects.

The output from the CDS was diluted by adding zero air, which could be enriched with ozone. Samples were collected on solid adsorbent cartridges with a custom-made autosampler (*52*). The four solid adsorbents used (Tenax TA, Tenax GR; Carbotrap, Carbotrap C, from Alltech, Deerfield, IL, and Supelco, Bellefonte, PA, respectively) have previously been found suitable in SQT analysis and were further investigated in this study to determine sampling interferences from ozone. An extensive review of the physical properties and analytical performances of these adsorbents was given by Dettmer and Engewald (*53*). Loaded adsorbent cartridges were thermally desorbed and quantified by GC-FID using a Perkin-Elmer-ATD-400 automated thermodesorption system interfaced to a PE Autosystem XL gas chromatograph (Perkin-Elmer, Boston, MA). The following ATD-400 parameters were used (experiments were conducted at ∼860 hPa, all reported volumes were corrected to standard conditions): He purge flow, 37 mL min^{-1}; primary desorption temperature, 300 °C; primary desorption time, 10 min; second stage trap temperature during primary desorption, −30 °C; second stage trap desorption temperature, 350 °C; hold time, 5 min. The second stage trap was filled with Unibeads (Alltech, Deerfield, IL). The ATD-400 outlet split flow during the second stage desorption was 7.7 mL min^{-1}. Other GC parameters were as follows: FID hydrogen, 45 mL min^{-1}; FID air, 350 mL min^{-1}; He carrier gas flow, 2.5 mL min^{-1}; GC oven program, 40 °C for 5 min, 20 °C min^{-1} to 100 °C, 2 °C min^{-1} to 160 °C, 40 °C min^{-1} to 250 °C, final time 5 min. The column was a DB-1, 0.32 mm i.d. × 30 m length with a 0.25 μm film thickness (J. & W. Scientific, Palo Alto, CA).

Ozone Generator. The dilution air was enriched with ozone to reach ozone mixing ratios between 5 and 150 ppbv with an UV ozone generator (Model OG-2, UVP, Upland, CA).

Ozone Analyzers. Ozone in the sample flow was recorded using two instruments. High ozone mixing ratios were quantified with a Monitor Labs ozone analyzer (Model 8810, Monitor Labs Inc., San Diego, CA). This analyzer has a 1 ppbv precision and a detection limit of approximately 2 ppbv. Ozone mixing ratios below 2 ppbv were measured with an

ozone−ethene chemiluminescence instrument (Model 8410, Monitor Labs). The detection limit of this instrument is ~0.2 ppbv.

Sodium Thiosulfate-Impregnated Ozone Filters. The ozone filters were prepared by flowing 10 mL of a 10% [w/w] aqueous solution of $Na_2S_2O_3$ through 25 mm diameter glass-fiber filter disks (1 μm pore size, polypropylene housing, product number 4523, Glass Acrodisk, Gelman Laboratory, Ann Arbor, MI) and subsequent drying under a nitrogen purge flow of 85 mL min^{-1} at 50 °C for 4 h. These filters were tested at 100 ppbv ozone and 255 mL min^{-1} flow rate. Several filters can be operated in series. One filter reduced the ozone mixing ratio to ~0.4 ppbv, while two and three filters in series reduced ozone mixing ratios to ~0.2 ppbv under these conditions.

Ozone Removal by NO Titration. The ozone mixing ratio in the sampling stream using the NO technique can be calculated by

$$[O_3] = [O_3]_0 e^{-kt[NO]} \quad (1)$$

Approximately 2 mL min^{-1} of a ~ 1% mixture of NO (Airgas, Loveland, CO) in nitrogen was added to the diluted standard flow, resulting in an NO mixing ratio of ~10 ppmv. The NO flow rate was controlled by the regulator pressure and by a 0.1 mm i.d. deactivated fused silica capillary flow restrictor. After the mixing of the two gas flows, the sample air was flown through Teflon tubing (length, 3 m; i.d., 0.4 cm) prior to the solid adsorbent trapping. Under these flow conditions, the Reynolds number was calculated to be 4300, which is clearly in the turbulent regime, allowing adequate mixing. This resulted in a residence time of ~1.5 s in the tubing and ensured enough time for the ozone + NO reaction to take place. According to eq 1, the expected ozone concentration by the time the sample reaches the adsorbent cartridge will be approximately 0.1% of the initial mixing ratio. At an initial ozone mixing ratio of 100 ppbv, the measured ozone at the outlet was below the 0.2 ppbv detection limit of the chemiluminescence instrument. In another study (*46*), NO addition resulting in a lower mixing ratio of 1 ppmv destroyed 90% of ambient ozone within a residence time of 8 s. Similar NO mixing ratios were also used by Komenda et al. (*47*).

Ozone Removal by a Manganese Dioxide Catalyst. In several previous studies, custom-made and carefully optimized manganese dioxide catalysts were used as ozone scrubbers (*24*, *25*, *28*). Here, we investigated whether a commercially available catalyst would be suitable for ozone removal in SQT quantification. The scrubber was a manganese dioxide catalyst canister (diameter, 9.5 cm; length, 4.5 cm) (O.B.E. Corp., Fredericksberg, TX) which contained 25 MnO_2-coated copper screens in a steel canister. This catalyst is normally used to provide an ozone-free reference gas in UV ozone analyzers. This scrubber reduced ozone mixing ratios from 100 ppbv to 0.6 ppbv at a flow rate of 300 mL min^{-1}.

Results and Discussion

SQT Losses in the Presence of Ozone. SQT sampling losses from reaction with ozone were investigated by loading cartridges of the four adsorbents with 1.6 L of standard sample air. The CDS output was diluted by a factor of 90, resulting in individual BVOC mixing ratios of 0.84 ppbv (*cis*-nerolidol), 0.91 ppbv (*trans*-nerolidol), 1.17 ppbv (δ-cadinene), 2.78 ppbv (α-humulene), 3.52 ppbv (α-copaene), 3.70 ppbv (α-cedrene), 3.73 ppbv (aromadendrene), 5.86 ppbv (isolongifolene), 6.25 ppbv (geranylacetone), 6.79 ppbv (longipinene), and 11.28 ppbv (*trans*-caryophyllene). These concentrations are somewhat higher (~10−100×) than typical BVOC concentrations in forest air but within the range of BVOC concentrations in branch or leaf enclosure experiments. Cartridges were loaded at a sampling flow rate of 160 mL min^{-1}. Ozone mixing ratios in the sampling stream were set to 0, 20 40, 60, 80, 100 ppbv (±2 ppbv at all levels). Two replicate cartridges were sampled under each condition. After this series another pair of samples was collected at 0 ppbv ozone to test the reproducibility of the initial conditions.

Analytes were quantified on the basis of their FID area counts and effective carbon numbers (*51*). The first cartridge of each series was loaded at an ozone mixing ratio of 0 ppbv and was used as the reference (100% value). Recovery rates for all compounds are listed in Table 1 of the Supporting Information. The bargraph results for the SQTs shown in Figure 1 reemphasize that ozone indeed severely affects recoveries. Significant SQT losses were observed for almost all compounds on all adsorbents. Loss rates varied widely, e.g., from approximately 2% (isolongifolene) to 90% (*trans*-caryophyllene, α-humulene) even at the lowest ozone level (20 ppbv) tested. At 100 ppbv ozone, the range of observed losses was from 10% (isolongifolene) to 100% (*trans*-caryophyllene, α-humulene). The aromatic compounds were stable with respect to ozone and had recoveries between 90 and 100% at all ozone mixing ratios. The adsorbent type had only a small impact on the SQT loss rate. The carbon based adsorbents Carbotrap and Carbotrap C displayed qualitatively similar behavior. The loss rates on Tenax TA appeared to be slightly lower than those observed on Carbotrap and Carbotrap C. SQT on Tenax GR generally showed 20% higher recovery rates than on the other adsorbents at elevated ozone levels.

SQT losses were related to the chemical structure of the respective compound. Compounds with only one double bond (i.e., all compounds except δ-cadinene, *trans*-caryophyllene and α-humulene) were depleted by up to 75% due to reaction with ozone. δ-Cadinene and *trans*-caryophyllene (two double bonds) as well as α-humulene (three double bonds) were more severely depleted and could not be recovered at 100 ppbv ozone mixing ratio. The observed loss rates appeared to correlate well with previously published atmospheric ozone reaction rate constants, i.e., *trans*-caryophyllene ~ α-humulene > α-copaene > α-cedrene [Hoffmann (*24*); Shu and Atkinson (*22*)]. Oxygenated SQTs experienced substantial losses and could only be recovered at the lowest ozone mixing ratios.

No apparent SQT oxidation reaction products were identified in the chromatograms. However, the analytical setup was not optimized for detecting either possible volatile ozone−SQT reaction products (such as acetone or formaldehyde as described in ref *23*) or oxygenated, heavier molecular weight products. Adsorbent degradation products, as identified previously by others (*33*), were not found in our measurements either.

As mentioned above, ozone did not affect the aromatic compounds, which demonstrates the stability of these molecules towards reaction with ozone. This observation proves that the SQT losses were due to SQT−ozone reactions and were not related to an ozone-induced degradation of the adsorbent material.

Estimates of SQT−Ozone Reaction Rate Constants. Gas-phase reaction rate constants (k) for the reaction of five SQTs with ozone were taken from the literature (*22*). Four of these compounds were also included in this study. Their published ozone reaction rate constants are (in 10^{-17} cm^3 $molecule^{-1}$ s^{-1}): α-cedrene (2.78), α-copaene (15.8), *trans*-caryophyllene (1160), and α-humulene (1170). A linear correlation was found when ln k was plotted vs the mean of the observed loss rates on the four adsorbents (see the previous section). This analysis was performed for the 20, 40, 60, 80, and 100 ppbv ozone experiments. These correlations were then used to estimate SQT−ozone reaction rate constants for the remain-

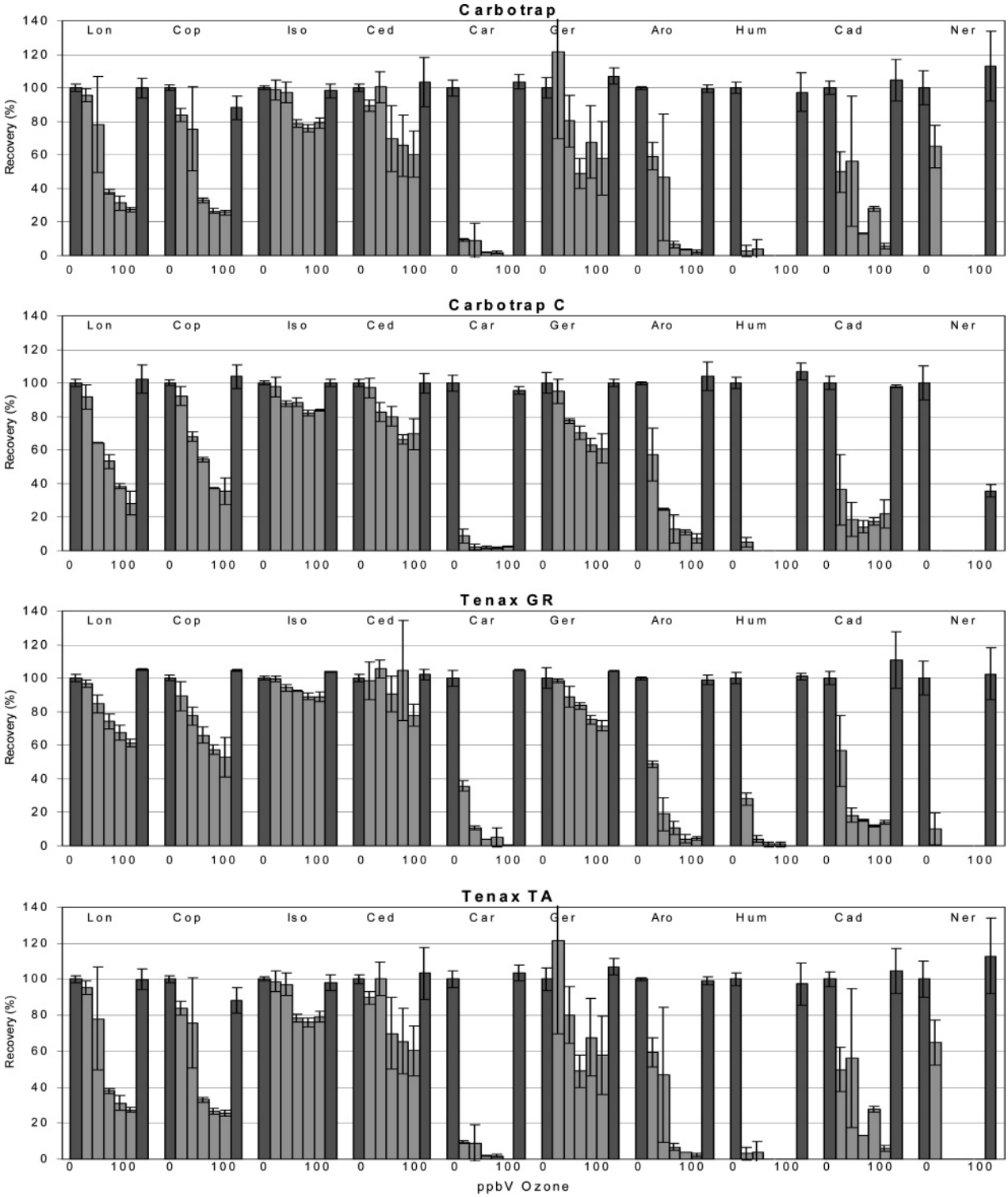

FIGURE 1. SQT recovery vs ozone concentration (0, 20, 40, 60, 80, 100, 0 ppbv) for 10 investigated BVOCs (from left to right in order of GC retention time). Abbreviations are as follows: Lon, longipinene; Cop, α-copaene; Iso, isolongifolene; Ced, α-cedrene; Car, *trans*-caryophyllene; Ger, geranylacetone; Aro, aromadendrene; Hum, α-humulene; Cad, δ-cadinene; Ner, nerolidol (average of the cis and trans isomer). Error bars represent the relative standard deviation over two experiments. Dark gray columns indicate experiments without the addition of ozone; light gray columns indicate runs with added ozone.

ing SQT compounds. The derived mean rate constants (with standard deviation) are listed in Table 1.

These rate constants rely on the data given by Shu and Atkinson (*22*), who reported relative uncertainties of ~50%. Furthermore, given the rather indirect approach of our analysis, the derived reaction rate constants should be regarded as rather approximate values. To the best of our knowledge, these are the first reaction rate estimates provided for these seven compounds with respect to ozone.

Sampling Flow Rate Effects. Experiments were performed at different sampling flow rates (keeping the sample volume constant) to determine if the SQT losses were occurring in the gas phase or on the adsorbent bed. Sample volumes of 1.6 L were collected at 100 ppbv ozone and at sampling flow

TABLE 1. Mean and Standard Deviation of SQT–Ozone Reaction Rate Constants That Were Estimated from Loss Rates on Four Adsorbents at 20, 40, 60, 80, and 100 ppbv, Respectively[a]

compound	reaction rate constant, 10^{-17} cm^3 molecule^{-1} s^{-1}
isolongifolene	2.6 ± 0.7
α-*cedrene*	*3.4 ± 0.2*
geranylacetone	7.6 ± 3.9
α-*copaene*	*29 ± 9*
longipinene	29 ± 11
γ-cadinene	320 ± 67
aromadendrene	650 ± 240
trans-caryophyllene	*1100 ± 51*
α-*humulene*	*1400 ± 88*
cis-nerolidol	3100 ± 2200
trans-nerolidol	2300 ± 1800

[a] Literature values (in 10^{-17} cm^3 molecule^{-1} s^{-1}) for α-cedrene (2.78), α-copaene (15.8), *trans*-caryophyllene (1160), and α-humulene (1170) were used to derive a correlation between observed sampling loss rates and reaction rate constants. The reaction rate constants that were obtained for these reference compounds from the correlation analysis are also included (in italics) in this table.

rates of 160, 120, 80, and 40 mL min^{-1} over 10 min, 13.3, 20, and 40 min, respectively. The estimated residence times in the sampling apparatus for the different flow rates are ~ 5 s (160 mL min^{-1} sampling), ~7 s, ~10 s, and ~20 s, respectively. At the highest flow rate (160 mL min^{-1}) and 100 ppbv of ozone, a maximum gas-phase depletion of 10% was calculated for the most reactive compounds (α-humulene and *trans*-caryophyllene) according to their literature reaction rate constants (*22*). Considering that the SQT mixing ratios for these compounds were approximately 2 ppbv (α-humulene) and 10 ppbv (*trans*-caryophyllene) and assuming that a 1:1 stoichiometric reaction between the SQT and ozone would occur, the maximum reduction of the ozone concentration from its gas-phase reaction with SQT was expected to be small (<2% at the highest flow rate and up to 10% at the lowest). However, it was possible that SQT oxidation products could further react with ozone which would decrease the ozone further than this estimate. Since the other compounds were either less concentrated or had significantly lower reaction rate constants, their contribution to a further decrease in the ozone mixing ratio was expected to be minor. Consequently, it was concluded that most of the ozone remained in the sampling air during the adsorption step. The time that the analytes were exposed to ozone in the gas phase increased by a factor of 4 as the sampling flow rates decreased from 160 to 40 mL min^{-1}. If the majority of SQT losses from ozone reaction would occur in the gas-phase, increased loss rates should be observed at the lower flow rates. The recovery rates for the different sample flows were calculated relative to experiments at 0 ppbv ozone and 160 mL min^{-1} sampling flow. Results for longipinene, a SQT that shows a moderate loss at 100 ppbv, were expected to yield a sensitive analysis of this effect. No significant differences (Figure 2) were seen for longipinene or any other less reactive SQT in this experiment. The most reactive compounds (α-humulene and *trans*-caryophyllene) were completely removed at all sampling flow rates at 100 ppbv ozone. This conclusion agrees with previous observations (*28*), which showed that monoterpenes similarly were lost due to ozone reactions on the adsorbent bed.

Sodium Thiosulfate Filter Technique. Two adsorbent cartridges were loaded initially without an ozone filter in the sampling stream at 0 ppbv ozone. The FID area counts of this analysis were used as a reference for the calculation of recovery rates. Cartridges were then loaded with the filter in the sampling stream at 0, 20, 40, 60, 80, and 100 ppbv ozone

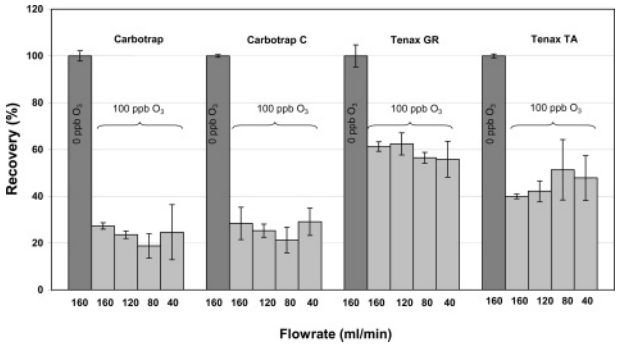

FIGURE 2. Recovery rates (n = 2) for longipinene at different sampling flows (same sampling volume) on four different adsorbents compared to a reference sample collected at 160 mL min^{-1} in the absence of ozone.

mixing ratios. The 0 ppbv ozone/filter sample was collected to investigate possible SQT losses to the filter materials. After these experiments, the filter was removed and two cartridges were loaded again without the filter at 0 ppbv ozone, replicating the initial experiment. Tabulated data for all compounds can be found in Table 2 of the Supporting Information; Figure 3 shows graphically the recoveries of the SQTs at the various ozone mixing ratios.

One $Na_2S_2O_3$-impregnated filter reduced ozone in the sampling air to approximately 0.4% of the initial value. The filter did not cause any significant SQT loss for the nonoxidized analytes and did not introduce any contamination peaks. Heavier, oxidized compounds (such as *cis*- and *trans*-nerolidol) were lost to the filter by approximately 50–65%. SQT losses due to ozone reaction were significantly reduced compared to the experiments without any ozone mitigation. SQT with one double bond (e.g., isolongifolene or longipinene) were quantitatively retrieved up to the highest ozone mixing ratio tested (100 ppbv). However, *trans*-caryophyllene and α-humulene still showed loss rates of 40–50% at 100 ppbv ozone on the different adsorbents. Results for the four studied adsorbents were quite similar.

These observations agree with earlier reports, where $Na_2S_2O_3$-impregnated filters were successfully used in monoterpene and light hydrocarbon analysis (*36*, *39*, *40*). Our results now expand on these results and demonstrate that $Na_2S_2O_3$-impregnated filters can also be utilized for sampling heavier molecular weight compounds such as SQT. However, compounds with higher polarity and lower vapor pressure than SQT (such as the oxygenated SQT) do suffer significant losses to this type of filter.

Experiments with Increasing Numbers of $Na_2S_2O_3$-Impregnated Filters. A significant reduction in SQT losses, though not a complete prevention of all analyte losses, was found for the most reactive SQT with one $Na_2S_2O_3$-impregnated filter in the sampling stream. Therefore, we investigated if several filters in series would yield a further improvement. A single $Na_2S_2O_3$-filter reduces the ozone mixing ratio from an initial value of 100 ppbv to ~0.4 ppbv. Several filters in series result in a further scrubbing of ozone (remaining ozone levels were <0.2 ppbv). However, this improvement may possibly be offset, especially for the heavier compounds, by higher adsorption losses to the filter material. One, two, and three sodium thiosulfate-impregnated filters were placed into the sampling stream at 100 ppbv ozone. The recovery rates for each experiment were compared to conditions at 0 ppbv ozone without any filters added. The average recovery rates for one selected SQT with high losses from ozone, i.e., α-humulene on four adsorbents, are displayed in Figure 4.

No additional absorption losses were observed for the non-oxygenated SQT in the two- and three-filter experiments.

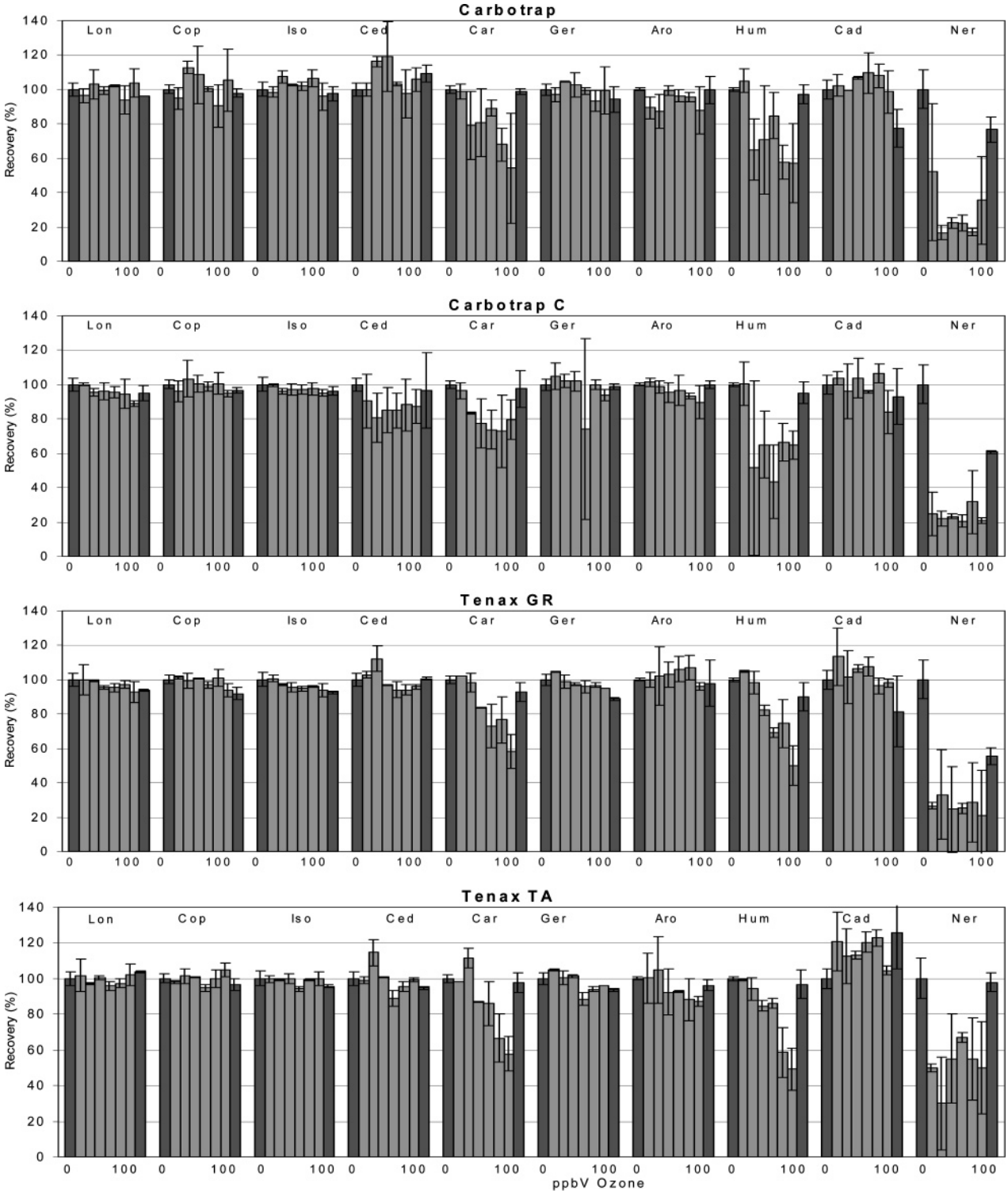

FIGURE 3. Recovery rates ($n = 2$) with a sodium thiosulfate-impregnated filter in the sampling stream in reference to samples without the filter at 0 ppbv ozone for 10 investigated BVOCs at 0, 0, 20, 40, 60, 80, 100, and 0 ppbv ozone. Abbreviations are the same as in Figure 1. Dark gray bars indicate runs without ozone added and no mitigation techniques applied; light gray bars indicate experiments at ozone mixing ratios from 0 to 100 ppbv with the filter in the sampling stream.

SQT loss rates from ozone reactions decreased slightly, but not substantially (~10% for α-humulene). However, the oxygenated compounds were almost completely lost to the additional filters. Similar to the findings reported above, no significant differences for the individual adsorbent materials were seen.

NO-Titration Technique. Two initial samples were taken (without NO added) at 0 ppbv ozone. The results of this analysis were used as a reference for the calculation of recovery rates. Cartridges were then loaded with 2 mL min^{-1} of 1% NO in N_2 added to the sampling stream at 0, 20, 40, 60, 80, and 100 ppbv ozone. After these experiments, the NO flow was turned off and two cartridges were loaded again without NO added at 0 ppbv O_3. All results are listed in Table 3 of the Supporting Information; bar graph results for SQTs are displayed in Figure 5.

Titration of ozone with NO did prevent most, but not all, of the SQT ozone sampling losses. However, it is apparent,

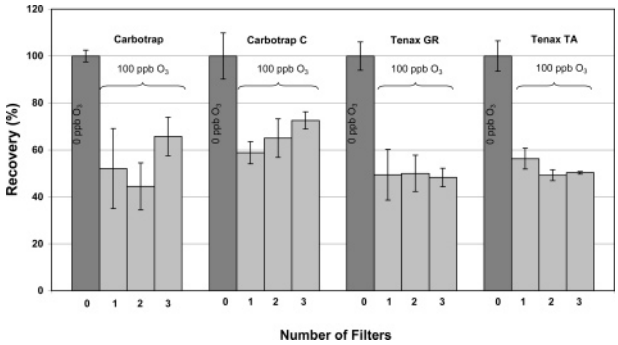

FIGURE 4. Recovery rates ($n = 2$) for α-humulene using an increasing number of sodium thiosulfate filters at 100 ppbv ozone in reference to measurements without the filter at 0 ppbv ozone.

that NO itself did cause analyte losses for some of the SQTs. On all four adsorbents loss rates of 5−45% were observed for *trans*-caryophyllene and α-humulene with NO added in the absence of ozone. Therefore, these losses have to be attributed to an interference stemming from NO in the sampling air. Recovery rates remained constant with increasing ozone concentrations. Results on the carbon-based adsorbents (Carbotrap and Carbotrap C) were somewhat better than for the Tenax-type adsorbents. No physical changes/degradation of the adsorbent materials or chromatographic interferences were observed in these experiments.

Manganese Dioxide Scrubber. The scrubber was placed into the sampling stream in the same location as the sodium thiosulfate filters. Almost complete removal of all analytes (>98%; see Figure 2 of the Supporting Information for a comparison of chromatograms) was observed when using this scrubber. A second, identical scrubber was tested to study if this result was reproducible. Results for the second scrubber agreed with the first observation. Since previous studies (*51*) have shown that SQT losses to walls of tubing and other internal surfaces can be overcome by heating these components, another experiment was performed with one of the scrubbers placed in a GC oven at 100 °C during sampling. Again, all analytes were lost under this condition. Higher temperatures than 100 °C were not investigated because of the temperature limit of the scrubber housing. Since all analytes were lost in these experiments, no numerical data for this experiment are given. Our findings agree with some earlier reports, where high loss rates for *trans*-caryophyllene (64%) were observed on a custom-made MnO_2 scrubber (*28*). The low cost and long lifetimes of commercially available manganese dioxide scrubbers make their use attractive. However, under our experimental conditions, they do not appear suitable for this application. These findings infer that, if manganese dioxide scrubbers are to be used as an ozone mitigation technique for VOC sampling, the total surface area that the analytes are exposed to, the sampling flow rate, and the residence time of analytes in the scrubber container need to be carefully investigated and optimized.

Implications for Research on Sesquiterpene Flux Studies

These experiments reemphasize the need of ozone management during the sampling of SQTs in air that contains even low ppbv levels of ozone. The degree of SQT analyte loss and its gas-phase reactivity towards ozone correlates with the number of double bonds in the SQT molecule. Highly unsaturated compounds (two or three double bonds) suffer the highest depletion rates. In contrast, aromatic compounds that were included in these experiments were inert toward ozone and did not experience sampling losses.

Substantial losses of SQTs were observed at even the lowest ozone levels tested (20 ppbv ozone), which is well within the range of expected ambient ozone concentrations. It is striking that *trans*-caryophyllene and α-humulene, two of the most common and most thoroughly investigated SQTs, were the two analytes that experienced the highest sampling losses among the compounds investigated and hence can be considered as two analytes that are the most difficult to analyze in ambient air.

Two out of three investigated ozone mitigation techniques were found to successfully remove ozone and to yield substantial improvements on all four of the adsorbents tested. The $Na_2S_2O_3$ filter and the NO titration techniques were equally effective in reducing ozone levels to concentrations required to quantify most SQTs reliably. However, for the NO titration technique, it is necessary to correct for eventual losses of SQT compounds due to reaction with NO. The commercial MnO_2 ozone scrubbers tested in these experiments were unsuitable for the sampling of SQTs and other organic compounds in the same volatility range.

We found that sodium thiosulfate-impregnated filters are the preferred method for field work due to their small size, ease of preparation, and low cost. Since these filters have a limited capacity for removing ozone, it is important to either replace them regularly or to monitor their effectiveness with an ozone monitor.

Nitric oxide titration is a more elaborate ozone mitigation technique. Nitric oxide is extremely toxic, and stringent safety procedures have to be followed for transport and storage of pressurized gas cylinders containing NO. Pure NO is difficult to acquire and this method is significantly more expensive than using sodium thiosulfate-impregnated filters. However, a 10 L volume gas cylinder filled with a 1% mixture of NO in N_2 at 100 psi will last much longer in a continuous application than a single sodium thiosulate filter. With this type of cylinder, it is possible to remove ozone from at least 50 m^3 of ambient air. For long-term, automated SQT sampling, NO titration may therefore be a preferred technique.

Substantial residual losses of *trans*-caryophyllene and α-humulene occurred even though it appeared that ozone levels were reduced well below the 1 ppbv level with these two techniques. These losses were significant enough to prohibit an accurate quantification of these compounds in the presence of ozone. These experiments reemphasize that an accurate quantification of reactive SQTs such as *trans*-caryophyllene and α-humulene in ambient air may not be feasible with adsorbent sampling techniques. These limitations particularly apply to flux measurements of these compounds by gradient or eddy accumulation techniques (with solid adsorbent sampling) where highly precise concentration measurements are needed to determine the difference in concentrations between updraft and downdraft samples or at different heights above the surface from a sampling tower. Laboratory SQT studies have shown that certain materials in the sampling stream require temperatures on the order of 150 °C to prevent adsorption losses and that long equilibration times are necessary for these components to reach steady state (*51*). These effects constitute another limitation for ambient eddy accumulation flux measurements, where a fast separation of updraft and downdraft air samples is needed and loss of temporal resolution of rapid concentration changes within sampling lines cannot be tolerated.

These observations further imply that atmospheric SQT probably will have high deposition losses to environmental substrates. Many SQT have short atmospheric lifetimes (minutes), which will result in low ambient mixing ratios, even close to their biogenic sources. Above-canopy flux measurements will likely underestimate flux estimates derived from leaf or branch level emission rate measurements because of losses occurring within the canopy. Conclusively,

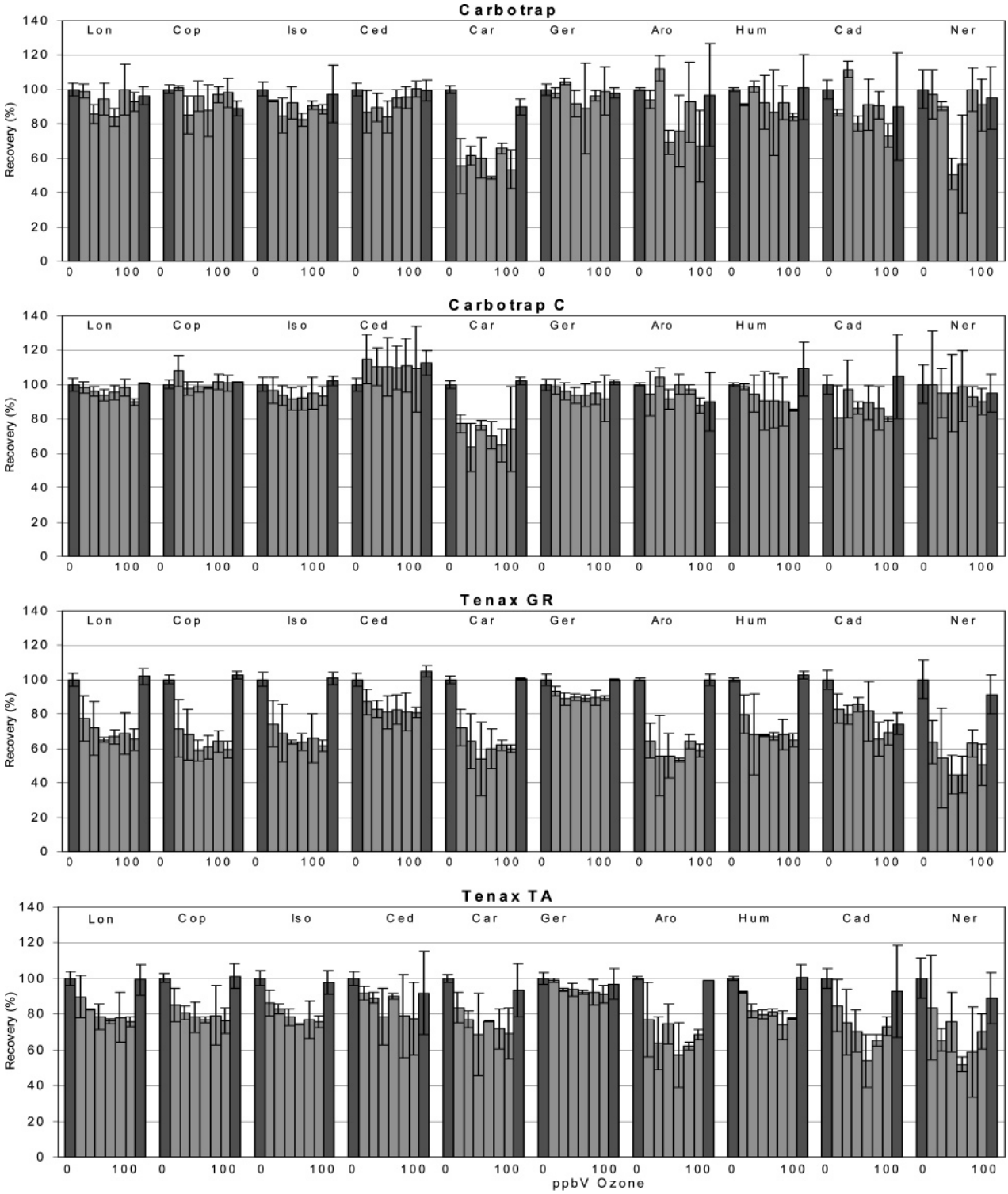

FIGURE 5. Recovery rates ($n = 2$) with NO added to the sampling stream in reference to samples with NO added at 0 ppbv ozone for 10 investigated BVOCs at 0, 0, 20, 40, 60, 80, 100, 0 ppbv ozone. Abbreviations are the same as in Figure 1. Dark gray bars indicate runs without ozone added and no mitigation techniques applied; light gray bars indicate experiments at ozone mixing ratios from 0 to 100 ppbv with 2 mL min^{-1} of 1% NO in nitrogen added to the sampling stream.

these effects pose severe limitations on ambient scale SQT flux measurements with currently available technology.

Vegetation enclosure experiments appear to be the best approach to estimate SQT emission rates. The experiments presented here emphasize the need to conduct enclosure experiments in an ozone-free environment. For these experiments, we recommend the following procedures when sampling on solid adsorbents:

(a) Use of either synthetic air or ozone-scrubbed air for the enclosure purge air so that BVOC emissions from the foliage are not exposed to ozone.

(b) Maintaining short residence times (~2−4 min) within the enclosure is necessary so that overheating is minimized. Typically under such conditions BVOC concentrations build up to high enough levels (1−10 ppbv) to obtain an adequate signal for BVOC emission rate quantification.

(c) Monitoring of ozone in the enclosure system to address the concerns listed above.

(d) Use of either NO titration or sodium thiosulfate-impregnated glass-fiber filters in the sampling flow prior to trapping analytes on the adsorbent materials.

By adhering to these procedures, analyte losses due to ozone reaction are minimized and the ability to quantitatively estimate emission rates and to infer SQT landscape fluxes is greatly improved.

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Supporting Information Available

Recovery rates for SQT, related compounds, and three aromatic compounds at varying ozone mixing ratios on four adsorbents without application of mitigation techniques, recovery rates at increasing ozone mixing ratios on four adsorbents using the $Na_2S_2O_3$-impregnated filter technique, recovery rates at increasing ozone mixing ratios on four adsorbents materials using the NO-titration technique, and chemical structures of investigated SQTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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