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Indoor Chemistry: Ozone, Volatile Organic Compounds, and Carpets

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■ Volatile organic compounds (VOCs) have been measured in a freshly carpeted 20-m³ stainless-steel room in both the absence and presence of ozone (ozone concentrations ranging from 30 to 50 ppb, with one experiment conducted at 400 ppb). Four different types of carpeting were exposed, and in each set of experiments, the room was ventilated at 1 air exchange/h. The gas-phase concentrations of selected carpet emissions (e.g., 4-phenylcyclohexene, 4-vinylcyclohexene, and styrene) significantly decreased in the presence of ozone. Conversely, the concentrations of other compounds (e.g., formaldehyde, acetaldehyde, and aldehydes with between 5 and 10 carbons) significantly increased. Furthermore, the total concentration of VOCs increased markedly in the presence of ozone. The additional VOCs appear to have been generated by reactions between ozone and relatively nonvolatile compounds associated with the carpets. These studies suggest that VOCs measured within a building at elevated ozone levels (>30 ppb) may differ from those measured at lower ozone levels (<10 ppb).

Introduction

Ozone is a very powerful oxidizing agent. Outdoors, it plays an important role in the chemistry of the atmosphere. Ozone reacts rapidly with certain classes of organics, especially those that contain unsaturated carbon-carbon bonds (3). In addition to gas-phase reactions, ozone also participates in heterogeneous reactions (e.g., ozone and rubber), often generating a series of volatile oxidation products.

Indoor ozone concentrations can be a significant fraction of those outdoors (refs 1 and 2, and references therein). Indoor-outdoor ratios for ozone depend on both the air exchange rate and the rate at which ozone is removed by indoor surfaces. At 2 air changes/h (ach), indoor ozone levels are typically 35% of outdoor levels. In locations with severe photochemical smog, indoor ozone often exceeds 50 ppb.

Carpets are a recognized source of indoor VOCs (4-7). Some of these compounds come from the carpet pile, but most come from the backing and backing adhesive. Carpets tend to have large surface areas and, hence, the potential to significantly impact indoor air quality. 4-Phenylcyclohexene (4-PCH, the predominant source of the "new carpet" odor), styrene (residual monomer), and 4-ethenylcyclohexene (4-VCH) each come from the styrene-butadiene rubber (SBR) latex adhesive, which is commonly used to bind the secondary backing of carpets. 2,6-Di-*tert*-butyl-4-methylphenol (BHT, an antioxidant) is added to certain types of carpets to preserve the secondary backing material. Ozone is known to or would be predicted to react quickly with each of these species.

In the present study, we examined reactions between ozone and new carpets covering the floor of a 20-m³ stainless-steel room. We also examined reactions between the carpets and a mixture of ozone and nitrogen dioxide. The latter experiments were intended to test the possibility that NO₃, produced as a consequence of O₃/NO₂ chemistry,

might affect VOC levels. With the exception of the initial experiment, the concentrations employed are representative of those which can be attained indoors.

Experimental Section

Environmental Chamber. The environmental chamber was a 20-m³ stainless-steel room with interior dimensions of 3.65 m (l) × 2.44 m (w) × 2.23 m (h). The materials used throughout the construction of the chamber were selected, in part, for their low emissions of VOCs. The chamber was equipped with a single-pass ventilation system. Inlet air was drawn from outside through a filter assembly (Model ECO Glide Pack, Farr Co.) containing a 30% particulate filter, 12 charcoal filters, and a high-efficiency particulate air (HEPA) filter, in series. The air entered the chamber through an inlet positioned high at one end of a long wall. The air exhaust was positioned low at the opposite end of the wall. The operating parameters for the environmental chamber were highly reproducible from experiment to experiment. The ventilation rate varied between 0.98 and 1.00 ach and the temperature varied between 22.8 and 23.5 °C for the five experiments (four carpets plus a chamber blank). These parameters were very stable throughout the 10-day-long measurement periods with relative standard deviations of only 1%. The relative humidity varied from 45 to 55%. Six small, variable-speed fans were positioned along the walls and were adjusted to produce an average velocity 5 cm above the floor of ~9 cm/s.

Carpets. The four new carpets investigated were typical of the types of carpets used in residences, school classrooms, and offices (7). Each is described in Table I. Three had all Nylon fibers, while carpet 4 had a combination of olefinic and Nylon fibers. The fibers were woven onto polypropylene primary backing in all cases. The secondary backings varied among the carpets. Carpets 1 and 4 had a coarse polypropylene mesh bonded to the primary backing with SBR latex adhesive. Carpet 3 had a secondary backing of poly(vinyl chloride) and was intended to be glued directly to a floor. Each carpet was packaged in double heat-sealed Tedlar bags shortly after manufacturing and remained so until the initiation of its chamber experiment.

Gases. O₃ was generated by passing ultrahigh-purity oxygen through an arc generator. NO₂ was from a pre-treated aluminum cylinder (Scott Specialty Gases) containing 496 ppm NO₂ in N₂. This mixture was further diluted with N₂ to yield a steady-state chamber concentration of 50 ppb. All flows and dilutions were regulated using electronic mass-flow controllers. O₃ was introduced into the chamber through the air inlet; NO₂ was introduced through a separate inlet on the opposite side of the chamber.

Analytical Measurements. O₃ concentrations were measured with a UV photometric ozone analyzer (Dasibi Model 1003 AH). The air was sampled at a rate of 2 L/min using Teflon tubing. Performance checks were

Table I. Descriptions of the Four Carpets Exposed to Ozone in the Environmental Chamber

parameter	carpet 1	carpet 2	carpet 3	carpet 4
construction	cut pile	cut pile	textured loop	textured loop
fiber	100% Nylon	100% Nylon	100% Nylon	75% olefin, 25% Nylon
dye method	piece	beck	solution	solution
fiber treatments	static control	not specified	Scotchguard and antimicrobial	not specified
secondary backing	polypropylene	polyurethane	poly(vinyl chloride)	polypropylene
backing adhesive	SBR latex	not specified	not specified	SBR latex
form	roll	roll	tiles	roll

conducted before each chamber experiment.

All samples for individual VOCs and total VOC (TVOC) were collected on multisorbent samplers (Part No. ST032, Envirochem, Inc.) packed with Tenax-TA, Carboxen carbon molecular sieve, and activated charcoal, in series. Replicate samples were collected from the chamber periodically throughout an experiment. The samples were drawn from the midpoint of the chamber through a stainless-steel sampling line connected to a manifold located outside the chamber. The typical sampling volume was 10 L collected over 1 h.

The analytical procedures for VOCs have been previously described (8). Briefly, a sample was thermally desorbed, concentrated, and introduced into a gas chromatograph (GC) with a Unacon 810A (Envirochem, Inc.) sample concentrating and inletting system. The GC was equipped with a 30 m \times 0.25 mm i.d. \times 1.0 μ m film capillary column, and the oven temperature was ramped over a range of 1–225 °C. The GC was connected via a direct capillary interface to a Hewlett-Packard 5970B mass selective detector, which was operated to scan a mass range of m/z 33–250. An internal standard, consisting of ~50 ng of 1-bromo-4-fluorobenzene, was added to samples immediately prior to their analysis. Authentic standards were used for both compound identification and calibrations. The analytical precision for individual compounds in replicate samples was typically 10% or better.

During the thermal desorption procedure, approximately 8% of each VOC sample was automatically split off and analyzed directly (without GC separation) by a flame ionization detector that is built into the Unacon system. This produced a measure of total carbon for compounds with boiling points between those of approximately C₃–C₁₄ hydrocarbons. The analysis was calibrated with a mixture of C₆–C₁₂ normal alkanes, and the results were expressed as mass of carbon. This method underestimates the mass of carbon in oxidized compounds (such as aldehydes).

Samples for formaldehyde and acetaldehyde were collected from the sampling manifold on C₁₈ Sep-Pak cartridges impregnated with an acid solution of 2,4-dinitrophenylhydrazine. Sample volumes were 180 L collected over 3 h. These samples were analyzed by high-performance liquid chromatography using a UV detector (9).

Experimental Protocol. On the day an experiment began, a carpet sample was placed over the floor of the chamber, producing a typical loading ratio of 0.44 m²/m³. Closing the chamber door established time “zero”. For the next 7 days the chamber was sampled for VOCs, TVOC, and aldehydes. After sampling on the seventh day (168 h), the ozone generator was turned on and the concentration of ozone in the chamber monitored. Ozone levels reached steady-state values within 10 h. Roughly 24 h after the ozone had been introduced into the chamber, three multisorbent samples (for VOCs and TVOCs) and a single aldehyde sample were collected. The ozone generator was then turned off; within 3 h the ozone levels were close to zero. Twenty-four hours after turning off the ozone, another set of samples was collected. Immediately following

Table II. Concentrations (ppb) of O₃ and Selected Reactants and Products during Chamber Study of Carpet 1

compound	concentrations ^a		
	prior to O ₃ ; 167 h	O ₃ present; 194 h	O ₃ absent; 217 h
O ₃	0	409	0
4-VCH	0.07	ND ^b	ND
styrene	0.35	ND	0.21
4-PCH	3.1	0.14	2.5
formaldehyde	NS ^c	NS	NS
acetaldehyde	NS	NS	NS
aldehydes			
C ₅	ND	1.6	0.28
C ₆	ND	4.6	0.51
C ₇	ND	6.6	1.0
C ₈	ND	2.9	0.55
C ₉	ND	4.8	2.2
C ₁₀	ND	0.44	0.14
TVOC (μ g of C/m ³)	22	84	32

^a At selected times after the new carpet was placed in the chamber. ^b ND, not detected. ^c NS, not sampled.

this sampling, in the experiments involving carpets 2–4, the ozone generator was turned back on. At the same time, nitrogen dioxide was introduced into the chamber to produce a steady-state NO₂ concentration of 50 ppb. Twenty-four hours later a final set of samples was collected in the presence of the mixture of ozone and nitrogen dioxide.

Results

Each new carpet was in the environmental chamber for 7 days prior to ozone exposure. During this 7-day period, the VOCs emitted from the carpets were monitored as part of a comprehensive study of emission rates (7). In addition to the four carpet experiments, there was a control experiment in which ozone was introduced into the environmental chamber with no carpet present. These experiments are presented in chronological order (which does not follow the numbering of the carpets).

Carpet 1. A relatively high steady-state ozone concentration (409 ppb) was used in this initial experiment, since the magnitude of potential effects was unknown. The results are summarized in Table II. Twenty-seven hours after ozone was introduced into the chamber (194 h after the start of the experiment), a set of samples was collected. The changes were substantial. The concentration of 4-PCH decreased from 3.1 ppb just prior to the introduction of ozone (167 h) to 0.14 ppb (194 h). In a similar fashion, the concentrations of 4-VCH and styrene were sharply reduced. On the other hand, a number of compounds were present which had not been previously detected. Dominant among these were linear aldehydes with from 5 to 10 carbons and concentrations ranging from 0.44 to 6.6 ppb (see Figure 1; in what follows, these compounds are designated C₅–C₁₀ aldehydes). The net effect on the TVOC level was an increase from 22 to 84 μ g of C/m³. (As noted, the TVOC measurement underestimates the mass of car-

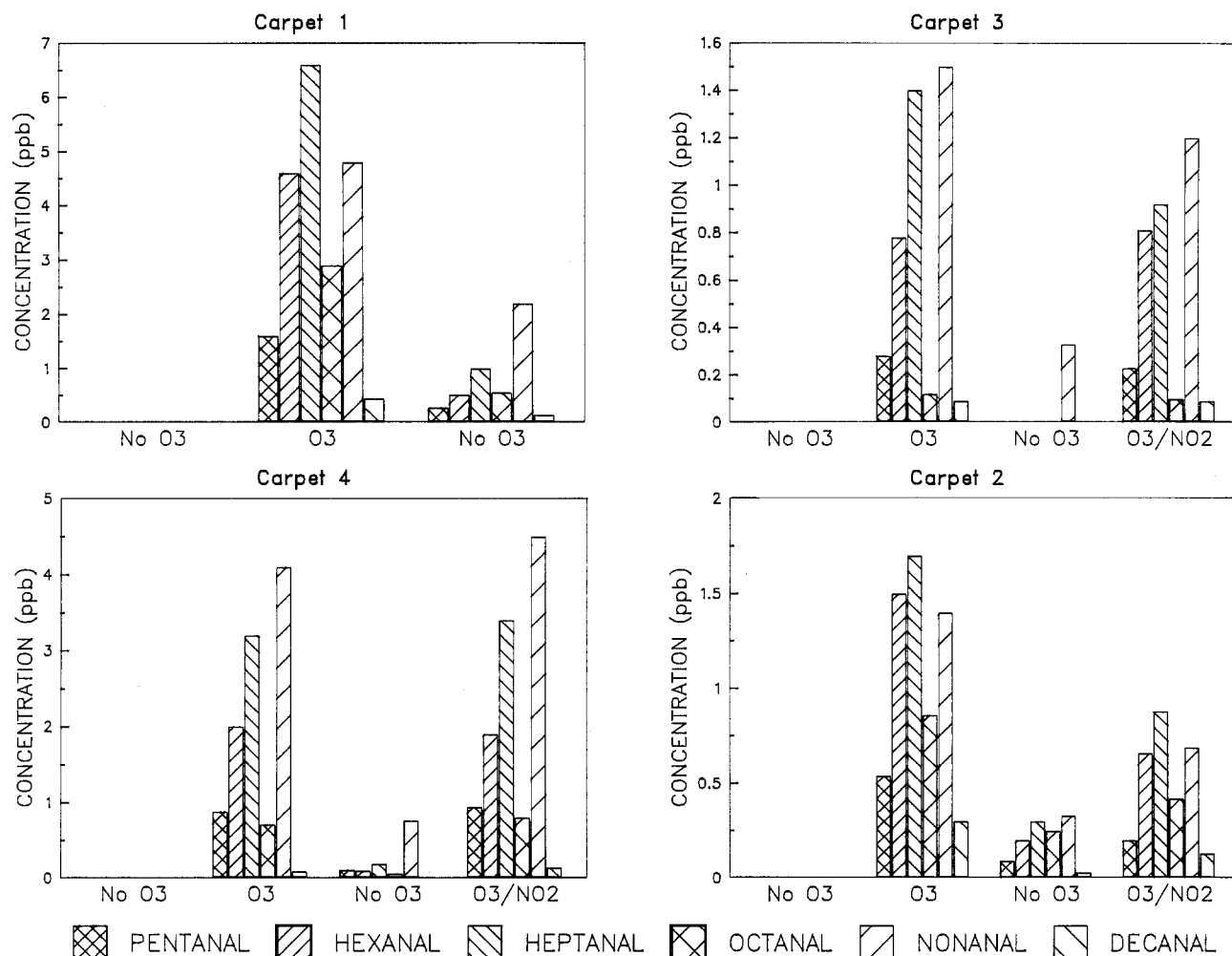


Figure 1. Aldehydes measured on successive days in the absence and presence of ozone (or ozone and 50 ppb nitrogen dioxide) for each of the carpet experiments. Note that prior to the initial ozone exposure, none of these aldehydes had been detected in any of the carpet experiments: carpet 1, 409 ppb O_3 ; carpet 3, 35 ppb O_3 ; carpet 4, 28 ppb O_3 ; carpet 2, 44 ppb O_3 .

bon present in oxidized compounds such as aldehydes. Therefore, the latter value should be considered a lower limit.) Following the sampling at 194 h, the ozone generator was turned off. Three hours later, the ozone concentration within the chamber was <2 ppb. After an additional 20 h, a final set of samples was collected (217 h). The concentrations of 4-PCH, 4-VCH, and styrene had increased to expected levels [i.e., levels consistent with the diminishing emission rates of these VOCs with time (7)], while the TVOC level decreased. Furthermore, the C_5 – C_{10} aldehydes decreased to low but still detectable levels.

Carpet 3. The steady-state concentration of ozone used in this second experiment (37–38 ppb) was 1 order of magnitude lower than that used in the initial experiment and was a level that is frequently exceeded indoors (1). However, even at this much lower ozone concentration, the effect on the VOCs was apparent (Table III). The concentration of BHT decreased from 0.67 (168 h, pre-ozone) to <0.06 ppb in the presence of ozone (197 h). With ozone present, the C_5 – C_{10} aldehydes were easily detected (see Figure 1), and the TVOC level had not decreased as much as would be expected on the basis of its rate of decay during the previous week (7). In this experiment, formaldehyde and acetaldehyde were also measured before, during, and after ozone exposures. The concentrations of both formaldehyde and acetaldehyde increased when ozone was present and then decreased when ozone was absent (221 h). Twenty-six hours after the ozone generator had been turned off, it was once again turned on, and nitrogen

Table III. Concentrations (ppb) of O_3 and Selected Reactants and Products during Chamber Study of Carpet 3

compound	concentrations ^a			
	prior to O_3 ; 168 h	O_3 present; 197 h	O_3 absent; 221 h	$O_3 + NO_2$ present; 247 h
O_3	0	37	0	38
vinyl acetate	9.9	6.3	5.7	4.8
BHT	0.67	<0.06	0.56	<0.06
formaldehyde	6.3	8.1	4.6	NS ^b
acetaldehyde	1.1	4.6	0.67	NS
aldehydes				
C_5	ND ^c	0.28	ND	0.23
C_6	ND	0.78	ND	0.81
C_7	ND	1.4	ND	0.92
C_8	ND	0.12	ND	0.1
C_9	ND	1.5	0.33	1.2
C_{10}	ND	0.09	ND	0.09
TVOC (μg of C/ m^3)	66	62	35	63

^a At selected times after the new carpet was placed in the chamber. ^b NS, not sampled. ^c ND, not detected.

dioxide was also introduced (50 ppb). The concentrations of VOCs measured in the presence of a mixture of ozone and nitrogen dioxide (247 h) are quite similar to those observed in the presence of ozone alone.

Carpet 4. Table IV lists the VOC and TVOC concentrations measured for carpet 4 under varying ozone scenarios. The steady-state ozone concentration in this ex-

Table IV. Concentrations (ppb) of O₃ and Selected Reactants and Products during Chamber Study of Carpet 4

compound	concentrations ^a			
	prior to O ₃ ; 168 h	O ₃ present; 197 h	O ₃ absent; 223 h	O ₃ + NO ₂ present; 245 h
O ₃	0	28	0	32
4-VCH	0.27	0.16	0.23	0.09
styrene	1.6	0.78	1.2	0.61
4-PCH	3.9	1.5	3.3	1.3
formaldehyde	0.98	2.8	1.1	2.4
acetaldehyde	0.2	3.3	0.2	3.6
aldehydes				
C ₅	ND ^b	0.88	0.11	0.94
C ₆	ND	2.0	0.10	1.9
C ₇	ND	3.2	0.19	3.4
C ₈	ND	0.71	0.06	0.80
C ₉	ND	4.1	0.76	4.5
C ₁₀	ND	0.09	ND	0.14
TVOC (μg of C/m ³)	41	56	28	70

^a At selected times after the new carpet was placed in the chamber. ^b ND, not detected.

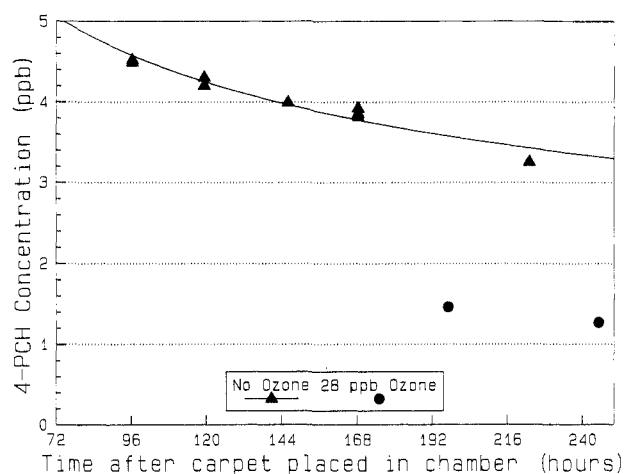


Figure 2. 4-PCH concentrations in the 20-m³ chamber from 74 to 245 h after carpet 4 was placed in the chamber. The concentrations at 197 and 245 h, when ozone was present, were significantly smaller than expected from the progressive reduction in the emission rate of 4-PCH.

periment was only 28–32 ppb. Similar to carpet 1, carpet 4 emitted significant levels of 4-PCH. In this case, 4-PCH dropped from 3.9 (pre-ozone) to 1.5 ppb in the presence of ozone. Figure 2 contrasts the actual levels of 4-PCH measured at 28 (or 32) ppb ozone with those expected at 197 and 245 h if no ozone were present. Similar decreases were observed for 4-VCH and styrene. With ozone present, the concentration of formaldehyde increased by roughly a factor of three, while that of acetaldehyde increased by 1 order of magnitude. Furthermore, the C₅–C₁₀ aldehydes were produced in measurable quantities, with the concentration of nonanal reaching 4.1 ppb. When ozone was absent (223 h), the concentrations decreased, moving toward pre-ozone values. When ozone and nitrogen dioxide were present together (245 h), the concentrations were similar to those measured in the presence of ozone alone (197 h). The TVOC concentrations were higher in the presence of ozone than in its absence.

Carpet 2. Table V summarizes results from the experiment with carpet 2. Even after 169 h, carpet 2 remained a strong source of BHT, with a chamber concentration of 8.2 ppb. In the presence of ozone (44 ppb) this level dropped to 1.2 ppb and then increased to 7.8 ppb when the ozone generator was turned off. The observations

Table V. Concentrations (ppb) of O₃ and Selected Reactants and Products during Chamber Study of Carpet 2

compound	concentrations ^a			
	prior to O ₃ ; 169 h	O ₃ present; 197 h	O ₃ absent; 221 h	O ₃ + NO ₂ present; 245 h
O ₃	0	44	0	53
BHT	8.2	1.2	7.8	1.0
formaldehyde	0.5	1.3	0.5	NS ^b
acetaldehyde	ND ^c	1.4	ND	NS
aldehydes				
C ₅	ND	0.54	0.09	0.20
C ₆	ND	1.5	0.20	0.66
C ₇	ND	1.7	0.30	0.88
C ₈	ND	0.86	0.25	0.42
C ₉	ND	1.4	0.33	0.69
C ₁₀	ND	0.30	0.03	0.13
TVOC (μg of C/m ³)	14	30	10	9.1

^a At selected times after the new carpet was placed in the chamber. ^b NS, not sampled. ^c ND, not detected.

pertaining to the aldehyde concentrations are similar to those reported for the other carpets, especially carpet 3 (Table III), which was also a source of BHT. The TVOC level increased in the presence of ozone (197 h) and decreased in the absence of ozone (221 h). The final TVOC reading (245 h) is not as high as expected, but given the uncertainty in the TVOC measurements, this discrepancy may not be significant.

Artifacts: Catalyst and Chamber Blank Experiments. Chamber air was drawn through three multisorbent samplers for each set of VOC/TVOC measurements. Two of these samples were duplicates. The third was collected with an ozone-destroying catalyst positioned upstream of the multisorbent sampler; hence, no ozone reached the sorbents. (The catalyst consisted of copper screens treated with a proprietary solution, Dasibi Part Z-0284-S, and reduced O₃ to O₂.) This sample was useful to distinguish between ozone reactions that occurred in the chamber and ozone reactions that may have occurred on the surface of the sorbent or with the sorbent itself. Analyses of the multisorbent samplers that had been downstream of ozone-destroying catalysts indicated that the reactions were not occurring within the multisorbent samplers. In the carpet experiments, when ozone was present, the C₅–C₁₀ aldehydes were still detected and the concentrations of compounds with unsaturated carbon-carbon bonds still decreased. (The samplers with the ozone-destroying catalysts were not used for quantitative analyses, since compounds with relatively low vapor pressures, such as 4-PCH, BHT, nonanal, etc., were partially adsorbed on the catalyst's surface.)

Sets of samples were collected from an empty chamber (no carpeting on the floor) with and without ozone present. The background concentrations with no ozone present were quite low (7). In the presence of 106 ppb ozone (24-h exposure), the background concentrations were again low and showed negligible production of C₅–C₁₀ aldehydes. Hence these aldehydes were not generated by the reaction of ozone with chamber materials. Furthermore, these experiments demonstrated that the C₅–C₁₀ aldehydes were not produced when ozone (106 ppb) was drawn through the multisorbent samplers.

Small-Chamber Carpet Pile and Backing Studies. A set of experiments with carpet 1, designed to identify sources of various VOCs, were conducted using small-volume 4-L chambers ventilated at 6.3 ach (7). Fibers were cut from the backing of carpet 1, and separate chamber experiments were performed with the fibers and the

backing. In both experiments, sampling and ozone exposure were conducted in an analogous fashion. The initial samples (0–0.5 and 0.5–1.5 h) were collected in the absence of ozone. Ozone was then introduced (600 ppb) and the final set of samples collected. Styrene, 4-VCH, and 4-PCH were emitted primarily from the carpet backing as opposed to the fibers, although this distinction was less pronounced for 4-PCH. With ozone present, the C₅–C₁₀ aldehydes were ~4 times more abundant in the chamber with the fibers compared to the chamber with the backing. Conversely, in the presence of ozone, benzaldehyde, benzoic acid, and acetophenone attained much higher concentrations in the chamber containing the backing than in that containing the fibers. These latter compounds are expected products of the reaction between ozone and styrene. They were also observed in the 20-m³ chamber experiments when carpets 1 and 4 were exposed to ozone, but were not quantified.

Discussion

Reactions among Ozone and VOCs. Atkinson and Carter (3) reviewed the kinetics and mechanisms of the gas-phase reactions of ozone with vapor-phase organic compounds under atmospheric conditions. The fastest reactions tend to be those with compounds containing unsaturated carbon–carbon bonds. The results presented in Tables II–V are consistent with the reported kinetics. With the exception of BHT, the VOCs that display a marked reduction in concentration in the presence of ozone are those that contain unsaturated carbon–carbon bonds (4-phenylcyclohexene, styrene, and 4-ethenylcyclohexene). Other VOCs (e.g., saturated alkylbenzenes and saturated alkanes) displayed no *unexpected* concentration decreases in the presence of ozone. However, not all compounds with unsaturated carbon–carbon bonds show a marked decrease in concentration. In the case of carpet 3 (Table III), the concentration of vinyl acetate was relatively unaffected by the presence of ozone. (The decrease in concentration shown in Table III is that expected from the decreasing emission rate of vinyl acetate measured in the initial 168 h of the chamber experiment.) Therefore, it appears that the rates at which ozone reacts with 4-PCH, 4-VCH, and styrene are significantly faster than the rate at which it reacts with vinyl acetate. Although a rate constant for the reaction of ozone with vinyl acetate has not been reported, the rate constants for the reaction of ozone with methacrolein [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$], vinyl fluoride, and vinyl chloride are at least 1 order of magnitude smaller than that with styrene (3).

Under steady-state conditions and in the presence of ozone, the concentration of a reactive VOC can be compared to its expected concentration if ozone were not present (e.g., Figure 2). Knowing the air exchange rate and the projected emission rate, one can then calculate a pseudo-first-order rate constant for the reaction between ozone and the VOC. Dividing this pseudo-first-order rate constant by the ozone concentration yields a second-order rate constant which can be compared with published values. Applying this procedure to 4-PCH emitted by carpet 1 (409 ppb ozone) yields a second-order rate constant of $5.2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction between ozone and 4-PCH at 23 °C. For the experiment with carpet 4 (28 ppb ozone), the calculated second-order rate constant for 4-PCH and ozone is $5.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is excellent agreement given that the ozone concentrations in these two experiments differed by a factor of 15. These values can be compared to a reported value of $1.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction between ozone and cyclohexene (3). The larger value for 4-PCH is consistent with the electron-donating properties

of the phenyl group, although this effect is expected to be tempered by the phenyl group's distance from the unsaturated bond.

Similar calculations were performed for styrene (carpet 4). The derived second-order rate constant for the reaction between styrene and ozone is $3.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is significantly larger than the reported value of $2.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (3). The larger value derived from the carpet experiment may indicate that styrene reacted with ozone on the surface of the carpet as well as in the gas phase or that ozone influenced the rate at which styrene was emitted from the carpet. On the other hand, this difference may simply reflect the limitation of the method at low styrene concentrations; in the presence of ozone, styrene levels were close to the estimated quantitation limit.

Butylated hydroxytoluene is an antioxidant commonly used to stabilize olefin-derived addition polymers. It inhibits autooxidation by serving as a labile hydrogen donor. In this manner, BHT effectively interrupts chain-propagating steps in the free-radical, chain mechanisms responsible for the oxidative degradation of many polymers (10). It performs a sacrificial role and yields, as a byproduct, a relatively unreactive, resonance-stabilized radical. In the chamber experiments involving carpets 2 and 3, ozone may have reacted directly with BHT. Alternatively, peroxy radicals generated from the reaction of ozone with VOCs, in turn, may have reacted with BHT. The relative contribution of these pathways is uncertain.

Both formaldehyde and acetaldehyde are common products of the reaction of ozone with unsaturated VOCs. Hence, the increases in their concentrations in the presence of ozone are expected. In each case, the increase in concentration was greater for acetaldehyde than for formaldehyde. This suggests that a major precursor was a compound with a double bond in the 2-position. Other potential products include organic acids. However, organic acids would not be detected using the analytical procedures employed in this investigation.

Sources of C₅–C₁₀ Aldehydes. The homologous series of C₅–C₁₀ aldehydes is not a logical consequence of the reaction of ozone with 4-PCH, 4-VCH, styrene, or BHT. Furthermore, in the presence of ozone, all four carpets are a source of the C₅–C₁₀ aldehydes, yet carpets 1 and 4 emit unsaturated VOCs that are quite different from those emitted by carpets 2 and 3. The sum of individual VOCs is higher when ozone is present than when it is absent. This observation is supported by the TVOC measurements (using FID), which increase in the presence of ozone. Together, the findings suggest that the source of this homologous series of aldehydes is the reaction of ozone with condensed-phase material, as opposed to VOCs (i.e., volatile material is produced from nonvolatile material). The small-chamber experiments with the fibers and backing from carpet 1 suggest that a reaction between ozone and some material associated with the fibers is likely responsible for the C₅–C₁₀ aldehydes. The condensed-phase reactant could be either semivolatile organic compounds (SVOC), such as unsaturated fatty acids, or nonvolatile material, such as a polymer with some degree of unsaturation.

Carpets as Sinks. The C₅–C₁₀ aldehydes were still detected in the chamber experiments 1 day after their ozone-induced production had presumably ceased. The ventilation rate in the chamber (1 ach) was sufficient to reduce the concentrations of these compounds to below the detection limit in several hours if they had no source. It is likely that these aldehydes adsorbed onto the carpet

Table VI. Rate Constants (s^{-1}) for the Decay of O_3 during the Chamber Studies of Selected Carpets

expt	$10^4 k_{obs}^a$	$10^4 k_{ex}$	$10^4 k_{chmb}$	$10^4 k_{car}$
no carpet	4.2	2.8	1.4	
carpet 1	6.7	2.8	1.1 ^b	2.8
carpet 2	7.8	2.8	1.1	3.9
carpet 3	9.7	2.8	1.1	5.8
carpet 4	17	2.8	1.1	13

^a $k_{obs} = k_{ex} + k_{chmb} + k_{car}$. ^b 80% of the "no carpet" value, reflecting that the chamber floor was covered with carpet.

surfaces during the period when their steady-state concentrations were elevated (i.e., when ozone was present). Then, in the absence of ozone, the carpets served as a source of these aldehydes as they desorbed from carpet surfaces. Consistent with this hypothesis, the less volatile of these aldehydes showed a proportionately smaller decrease in concentration than the more volatile species. For example, in the case of carpet 1, nonanal decreased from 4.8 (ozone) to 2.2 ppb (post-ozone), while pentanal decreased from 1.6 (ozone) to 0.28 ppb (post-ozone).

Rate of Ozone Decay. For the carpet experiments, as well as the experiment with no carpet present, the rate at which ozone decayed (a first-order process) was monitored when the ozone generator was turned off. Table VI lists the observed first-order rate constants (k_{obs}) for these experiments. In the case of the experiment with no carpet present, k_{obs} can be separated into a contribution from the air exchange rate (k_{ex}) and a contribution from heterogeneous decay on the chamber surfaces (k_{chmb}). For the experiments with carpets, the contribution from heterogeneous decay on the carpet surface must also be considered (k_{car}). These derived rate constants are also listed in Table VI. It is apparent that the carpet surfaces have a significant influence on the rate at which ozone decays since k_{car} is much larger than k_{chmb} . It is also interesting that this influence varied significantly among the carpets (more than a factor of four between carpet 1 and carpet 4). Presumably, the heterogeneous decay of ozone on the carpet surface includes (but is not limited to) the production of the C_5 – C_{10} aldehydes. Consistent with this, the sum of these aldehyde concentrations (normalized for the varying ozone concentrations) is largest for carpet 4, the carpet with the largest value for k_{car} .

This discussion has ignored the contribution of homogeneous reactions to ozone decay. For the chamber experiments with no carpet present, gas-phase reactions can obviously be neglected. This is also reasonable for carpets 1 and 3, since in these cases, the steady-state ozone concentration was 1 order of magnitude greater than the sum of reactive VOC concentrations prior to the introduction of ozone. For carpets 2 and 4, the ozone concentration was roughly 5 times that for the sum of the reactive VOCs (carpet 2, 44 vs 8 ppb; carpet 4, 28 vs 5 ppb). In these two experiments, homogeneous chemistry should be considered. However, for at least the first two half-lives of ozone decay, the impact of homogeneous chemistry would be minor compared with air exchange and heterogeneous removal.

Ozone and Nitrogen Dioxide. When NO_2 was added to the chamber, together with O_3 , the effect on reactive VOCs was comparable to that observed with O_3 alone. In the absence of sunlight, O_3 and NO_2 are expected to react to produce the nitrate radical (NO_3). At 50 ppb NO_2 and with O_3 values from 32 to 53 ppb, the estimated production rate of NO_3 is roughly 0.001 – 0.002 $ppb^{-1} s^{-1}$ (11). Given wall losses in the stainless-steel chamber, an air exchange rate of 1 ach, and equilibrium with N_2O_5 , the steady-state

value of NO_3 is expected to be less than 0.05 ppb. Hence, the lack of a discernible effect on VOC concentrations is not surprising. A more sensitive indicator of possible O_3/NO_2 chemistry (12) would be measurements of nitric acid and peroxy radical concentrations in future $O_3/NO_2/VOC$ chamber experiments.

Conclusions

This study presents the first demonstration of reactions between ozone and selected VOCs under frequently encountered indoor conditions. The greatest effects were seen at the highest ozone concentration (carpet 1). However, it is striking that at modest ozone concentrations (28–44 ppb), major effects were still observed: selected VOC concentrations were reduced to levels one-third to one-tenth their pre-ozone levels; formaldehyde levels increased as much as a factor of 3; acetaldehyde levels increased even more—up to a factor of 20 (carpet 4); and C_5 – C_{10} aldehydes, previously undetected, attained steady-state levels as high as 4.1 ppb in the presence of 28 ppb ozone.

In these experiments, reactions with ozone reduced the concentrations of some potentially irritating compounds (e.g., 4-PCH, styrene, and 4-VCH) while at the same time generating a different set of irritants (e.g., formaldehyde and the C_5 – C_{10} aldehydes). The evidence suggests that the higher molecular weight aldehydes were generated from the reaction of ozone with relatively nonvolatile substances such as unsaturated fatty acids or unsaturated polymers.

In addition to carpets and carpet emissions, ozone can react with many other substances commonly found indoors. Especially important are products that contain compounds with unsaturated carbon–carbon bonds [e.g., paints based on linseed oil, linoleum floor coverings, products made from natural latex or styrene–butadiene rubber, polyvinyl resins, detergents containing dodecylbenzene derivatives (source of dodecene), waxes and lubricants with unsaturated fatty acids, untreated wood surfaces (terpenes), and cleaners or "room fresheners" scented with limonene or α -pinene]. Note that a number of these products may cover large areas in typical indoor applications.

Indoor chemistry can impact indoor VOCs. Since VOC measurements within a building at low ozone levels (<10 ppb) may differ from those at higher ozone levels (>30 ppb), a single sampling under one set of conditions may not be sufficient to associate indoor pollutants (kind and concentration) with occupant complaints.

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Registry No. 4-PCH, 4994-16-5; 4-VCH, 100-40-3; BHT, 128-37-0; O_3 , 10028-15-6; vinyl acetate, 108-05-4; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; styrene, 100-42-5.

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Carbon Limitation of Denitrification Rates in an Anaerobic Groundwater System

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■ Rates of potential denitrification were determined for anaerobic aquifer sediments collected at a site where groundwater NO_3^- concentrations ranged from 0.7 μM to 8.6 mM. A significant relation ($p = 0.046$) was observed between denitrification rates and the in situ concentration of NO_3^- , but NO_3^- concentration only accounted for approximately 34% (r^2) of the variation in activity. The highly significant relation ($p < 0.001$; $r^2 = 0.80$) between potential denitrification and sediment total organic content and the enhanced activity of sediments amended with glucose indicated that denitrification rates in this aquifer system were carbon limited. No significant relation was observed between denitrification and the in situ groundwater pH, but short-term variations in pH influenced both the magnitude and the end products of denitrification.

Introduction

The accumulation of nitrate in groundwater beneath cultivated land commonly reflects the leaching of fertilizer from the surface at rates that exceed the nitrogen requirements of the underlying soil community. In such cases, delivery of NO_3^- to groundwater via vertically percolating recharge typically exceeds the denitrification potential of aquifer material. In aerobic groundwater systems, the limitation of denitrification is readily attributed to repression of nitrogen oxide reductase activity by molecular oxygen. In anaerobic aquifers, however, the conditions limiting denitrification are less obvious. Numerous studies have demonstrated that nitrogen and carbon availability as well as pH may limit potential denitrification rates in soils (see refs 1 and 2 for review). It is reasonable to hypothesize, therefore, that similar processes may limit denitrification in groundwater systems and that these limitations may contribute to NO_3^- accu-

mulation in anaerobic aquifers. The purpose of the studies reported here was to evaluate potential denitrification rates in a shallow anaerobic groundwater system underlying a golf course near Tampa, FL, as a function of NO_3^- concentrations, carbon availability, and pH. The results of this investigation indicate that carbon limitation in anaerobic aquifer sediments can be a primary cause for the accumulation of nitrate in groundwater underlying cultivated lands. Further, this study is intended to illustrate the use of such evaluations to provide practical guidelines for surface applications of nitrogen fertilizers and waste.

Study Location

Sediment samples were collected from a golf course near Tampa, FL. The elevation at the course ranges from 0 to 3 m above sea level. The course is underlain by a fine sand layer which functions as a shallow aquifer. Particle size analysis indicates that the sediment is primarily sand with a maximum silt/clay content of 2% of dry weight (Bradley, unpublished results). The aquifer is confined at a depth of approximately 4.5 m by a sandy-clay layer which ranges in thickness from 4.5 to 7.5 m. The depth to the water table typically ranges from 1 to 3 m across the site.

Sample Collection

Water quality characteristics of the shallow groundwater were determined for the six sites at which sediment was collected. Water samples were collected from steam-sterilized, stainless-steel drive-point samplers after approximately 2 L was purged from each sampler. The groundwater pH and oxygen concentration were measured immediately with calibrated pH and dissolved oxygen meters, respectively. Samples for NO_3^- nitrogen analysis were collected in 250-mL dark brown plastic bottles containing 13 mg of HgCl_2 , stored on ice, and shipped immediately to a U.S. Geological Survey laboratory.

Aquifer sediment samples were collected at depths of 1-2 and 3-4 m at six sites using a hollow-stem auger drilling rig equipped with a split-spoon sampler. Cores

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