

**FILTRATION OF OZONE BY CARBONACEOUS
MATERIALS: REMOVAL EFFICIENCIES AND
REACTIONS WITH VOLATILE ORGANIC
COMPOUNDS**

by

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DEDICATION

This dissertation is dedicated to Albert Metts in appreciation of his enduring support and encouragement.

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LIST OF ACRONYMS

AC	Activated Carbon
ACF	Activated Carbon Fiber
DPM	Diesel Particulate Matter
GAC	Granular Activated Carbon
GC	Gas Chromatography
EPA	Environmental Protection Agency
HPLC	High Performance Liquid Chromatography
IAQ	Indoor Air Quality
MS	Mass Spectrometry
NAAQS	National Ambient Air Quality Standard
OPC	Optical Particle Counter
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
TD	Thermal Desorption
TLV	Threshold Limit Value
VOC	Volatile Organic Compound

CHAPTER 1. INTRODUCTION

1.1 Background

Indoor air is the major exposure source for many pollutants because most humans spend 70-90% of their time indoors and many pollutants are present in even higher concentrations indoors than outdoors (Brown et al., 1994). Both human health and comfort can be adversely affected by buildings with poor indoor air quality (IAQ). Headaches, fatigue, eye and mucous membrane irritation, respiratory problems, and unpleasant odors are common symptoms and complaints associated with poor IAQ (Zhang and Smith, 2003).

Ideally, controlling or eliminating emission sources would reduce indoor air pollutant levels; however this is not always practical or cost-effective. As such, filtration and dilution systems are often used to control indoor air contaminants. When properly designed, selected and used, these can be very effective means to control certain indoor air pollutants. Many types of filter media are available for various classes of pollutants (e.g., bioaerosols, respirable particulates). This research will focus on the use of granular activated carbon (GAC) for the filtration of low concentrations of ozone (O_3) and volatile organic compounds (VOCs).

Ozone, even in trace amounts, can cause acute and possibly chronic health effects (US EPA, 1996). Ozone can also adversely affect plants, materials, cultural artifacts, and works of art. Ambient O_3 levels frequently exceed the current National Ambient Air

Quality Standard (NAAQS) in many urban areas. Indoors, O₃ originates mainly from infiltration of O₃ from outdoors. It can also be formed from indoor sources such as photocopiers, laser printers, and certain “air purifiers.” Although once regarded largely as an outdoor problem, indoor O₃ exposure is now recognized to compose a major portion of total O₃ exposure and to exceed outdoor exposure for many people (Weschler et al., 1989). Ozone is very reactive and is rapidly scavenged by indoor surfaces, which are the main sinks of indoor O₃. Ozone can also react with gaseous pollutants. These reactions, important for O₃ removal, also may produce gas and particulate-phase reaction products called secondary pollutants. Activated carbon (AC) filters can be very effective for the removal of O₃; however, they do not work indefinitely because chemical reactions ultimately change the composition, structure and surface area of the carbon. Few studies have documented the efficiencies of AC filters for the removal of O₃ at concentrations normally found indoors. Most of the data have come from field studies or have been extrapolated from high-concentration laboratory experiments.

Hundreds of VOCs have been identified in indoor air (Brown et al., 1994) which can also impair IAQ. VOCs are usually present at low concentrations, arising from sources including infiltration of outdoor air, electronic and office equipment, carpets, solvents, building materials, human body effluents, tobacco smoke, cleaning products, and ventilation systems (Sundell et al., 1993; Brown et al., 1994; Leovic et al., 1996; Zhang and Smith, 2003). As mentioned, certain VOCs can react with O₃ and other oxidants to form secondary pollutants, some of which can be more irritating than their precursors. For example, Clausen et al. (2001) subjected mice to a limonene/O₃ mixture and measured a 33% reduction in respiratory rate, representing sensory irritation. The

reduction in respiratory rate was significantly greater than the effects of pure air, O₃, or limonene exposures at concentrations equal or above those measured. There is mounting, though indirect, evidence that chemical reactions that take place on surfaces or in the air are associated with sick building syndrome (SBS). It has been proposed that reactions between oxidants such as O₃ and unsaturated VOCs such as terpenes, which are major components of citrus and pine oils that are widely used as fragrances, produce chemically reactive compounds that are more likely to cause eye and respiratory irritation than the non-reactive VOCs typically measured indoors (Wolkoff et al., 1997; 1999, 2000; Wolkoff and Nielson, 2001; Clausen et al., 2001). The use of AC to control VOCs at moderate-to-high concentrations has been well documented. However, as with O₃, there is little information available on the effectiveness of AC to remove VOCs at the low concentrations (ppb range) that are normally found in indoor air.

O₃ may also be removed by soot present in air or deposited on surfaces. Soot, a by-product of fuel combustion, is a fine aerosol mixture that has a large surface area making it ideal for heterogeneous chemical reactions. Although several studies (e.g., Lelievre et al., 2004) have explored the potential of aircraft-generated soot to deplete O₃ in the upper troposphere/lower stratosphere, little is known about whether soot particles affect O₃ levels in the lower atmosphere or whether soot particles collected on ventilation filters affect O₃ levels in indoor air.

1.2 Research focus and hypotheses

The primary purpose of this research was to study the interactions of O₃, VOCs and AC using conditions normally found in indoor air in order to better understand the performance and application of carbon filtration of indoor air. In addition, the ability of

diesel particulate matter (DPM) to remove O_3 from air was measured and extended to ambient air and indoor air filtration applications.

The specific hypotheses tested were as follows:

Hypothesis 1a. The efficiency of AC to remove O_3 at low concentrations will decrease over time and can be predicted by results of tests performed at higher concentrations.

An understanding of the O_3 filtration process using concentrations typically found in indoor air will enable the optimal design and use of filtration systems that are protective of human health and welfare. At present, there is little guidance regarding design, use and replacement of AC filters in ventilation or IAQ filtration systems.

Several studies have measured the O_3 removal efficiency of AC filters (non-chemically treated) either at high O_3 concentrations, e.g., 250 ppb to 5 ppm (Ellis and Tometz, 1972; Johnston et al., 1989), or in uncontrolled field studies (Shair, 1981; Weschler et al., 1994; Shields et al., 1999; Salmon et al., 2000). In the laboratory, Parmar and Grosjean (1991), tested the ability of several sorbents to remove O_3 and other pollutants from a museum display case and found that 200 g of AC could remove an amount of O_3 equivalent to 20 ppb for one yr at a flow rate of 0.1 L min^{-1} ; this gives a wt. % of 0.0010. Lee and Davidson (1999) tested various types of AC filters at an O_3 concentration of 120 ppb; efficiency tests were based on measurements of breakthrough times for 10% (C_t/C_0) penetration. Half of the filter samples had initial efficiencies below 90%, so breakthrough times could not be measured. They also constructed an isotherm by exposing thin (0.26 cm) activated carbon fiber (ACF) filter samples to O_3 concentrations of 120, 300, 500, and 800 ppb until they reached 95% penetration. However, because of differences in pore size distributions (Lee and Davidson, 1999) and

other factors, ACF may behave differently than AC. No studies were found that used O₃ concentrations below 100 ppb, probably because low concentration tests of AC filters require prohibitively long times for breakthrough to occur.

AC is expected to be quite effective at removing low concentrations of O₃, in contrast to physical adsorption processes where filter efficiencies may decrease at low contaminant levels (Robinson and Ouellet, 1999). The irreversible reaction of O₃ with unsaturated bonds on the carbon's surface should cause a strong concentration gradient to be maintained, resulting in high removal efficiency, at least initially. This is supported by Kelly and Kinhead (1993) in removal tests of chemically treated air purifiers for O₃ (120 ppb for 80 h) and other gaseous pollutants. The O₃ removal efficiency at low-concentrations is also expected to decrease over time due to irreversible changes in the carbon's structure.

Although O₃ removal efficiency can be measured experimentally for an individual sorbate-sorbent system, no predictive models were identified that can generalize O₃ adsorption. In contrast, many models have been developed for physical adsorption of VOCs on AC. The applicability of these models for O₃ has not been demonstrated. Because O₃ adsorption is an irreversible process involving chemical reactions with AC in addition to adsorption, it is likely that different and more sophisticated models are necessary to predict O₃ removal by AC.

This research also investigates whether laboratory tests conducted at higher O₃ concentrations can be used to predict the efficiency of AC for O₃ removal at lower concentrations. This was accomplished by estimating a number of empirical and

physically-based models and determining whether they fit the data with reasonable estimates of parameters.

Hypothesis 1b. Extremely small quantities of AC can be used to expedite tests of O₃ removal efficiencies of AC, which will facilitate the testing of AC using low O₃ concentrations.

As discussed above, previous methods for evaluating O₃ removal efficiency of AC filters have relied on high O₃ concentrations, questionable extrapolations, or uncontrolled field studies. Although these approaches have avoided the extremely long exposure times required for breakthrough to occur, it is not yet known whether they can accurately estimate the actual low-concentration efficiency. The use of extremely small quantities of carbon may afford testing of AC in a timely manner and then facilitate predictions of O₃ removal efficiency at low concentrations.

Hypothesis 2. The loading of AC by VOCs affects O₃ removal efficiency.

In addition to O₃, other pollutants can be removed by AC filtration. Indeed, VOC removal has been the primary use of AC. Thus, it is important to understand what occurs when AC filters are exposed to contaminants in addition to O₃. Additionally, an understanding of the effect of VOC loading on O₃ removal efficiency would be useful for choosing the optimal placement and design of filters relative to VOC sources.

The literature is very limited with respect to filter performance and environmental factors. Soiling of carbon filters by submicron particles contributes to a faster decrease in O₃ removal efficiency (Weschler et al., 1994). Dusenbury and Cannon (1996) and Cannon et al. (1996) studied the effect of VOC loading on the ability of O₃ to penetrate GAC beds and found that VOCs did indeed alter O₃ penetration. However, their research

used high ozone concentrations (250-350 ppm) and focused on the ability of oxidants to regenerate spent GAC used in air pollution control applications. No peer-reviewed literature was found regarding the effect of VOC loading on the O₃ removal efficiency of AC filters at low O₃ concentrations. The effect of VOC loading should depend on the reactivity of the particular VOC with O₃ and the strength or reversibility of VOC adsorption on AC (Dusenbury and Cannon, 1996). If present in high enough amounts, VOCs may decrease the O₃ removal capacity. On the other hand, the presence of certain reactive VOCs adsorbed on the AC might enhance O₃ removal efficiencies of AC because of chemical reactions with O₃ that occur on the carbon's surface.

Hypothesis 3. O₃ will react heterogeneously with certain VOCs adsorbed on the surfaces of AC forming oxidation products.

The purpose of AC filtration is to remove pollutants from air; it should not be a source of pollutants. Thus, it is important to determine if O₃ reacts with VOCs adsorbed onto AC to form secondary VOCs or other products to an extent that might impair IAQ. Both atmospheric and indoor air studies have documented that several reaction products are formed during the gas-phase reaction of unsaturated VOCs (Grosjean, et al., 1992, 1993; Zhang et al., 1994; Atkinson et al., 1995; Griesbaum et al., 1996; Weschler and Shields, 1999; Wolkoff et al., 1999; 2000; Koch et al., 2000; Wainman et al., 2000; Feltham et al., 2000; Glasius et al., 2000; Clausen et al., 2001). Some of these reactions may occur at fast enough rates to impact IAQ (Weschler, 2000). These reactions can produce formaldehyde, other carbonyls, and organic acids, some of which are strong airway irritants (Wolkoff et al., 1999; 2000). However, no study has yet evaluated

whether reaction products are formed by the heterogeneous reaction of O_3 and VOCs adsorbed onto AC.

Hypothesis 4. Diesel particulate matter can remove significant amounts of O_3 from air, potentially affecting ambient or indoor O_3 levels

In urban areas, high concentrations of O_3 often co-exist with other air pollutants, including particulate matter ($PM_{2.5}$, PM_{10}). As mentioned, most previous studies exploring O_3 removal by soot particles have focused on stratospheric depletion of O_3 by aircraft-generated soot. However, few studies have explored the potential for soot particles to act as O_3 scavengers in the lower atmosphere. Kotzick et al. (1999) and Decesari et al. (2002) found that ozonation causes soot particles to become more hydrophilic, potentially acting as cloud condensation nuclei. Berkowitz et al. (2001) proposed a heterogeneous reaction for aerosol particles in the lower troposphere as one explanation for O_3 depletion observed in a nighttime urban plume. Even less is known about how the diesel particulate matter (DPM), a potentially important class of soot in urban areas, affects O_3 . DPM collects on ventilation filters and other surfaces and may remove O_3 from indoor air.

1.3 Importance

This research was aimed at increasing the understanding of gas-phase filtration of O_3 by AC and filling several important gaps in the literature, including the lack of studies using low O_3 concentrations typical of indoor air. Novel aspects of this research included the development of empirical models to generalize O_3 and DPM adsorption, the use of extremely small quantities of carbon to expedite low-concentration efficiency testing, the examination of heterogeneous reaction products, and the use of a laboratory system that

allowed rapid testing of O₃ removal capacity. This research should have numerous applications aimed at enhancing indoor air filtration to remove O₃ and VOCs, and it should contribute to the understanding and mitigation of IAQ problems, including SBS-type complaints.

1.4 Organization of this dissertation

This dissertation is organized into seven chapters. Chapter 2 provides a review of the literature relevant to this research. Chapters 3 through 6 are research chapters, each separately devoted to the four hypotheses discussed above. Chapter 3 examines whether O₃ removal efficiency tests can be expedited by using extremely small quantities of AC. It also investigates whether changes in the efficiency of AC to remove low-concentrations of O₃ over time can be predicted by tests performed using higher O₃ concentrations. Chapter 4 determines whether VOC loading affects the O₃ removal efficiency of AC. Chapter 5 investigates heterogeneous reactions of O₃ with VOCs adsorbed onto AC. Chapter 6 studies the O₃ removal capability of DPM. These chapters have been written as stand-alone sections, in anticipation of submission to journals as article manuscripts. This approach is also believed to facilitate understanding of the research, though at the cost of some repetition in methods. Chapter 7 presents the conclusions of this research and offers suggestions for further study.

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CHAPTER 2. LITERATURE REVIEW

This chapter presents a review of the literature relevant to the removal of ozone (O_3) and volatile organic compounds (VOCs) by activated carbon (AC) and diesel particulate matter (DPM) and expands on the literature reviews provided in the following chapters. Section 2.1 discusses general principles of gas-phase filtration. Section 2.2 discusses O_3 filtration by AC. Section 2.3 discusses the effects of VOC loadings on the gas-phase filtration of O_3 by AC. Section 2.4 discusses reactions of O_3 with unsaturated VOCs, emphasizing *d*-limonene. It also discusses heterogeneous reactions of O_3 with compounds adsorbed on surfaces. Some considerations for the sampling and analysis of terpenes and terpene oxidation products are presented in Section 2.5. Section 2.6 discusses uptake of O_3 by DPM. Finally, Section 2.7 presents four chemisorption models that have been successfully applied to various sorbate/sorbent systems that may also have application for O_3 uptake on carbonaceous materials.

2.1 Principles of gas-phase filtration by AC

2.1.1 Structure and properties of AC

Porous carbon solids, which are known as AC or activated charcoal, have for many years been widely used in air cleaning filters due to their ability to remove gases and vapors from the air. They are also used in occupational respirators, air-sampling devices, and vapor recovery operations.

Activated carbon is generally produced in a two-step process (Balieu, 1989). In the first step, the carbonaceous material is heated in an inert atmosphere, a process called *carbonization*. The second step is called *activation*; methods include steam distillation and chemical activation. Activation cleans and modifies the pores, which transforms the carbonized material into a high purity sorbent that is very porous with an internal surface area ranging from 1000-1600 m² g⁻¹ (Balieu, 1989). The pores differ in diameter; macropores have diameters of >1000 Å and micropores have diameters 10-1000 Å. The micropores constitute the major portion of the surface area (Cookson, 1978).

Structurally, AC is basically microcrystalline graphite. However, the microcrystals have imperfect edges where heterocyclic ring structures can be found with oxygen as the heterocyclic element, such as lactone groups, peroxide groups, and carboxylic acid anhydride groups. Besides the heterocyclic ring structures, other functional groups such as carboxylic acid groups, phenolic groups, and carbonyl groups may also be present (Cookson, 1978). Although many of the functional groups are formed during the manufacturing process, some may be formed during storage at room temperature as a result oxidation, which is referred to as “aging” (Balieu, 1989).

Activated carbon filters have traditionally consisted of a packed bed of GAC, but in recent years there have been alternative designs using AC fibers or fabrics. The granular activated carbon (GAC) in air cleaning filters are typically about 1-3 mm in size. In general, the smaller the granules, the higher the sorption capacity will be per unit volume of granules. However, the smaller the granules, the higher the resistance to air flow will be through the filter (Balieu, 1989).

2.1.2 Filtration process

The filtration process progresses as follows: incoming air (with influent concentration, C_i , of the gas to be removed) passes through the porous bed of GAC. Initially, the gas molecules are adsorbed near the inlet but as filtration continues, they will penetrate further into the filter bed due to the reaching of equilibrium adsorption in the area near the filter inlet. Eventually, the entire filter will reach equilibrium adsorption and the concentration of the gas in the effluent air, C_e , will be equal to C_i and *breakthrough* occurs. According to classical filtration theory, the filter can be divided into three regions: the region nearest the inlet (zone A) where the sorbent has reached equilibrium adsorption, the region immediately downstream of zone A where the sorbent is in partial equilibrium (zone B, also called the wave front or mass transfer zone), and zone C, the region where the sorbent is unused and has its full adsorption capacity (Balieu, 1989). Ideally, in air cleaning, a state of total equilibrium adsorption should not be reached; the filter should be changed before C_e reaches an unacceptable level.

If several pollutants are present in the air stream, several mass transfer zones (MTZs) may exist due to the different adsorbabilities and diffusion rates of the components. The MTZ of a more strongly adsorbed component is located upstream of a less strongly adsorbed component (Gong and Keener, 1993). If the adsorbate concentration decreases after equilibrium is reached, desorption begins to occur. Desorption can also occur when a less strongly adsorbed component is replaced by a more strongly adsorbed component, called competitive sorption. For example, because GAC better adsorbs non-polar compounds, polar compounds (especially low-molecular weight compounds) tend to be displaced by non-polar compounds (Goller, 1985).

There are two types of sorption process that can occur between AC and a sorbate, *physical sorption* and *chemisorption*. In physical sorption, the sorbate molecules interact with the AC surface by van der Waals' forces. It is a physical phenomenon because chemical bonds are not formed; the attraction is electrostatic. Physical sorption of VOCs will be discussed in more detail in Section 2.3.1. In chemisorption, electron bonds are formed between the sorbent and the sorbate by chemical reaction (Balieu, 1989). (Chemisorption of O₃ will be discussed in greater detail in Section 2.2.4.) Filter media can also be impregnated with chemicals such as potassium permanganate, which are used to remove certain reactive gases by chemisorption.

2.1.3 Measures of filter performance

A property of AC that is very important from a practical standpoint is sorption capacity, defined as the maximum amount of a specific substance that can be adsorbed under given conditions (temperature and partial pressure). Although sorption capacity depends primarily on the specific surface area (micropore volume), it is also affected by the amount of metal ions and oxygenated surface functional groups (Chiang et al., 1999). Sorption capacity can be determined experimentally by constructing sorption curves. The most frequently used type of sorption curve for evaluating filter materials is the *isotherm*, which shows the equilibrium amount of sorbate adsorbed by a sorbent as a function of sorbate concentration at constant temperature (Balieu, 1989). There are five main types of isotherms: Type I corresponds to adsorption of a monolayer of sorbate molecules; Types II and III correspond to multilayer adsorption; and Types IV and V correspond to multilayer adsorption with simultaneous capillary condensation in the micropores (Balieu, 1989). Types I and V are of special interest in filtration applications because they describe the equilibrium sorption capacity for numerous VOCs and water vapor,

respectively. Several equations are available for approximating Type I isotherms. Two of the simpler equations, the Freundlich equation and the Langmuir equation are shown below. The Freundlich isotherm is an empirical equation that has been shown to fit the parabolic shape of a typical adsorption isotherm. The Langmuir isotherm, on the other hand, was theoretically derived (Balieu, 1989). Both have limited predictive ability (Werner and Winters, 1986).

$$\text{Freundlich equation: } \log S = \log \gamma + \delta \log C \quad (2.1)$$

$$\text{Langmuir equation: } C/S = 1/\gamma + \delta C/\gamma \quad (2.2)$$

where S = equilibrium amount of sorbate per g of sorbent; C = concentration in the gas phase; and γ and δ = empirical constants, unique for each sorbent-sorbate system.

The symbols S and C are interchangeable between the two equations, but the two empirical symbols are not. The empirical constants may be derived from graphs of experimental data. In general, isotherms are not linear because sorption capacity decreases with decreasing concentration, though they can be considered linear over a limited concentration range. Although predictive equations often assume linearity, this assumption can lead to errors in estimating performance of filters working under a broad concentration range (Balieu, 1989). Many models have been developed to predict gas-phase AC adsorption (Werner and Winters, 1986).

Filters can also be evaluated by constructing breakthrough curves. The breakthrough time (t_b) is defined as the time required for the effluent concentration (C_e) to reach a threshold percentage (for example, 1%) of the influent concentration (C_i). Generally, t_b corresponds to a maximum acceptable level of the pollutant in the effluent air, for example a fraction of the threshold limit value (TLV). Many variables can affect

breakthrough times, including C_i , airflow rate, humidity, temperature, and filter design factors (Balieu, 1989).

The kinetic adsorption constant (k) and the equilibrium sorption capacity (S) for a particular sorbate-sorbent system can be derived from experimental breakthrough curves. Although S is concentration dependent, if its value is determined over a wide concentration range and if the results can be expressed by an appropriate isotherm (i.e., the Langmuir equation), empirical constants γ and δ can also be determined. Thus, the values of k , γ , and δ can be used in an appropriate predictive equation to generalize the experimental results (Balieu, 1989). Breakthrough curves can be affected by the presence of metal salts or impregnated chemicals that cause catalysis or chemical reactions to occur.

Another measure of filter performance is efficiency E (%) defined as:

$$E = \frac{(C_i - C_e) \times 100}{C_i} \% \quad (2.3)$$

and the penetration P (%) is $100 - E$. The reduction factor (R),

$$R = C_i/C_e \quad (2.4)$$

is used in several predictive equations.

Predictive equations have attempted to describe the sorption process in quantitative terms. Many predictive equations have a generalized linear form,

$$\ln R = \alpha t + \beta \quad (2.5)$$

or

$$\ln(R-1) = \alpha t + \beta \quad (2.6)$$

where α and β are constants that depend on k , S , the filter dimensions, C_i , and the airflow rate (Balieu, 1989). If R is high, then $\ln(R)$ is approximately equal to $\ln(R-1)$.

Practically, whether to use $\ln(R)$ or $\ln(R-1)$ only matters generally when tests are conducted to 10% breakthrough or higher, and then should be used as specified with the chosen type of predictive equation (Balieu, 1989). One example is the Wheeler-Jonas equation:

$$\ln(R) = \frac{k C_i t}{S d} + \frac{A h k}{v} \quad (2.7)$$

where A = sorbent bed cross-section (cm^2); h = sorbent bed depth (cm); v = volumetric flow rate through the sorbent bed ($\text{cm}^3 \text{ min}^{-1}$); d = bulk density of the sorbent (g cm^{-3}); and k (min^{-1}), C_i (g cm^{-3}), t (min), and S (g g^{-1}) as defined above (Balieu, 1989). Other useful measures of filter performance are activity and retentivity (VanOsdell et al., 1996). Activity is defined as the equilibrium mass percentage of sorbate collected by AC in contaminated air. If the AC is removed from contaminated air and allowed to equilibrate in clean air, retentivity can be calculated. Retentivity is defined as the maximum amount of sorbate that AC can retain in clean air, following saturation in contaminated air.

2.2 Ozone filtration by AC

2.2.1 Sources of indoor O_3

Although air contains approximately 21% diatomic oxygen, it contains only trace amounts of triatomic O_3 (usually 10-100 ppb). However, even trace amounts can be harmful to human health, plants, and materials (EPA, 1996). Ozone production and destruction occurs through a complex set of chemical reactions involving VOCs, nitrogen oxides, carbon monoxide, and sunlight and is described in detail elsewhere (U.S. EPA, 1996). Ozone concentrations are generally highest in urban areas where the concentrations of VOCs and nitrogen oxides are high. Ozone concentrations are also

generally highest in areas with frequent atmospheric temperature inversions and ample sunshine. Outdoor O₃ is a major concern and there have been many efforts to reduce it. Even so, O₃ measurements in relatively remote sites indicate that tropospheric O₃ has been increasing between 1 and 2% annually over the past 3 decades (Seinfeld and Pandis, 1998).

Much of the O₃ found indoors originates from outdoor air due to infiltration. Thus, efforts to reduce outdoor O₃ concentrations will also reduce indoor concentrations. However, increased ventilation of buildings to reduce the concentrations of indoor pollutants can have the negative result of increasing O₃ levels indoors.

Indoor sources of O₃ include laser printers, photocopy machines, and other types of office equipment. These devices sometimes include AC filters to help reduce the amount of O₃ emitted. Ozone emissions from dry process photocopy machines have been measured as high as 7,900 µg h⁻¹ (Leovic et al., 1996). Lee et al. (2001) measured O₃ emission rates from laser printers as high as 1.20 µg/copy. Electrostatic air cleaners can also generate O₃. Although manufacturers design them to produce less O₃, air cleaners can still release significant amounts of O₃ in indoor air. Finally, many commercial O₃ generators remain on the market that are purported to remove indoor pollutants. These generators can emit from tens to thousands of milligrams of O₃ per hour (Weschler, 2000). The effectiveness of these devices is controversial.

Indoor O₃ concentrations depend on the outdoor O₃ concentration, air exchange rate, indoor O₃ sources, homogenous reactions with other chemicals, and removal by surfaces (Weschler, 2000). Indoor O₃ concentrations closely follow outdoor trends, barring any significant indoor O₃ sources (Sabersky et al., 1973; Weschler et al., 1989,

1994b; Zhang and Liou, 1994). Assuming a constant air exchange rate and nonvarying indoor O_3 sources, the ratio of indoor O_3 concentration divided by the outdoor concentration (I/O ratio) tends to remain constant for a given site (Weschler, 2000 and references therein). Excluding extreme values, I/O ratios typically range from 0.2 to 0.7 (Weschler, 2000). Buildings that are tightly sealed or that use charcoal filtration tend to have very low I/O ratios, while buildings that have very high air exchange rates have much higher I/O ratios with indoor O_3 levels exceeding 100 ppb as found in Southern California (Weschler et al., 1994b).

2.2.2 Reactions of O_3 with substances found indoors

Although O_3 itself is a very harmful pollutant, its reactivity with other chemicals is also a concern for IAQ. Ozone tends to be a relatively stable molecule. It will only decompose to oxygen at a significant rate at high temperatures or high concentrations (Cotton and Wilkinson, 1988). Generally, spontaneous decomposition is negligible at concentrations normally found in ambient or indoor air. However, O_3 is a very powerful oxidant. Only a few other species, e.g., fluorine, atomic oxygen, and the hydroxyl radical, are stronger oxidants (Cotton and Wilkinson, 1988). Although O_3 can oxidize many species, many of these reactions occur at relatively slow rates indoors. Gas-phase reactions of O_3 with most other chemicals are thermodynamically possible; however, reaction rates are generally very slow at ambient temperatures and concentrations.

For a chemical reaction to be important indoors, it must react at a rate that is at least as fast as the air exchange rate (Weschler and Shields, 1999). For reactions to occur among indoor pollutants, there must be sufficient time for the pollutants to interact, which is determined by the ventilation rate, air exchange rates, mixing, and other factors. As the ventilation rate decreases, the residence time of indoor air increases, which

increases the time pollutants have to decompose or react with one another. Ventilation also affects indoor air chemistry by changing the concentrations of the chemical compounds. As the ventilation rate decreases, pollutants of outdoor origin decrease in concentration, pollutants of indoor origin increase in concentration. The concentrations of reactants influence the rate at which a chemical reaction occurs. Since most indoor reactions are bimolecular processes, their rates scale linearly with the concentration of each species (Weschler, 2000).

Ozone can react with VOCs, which are defined as organic compounds (excluding pesticides) having boiling points ranging from 50 to 260 °C (Brown et al., 1994). O₃-VOC reactions are thermodynamically favorable (i.e., given enough time, they will occur). The amount of time required for reactions to occur varies from compound to compound, and reaction rate constants are available in the literature. When a VOC is present at a concentration significantly lower than that of O₃, its half-life is independent of its concentration and depends only on the O₃ concentration. Thus, if the rate constant is known, the half-life of a VOC can be calculated for a given O₃ concentration (Weschler, 2000). Some half-lives of common VOCs and their rate constants for reaction with O₃ are shown in Table 2-1.

The half-life concept can also be applied to air exchange rates. The air exchange rate half-life is the time required for half of the indoor air to be replaced. Typical half-lives for air exchange rates range from 15 min to 3 h (Weschler, 2000). As stated earlier, if the half-life of a parcel of air is significantly less than the half-life of a given chemical reaction, the reaction will not have enough time to impact the indoor environment. Most

O₃/VOC reactions do not occur quickly enough to compete with typical air exchange rates and significantly impact the indoor environment.

One group of VOCs does react quickly enough with O₃ to compete with air exchange rates. This O₃-reactive group, which shares one carbon-carbon double bond, includes compounds such as 1,2-dichloroethylene, isoprene, *d*-limonene, and styrene (Weschler, 2000). Chemical reactions between unsaturated VOCs and O₃ will be discussed in more detail in Sections 2.4.2 and 2.4.3.

Organic compounds present in indoor air that are more volatile than VOCs are called *very volatile organic compounds* (VVOCs) and include such compounds as formaldehyde, acetaldehyde, and propane. Also present in indoor air are inorganic gases such as carbon monoxide, nitrogen oxides, ammonia, and sulfur dioxide. Reactions between O₃ and most VVOCs or inorganic gases are negligible at typical indoor air concentrations; they are too slow to compete with typical air exchange rates (Weschler, 2000). One important exception is nitric oxide, which reacts with O₃ to form nitrogen dioxide. Indoor O₃ and nitric oxide concentrations negatively correlate; significant levels of O₃ accumulate only when there is little nitric oxide and vice versa (Weschler et al., 1994b). Although 500 times slower, nitrogen dioxide can also react with O₃ quickly enough to form highly reactive nitrate radicals, which are ultimately converted to nitric acid indoors (Weschler, et al., 1994). Other compounds that can react fast enough with O₃ to compete with typical air exchange rates are hydrogen sulfide forming sulfur dioxide and ethene, propene, or isobutene, which can all form formaldehyde (Weschler, 2000).

2.2.3 Heterogeneous reactions of O₃

Although O₃ readily reacts with only a small group of indoor gases, it can also react with certain chemicals that constitute or are adsorbed onto surfaces. These

reactions are classified as *heterogeneous* in contrast with the *homogeneous* gas-phase reactions discussed earlier. These reactions are the main reason that O_3 concentrations are lower indoors than outdoors. Some examples are O_3 's reaction with natural rubber, neoprene, compounds associated with latex paints, carpets, and linoleum flooring; unsaturated components of floor waxes and polishes; and unsaturated compounds adsorbed on surfaces (Weschler et al., 1992; Weschler, 2000). The reaction of O_3 with AC is discussed in detail in Section 2.2.4. Ozone has a half-life ranging from about 9-26 min in offices and 8-21 min in residential rooms (Sundell and Zuber, 1996). Heterogeneous reactions are important as they often have undesirable consequences such as deterioration of rubber, fading of paints, and damage to photographic materials. Sometimes these reactions can also be the source of highly volatile and odorous carbonyl compounds (Weschler, 2000).

The rate of removal of O_3 by indoor surfaces depends on a first-order rate constant, which is defined as the product of the deposition velocity, k_d , and the surface area-to-volume ratio (A/V). The A/V ratio depends on the room dimensions, surface coverings, and furnishings. Generally, smaller rooms have larger A/V ratios than larger ones. Thus, O_3 removal is usually faster in smaller rooms. The deposition velocity, k_d , varies depending on the type of surface as well as the indoor ventilation conditions. Textured surfaces such as carpets, drapes, and upholstery typically have larger surface removal rates compared to rooms with smooth surfaces. Surface removal rate constants are analogous to air exchange rates and range from 1.4 h^{-1} in a stainless steel chamber to 7.6 h^{-1} in a highly ventilated cleanroom (Weschler, 2000 and references therein). The interaction of O_3 with surfaces will be discussed in greater detail in Section 2.4.5.

2.2.4 Chemisorption of O_3 by AC

Ozone removal by AC filters is a chemisorption process. Initially, ozonation causes a significant increase in the AC weight, reaching a maximum and then slowly decreasing (Deitz and Bitner, 1972). Corresponding elemental analyses of charcoals have shown a continuous increase in oxygen content coupled with a continuous decrease in carbon (Deitz and Bitner, 1972). O_3 reacts with the carbon-carbon double bonds on the surface of AC to form epoxides and ozonides (Takeuchi and Itoh, 1993), which can then further react to form CO, CO_2 , and surface functional groups. Ozone oxidation has been found to lead to the formation of hydroxyl, carbonyl, -C-O-, and -COOH surface functional groups (You et al., 1994; Mawhinney and Yates, 2001). Chiang et al. (2002) found that the amounts of oxygen-containing functional groups (OCGs) on carbon samples increased by 22% upon O_3 exposure (40 mg L^{-1} for 30 min at 2.5 L min^{-1}), which they found was mainly due to an increase in hydroxyl and carboxyl groups. These OCGs were found to be thermally stable from 30-250 °C but began to decompose at higher temperatures with virtually none remaining at 1200 °C. Valdés et al. (2002) found a positive linear relationship between ozone exposure and the number of acid sites on the AC. For every 1 mmol of ozone consumed, 16 μequiv of acid sites were generated per gram of AC ($R^2 = 0.989$). In addition, an increase in acid sites was accompanied by a linear decrease in basic sites; approximately five acid sites were formed for each basic site that disappeared ($R^2 = 0.99$).

In addition to forming OCGs, ozone also changes the structure of AC. Ozone reactions cause enlargement of pores and the creation of new pores. Initially the surface area increases slightly, as a result of O_3 slightly increasing the porosity of the carbon (Deitz and Bitner, 1972; Valdés et al., 2002). Eventually, the pore walls are destroyed by

the gasification of carbon, which results in a decrease of surface area (Valdés et al., 2002). Gasification occurs when the AC surface is oxidized by O₃ forming CO₂, which then exits the carbon surface and creates new micropores (You et al., 1994). Dietz and Bitner (1972) provided two possible explanations for the decrease in surface area: chemisorbed oxygen atoms plugging the narrow micropore openings or destruction of pore walls. In addition, because the reaction of O₃ with AC is exothermic, the increased temperature causes the reaction rate to increase, which causes the formed CO₂ to also react with the AC. This mechanism, which is very similar to the activation step that occurs during AC manufacture, is shown in the following equations (You et al., 1994):



Takeuchi and Itoh (1993) found that unexposed carbon samples show a uniform distribution from micropore to macropore range. However, after O₃ treatment there was a large increase in the volume of pores in the 10⁴-10⁵ Å (macropore) size range because of breakage of the carbon substrate structure. By calculating the overall effective mass transfer coefficients (K_D), which depend on the diffusivity of the VOCs into the adsorbents' pores, You et al. (1994) found that an increase in K_D values for the oxidized carbon indicated that the micropores may be enlarged to form macropores. In contrast, Chiang et al. (2002) found that AC exposed to O₃ showed an increase in BET surface area (8.7%), micropore area (7.4%), total pore volume (9.0%), and micropore volume (7.5%) due in part to increased micropores. They did not find a significant difference in the macropore and mesopore volume distribution between the virgin and ozonated carbon

samples. Scanning electron microscope photographs have clearly shown macropore enlargement following exposure to O_3 , which is an indicator of material loss due to chemisorption (Lee and Davidson, 1999).

Atyaksheva and Emel'yanova (1989) found that there are three competing processes that occur when O_3 interacts with AC: (a) partial oxidation with formation of surface functional groups, (b) extensive oxidation with formation of CO_2 , and (c) catalytic decomposition. In their study of the interaction of O_3 on the surface of an activated carbon fabric, they found that catalytic decomposition made the main contribution (80-90%) while the remaining O_3 reacted with the AC forming gaseous carbon oxides and surface functional groups. Their findings contrasted with earlier studies that did not find any evidence of catalytic decomposition on charcoal (Deitz and Bitner, 1973; Stephens et al., 1986). However, ozone may interact differently with AC fabrics than charcoal.

There eventually comes a point where charcoal, as such, no longer exists. Deitz and Bitner (1973) proposed that this occurs when the adsorption of nitrogen at 77.4 K, a measure of surface area, declines rapidly. This generally corresponds to an oxygen content greater than 20% by weight (Deitz and Bitner, 1972).

2.2.5 Efficiency of AC filters for removing O_3

The ability of AC to remove O_3 can be determined by several factors including breakthrough time and efficiency. The selection of an O_3 filter is often a compromise between high efficiency and low pressure drop. Generally, high efficiency filters have high pressure drops, which can greatly increase operating cost. Lee and Davidson (1999) found that initial efficiency was not always the best indicator of the quality of O_3 filters.

Instead, they suggested that a quality factor, which equals the ratio of a threshold breakthrough time and pressure drop, be used to compare O₃ filters.

Most of the studies in the literature regarding O₃ and AC have focused on determining the O₃/AC reaction mechanism or studying changes in the carbon structure due to ozonation. Few laboratory studies specifically address the efficiency of AC to remove O₃ from air, and most of these studies used O₃ concentrations much higher than those typically found in indoor air. Ellis and Tometz (1972) found that coconut charcoal and AC had the highest O₃ removal efficiencies (>90% after 15 min) of 26 different materials tested with an influent O₃ concentration of 250 ppb. Further tests using coconut charcoal indicated that O₃ efficiency decreased with time and increasing flow rate. They also tested the effect of O₃ concentration (45 ppb to 1 ppm) and found that efficiency decreased moderately up to 200 ppb and then decreased very slowly over the rest of the range. However, they used charcoal that had been previously exposed to O₃ for 65 h for these tests. Johnston et al. (1989) used O₃ challenge concentrations of 5 ppm to evaluate O₃ removal capabilities of welding fume respirators. They found that the average time to 0.1 ppm breakthrough (2%) was about 126 min. Parmar and Grosjean (1991) tested the ability of several sorbents to remove O₃ and other pollutants from a museum display case and found that 200 g of AC could remove an amount of O₃ equivalent to 20 ppb for one yr at a flow rate of 0.1 L min⁻¹. The only other prior laboratory study of the ability of AC to remove relatively low concentrations of O₃ that was found was a study of the performance of 10 commercial filters using influent O₃ concentrations of 120 ppb (Lee and Davidson, 1999). The most-likely reason that more studies using low O₃ concentrations have not been conducted is that the time required for such tests is

prohibitively long. For example, Lee and Davidson (1999) estimated (by extrapolation from 10% breakthrough times) that the time required for 50% breakthrough on a 1.27-cm thick filter sample was as high as $40,000 \pm 10,000$ min (3-5 weeks).

In a review of test methods for determining the effectiveness of gas-phase filtration equipment, VanOsdell (1994) recommended the use of an accelerated loading method for testing of O_3 , acid gases, and other irreversibly adsorbing compounds. This recommendation was based on earlier work by Ostojic (1985) who found that the method gave acceptable results for the measurement of breakthrough times based on the total capacity of the adsorbent. The method consists of “accelerated loading” of high concentrations of O_3 for about an hour followed by a short period of low concentration loading. This sequence is repeated until the desired breakthrough level is achieved, which takes about 8 hours. However, the method requires additional testing to validate the results that were obtained in limited runs.

Although few laboratory studies have specifically addressed low concentration filtration by AC, chemisorption processes are likely to be quite effective in removing low concentrations (ppb) of O_3 , as has been found in tests of chemically treated air purifiers for the removal of O_3 (120 ppbv for 80 h) and other gaseous pollutants (Kelly and Kinkad, 1993). In contrast to physical adsorption processes where efficiencies are expected to decrease when the contaminant levels are low, the irreversible reaction of O_3 with chemical reagents on the carbon’s surface allows a strong concentration gradient to be maintained resulting in a high removal efficiency. However, in the case of non-chemically treated AC, efficiency is expected to decrease over time due to irreversible changes to the carbon’s structure.

Although field studies in the literature are limited, AC filters have been shown to be effective in reducing indoor O_3 concentrations in buildings with mechanical ventilation systems. In a 3-yr study conducted in the Los Angeles area, AC filters used intermittently were found to remove O_3 fractions of 0.95, 0.8, and 0.5 of the O_3 at the end of the first, second, and third years, respectively (Shair, 1981). In a 37-mo. study, Weschler et al. (1994a) measured the O_3 removal efficiencies of commercial AC filters in a test plenum, an air handler providing outside air to a clean room, and a plenum downstream of an air handler providing outside air to another clean room. Updated data from this study were published five years later in a subsequent paper (Shields et al., 1999) and are summarized in Table 2-2. They concluded that adequately sized AC filters have very long service lives for O_3 removal as long as they are not excessively soiled by submicron particles, which contributes to a faster decrease in O_3 removal efficiency. Salmon et al. (2000) determined that the National Museum of Poland's AC filtration system averaged an O_3 removal efficiency of 77% over a 33-day measurement period.

Few models exist that can be used to predict O_3 removal efficiency. Although, Afanas'ev et al. (1981) showed that adsorption of O_3 by AC exhibits a Type I isotherm, Stephens et al. (1986) found that ozonation causes significant and permanent changes to carbon structure that are not easily explained by classical adsorption isotherms. Ellis and Tometz (1972) attempted to model the decomposition of O_3 on coconut charcoal, but their model only accounted for catalytic decomposition and hence could not explain the concentration-dependence of O_3 adsorption.

In a field experiment, Weschler et al. (1994a) used a one-compartment mass balance model to predict O_3 to estimate O_3 removal efficiency:

$$I/O = E_x(1 - F_s)/[v_d (A/V) + E_x] \quad (2.11)$$

where I/O = ratio of indoor and outdoor O_3 concentrations; E_x = air exchange rate (h^{-1}); F_s = fractional efficiency of carbon filters for O_3 removal and $v_d (A/V)$ = rate at which O_3 is removed by indoor surfaces (product of the deposition velocity and the surface-to-volume ratio (h^{-1})). Equation 2.12 assumes continuous fan operation, no recirculated air, negligible infiltration of untreated air and no indoor O_3 sources, and was used in a situation where it was difficult to directly measure upstream and downstream ozone concentrations.

Stephens et al. (1986) attempted to model the heterogeneous reaction of ozone on carbonaceous surfaces. Their crude mechanistic model included a Langmuir-type adsorption-desorption equilibrium component followed by a surface reaction component. However, they did not have enough high quality data to develop a quantitative model at the time. Gómez-Serrano et al. (2002) proposed a kinetic model for the ozonation of cherry stone char that was based on a Langmuir-Hinselwood adsorption-desorption mechanism.

2.2.6 Effect of humidity on O_3 removal efficiency

It is generally accepted that in physical adsorption, the presence of water vapor decreases the efficiency and capacity of AC to remove non-reactive gases (Werner, 1985; Gong and Keener, 1993). However, there have been mixed results in studies that have investigated the effect of humidity on chemisorption processes. Ellis and Tometz (1972) did not notice any effect of changing the relative humidity over a range of 10-70%. Lee and Davidson (1999) found that changes in relative humidity from 20-50% did not significantly affect the performance of granular AC (GAC). They did observe a slight increase in efficiency when the relative humidity was increased from 50% to 80%, which

they suggested was due to increased decomposition of O_3 by water. However, performance of AC fibers (ACF) was negatively affected by increasing the humidity. The 10% breakthrough time was 140 min at 20% RH, but only 10 min at 50% RH. When the relative humidity was increased from 50% to 80%, efficiency improved slightly, which was once again attributed to decomposition of O_3 by water. The reason for the difference in performance between GAC and ACF, they proposed, was because water molecules more easily block the micropores in ACF. In contrast, Dusenbury and Cannon (1996) found that humidity allowed more ozone to penetrate into a GAC bed as compared to dry air; humidity levels were not specified.

2.2.7 Effect of O_3 exposure on VOC adsorption capacity of AC

Ozone exposure affects adsorption capacity by decreasing the surface area of AC and increasing the amount of oxygen chemisorbed on the carbon surface. The VOC adsorption capacities for nonpolar compounds such as n-hexane have been shown to be much lower for AC that was treated with O_3 even though the O_3 -exposed AC had a larger specific area (You et al., 1994). The authors suggested that in addition to the O_3 causing the formation of C-O and C=O surface functional groups, some of the O_3 is adsorbed onto the carbon's surface. This causes many of the active sites to be covered by either O_3 or O, which limits the amount of nonpolar molecules that can be adsorbed by van der Waals forces. However, You's group found that when the adsorbate is a polar compound such as methyl ethyl ketone, the adsorption capacity of virgin and O_3 exposed AC is roughly equal. This, they proposed, is because the more oxygenated surface functional groups there are on AC, the higher the affinity of the sorbent to adsorb polar compounds.

2.3 Effect of VOC loading on gas-phase filtration of O₃ by AC

2.3.1 *Low concentration gas-phase filtration of VOCs*

Physical sorption, which is also known as adsorption condensation, occurs when VOC molecules diffuse onto the surface of the AC. Generally, VOCs with boiling points greater than 100° C are physically adsorbed quite readily. These VOCs exist as vapors but will readily condense to their liquid phase when diffused onto the surface of the AC (Robinson and Ouellet, 1999). VOCs can then move further into the sorbent by secondary diffusion until all external and internal surface area is utilized. However, the diffusion gradient in most indoor environments is low due to the very low VOC levels (ppb range). Because of this low diffusion gradient, secondary diffusion will not readily occur and low-concentration gas-phase filtration remains a surface phenomenon (Robinson and Ouellet, 1999). In addition, since physical adsorption is reversible, compounds may desorb at low concentrations (VanOsdell et al., 1996).

Humidity decreases the efficiency and capacity of AC to remove VOCs (Werner, 1985; Gong and Keener, 1993). Although water vapor is less strongly adsorbed than VOCs, its concentration in air is much higher than VOC concentrations. Thus, water may displace weakly adsorbed compounds while strongly adsorbed compounds may displace water (Werner, 1985). There are four factors that determine the extent that humidity affects VOC adsorption (Werner, 1985): the manner in which the carbon is preconditioned with humidity, the concentration of the VOC, VOC type, and AC type. In general, an increase in humidity level will decrease the adsorptive capacity of the carbon. However, the effect is even more pronounced when the VOC concentrations are low.

2.3.2 Effect of VOC loading on O₃ removal efficiency

Only two peer-reviewed studies were found that measured the effect of VOC loading on O₃ penetration, and both focused on use of advanced oxidants (O₃, OH[•], HO₂, etc.) and the regeneration of spent carbon. Dusenbury and Cannon (1996) exposed 1/8" GAC beds that were saturated with VOCs to high concentrations of ozone (250-350 ppm at 1.5 L min⁻¹) and measured ozone penetration as a function of time. Results are summarized in Table 2-3. Four VOCs were tested, which represented a wide range of ozone reactivity (methyl isobutyl ketone (MIBK), acetone, benzene, and 2,3-dimethyl-2-butene (DMB)). The data indicated that for the first two hours of ozone exposure, the extent of O₃ penetration was a function of the VOC type. Benzene, one of the least reactive of the four VOCs, allowed the most O₃ to penetrate the AC bed, while DMB (the most reactive VOC) allowed none of the O₃ to penetrate. After 24 hr, the penetration of O₃ into the GAC bed was similar to that of virgin carbon, with the exception of MIBK. MIBK behaved quite differently than the other three VOCs in that O₃ penetration increased continuously with time. The authors proposed that the presence of MIBK and its partial oxidation products protected the GAC surface from further oxidation by O₃. In the second study, Cannon et al. (1996) loaded GAC beds (3.8 cm dia x 15.2 cm depth) with MIBK that were then exposed to advanced oxidants for 24 hr. Oxidant regeneration was most effective in the first 2.5 cm of the GAC bed, with most of the MIBK desorbed or destroyed; ~25% of the initial MIBK mass was removed in the remainder of the bed. Only 10-15% of the MIBK was converted into reaction products. Cannon et al. (1996) suggest that the oxidants penetrated only 2-3 cm into the GAC bed, displacing the MIBK.

Soiling of AC filters by submicron particles contributes to a faster decrease in O₃ remove efficiencies (Weschler et al., 1994a). However, Weschler (in the discussion

section following the article) stated that the loading of carbon by other gas-phase contaminants (excluding submicron particles) had little effect on the O₃ removal efficiency. The measured VOC loadings for filters servicing two clean rooms, which were not reported in the article's text, were close to the expected saturation levels for VOCs (4.7% and 3.6% of the original carbon weight), yet the filters continued to remove O₃ with efficiencies of 60% and 90%, respectively. No further information was given regarding the characteristics of the VOC loadings. No peer-reviewed articles were found regarding the effect of VOC loading on O₃ removal efficiency at low concentrations.

2.4 Heterogeneous reactions of O₃ and unsaturated VOCs on AC

2.4.1 Sources of indoor unsaturated VOCs

Many of the unsaturated VOCs that are found indoors are of biogenic origin. Plants naturally emit hundreds of different VOCs into the atmosphere including aldehydes, ketones, carboxylic acids, alkanes, alkenes, isoprene, and terpenes. Terpenes, organic compounds with structures divided into isoprene units, are found in the natural oils of many plants. Monoterpenes (C₁₀), sesquiterpenes (C₁₅), and isoprene (C₅) are very volatile and are emitted from vegetation in large amounts, e.g., the annual global biogenic VOC flux has been estimated to be 1150 Tg yr⁻¹ and consists of approximately 44% isoprene, 11% monoterpenes, and 45% other VOCs (Guenther et al., 1995). Terpenes and isoprene are highly reactive in the atmosphere due to their olefinic double bonds and hence usually have short lifetimes. In addition to playing an important role in indoor air chemistry, terpenes also are important in the formation of photochemical O₃ and secondary atmospheric organic aerosols.

Some commonly occurring unsaturated VOCs and their indoor sources are shown in Table 2-4. Plant oils containing monoterpenes are ingredients in many consumer products such as cleaning products, degreasers, solvents, toiletry items, and insecticides. Unsaturated VOCs are also emitted from office equipment. Leovic et al. (1996) measured emission rates from dry process photocopy machines as high as 12,000 and 1,100 $\mu\text{g h}^{-1}$ for styrene and limonene, respectively. Peak styrene levels from laser printers of 5.27 ppbv have been measured in chamber tests (Lee et al., 2001). Terpenes are also emitted from wood products such as flooring and furniture. In 48-hour chamber tests, terpenes accounted for 7-21% of total VOC emissions (calculated as α -pinene) from particleboard samples (Bauman et al., 1999). Monoterpenes are themselves eye, mucous membrane and skin irritants as observed during inhalation exposure studies in humans and animals (Kasanen et al. 1999).

Because of its reactivity with O_3 and its common occurrence in indoor air, *d*-limonene will be discussed in more detail (Section 2.4.3).

2.4.2 Homogeneous reactions of unsaturated VOCs with O_3

As mentioned earlier (Section 2.2.2), O_3 can react with certain unsaturated VOCs at a fast enough rate to impact IAQ. Ozone attacks a carbon-carbon double bond to form an ozonide that quickly decomposes into one of two possible carbonyl and biradical combinations as shown in the following mechanism (Griesbaum et al., 1996; Feltham et al., 2000; Weschler, 2000):



where: $\bullet$ = an unpaired electron and $*$ represents an excited state. The biradicals are very energy rich and can rearrange or react by different mechanisms, which are not entirely understood (Atkinson et al., 1995). The intermediate products are highly reactive and include such species as the hydroxyl, hydroperoxyl, and alkylperoxyl radicals. The end-result is the formation of stable products such as carbonyl compounds and organic acids. In humidified air, water vapor can also play an important role in O_3 /alkene chemistry leading to an increase in the formation of hydrogen peroxide (Sauer et al., 1999) and formic acid (Zhang et al. 1994). Humidity has also been shown to influence the degree of upper airway irritation, with greater irritation reported in mice exposed to terpene/ O_3 reaction mixtures at low humidity levels compared to high levels (Wilkins et al., 2003) suggesting that some intermediates react with water to form less irritating compounds.

Indoors, the reaction between O_3 and unsaturated VOCs can cause the formation of hydroxyl radicals in concentrations that approach or even exceed outdoor concentrations (Weschler and Shields, 1996). Indoor hydroxyl radical levels track non-linearly with outdoor O_3 levels, indoor alkene emission rates, and air exchange rates (Sarwar et al., 2002). The hydroxyl radicals can go on to react with other indoor pollutants and generate other radicals leading to the formation of additional stable products with one or more carbonyl, carboxylate, or hydroxyl functional groups (Weschler, 2000). Reactions of O_3 with *d*-limonene, α -pinene, 2-methyl-2-butene, and α -terpinene are important sources of OH radicals indoors. Reactions of OH radicals with *d*-limonene, nitrogen dioxide, ethanol, formaldehyde, carbon monoxide, and isoprene are important sinks (Weschler and Shields, 1996). Atkinson et al. (1992) suggested that the

OH radical formation yields depend on the location of the carbon-carbon double bond. Alkenes with internal double bonds have higher OH radical formation yields than those with terminal double bonds. For compounds with multiple double bonds, the O₃ reactions proceed mainly at the internal double bonds.

One of the major products resulting from the reaction of O₃ and most unsaturated VOCs containing a terminal carbon-carbon double bond is formaldehyde. Other products from the reaction of O₃ with common indoor unsaturated VOCs are shown in Table 2-5. Reaction products of *d*-limonene will be discussed in more detail later (Section 2.4.4).

As discussed, reactions between O₃ and unsaturated VOCs produce both reactive free radicals and stable products. The stable products can be further classified as gas-phase or aerosol species. In smog chamber experiments, Glasius et al. (2000) identified three classes of secondary aerosols from the reaction of cyclic monoterpenes with O₃: dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids. Because carboxylic acids are highly polar and have lower vapor pressures than their corresponding aldehydes, they may play an important role in the formation of secondary organic aerosols (SOAs). Recent studies (Weschler and Shields, 1999; Wainman et al., 2000, Rohr et al., 2002; Fan et al., 2003; Sarwar et al., 2004) have shown that O₃/terpene reactions are a significant source of indoor sub-micron particles. Acetic acid and formic acid are the most abundant organic acid products for most terpene/O₃ reactions. Of the higher molecular weight organic acids, dicarboxylic acids are the most abundant with yields ranging from 1-5 mol% (Koch et al., 2000). Dicarboxylic acid yields were found to be slightly lower when cyclohexane was used as an OH radical scavenger, indicating a small contribution by OH radicals in the formation of these acids (Koch et al., 2000).

2.4.3 *d*-Limonene: sources and properties

Limonene (4-isopropenyl-1-methyl-cyclohexene) is a common monoterpene that is present in the oils of pine and citrus trees. It is also found in citrus peels, dill, caraway, fennel, celery, and turpentine. It has a lemon-like odor and is used in many industrial and household products. It is a colorless liquid at room temperature. The commercial purity is usually 90-98%. Impurities usually are other terpenes, including myrcene, α -pinene, β -pinene, sabinene, and Δ^3 -carene (Filipsson et al., 1998). Some of the physical and chemical properties of *d*-limonene are shown in Table 2-6. There are two optical isomers of limonene, *d*-limonene and *l*-limonene. The *d*-limonene isomer rotates a plane of polarized light clockwise and the *l*-limonene isomer causes rotation in the opposite direction. A racemic mixture of the two limonenes (*dl*-limonene) is called “dipentene,” which should not be confused with “commercial dipentene solvent,” which is a mixture of several terpenes including limonene isomers and is often referred to as simply “dipentene.” In recent years, commercial dipentene has been used as an environmentally friendly alternative to chlorinated hydrocarbons and chlorofluorocarbons (Karlberg et al., 1994). Limonene is also used as a flavor or fragrance additive in many foods, cleaning products, and perfumes. It is also used as an industrial solvent and metal degreaser (Filipsson et al., 1998).

Based upon data from many studies since the early 1970s, typical concentrations of limonene in urban/suburban air range from 0.1 to 2 ppb ($0.6\text{--}11.1\ \mu\text{g}/\text{m}^3$), but concentrations as high as 41,000 ppb have been measured near landfill sites (Filipsson et al., 1998). Concentrations vary considerably depending on type of vegetation, season, and time of day, with highest emissions usually in the summer (Filipsson et al., 1998). Indoor concentrations also vary considerably. A 1995-98 study by the U.S. EPA detected

d-limonene in air samples from at least 81% of 56 randomly selected office buildings at levels of 0.3 – 140 $\mu\text{g}/\text{m}^3$ (Girman et al., 1999). Wallace et al. (1991) studied the exposure of 51 Los Angeles residents to VOCs including limonene. They found the arithmetic mean 24-h indoor limonene concentration in February and July to be 37 and 20 $\mu\text{g}/\text{m}^3$, respectively. They also found the arithmetic mean ratios of indoor to outdoor concentrations (12-h overnight) to be 23 and >8 for winter and summer, respectively. Subramanian et al. (2000) suggested that limonene levels indoors could be an effective indicator of indoor air quality and that indoor limonene levels correlated with upper respiratory symptoms reported by office workers in the Midwest. Batterman et al. (2004) recently found limonene in all but one of 49 single family homes tested (average concentration of 14 $\mu\text{g}/\text{m}^3$) and in all 63 public school class rooms tested (4.4 $\mu\text{g}/\text{m}^3$).

*2.4.4 Gas-phase reactions of O_3 with *d*-limonene*

As discussed earlier (Section 2.4.2), reactions between unsaturated VOCs and O_3 can produce both gas-phase and aerosol products. Much of the data regarding the homogeneous reactions of O_3 and limonene have come from studies focusing on atmospheric smog formation. In a review of gas-phase terpene oxidation products (Calogirou et al., 1999), major reaction products were identified as limonon aldehyde (3-isopropenyl-6-oxo-heptanal), keto-limonon aldehyde (3-acetyl-6-oxo-heptanal) and a decarbonylized analogue, limononic acid (3-isopropenyl-6-oxo-heptanoic acid), and keto-limononic acid (3-acetyl-6-oxo-heptanoic acid). Structures of these products are shown in Figure 2-2. Other major reaction products included formaldehyde and lesser amounts of 4-acetyl-1-methylcyclohexene (also known as AMCH or limona ketone). AMCH can also react with O_3 forming two biradicals that may eventually form low-volatility C_9 and C_{10} oxidation products (Grosjean et al., 1993). It can also react with $\text{OH}^\bullet$ forming

smaller carbonyls such as formaldehyde, glyoxal, and 3-oxobutanal (Grosjean et al., 1992). Calogirou et al. (1999) estimated the chemical lifetimes of limona ketone and limonon aldehyde in the troposphere ($[O_3]=30\text{ppb}$) to be 2.6 hours and 2 d, respectively. Other products that have been identified following limonene/ O_3 reaction are ethanol, acetone, isopropanol, octanal, nonanal, limonene oxides, decanal, acetaldehyde, acrolein, propanal, hexanal, formic acid, acetic acid, C2-C6 linear saturated aldehydes, and carvone (Clausen et al., 2001; Wolkoff et al., 2000). It is anticipated that with the application of new analytical techniques, even more limonene oxidation products will be identified.

Using reaction conditions typical of indoor air, Zhang et al. (1994) obtained concentrations of $81\text{--}509\text{ }\mu\text{g m}^{-3}$, $31\text{--}39\text{ }\mu\text{g m}^{-3}$, and $6\text{--}58\text{ }\mu\text{g m}^{-3}$ for formaldehyde, formic acid, and acetic acid, respectively. They also found that formaldehyde yields ($125 \pm 28\%$) depended on the initial reactant concentrations, with the greater than unity stoichiometry indicating additional reactions involving Criegee biradicals.

Limonene/ O_3 reactions may also be a source of hydroxyl and other radicals. Atkinson et al. (1992) obtained an OH radical formation yield for the gas-phase reaction of limonene and O_3 of 0.86 (uncertainty factor of ~ 1.5). However, Fick et al. (2002) did not find any evidence of hydroxyl radical formation in limonene/ O_3 experiments conducted with/without an $OH^\bullet$ scavenger. Li et al. (2002) introduced controlled levels of O_3 and limonene into an unoccupied office and measured total hydroperoxide levels of 0.6 – 0.8 ppb and 1.0 – 1.5 ppb, at high and low air exchange rates, respectively.

Limonene/ O_3 reactions are a significant source of submicron particles. Using varying reactant concentrations and experimental conditions in limonene/ O_3 chamber

studies, Rohr et al. (2003) measured particle concentrations ranging from 51-11213 $\mu\text{g m}^{-3}$ and particle counts ranging from 4.2×10^5 to $1.6 \times 10^7 \text{ cm}^{-3}$ with O_3 as the limiting reagent. Mean particle diameters ranged from 45 to 107 nm and the time to reach steady state was 21-30 min. In addition, particle growth occurs over time due to condensation and coagulation and is greatest at low air exchange rates (Rohr et al., 2003; Weschler and Shields, 1999; Koch et al., 2000, Weschler and Shields, 2003). Koch et al. (2000) analyzed aerosol samples from the ozonolysis ($4 \times 10^{13} \text{ molecule cm}^{-3} \text{ O}_3$) of limonene ($1 \times 10^{14} \text{ molecule cm}^{-3}$) and found molar yields of 6.1% for formic acid, 6.2% for acetic acid, 1.3% for dicarboxylic acids, 0.6% for acetylcarboxylic acids, and <2% for other acids. Using reaction conditions typical of indoor air, Zhang et al. (1994) found average molar yields of $42 \pm 17\%$ and $30.3 \pm 14.7\%$ for formic acid and acetic acid, respectively. Weschler and Shields (1999) measured net particle mass concentration increases as large as $95 \mu\text{g m}^{-3}$ in simulated office settings with supplemental O_3 and limonene.

2.4.5 Interactions of O_3 with surfaces

As discussed earlier (Section 2.2.2), heterogeneous reactions of O_3 with chemicals that constitute or are adsorbed on surfaces are the main O_3 removal processes indoors. The interactions of O_3 with surfaces are not as well understood on a molecular level as are the interactions with gaseous species. There are two processes that must occur in surface deposition: transport of the pollutant to the surface, and the subsequent uptake onto the surface. The transport of the pollutant to a surface depends on the thickness of the boundary layer, which depends on the airflow near the surface, and the diffusion rate of the pollutant in air. Surface uptake depends on the *mass accommodation coefficient*, which is defined as the number of “sticks” of an O_3 molecule colliding with a surface per total number of collisions (Reiss et al., 1994). The mass accommodation coefficient

varies with the nature of the surface, compounds adsorbed onto the surface, temperature, and relative humidity (Weschler, 2000). Typical mass accommodation coefficients for indoor surfaces such as glass, latex paint, and wallpaper have been experimentally determined to range from 10^{-5} to 10^{-7} (Reiss et al., 1994). For a clean carbon surface at steady state, Stephens et al. (1986) determined the “sticking coefficient” to be in the order of 10^{-3} and 10^{-5} . Fendel et al. (1995) found the “sticking coefficient” for submicron carbon aerosol particles to be in the order of 10^{-4} under typical stratospheric O_3 concentrations. Once a “stick” occurs, the O_3 molecule can react with surface constituents to produce products such as VOCs or it can decompose through a series of surface assisted steps (Weschler, 2000). For a given VOC, the VOC *formation factor*, κ , is defined as the number of molecules of VOC formed on the surface divided by the total number of “sticks” (Reiss et al., 1995). Each VOC formed by reaction with O_3 has a specific κ . Reiss et al. (1995) developed an experimental method for measuring values of κ for latex paints. However, no studies were found in which κ values were measured for AC.

2.5 Sampling and analysis of terpenes and terpene oxidation products

2.5.1 Sampling and analysis techniques.

Modern analytical techniques allow for efficient measurement of most terpenes. This is especially true for the least reactive terpenes such as limonene and pinene when sampling at low O_3 concentrations. Highly reactive terpenes can be difficult to sample because of their short atmospheric residence times. For example, β -ocimene isomers, which has a atmospheric half-time on the order of minutes, contains 3 C-C double bonds and reacts 40-50 times faster than β -pinene (Atkinson et al., 1990).

Most published methods include trapping the terpenes on an adsorbent medium (polymers or carbon-type sorbents) followed by thermal desorption, cryofocusing, and gas chromatography with either a FID or MS detection system. These methods can also be used to sample and analyze many terpene oxidation products. However, some compounds such as formaldehyde and other low molecular weight carbonyls require the use of special derivatization techniques as discussed below.

Potential problems in the sampling and analysis of terpenes include reaction with O_3 and other oxidants during sampling, rearrangement during thermal desorption, retention of polar, oxygenated terpenes by humidity-removal systems, and chromatographic interference from trace organic compounds (Larsen et al., 1997). Interferences from O_3 and other oxidants will be discussed in greater detail in a later section (Section 2.5.2)

Special methods are required for the sampling and analysis of formaldehyde and other low molecular weight carbonyls. The most commonly used method for the analysis of formaldehyde in ambient air is U.S. EPA Compendium Method TO-11A (1999), although other methods are available. In addition to formaldehyde, at least 14 other carbonyl compounds can be identified using this method. The TO-11A method is based on the reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (DNPH) in the presence of a strong acid that acts as a catalyst forming a stable hydrazone derivative. Compounds are collected using DNPH-coated silica gel cartridges. Pre-coated DNPH cartridges are available commercially and are preferred by most users because cartridges are quite tedious to prepare and easily contaminated. Samples are separated and analyzed by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection.

Long-term active sampling (1-24 h) can detect formaldehyde levels in the low ppbv range, while short-term sampling (5-60 min) can be used for concentrations in the ppmv range. As with the sampling and analysis of terpenes, O_3 can present many problems, which will be discussed in the next section.

2.5.2 Interferences from O_3 .

It is necessary to remove O_3 prior to sampling because it can cause significant interferences when analyzing trace gases. Helmig (1997) provides an extensive review of O_3 interferences that have been observed. Briefly, O_3 can cause interferences in cryogenic enrichment techniques (losses of unsaturated and sulfur compounds), solid adsorbent sampling (losses of unsaturated compounds, artifacts, rearrangements), and derivatization techniques (losses of carbonyl compounds, artifacts, degradation of derivatizing agents). O_3 interferences during solid adsorbent sampling will be discussed in more detail below.

Numerous studies have demonstrated that unsaturated VOCs such as monoterpenes, styrene, and isoprene trapped on Tenax-TA can react with O_3 to form oxidized reaction products. Reduction of analyte yields depends on the structure of the compounds. Saturated and aromatic compounds are generally stable even at concentrations much higher than ambient. Terpene losses increase with the number of carbon-carbon double bonds (Calogirou et al., 1996). The amount of oxidation depends on both the duration of sampling time and the O_3 concentration. Measured losses of limonene under ambient conditions have ranged from negligible to as high as 97% (Helmig, 1997).

In addition to reacting with unsaturated compounds adsorbed on solid adsorbents, O_3 can also react with the sorbent itself to form artifacts. The type and amount of

artifacts formed are dependent on the sorbent composition. Cao and Hewitt (1994) exposed four commonly used sorbents (Chromosorb 106®, Carbotrap®, Tenax-TA®, and Tenax-GR®) to 180 ppb of O₃ for one week. They found that the Chromosorb and Carbotrap adsorbents were generally unaffected by O₃. However, chromatograms of both Tenax-TA and Tenax-GR had several new peaks, with benzaldehyde and acetophenone being the most significant. There were also slight increases in benzene, toluene, and n-heptane. The amounts of artifacts produced from Tenax-GR were much smaller than those of Tenax-TA, which can be attributed to it containing 23% graphitized carbon. Other studies have noted the presence of artifacts in addition to (but not limited to) those mentioned above including phenol, C₇-C₉ n-alkanes, and C₆-C₁₀ n-aldehydes (Helmig, 1997, Klenø et al., 2002). Pellizzari et al. (1984) found that when sampling in ambient air with a high relative humidity, the quantities of artifacts on Tenax GC increased. They also found that there were significantly fewer artifacts on aged Tenax GC than on virgin Tenax GC.

Ozone may also cause interferences when using derivatization techniques for air sampling. Several kinds of interferences have been identified as reviewed in Helmig (1997). The sampling and analysis of carbonyl compounds by reaction with the derivatizing agent 2,4-dinitrophenylhydrazine (DNPH) to form carbonyl hydrazones has been the most extensively studied. Ozone has been found to deplete the derivatization agent DNPH as well as deplete the carbonyl hydrazones (negative interference). It can also lead to the formation of artifact carbonyl hydrazones (positive interference) or other DNPH products that can interfere with chromatographic analysis.

Ozone removal typically involves one of the following techniques: annular denuder, impregnated filter or glass wool, sampling through tubes containing a crystalline reactant retained by glass wool plugs, metal oxide catalysts, gas-phase titration of O₃ with nitrogen oxide, or direct pretreatment of the adsorbent (Helmig, 1997). Helmig (1997) published an extensive review of several O₃ removal techniques that have been previously tested or that have potential for the use in atmospheric sampling. In addition, there are several techniques that have been successfully used for the sampling of other organic compounds such as carbonyls and organic sulfur compounds but have not been tested for the sampling of terpenes. One additional technique that can be used to minimize interferences by O₃ is to limit the time available for ozonolysis. Calogirou et al. (1996) found that by increasing the flow rate and limiting the sampling duration from 10 min to 30 s, significant enhancement of analyte recoveries resulted, while allowing the same volume of air to be collected.

Techniques that remove O₃ prior to sampling also can remove oxygenated reaction products, a potentially serious issue when sampling for oxidation products. Fick et al. (2001) tested several different O₃ scrubbing materials for both for their effectiveness in recovery of four different common terpenes and isoprene as well as five major oxidation products. Of the nine scrubbers tested, potassium iodide (KI) was found to be the best scrubber overall for the recovery of both terpenes and their oxidation products. In addition, KI has been frequently used for the sampling of aldehydes by the DNPH method and has been shown to effectively remove O₃ in several field and smog chamber experiments as reviewed by Helmig (1997). The main disadvantage of potassium iodide is its ability to form alkyl iodide artifacts. However, these artifacts, if

present, should be easily identified by their mass spectra. Common fragments of these compounds are H^+ , HI^+ , and an alkyl group, with abundant signals observed at 127 and 128 (Helmig and Greenberg, 1995).

It is believed that O_3 is destroyed by KI in the presence of moisture by the following reaction (Helmig and Greenberg, 1995):



When O_3 -laden air is drawn through a KI scrubber, iodide is oxidized to iodine, which destroys the O_3 . Stoichiometrically, one gram of KI has the capacity to destroy 144 mg of O_3 . Previous studies have found O_3 removal capacities to be as high as 25,000 ppb-h for KI scrubbers at 50% relative humidity. However, their capacities are greatly reduced when sampling in dry air (Helmig, 1997), which is plausible because water is a reactant in the above reaction.

There are three general techniques for the use of KI-based O_3 traps: annular denuder traps, impregnated glass wool traps, and crystalline KI traps. Their preparation is described in Helmig and Greenberg (1995) as well as several other references.

2.5.3 Interferences other than O_3

High concentrations of HO_x radicals can be generated from ozonators used in certain types of artificial air generators (Koppmann et al., 1995). Thus, it is possible that some of the effects of HO_x radicals may be erroneously attributed to O_3 . In addition, other compounds may be present that enhance (radicals) or quench (NO , unsaturated hydrocarbons) the effect of O_3 .

Squalene, a straight-chain triterpene ($C_{30}H_{50}$) containing six carbon-carbon double bonds, may also cause interferences. Because of its structure, it is very reactive with O_3 . Squalene is a metabolic precursor of sterols and steroids and is also a major component

of human skin lipids. It has been shown that contamination of samples with human skin lipids can cause interferences when exposed to O₃. Accidentally touching any material that is exposed to O₃ can result in significant artifact formation. Artifacts include geranyl acetone, 6-methyl-5-hepten-2-one (6-MHO), 4-oxopentanal (4-OPA), nonanal, decanal, and acetone (Fruekilde et al., 1998). Thus, great care must be taken to avoid touching test samples, glass wool, adsorbent material, and any other material that will be exposed to O₃ with bare hands.

Auto-oxidation may also cause interferences. When *d*-limonene is exposed to air and daylight, it rapidly undergoes auto-oxidation (Karlberg et al., 1992, 1994). The main auto-oxidation products include cis-and trans-limonene-1,2-oxide, carvone, cis-and trans-carveol, and several limonene hydroperoxides. Several of these auto-oxidation products have been shown to be potent contact allergens. In addition, prolonged oxidation causes a change in the technical properties of limonene such as an increase in viscosity, which is due to the polymerization of the oxidation products (Karlberg et al., 1994). Cold and dark storage of *d*-limonene in closed vessels has been shown to prevent auto-oxidation for a year without the addition of an anti-oxidant (Karlberg et al., 1994).

In addition to auto-oxidation products, terpene impurities may also lead to erroneous results. The highest available purities of limonene are typically 98% and 99%. The impurities in 98% *d*-limonene are mainly other terpenes, while the impurities in the 99% *d*-limonene are mainly limonene auto-oxidation products (Clausen et al., 2001).

Finally, the presence of trace amounts of acids in the atmosphere or on solid adsorbents may cause chemical rearrangements. For example, α - and β -pinene isomers were found to be converted into camphene, limonene, *p*-cymene, and other monoterpenes

in the presence of trace amounts of sulfuric acid on Tenax adsorption cartridges (Strömvall and Petersson, 1992). Pretreatment of the sorbent with a hydrogen carbonate solution was found to prevent these acid rearrangements. In addition, high levels of halogens have been shown to cause chemical transformations of olefins in the presence of O_3 during ambient air sampling (Pellizari and Krost, 1984).

2.6 Ozone uptake by diesel soot

2.6.1 Background.

Tropospheric ozone (O_3) is the most widespread air pollutant in the US and in many other countries. Ambient O_3 concentrations in many areas exceed standards (120 ppb, 1-hr average; 80 ppb, 8-hr average in the US), and it has proven exceedingly difficult to reduce O_3 concentrations. In urban areas, high concentrations of O_3 often co-exist with other air pollutants, including particulate matter ($PM_{2.5}$, PM_{10}). O_3 removal mechanisms include a number of homogeneous and heterogeneous mechanisms, the most significant being deposition on dry surfaces or water, photolysis by UV radiation, and photochemical reactions involving the HO_2 radical (Paluch et al., 1995).

Soot is a by-product of diesel fuel combustion and consists of both elemental carbon (EC) and organic carbon (OC) fractions as well as up to 10 mol % of hydrogen and other trace elements (Seinfeld and Pandis, 1998). Soot itself is of interest since it is associated with adverse health and visibility impacts, and because it is an important component of $PM_{2.5}$ and PM_{10} . The US EPA (1996) estimated EC emission rates of 0.1-0.2 g km^{-1} and 0.5-1.2 g km^{-1} for light and heavy-duty diesel vehicles, respectively. Greater than 90 wt % of the EC emitted by diesel engines is in the submicron range with mean volume diameters from 50 to 250 nm (Seinfeld and Pandis, 1998). Braun et al.

(2004) characterized diesel particulate matter into three size ranges: fractal aggregates (70-100 nm); primary particulates (10-20 nm); and particulate subunits (~ 2 nm). Soot particles can adsorb a significant amount of organic vapors as the combustion products cool. Although soot particles have “unique” chemical and physical properties, aging processes, such as coagulation and condensation, cause them to become mixed with other types of atmospheric PM, thereby becoming more similar to other particles in the atmosphere (Seinfeld and Pandis, 1998).

Due to its large surface area, the graphitic structure of soot particles provides an ideal surface for heterogeneous chemical reactions. For fuel combustion soots, specific surface areas typically range from 60-150 m² g⁻¹ and track linearly with increasing air/fuel combustion ratio (Chughtai et al., 2002). Reactions of O₃ and other oxidants can affect the structure and properties of soot and other carbonaceous particles. Whether atmospheric O₃/soot reactions are significant depend both on soot concentration and its structure and properties, which in turn depend on the fuel composition, combustion conditions, and aging processes (Pöschl et al., 2001; Wei et al., 2001; Chughtai et al., 2002; Seinfeld and Pandis, 1998). Atmospheric soot chemistry may also be affected by the presence of other contaminants, such as volatile organic compounds (VOCs), inorganic compounds, and radicals, which can potentially affect soot surface reactivity or lead to indirect O₃ losses. For example, Lary et al. (1999) suggested that heterogeneous reduction of NO₂ and HNO₃ on soot could form an O₃ sink. Fan et al. (1996) found that particle-associated nitro polycyclic aromatic hydrocarbons (NPAH) and PAH are degraded by O₃, which may be the dominant loss process for these compounds at night.

2.6.2 O_3 loss on soot.

Much of the literature regarding O_3 loss on particulate matter has focused on O_3 reactions with soot emitted by aircraft in the upper troposphere/lower stratosphere and the potential contribution to stratospheric O_3 depletion (Bekki, 1997; Gao et al., 1998; Lary et al., 1999). Generally, these reactions are believed to have negligible effects on atmospheric O_3 concentrations (Kamm et al., 1999; Disselkamp et al., 2000; Longfellow et al., 2000; Wei et al., 2001; Chughtai et al., 2003; Lelievre et al., 2004).

A few studies have explored the potential for soot particles to act as O_3 scavengers in the lower atmosphere. While soot particles are normally hydrophobic, ozonation causes them to become more hydrophilic, potentially acting as cloud condensation nuclei (Kotzick and Niessner, 1999; Decesari et al., 2002), which in turn could also affect atmospheric residence times of particles as since rain-out is a major removal mechanism for atmospheric soot aerosols. Berkowitz et al. (2001) proposed a heterogeneous reaction for aerosol particles in the lower troposphere as one explanation for O_3 depletion observed in a nighttime urban plume. O_3 removal by DPM probably occurs both day and night as sunlight does not appear to affect O_3 loss. In studying the effect of simulated sunlight irradiation on the loss of O_3 on n-hexane soot, Smith and Chughtai (1997) found that although solar radiation shifted product formation toward gaseous CO_2 , CO and H_2O rather than functional groups on the soot surface, it did not significantly affect the overall rate or quantity of O_3 loss.

The O_3 loss rate on soot aerosol appears to depend on specific surface area, reaction time, O_3 concentration, relative humidity, and temperature (Kamm et al., 1999; Chughtai et al., 2002; 2003). Current understanding is based on laboratory experiments generally using n-hexane soot as a surrogate for fuel combustion aerosols (from diesel,

kerosene, JP8). Most chemical properties are similar, the main difference being the presence of trace elements or commercial additives in fuels (Chughtai et al., 2002). Still, O_3 removal mechanisms are not completely understood. Smith and Chughtai (1997) characterized O_3 loss on n-hexane soot particles by an initial rapid, catalytic decomposition stage, followed by slower stages during which surface carboxylic groups are formed, gaseous CO_2 , CO , and H_2O are desorbed, and further O_3 is lost by a second-order process. During the catalytic stage, in which O_3 is converted to O_2 , the soot is treated as a catalyst and is not destroyed by O_3 (Wei et al., 2001). During the non-catalytic stages, an O_3 molecule oxygenates one active site on the soot's surface, thereby inactivating or "poisoning" the site (Wei et al., 2001). "Poisoned" soot may be regenerated by further reaction with O_3 to liberate O_2 (Wei et al., 2001; Smith and Chughtai, 1997). Kamm et al. (1999) proposed a set of four equations for modeling O_3 loss on soot aerosol: rapid surface reaction resulting in a loss of a monolayer-equivalent of O_3 ; O_3 -induced recovery of surface sites; spontaneous recovery of surface sites; and spontaneous conversion of active sites into inactive sites (passivation). The first three equations represent a catalytic cycle that continues until either all active sites or O_3 is depleted.

The reversibility of O_3 loss on soot also remains an open question. Fendel et al. (1995) and Kamm et al. (1999) proposed that O_3 loss was irreversible, characterized by an initial adsorption process where an O atom is adsorbed and liberated as O_2 . Earlier, Stephens et al. (1986) proposed that O_3 adsorption on charcoal is reversible consistent with a Langmuir isotherm, with O_3 molecules subsequently reacting heterogeneously to form oxygenated surface groups, CO and CO_2 . Pöschl et al. (2001) extended this

mechanism to fresh spark-discharge soot particles coated with benzo[*a*]pyrene, a polycyclic aromatic hydrocarbon (PAH), suggesting that gaseous O₃ loss initially proceeds via fast reversible adsorption and then continues through irreversible oxidation reactions with surface PAH or carbon leading to the formation of oxygenated surface functional groups. These functional groups can then be further oxidized to form CO, CO₂, and semi-volatile organic compounds.

Also controversial is the extent of catalytic decomposition of O₃ on soot. Pöschl et al. (2001) suggested that catalytic decomposition of O₃ may occur in parallel with oxidation reactions on the particle surface, but stated the need for more studies to determine whether decomposition was significant. While Smith and Chughtai (1997) attributed initial, rapid O₃ loss to catalytic decomposition, Stephens et al. (1986) and Disselkamp et al. (2000) stated that their results did not show any evidence of a catalytic process.

2.7 Chemisorption models.

Several models have been developed to characterize the kinetics of chemisorption processes on solid surfaces, including the Elovich, Ritchie, Lagergren pseudo-first order, and pseudo-second order equations (e.g., Ho and McKay, 1998; Cheung et al., 2000). These models have been used for a myriad of sorbents (e.g., moss, clay, fly ash) and sorbates (e.g., metal ions, dyes, VOCs). However, they have not yet been validated for O₃/AC or O₃/soot reactions. The basis and form of these four models are summarized below.

2.7.1 Lagergren pseudo-first order model.

The pseudo-first order Lagergren equation has been used to describe the kinetics of a variety of sorbate/sorbent systems (Ho and McKay, 1998):

$$dq_t/dt = k_1 (q_e - q_t) \quad (2.16)$$

where q_t = sorption capacity at time t ($\mu\text{g mg}^{-1}$), q_e = the equilibrium sorption capacity ($\mu\text{g mg}^{-1}$), and k_1 = pseudo-first order rate constant (hr^{-1}). Eq. (2.16) can be integrated to:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2.17)$$

Plots of $\ln(q_e - q_t)$ vs. t should be linear if pseudo-first order kinetics apply. Since q_e is rarely known and is generally impractical to measure, the data can be extrapolated to $t = \infty$ or q_e can be determined by trial-and-error. Pseudo-first order kinetics often only apply to the first 20 – 30 minutes in many sorbate/sorbent systems.

2.7.2 Pseudo-second order model.

Pseudo-second order kinetics may be represented by the following equation (Ho and McKay, 1998):

$$dq_t/dt = k (q_e - q_t)^2 \quad (2.18)$$

which following integration and rearrangement becomes:

$$t/q_t = 1/h + t/q_e \quad (2.19)$$

where h = initial sorption rate as $q_t/t \rightarrow 0$ ($\mu\text{g mg}^{-1} \text{ hr}^{-1}$). Thus, a plot of t/q_t vs. t should yield a straight line from which q_e , k , and h can be directly determined from the regression coefficients if pseudo-second order kinetics apply. Unlike the pseudo-first order model, there is no need for extrapolation or solving by trial-and-error to obtain q_e . Also, if applicable, this model has the advantage of fitting the entire range of data rather than just the first few minutes of chemisorption.

2.7.3 Elovich equation.

The Elovich equation has been applied successfully to some chemisorption data where the adsorbing surface is heterogeneous (Cheung et al., 2000). The Elovich equation uses additional terms,

$$dq_t/dt = a \exp (-b q_t) \quad (2.20)$$

where a = initial sorption rate ($\mu\text{g mg}^{-1} \text{ hr}^{-1}$), and b = adsorption constant ($\text{mg } \mu\text{g}^{-1}$) for a given experiment (Ho and McKay, 1998). Following integration, eq. (2.20) becomes:

$$q_t = 1/b \ln (a b) + 1/b \ln (t + t_0) \quad (2.21)$$

where t_0 = time constant (hr) and is estimated by trial-and-error to achieve a linear plot of q_t versus $\ln (t + t_0)$. If the Elovich model applies, the constants, a and b , can then be calculated from the slope and intercept. If $q_t = 0$ at $t = 0$, $t_0 = 1/ab$. However, if an amount of gas is instantaneously adsorbed, the integrated form of eq. (2.20) becomes (Low, 1960):

$$q_t = 1/b \ln (a b) + 1/b \ln (t + k) \quad (2.22)$$

where $k \text{ (hr)} = t_0 \exp (b q_0)$. Because of rapid initial adsorption or other kinetic processes that may displace plots, the Elovich equation is not practical for determining values of q_t . Rather, it is most useful for determining adsorption rates and not sorption capacities (Low, 1960).

2.7.4 Ritchie model.

The Ritchie equation was originally proposed for modeling chemisorption of gases on carbon and has since been applied to the adsorption of cadmium ions on bone char in aqueous solutions (Cheung et. al, 2000). The differential form is:

$$d\theta/dt = k (1 - \theta)^n \quad (2.23)$$

where θ = fraction of surface sites occupied by the adsorbed gas, k = rate constant ($\text{mg } \mu\text{g}^{-1} \text{ hr}^{-1}$), and n = number of surface sites occupied by each gas molecule. At time, t , $\theta = q_t/q_e$. Assuming second-order kinetics and that $\theta = 0$ at $t = 0$, eq. (2.23) can be integrated, simplified and rearranged to a linear form,

$$1/q_t = 1/(k q_e t) + 1/q_e \quad (2.24)$$

from which q_e and k can be determined from the regression of $1/q_t$ vs. $1/t$.

2.8 References

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Table 2-1 Half-lives and rate constants for the reaction of some common indoor VOCs with O₃.

Compound	Half life		Rate Constant (ppb ⁻¹ hr ⁻¹)
	50 ppb O ₃ (hr)	100 ppb O ₃ (hr)	
Toluene	1,040,000	522,000	3.69x10 ⁻¹²
o-Xylene	15,000	7,850	2.46x10 ⁻¹⁰
Isoprene	13	6.5	2.95x10 ⁻⁷
<i>d</i> -Limonene	0.75	0.37	5.14x10 ⁻⁶
α -Pinene	1.8	0.9	2.14x10 ⁻⁶
Styrene	7.25	3.62	5.31x10 ⁻⁷

*From various sources as summarized in Weschler (2000).

Table 2-2 Ozone removal efficiencies by charcoal filters for eight years of continuous service.

Filter location	Ozone removal efficiencies (%)				
	0 yr ^a	3.1 yr ^a	5 yr ^b	7 yr ^b	8 yr ^b
Test plenum	95	90	90	-	-
Cleanroom 1	85	60	60	-	60
Cleanroom 2	95	95	92	70	-

^a Weschler et al. (1994)

^b Shields et al. (1999)

Table 2-3 Ozone penetration into a 1/8-in VOC-saturated GAC bed. The O₃ concentration was 250-350 ppm and had a flow of 1.5 l min⁻¹ (data taken from Dusenbury and Cannon, 1996).

Compound	O ₃ rate constant (cm ³ molecule ⁻¹ s ⁻¹)	O ₃ penetration at onset (%)	O ₃ penetration after 24 hr (%)
Virgin carbon	-	4	26
Methyl isobutyl ketone	~ = 10 ^{-20a}	18	62
Acetone	~ = 10 ^{-20a}	20	22 ^b
Benzene	7 x 10 ⁻²³	68	27 ^b
2-3-Dimethyl-2-butene	1.2 x 10 ⁻¹⁵	0	33 ^b

^a Value was inferred by the authors from established values for similar saturated ketones.

^b Value was estimated from a graph.

Table 2-4 Some unsaturated VOCs commonly found indoors and their sources.

Compound	Sources ¹
<i>d</i> -Limonene	Commercial "dipentene" solvent, pine oil, citrus oils, fragrances, photocopiers ²
α -Pinene	Oil of turpentine, pine oil, fragrances
α -Terpinene	Commercial "dipentene" solvent, pine oil, fragrances
Camphene	Fragrances
Styrene	Tobacco smoke, carpets, adhesives, office equipment ^{2,3}
Isoprene	Human body effluent, houseplants

¹ From Weschler and Shields (1996), unless otherwise noted.

² Leovic et al. (1996)

³ Lee et al. (2001)

Table 2-5 Some common indoor unsaturated VOCs and their major O₃-reaction products.

Unsaturated VOC	Major products
Isoprene	Formaldehyde, methacrolein, methyl vinyl ketone
Limonene	Formaldehyde, 4-acetyl-1-methylcyclohexene, limonic acid, limononic acid, 7-hydroxylimononic acid, 7-hydroxy-keto-limononic acid
Styrene	Formaldehyde, benzaldehyde
α -Pinene	Formaldehyde, pinonaldehyde, norpinonaldehyde, pinic acid, C10 hydroxy dicarbonyls

From Weschler (2000) and references therein.

Table 2-6 Properties of d-limonene.

Property ¹	<i>d</i> -Limonene
Cas. no.	5989-27-5
Empirical formula	C ₁₀ H ₁₆
Molecular weight	136.23
Boiling point (°C)	175.5-176.0
Melting point (°C)	-74.35
Density (g cm ⁻³ at 25 C)	0.8411
Vapor pressure (Pa at 20 C)	190
Water solubility (mg L ⁻¹ at 25 C)	13.8
Henry's law constant (kPa m ³ mol ⁻¹ at 25 C)	34.8
Log K _{ow}	4.23

¹ From Filipsson et al. (1998)

Figure 2-1 Structure of *d*-limonene.

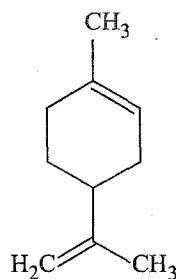
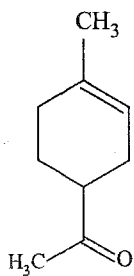
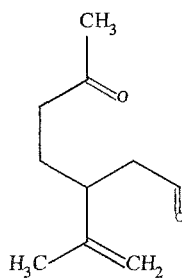


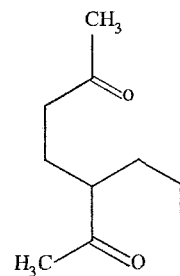
Figure 2-2 Compounds that have been identified as reaction products of *d*-limonene and O₃.



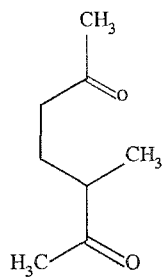
Limona ketone (AMCH)



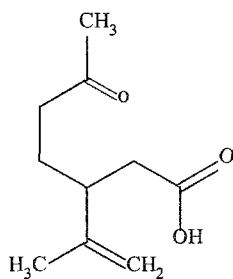
Limonon aldehyde



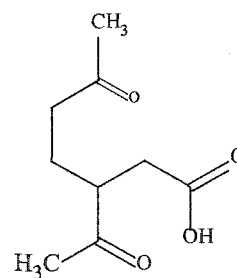
Keto-Limonon Aldehyde



Decarbonylized analogue



Limononic acid



Keto-limononic acid

CHAPTER 3. OZONE REMOVAL BY ACTIVATED CARBON FILTERS

3.1 Abstract

The removal of ozone (O_3) by activated carbon (AC) at the low concentrations found in environmental applications has not been well characterized, in part due to experimental difficulties and the length of time required for analysis. A sequence of experiments was performed to investigate the performance and use of chemisorption models for O_3 -AC systems and to determine whether O_3 removal efficiencies of AC at low concentrations could be predicted using tests conducted at high O_3 concentrations. Using a flow-through experimental system, small quantities (0.5 - 20 mg) of AC were exposed to O_3 concentrations from 0.12 to 1.8 ppm and O_3 breakthrough curves for up to seven AC samples were measured simultaneously. To further decrease breakthrough times, experiments also were conducted using a mixture of AC and glass beads, with other variables kept constant, e.g., bed depth and geometry.

Experimental results show that O_3 removal by glass beads alone was negligible. O_3 removal by the AC-glass bead mixture was slightly enhanced compared to AC alone. Estimated O_3 removal rates per unit AC mass greatly increased with O_3 concentration and decreased with bed depth. At any O_3 penetration fraction, a curvilinear relationship existed between time to breakthrough and bed mass, which depended on exposure time and O_3 concentration. Relationships between O_3 penetration, breakthrough time, bed

depth, and AC mass were characterized using Lagergren pseudo-first order, pseudo-second order, Elovich, and Ritchie chemisorption models. The Elovich and Ritchie models provided the best fit to the experimental data; however, the lack of generalizable parameters for these models means that O₃ removal on AC must be determined experimentally, and that results obtained at high O₃ concentrations cannot be scaled to environmental conditions. This work demonstrated the feasibility of measuring, in a reproducible manner and within a reasonable time frame, O₃ breakthrough curves and other parameters for AC at environmentally relevant conditions in a controlled laboratory setting using very small quantities of AC. This study indicates critical bed depths, removal rates, and removal capacities relevant for AC filters operating at both low (<200 ppb) and high (500 – 2000 ppb) O₃ concentrations.

3.2 Keywords

Activated carbon, chemisorption models, filters, ozone.

3.3 Introduction

Activated carbon (AC) has been widely used for VOC removal and odor control for decades. The ozone (O₃) removal achieved by AC is an added benefit. Outdoors, O₃ is harmful to human health, plants and materials, even at low concentrations (EPA, 1996). Indoors, the presence of moderate or high levels of O₃ degrades indoor air quality (IAQ). O₃ will also react with unsaturated VOCs, such as monoterpenes that are commonly found in citrus and pine oils and nearly ubiquitous indoors, to produce secondary pollutants that are eye and respiratory irritants (Clausen et al., 2001).

Much of the O₃ found indoors originates from outdoors, where it results from a complex set of chemical reactions involving VOCs, nitrogen oxides, carbon monoxide, and sunlight (EPA, 1996). Outdoor concentrations of O₃ vary considerably, typically peaking in the summer. Many locations exceed the US National Ambient Air Quality Standards (NAAQS) of 80 ppb (8-hr average) and 120 ppb (1-hr average). Indoor O₃ concentrations depend on outdoor levels, air exchange rates, indoor O₃ sources, homogenous reactions with other chemicals present, and removal by surfaces (Weschler et al., 1994; Weschler, 2000). The U.S. Occupational Safety & Health Administration (OSHA) permissible exposure limit (PEL) for occupational exposures is 100 ppb for an 8-hr time-weighted average (TWA). Typical indoor/outdoor (I/O) ratios for O₃ range from 0.2 to 0.7 (Weschler, 2000). Significant indoor sources of O₃ include laser printers, photocopy machines, and electrostatic air cleaners (Weschler, 2000). Because source elimination of O₃ is often impractical, AC filters can be used to help reduce indoor concentrations to acceptable levels.

Available methods for evaluating O₃ removal efficiency of carbon filters have relied on high O₃ concentrations, questionable extrapolations from low or moderate concentration tests, or poorly controlled field studies. Few studies have been performed at environmentally relevant concentrations due to the prohibitively long times required to quantify removals and the difficulty of maintaining the desired test conditions over the tests. Moreover, no generalizable physically-based or empirical models of O₃ removal by AC have been validated. Thus, available information and models provide little guidance regarding the performance of AC filters at low concentrations.

3.4 Purpose

The research in this chapter evaluates whether O₃ removal efficiency of AC at low and environmentally-relevant concentrations can be predicted using laboratory tests conducted at moderate O₃ concentrations, or by the use of extremely small quantities of AC at low O₃ concentrations. Both approaches may afford the ability to evaluate the performance of AC in removing O₃ in a timely manner. Additionally, several models are evaluated that may extend experimental results and potentially provide insight into controlling processes. An improved understanding of O₃ filtration will enable more optimal design and use of filtration systems that are protective of human health and welfare in indoor air quality and other applications.

3.5 Background

3.5.1 Mechanisms of O₃ removal by activated carbon.

Many studies have been conducted to elucidate AC/ O₃ reaction mechanisms. O₃ removal by AC is a chemisorption process. Initially, ozonation increases AC weight, which reaches a maximum and then slowly decreases (Deitz and Bitner, 1972). Elemental analyses have shown a continuous increase in oxygen content coupled with a continuous decrease in carbon (Deitz and Bitner, 1972). Chiang et al. (2002) proposed that O₃ reacts with carbon-hydrogen bonds to form hydroxide compounds or hydrotrioxide intermediates, which are ultimately transformed to carboxyl and carbonyl compounds. Stephens et al. (1986) used a mass balance to show that an oxygen molecule is found for every O₃ molecule lost on the carbon's surface, with the odd oxygen leading to product formation. Takeuchi and Itoh (1993) studied the contribution of unpaired

electrons on AC surfaces in O_3 removal and found that unpaired electrons are partially responsible for initiating O_3 removal. O_3 reacts with the carbon-carbon double bonds on the surface of AC to form epoxides and ozonides (Takeuchi and Itoh, 1993), which can then further react to form CO, CO_2 , and surface functional groups. O_3 oxidation has been found to lead to the formation of hydroxyl, carbonyl, -C-O-, and -COOH surface functional groups (You et al., 1994; Mawhinney and Yates, 2001; Chiang et al., 2002). Valdéz et al. (2002) found a positive linear relationship between O_3 exposure and the number of acid sites on the AC, which was accompanied by a decrease in basic sites. Atyaksheva and Emel'yanova (1989) found three competing processes that occur when O_3 interacts with AC: (a) partial oxidation with formation of surface functional groups, (b) extensive oxidation with formation of CO_2 , and (c) catalytic decomposition. In their study of the interaction of O_3 on the surface of an AC fabric, they found that catalytic decomposition made the main contribution (80-100%) while the remaining O_3 reacted with the AC forming gaseous carbon oxides and surface functional groups. These findings differ from earlier studies that found no evidence of catalytic decomposition on charcoal (Deitz and Bitner, 1973; Stephens et al., 1986). However, O_3 may interact differently with AC fabrics than charcoal.

3.5.2 Chemical and structural changes of O_3 -exposed AC.

In addition to forming oxygen-containing functional groups, O_3 changes the structure of AC. O_3 reactions enlarge existing pores and create new pores. Initially the surface area slightly increases, a result of increased porosity (Deitz and Bitner, 1972; Valdés et al., 2002). Eventually the pore walls are destroyed by the gasification of carbon, which decreases surface area (Valdés et al., 2002). Gasification occurs when the

AC surface is oxidized by O_3 forming CO_2 , which then exits the carbon surface and creates new micropores (You et al., 1994). Deitz and Bitner (1972) provided two possible explanations for the decrease in surface area: chemisorbed oxygen atoms plugging the narrow micropore openings, and the destruction of pore walls. In addition, because the O_3 /AC reaction is exothermic, the increased temperature accelerates reaction rates, and causes the formed CO_2 to react with the AC.

Takeuchi and Itoh (1993) found that unexposed carbon samples have a uniform pore size distribution over the micropore to macropore range. However, O_3 treatment significantly increases the macropore ($10^4 - 10^5 \text{ \AA}$) size range due to breakage of the carbon substrate structure. You et al. (1994) found an increase in the overall effective mass transfer coefficient (K_D) for oxidized carbon, indicating that micropores may be enlarged to form macropores. In contrast, Chiang et al. (2002) found that O_3 -exposed AC had increased BET surface area, micropore area, total pore volume, and micropore volume, due in part to increased micropores, and no significant difference in the macropore and mesopore volumes between virgin and ozonated AC. However, scanning electron microscope micrographs clearly have shown macropore enlargement following O_3 exposure, an indicator of material loss due to chemical reaction (Lee and Davidson, 1999).

3.5.3 Indicators of O_3 removal performance

The ability of AC to remove O_3 is measured by several indicators, including *breakthrough time* and *removal efficiency*. The breakthrough time (t_b) is the time required for the effluent concentration (c_e) to reach some threshold percentage (e.g., 5%) of the influent concentration (c_i). Often, the threshold corresponds to a maximum acceptable level of the pollutant in the effluent air, for example, a fraction of an exposure

limit such as a threshold limit value (TLV). Typically, filters are evaluated by constructing breakthrough curves showing the penetration of O₃ through the filter as a function time.

Filter efficiency or removal efficiency (E) is defined as:

$$E = \frac{(C_i - C_e) \times 100\%}{C_i} \quad (3-1)$$

where C_i and C_e are the influent and effluent O₃ concentrations, respectively.

The *critical bed depth* is the minimum amount of AC required to contain the O₃ mass transfer zone. When the bed depth is less than the critical bed depth, O₃ will immediately appear in the effluent air stream (ASTM, 1998).

Another important property of AC is *sorption capacity*, defined as the maximum amount of a specific substance that can be adsorbed under a given condition (temperature and partial pressure). Sorption capacity depends primarily on the specific surface area (micropore volume), and also on the concentration of metal ions and oxygenated surface functional groups (Chiang et al., 1999). Sorption capacity can be determined experimentally by constructing sorption curves, and most frequently using *isotherms*, which show the equilibrium amount of sorbate adsorbed by a sorbent as a function of sorbate concentration at constant temperature (Balieu, 1989). O₃ adsorption by AC exhibits a Type I isotherm (Afanas'ev et al., 1981), which is characteristic of chemisorption processes on microporous materials such as AC. However, isotherms for AC-O₃ systems are generally not practical to measure due to the prohibitively long time required to reach equilibrium sorption capacity at conditions typical of indoor air filtration applications. Lee and Davidson (1999) constructed an isotherm by exposing very thin (0.26 cm) ACF (activated carbon fiber) filter samples to O₃ concentrations of

120, 300, 500, and 800 ppb until they reached steady state, which corresponded to 95% O_3 penetration fraction of the filter. However, because of differences in pore size distributions and other factors, ACF may behave differently than AC.

Breakthrough time, efficiency, and critical bed depths often are used to select filters appropriate for a given application, along with other parameters such as pressure drop. Typically, high efficiency filters have high pressure drops, which increase operating cost. Lee and Davidson (1999) found that the initial O_3 removal efficiency was not always the best indicator of filter performance. Instead, to compare O_3 filters, they suggested the use of a quality factor, defined as the ratio of a threshold breakthrough time and pressure drop.

Many factors can affect O_3 removal and the performance indicators discussed above, including incoming concentration C_i , flow rate, humidity, temperature, and filter configuration (bed depth, grain size, etc.). Generally, performance indicators pertain to the specific experimental conditions used, and it can be difficult to extrapolate to other conditions. For some sorbate-sorbent systems, e.g., AC with a specific solvent, breakthrough data are often used to estimate the kinetic adsorption constant k and the equilibrium sorption capacity S , e.g., using the Wheeler or similar equation (Balieu, 1989). Although S is concentration-dependent, if its value is determined over a wide concentration range and if the results can be expressed by an appropriate isotherm (i.e., the Langmuir equation), predictive equations often can be used to generalize experimental results (Balieu, 1989). However, AC- O_3 interactions cannot be easily characterized using this approach or other existing predictive models due to its complicated, chemisorptive nature.

3.5.4 Laboratory studies

Most studies addressing O₃ and AC focus on determining the reaction mechanisms or the changes in carbon structure due to ozonation. Only a few laboratory studies specifically address the efficiency of AC to remove O₃ from air, and most of these have used O₃ concentrations that considerably exceed levels found in environmental applications. Ellis and Tometz (1972) found that coconut charcoal and AC had the highest O₃ removal efficiencies (>90% after 15 min) among 26 materials, as tested with an influent O₃ concentration of 250 ppb. Further tests using coconut charcoal indicated that O₃ efficiency decreased with time and increasing flow rate. Increasing O₃ concentrations from 45 to 200 ppb moderately decreased efficiencies, after which efficiencies decreased very slowly as concentrations increased to 1 ppm. However, the tested charcoal had been previously exposed to O₃ for 65 h. Johnston et al. (1989) used O₃ challenge concentrations of 5 ppm to evaluate the O₃ removal capabilities of welding fume respirators. Parmar and Grosjean (1991) tested the ability of several sorbents to remove O₃ and other pollutants from a museum display case and found that 200 g of AC could remove an amount of O₃ equivalent to 20 ppb for one yr at a flow rate of 0.1 L min⁻¹ (0.0010 wt %). The only other laboratory study identified using low O₃ concentrations examined 10 commercial filters (including 8 AC) using influent O₃ concentrations of 120 ppb, and found them to be quite effective at O₃ removal but not indefinitely due to irreversible structural changes (Lee and Davidson, 1999). They also found that the initial O₃ removal efficiency of 1.27 cm thick filter samples varied considerably, e.g., efficiencies from 4.6 to 98% were reported.

Tests at low O₃ concentrations require long exposure times to achieve breakthrough. For example, Lee and Davidson (1999) extrapolated results for 10%

penetration at 120 ppb to estimate that up to $40,000 \pm 10,000$ min (3-5 weeks) was required for 50% breakthrough on a 1.27-cm thick filter sample. Experimental conditions must be stable during these long exposure periods to obtain valid results. It is likely that few studies have been performed at low concentrations due to the prohibitively long time required and the difficulty of maintaining the desired test conditions.

In a review of test methods for gas-phase filtration equipment, VanOsdell (1994) recommended the use of an accelerated loading method for testing of O₃, acid gases, and other irreversibly adsorbing compounds. This recommendation was based on earlier work by Ostojic (1985) who found that the method gave acceptable results for the measurement of breakthrough times based on the total capacity of the adsorbent. The “accelerated loading” method uses high concentrations of O₃ for about an hour, followed by a short period of low concentration loading. This sequence is repeated until the desired breakthrough level is achieved, which takes about 8 hours. This method requires further testing to validate results.

3.5.5 Field studies

Several field studies have shown that AC filters installed in buildings with mechanical ventilation systems can reduce indoor O₃ concentrations. In the Los Angeles area, AC filters used intermittently were found to remove 95, 80, and 50% of the O₃ at the end of the first, second, and third years, respectively (Shair, 1981). In a 37-mo. study, Weschler et al. (1994) measured the O₃ removal efficiencies of commercial AC filters in a test plenum, an air handler providing outside air to a clean room, and a plenum downstream of an air handler providing outside air to another clean room. Updated data from this study were published five years later in a subsequent paper (Shields et al., 1999). They concluded that adequately-sized AC filters have very long service lives for

O₃ removal as long as they are not excessively soiled by submicron particles, which contributes to a faster decrease in O₃ removal efficiency. Salmon et al. (2000) determined that the National Museum of Poland's AC filtration system averaged an O₃ removal efficiency of 77% over a 33-day measurement period. Filters used in each of these studies contained a large amount of granulated AC, and results are not likely to apply for AC-impregnated fiber filters, which have little carbon and very short bed depths, that are commonly found in residential and commercial applications.

3.5.6 Low-concentration O₃ filtration

Although few laboratory studies have specifically addressed low concentration filtration by AC, chemisorption processes may be effective in removing low concentrations (ppb) of O₃. This is in contrast to physical adsorption processes where filter efficiencies are expected to decrease when the contaminant levels are low (Robinson and Ouellet, 1999). The irreversible reaction of O₃ with unsaturated bonds on the carbon's surface should maintain a strong concentration gradient, resulting in high removal efficiency (at least initially). Kelly and Kinkead (1993) found high removals of O₃ (120 ppbv for 80 h) and other gaseous pollutants in tests of chemically-treated air purifiers (carbon composite treated with potassium iodide and potassium hydroxide). However, removal efficiency for non-chemically treated AC is expected to decrease over time due to irreversible changes to the carbon's structure.

3.5.7 Models of O₃ removal by AC

No generalizable model was identified that can predict overall O₃ adsorption and removal by AC. However, several models have been constructed and tested for selected processes or specialized applications. Ellis and Tometz (1972) modeled O₃ decomposition on coconut charcoal, representing only catalytic decomposition;

concentration dependence of O_3 adsorption was not explained. Fendel et al. (1995) and Stephens et al. (1996) developed kinetic models representing the interaction of O_3 with atmospheric carbon particles. Gómez-Serrano et al. (2002) proposed a kinetic model for the ozonation of cherry stone char that was based on a Langmuir-Hinselwood adsorption-desorption mechanism.

Several models have been developed to characterize chemisorption kinetics on solid surfaces, including the Elovich equation, Ritchie equation, Lagergren pseudo-first order equation, and pseudo-second order equation (e.g., Ho and McKay, 1998; Cheung et al., 2000). While these models have been used for a myriad of sorbents (e.g., moss, clay, fly ash) and sorbates (e.g., metal ions, dyes, VOCs), they have not yet been validated for AC- O_3 systems. Many models have been developed for physical adsorption of VOCs on AC and other substrates, but again, these models have not been validated for O_3 . As mentioned, isotherms are generally not practical to construct due the prohibitively long time required to reach equilibrium sorption capacity. Additionally, O_3 adsorption is an irreversible process involving chemical reactions with AC in addition to adsorption, thus, there are limitations in extending physical adsorption models that consider only adsorption/desorption processes.

3.6 Methods

A sequence of laboratory experiments was conducted to determine whether results of high O_3 concentration experiments could be used to predict results of low concentration experiments. Initially, breakthrough curves were measured at high O_3 concentrations using AC quantities from 5 - 15 mg. To determine if even smaller amounts of AC could be used to expedite breakthrough, tests were repeated using smaller

quantities of AC (0.5 – 3.0) in a glass bead mixture that maintained the bed geometry of the earlier tests. Additional tests were conducted to ensure that adsorption by the glass beads was negligible. Finally, tests were conducted using AC/glass bead samples exposed to low O₃ concentrations to determine the relationship between O₃ concentration, O₃ penetration fraction (C_t/C_0 , %), exposure time, and bed depth.

The AC filter bed depths (0.6 – 18 mm) and face velocity (21.2 cm s⁻¹) were selected to match typical values in filter applications. Each test held the following variables constant: temperature (24 C), relative humidity (50% RH), and flow rate/face velocity (160 cm³ min⁻¹ or 21.2 cm s⁻¹). Test durations ranged from 50 to 145 hrs, O₃ concentrations ranged from 122 to 1845 ppb, and AC bed masses ranged from 0.5 to 15 mg. Replicate samples were tested for each experimental condition.

3.6.1 Filter beds

The filter beds were prepared as a cylindrical disk between stainless steel screens in Teflon® tubes (8.5-cm long, 4 mm ID) equipped with Swagelok® fittings. AC particle size (250-300 µm dia) and glass bead size (100-120 µm dia) were selected to minimize wall effects that might lead to short-circuiting within the tube assembly. In the initial experiments, the AC/glass bead samples contained 130 mg of glass beads. The bead mass was reduced to 65 mg in subsequent runs.

The AC was acquired as mesh size 30-60 (Standard Coconut Shell Carbon, G55-C, PICA USA, Columbus, OH), ground using a mortar and pestle, and sieved between 50 and 60 mesh screens. AC samples were weighed to within 0.1 mg on an analytical balance (Mettler Instrument Corp.; Hightstown, NJ). Glass beads (Fisher Scientific; Pittsburg, PA) were weighed to within 1 mg on an electronic balance (Ohaus Corp.; Florham Park, NJ). The samples were loaded into the tube assemblies under vacuum and

held in place with stainless steel screens secured against the tube wall by stainless steel springs. A small plug of glass wool was placed in each end to trap any particles that might escape through the screens. This system maintained a cylindrical bed with flat and near parallel faces. AC bed masses ranged from 0.5 to 3.0 mg for the low concentration experiments, corresponding to bed depths from 0.6 to 3.6 mm. AC masses for the high concentration experiments ranged from 1.0 to 15.0 mg, corresponding to bed depths from 1.2 to 18 mm. When not in use, the AC and packed tubes were stored in a dessicator containing Drierite[®] material to minimize ageing effects.

3.6.2 Exposure and monitoring system

The exposure system (Fig. 3-1) generated the desired O₃ concentration in humidified air and provided very stable O₃ concentrations (within 5.5%). A controlled flow of hydrocarbon-free air was supplied by a pure air generator (Model 737-12A, AADCO Instruments, Inc., Clearwater, FL) to an ultraviolet-based O₃ generator (Model MZ-250, Clearwater Tech Inc., San Luis Obispo, CA). This flow was then diluted with 50% RH air, obtained using temperature controlled bubblers filled with distilled water. After mixing, the flow was split into eight identical streams by rotameters. Seven of the streams were used to expose media; the eighth provided a control for monitoring the O₃ concentration. A Teflon[®] solenoid valve (Cole-Parmer Instrument Co., Vernon Hills, IL) downstream of each sample assembly vented the flow to an exhaust hood in the normally-opened position. When the solenoid valve was energized, the flow was diluted with a clean, dry air (1.50 L min⁻¹) for measurement with a continuous O₃ UV absorption analyzer (Model 400A, Advanced Pollution Instrumentation, Inc., San Diego, CA) and a continuous chemiluminescence NO_x monitor (Model CLD 700 AL, EcoPhysics, Ann

Arbor, MI). A datalogger (Model 21X, Campbell Scientific, Inc., Logan UT) controlled the solenoid valves and recorded outputs from the O₃ and NO_x analyzers.

Both O₃ and NO_x analyzers were modified to improve response time by eliminating signal smoothing. Both analyzers had low detection limits (LDLs) and large dynamic ranges. The O₃ analyzer, which had a performance range of 0 - 10 ppm and an LDL of <0.6 ppb, was calibrated using a certified transfer standard (UV photometer, 401X, Advanced Pollution Instrumentation, Inc., San Diego, CA). The NO_x monitor, with a performance range from 0 - 100 ppm and a LDL of 1 ppb, was calibrated using a certified NO standard (Scott Specialty Gases, Plumsteadville, PA).

The datalogger was programmed to advance the solenoid valves every 2 min. The first 1 min of data was discarded to allow the O₃ analyzer and the system to stabilize. The second 1 min of data was recorded (at 1 Hz) and averaged to obtain a 1-min average. Thus, O₃ and NO_x concentrations were obtained for each tube assembly every 16 min.

The NO_x data were used to monitor for presence of nitrogen oxides (NO_x), which can be produced when using an air-fed ozonator (Fendel et al., 1995). Significant amounts of NO_x would be undesirable in this study because nitric oxide (NO) readily reacts with O₃. Continuous monitoring showed no evidence of NO_x production at any time during the experiments. (The original experimental setup, which used a high voltage spark discharge O₃ generator, at times did generate NO_x. However, switching to a UV O₃ generator eliminated this problem.)

3.6.3 Data and statistical analysis

Collected data were downloaded to a personal computer and imported into Microsoft Excel (2002) for analysis. Data were smoothed using an exponential smoothing function (damping factor = 0.3). Smoothing was not used at early times to

capture rapid changes in the concentration. O_3 concentration data were used to construct breakthrough curves and to calculate breakthrough times. Breakthrough curves were constructed for each sample by trending O_3 penetration fractions, calculated by dividing effluent O_3 concentrations by the blank concentrations for each 16 minute reading.

Unless noted, results are based on 1-hr averages of replicates.

Initially, an exploratory analysis of the data was performed by trending O_3 breakthrough penetrations and removal rates. Selected data were then fit to four physically-based chemisorption models, and predictions and model fit evaluated. Regression coefficients and other statistics were estimated using Microsoft Excel (2002)

3.7 Results and Discussion

Fig. 3-2 shows a typical set of O_3 breakthrough curves for 4 AC bed depths (2.4 to 15.6 mm, equivalent to 2 to 13 mg of AC) obtained at an O_3 concentration of 1680 ppb. As expected, deeper beds show lower penetrations at all exposure times. Also, O_3 penetration occurred immediately for the 2 mg sample, indicating that this sample did not exceed critical bed depth.

In most cases there was good agreement between replicates of the same bed mass ($COV < 10\%$), especially after 10 hr. Generally, reproducibility was higher with larger amounts of AC, probably because very small quantities (e.g., 2 mg) of AC were difficult to pack consistently. Agreement among replicates during the first 10 hr was sometimes poor, but samples often would “catch up” to one another. The initial variability seen among replicates also may have resulted from differences in tube packing, i.e., slightly uneven bed depths might cause a portion of the gas flow to bypass some of the AC bed.

Additional sources of variability might include changes in flow rates, different quantities of AC in the tubes, and minor conditioning differences in the bed.

3.7.1 Comparison of pure AC versus AC/glass bead mixtures

Breakthrough curves comparing the various amounts of AC (5, 10, 15 and 20 mg) with and without 130 mg of glass beads show several trends (Fig. 3-3). First, as seen earlier (Fig. 3-2), additional AC reduced penetration and increased breakthrough times. Second, penetration fractions of the AC/glass bead mixtures at any given time were lower than those of the AC alone, indicating that the glass beads increased O₃ removal. Two separate tests were performed in which four glass bead samples (130 mg each) along with four blank tubes (no beads) were exposed to O₃ (1.845 ppm) for 22 - 52 hr. In each experiment, effluent O₃ concentrations of bead samples and blanks were within 2% (37 ppb) indicating negligible O₃ removal by the glass beads. Thus, the differences seen in Fig. 3-3 are not due to removal by the glass beads directly. Third, the effect of the beads appeared to increase with greater weights of AC, i.e., the presence of the beads only slightly increased the O₃ removals achieved by 5 mg of AC; but the effect (on a relative basis) was much larger with 20 mg of AC. It should be noted, however, that effects of the glass beads were generally small when considering differences in penetration fraction, e.g., most differences were under 4% for any given exposure time, though the 10 mg samples differed by up to 12%.

While the glass beads themselves did not remove O₃, their presence slightly increased removal. The beads may provide more opportunity for O₃ to contact an AC surface due to the longer residence times in the bed, more uniform packing of AC grains, less likelihood that two or more AC grains will be adjacent impose diffusion barriers to O₃, and less likelihood of partial or complete short-circuiting due to non parallel bed

faces or wall effects. Also, the increased resistance from with the glass beads may have slightly decreased flow rates and lowered the apparent O_3 concentration, though this effect is expected to be small. To test this idea, flow rate drops were compared in 130 mg glass bead samples relative to 10 mg AC (no beads) samples. The glass bead samples had an average ($n=2$) flow rate decrease of $1.2 \pm 0.6 \text{ mL min}^{-1}$ relative to the AC samples, resulting in only a 0.7% decrease in apparent O_3 concentration. To minimize differences between AC/glass bead samples and pure AC samples, glass beads used in subsequent experiments were reduced to 65 mg, still allowing the use of small amounts of carbon while maintaining an acceptable bed depth.

3.7.2 Critical bed depth

Critical bed depths were determined for each experiment, as shown in Table 3-1. Since the same size tubes were used throughout all experiments, i.e., cross sectional area was constant, the bed depth is proportional to bed mass. Only approximate critical bed depths can be determined from experimental data since a limited number of discrete bed depths were tested at each O_3 concentration, and because up to 16 min may elapse before O_3 concentrations were measured for an individual AC bed. Estimated critical bed depths/AC weights ranged from $<0.6 \text{ mm}/<0.5 \text{ mg}$ at an O_3 concentration of 120 ppb, 8 mm/7 mg at ~ 750 ppb, to 18-24 mm/15–20 mg at 1740 ppb. Average critical bed masses were $\sim 4.8 \text{ mg}$ for O_3 concentrations ≤ 980 ppb and $\sim 9.2 \text{ mg}$ for O_3 concentrations ≥ 1.41 ppm.

3.7.3 Bed depth and breakthrough time

Although nine different bed masses (1 – 13 mg) were tested, the smaller masses were under the critical bed depth and the larger masses reached only low penetration fractions, e.g., 13 mg AC samples only achieved 16% penetration. Using the available

data, Fig. 3-4 plots the time to reach various penetration fractions versus bed mass.

These data fit a power law relationship:

$$t_{b,p} = \alpha_p (M_{bed} - M_{crit})^{\beta_p} \quad (3-2)$$

where $t_{b,p}$ = time to reach breakthrough penetration p ; M_{bed} = mass of the bed (mg); M_{crit} = estimated critical bed mass (mg); and α_p and β_p = estimated parameters. Curves were fit using a curve fitting function (Microsoft Excel); R^2 values ranged from 0.97 to 1.00. Interestingly, exponent β_p did not strongly depend on the penetration fraction (β_p values of 1.6, 1.8, and 1.6 were obtained for the penetration fraction of 5, 10 and 15%). This model tended to underpredict the measured t_b at lower bed masses, especially at penetration fractions beyond 15% (not shown in Fig. 3-5). This empirical model is limited to an O_3 concentration of 1.68 ppm and applies to filter beds that exceeded the critical bed mass (~5 mg for the tested conditions).

3.7.4 Relationship between bed depth and O_3 penetration fraction

Penetration fractions for particular exposure times showed a curvilinear relationship with bed depth (Fig. 3-5). These results apply to the particular O_3 concentration and other conditions used. Curvature tended to increase at short O_3 exposure times, e.g., <10 hr, and at low O_3 concentrations (196 ppb). To further explore effect of O_3 concentration, Fig. 3-6 plots the O_3 penetration fraction at 20 hr versus bed mass at three different O_3 levels. Again, linearity decreased with lower concentrations, e.g., linear models had R^2 fits of 0.97 and 0.96 for the 1680 and 540 ppb experiments, respectively, compared to R^2 of 0.83 for the 120 ppb experiment. Data sets at other concentrations yielded similar results. No simple relationship between bed mass and O_3 penetration fraction applying to all O_3 exposure times was found, rather, the relationship between O_3 penetration and bed mass changed with O_3 concentration.

3.7.5 O₃ removal rates

Rates of O₃ removal per bed mass (mg g⁻¹ hr⁻¹) were calculated for each bed mass (1 to 13 mg) and plotted vs. time for O₃ concentrations of 196 and 1680 ppb (Fig. 3-7). Masses of O₃ removed were calculated by multiplying the O₃ removal efficiency by the mass of O₃ available (calculated by converting blank ppb levels to µg mL⁻¹ and multiplying by the flow rate). Rates were then estimated by dividing the O₃ removed per unit time by the bed mass. At 196 ppm, the initial rates measured during first 16 min of ozonation decreased with bed mass, e.g., 11 and 1 mg samples had removal rates of 0.37 and 3.92 mg g⁻¹ hr⁻¹, respectively. O₃ removal rates of all samples decreased with exposure time, especially for the smaller bed masses, e.g., for the 1 mg sample, rates fell 3-fold (from 3.92 to 1.13 mg g⁻¹ hr⁻¹) after 45 hr, while for the 11 mg sample, rates drop only slightly (from 0.37 to 0.35 mg g⁻¹ hr⁻¹) after 135 hr.

O₃ removal rates were much faster at the high (1680 ppb) concentration (Fig. 3-7A), but otherwise the same patterns were seen, e.g., rates were highest with small bed masses and early exposure times. Initial O₃ removal rates ranged from 2.4 to 17.2 mg g⁻¹ hr⁻¹ for the 13 and 1 mg samples, respectively, about 4 to 6 times higher than rates at 196 ppb. Again, O₃ removal rates decreased over the test period, especially for the small bed masses.

Removal rates tended to stabilize, especially for the larger AC masses, after ~10 hr of 196 ppb O₃ exposure, and after ~40 hr in the 1680 ppb exposure. O₃ removal rates at these concentrations were not proportional at any given bed depth, rather, ratios of the rates of the high concentration samples to the low concentration samples increased with bed mass. For example, at 50 hrs the rates for 1680 ppb compared to 196 ppb were from 2.65 to 7.02 times higher for the 2 mg and 11 mg filter samples, respectively. Also, these

O₃ removal rate ratios decreased with time, e.g., ratios ranged from 2.22 to 6.49 at 60 hrs for the 2 and 11 mg samples, respectively. At 70 hrs, the rate ratio dropped to 5.97 for the 11 mg samples.

Like the penetration fraction, this analysis shows that O₃ removal rates vary nonlinearly with bed mass, concentration and exposure time. Thus, first-order and other simple models will not suffice to O₃ removals at low concentrations using data from high concentration experiments.

3.7.6 Chemisorption models

Four chemisorption models with potential applicability to the AC-O₃ system were evaluated using a portion of the experimental data, specifically, results from the 1680 ppb O₃ experiments on two AC samples using bed masses of 2 and 11 mg.

Pseudo-first order equation. The pseudo-first order equation of Lagergren has been used extensively to describe the kinetics of a variety of sorbate/sorbent systems and can be expressed as follows (Ho and McKay, 1998):

$$dq_t/dt = k_1 (q_e - q_t) \quad (3-3)$$

where q_t = sorption capacity at time t ($\mu\text{g mg}^{-1}$), q_e = the equilibrium sorption capacity ($\mu\text{g mg}^{-1}$), and k_1 = pseudo-first order rate constant (hr^{-1}). Pseudo-first order kinetics often only apply to the first 20 – 30 minutes in many sorbate/sorbent systems (Ho and McKay, 1998). Eq. (3-3) can be integrated to:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3-4)$$

indicating that a plot of $\ln(q_e - q_t)$ vs. t should be linear if pseudo-first order kinetics apply. Since q_e is rarely known and is generally impractical to measure, the data must be extrapolated to $t = \infty$ or q_e can be determined by trial-and-error or various search algorithms.

The fit of the data collected in the 1680 ppb O₃ experiments for 2 and 11 mg AC samples to the pseudo-first order model is shown in Fig. 3-8A. Using trial-and-error, q_e was estimated as 44.9 and 200.2 wt % for the 2 and 11 mg samples, respectively. Pseudo-first order rate constants, k_1 , estimated by regression, were 0.045 and 0.00135 hr⁻¹ for 2 and 11 mg samples, respectively. In both cases, $R^2 > 0.999$, indicating a linear fit over the entire data range. However, because q_e was not experimentally measured, it is impossible to determine the accuracy of this model. Predicted penetrations (Fig. 3-8B) using the pseudo-first order model show departures from observed values, especially at early and late exposure times.

Pseudo-second order equation. Pseudo-second order kinetics represent the governing equation for chemisorption as (Ho and McKay, 1998):

$$dq_t/dt = k(q_e - q_t)^2 \quad (3-5)$$

which following integration and rearrangement becomes:

$$t/q_t = 1/h + t/q_e \quad (3-6)$$

where h = initial sorption rate as $q_t/t \rightarrow 0$. In this case, plots or regressions of t/q_t vs. t should yield a straight line from which q_e and h can be directly determined. Unlike the pseudo-first order model, there is no need for extrapolation or solving by trial-and-error to obtain q_e . If applicable, this model has the advantage of fitting the entire range of data, rather than just the initial period.

The pseudo second-order model fit to the experimental data shows some curvature during the first ~10 hours, after which the fit appears quite linear (Fig. 3-9A). Values of R^2 were high, 0.99 and 0.89 for the 2 mg and 11 mg samples, respectively. Estimates of initial sorption rate h were 0.74 and 0.28 wt %⁻¹ hr⁻¹, and equilibrium

sorption capacity q_e were 66.3 and 191.9 wt %, for the 2 mg and 11 mg samples, respectively. Omitting the first 10 hr from the regression slightly increased the R^2 . Since this model does not yield linear results over the exposure period, other processes are occurring that are not pseudo-second order. However, the model does provide reasonable predictions of the breakthrough plots (Fig. 3-9B), somewhat better than that provided by the pseudo-first order model (Fig. 3-8B).

Elovich equation. The Elovich equation has been applied successfully to some chemisorption data where the adsorbing surface is heterogeneous (Cheung et al., 2000). The Elovich equation uses additional terms,

$$dq_t/dt = a \exp (-b q_t) \quad (3-7)$$

where a = initial sorption rate (wt % hr⁻¹), and b = adsorption constant (wt %⁻¹) for a given experiment (Ho and McKay, 1998). Following integration, eq. (3-7) becomes:

$$q_t = 1/b \ln (a b) + 1/b \ln (t + t_0) \quad (3-8)$$

where t_0 = time constant (hr) and is estimated by trial-and-error to achieve a linear plot of q_t versus $\ln (t + t_0)$. If the Elovich model applies, constants a and b can then be calculated from the slope and intercept. If $q_t = 0$ at $t = 0$, $t_0 = 1/ab$. However, if an amount of gas is instantaneously adsorbed, the integrated form of eq. (3-7) becomes (Low, 1960):

$$q_t = 1/b \ln (a b) + 1/b \ln (t + k) \quad (3-9)$$

where k (hr) = $t_0 \exp (b q_0)$. Because of rapid initial adsorption or other kinetic processes that may displace plots, the Elovich equation may not be practical for determining values of q_t . Rather, it is most useful for determining adsorption rates and not sorption capacities (Low, 1960).

Fig. 3-10A shows chemisorption of 1680 ppb O₃ on two AC samples (2 mg and 11 mg bed masses) plotted using the Elovich equation. The time constant k was estimated by maximizing the R^2 value of a plot of q_t versus $\ln(t + k)$; R^2 values were greater than 0.999 in both cases. Fig. 3-10B shows breakthrough curves estimated using eq. (8). Although Low (1960) recommended using the Elovich equation to determine rates rather than sorption capacities because of potential plot offsets, the Elovich equation fit the experimental data well, except for a large offset that occurred in the first data point only. Compared to pseudo-first order and pseudo-second order models discussed previously, predictions better followed the observed breakthrough curve during the early hours of O₃ exposure, except for the large first-point offset mentioned above.

Table 3-2 shows the Elovich parameters (k , a , and b) obtained from plots of q_t versus $\ln(t + k)$ and measured initial rates for two O₃ concentrations (1680 and 196 ppb). Time constants varied widely for both the high and low concentration experiments. Estimated initial rates decreased nonlinearly with bed mass for both concentrations. Estimated initial O₃ removal rates were in close agreement with measured initial rates for samples that exceeded the critical bed mass. However, the Elovich equation tended to underestimate the initial rates for samples under the critical bed mass. The adsorption constant b varied considerably among the different bed masses with $b = 0.019 \pm 0.012$ wt %⁻¹ and 0.021 ± 0.027 wt %⁻¹ for the 1680 ppb and 196 ppb experiments, respectively. However, average b values were similar at both high and low O₃ concentrations and did not appear dependent on bed mass. Table 3-3 shows observed and predicted O₃ penetration fractions for selected bed masses in the 1680 ppb experiment. Generally,

excellent agreement was obtained between observed and predicted values, especially at longer exposure times.

Ritchie equation. The Ritchie equation was originally proposed for modeling chemisorption of gases on carbon and has since been applied to the adsorption of cadmium ions on bone char in aqueous solutions (Cheung et. al, 2000). The differential form is:

$$d\theta/dt = k (1 - \theta)^n \quad (3-10)$$

where θ = fraction of surface sites occupied by the adsorbed gas, k = rate constant ($\text{mg } \mu\text{g}^{-1} \text{ hr}^{-1}$), and n = number of surface sites occupied by each gas molecule. At time, t , $\theta = q_t/q_e$. Assuming second-order kinetics and that $\theta = 0$ at $t = 0$, eq. (3-10) can be integrated, simplified and rearranged to a linear form,

$$1/q_t = 1/(k q_e t) + 1/q_e \quad (11)$$

from which q_e and k can be determined from the regression of $1/q_t$ vs. $1/t$.

The Ritchie equation provided an excellent fit to the AC-O₃ data, e.g., $R^2 > 0.999$ for both 2 and 11 mg samples (Fig. 3-11A). Estimates of q_e were 71.4 and 212.2 wt %, and k were 0.010 and 0.0013 wt %⁻¹ hr⁻¹ for the 2 mg and 11 mg samples, respectively. Breakthrough curves using values derived from the Ritchie model compared favorably to measured values (Fig. 3-11B). Overall, this model appeared to fit the experimental data reasonably well, especially after the first few hours of breakthrough, and better than the three other models evaluated.

3.7.7 Model evaluation

No studies were identified in the literature regarding the removal capacity or the removal rates for O₃ on activated carbon. Thus, experimental results obtained here cannot be compared to literature values or previously estimated parameters. Also, no

comparable applications of AC-O₃ chemisorption models were identified in the literature. Thus, this research may represent one of the first attempts to use and evaluate models representing O₃ chemisorption on AC for air filtration applications.

Based on the four chemisorption models tested, O₃ removal by AC was best predicted by the Elovich and Ritchie models; the two pseudo first- and second-order models did not provide good fits at both short and long exposure times. Additional data, especially at both very short and very long times, would be helpful in selecting and evaluating these models. Because most parameters of the four models were specific to the experimental conditions, e.g., O₃ concentration, bed depth and exposure time, it was not possible to develop a generalized model. O₃ chemisorption is clearly a complex process involving nonlinear and dynamic (time changing) processes.

The lack of a generalized model means that prediction of O₃ removal by AC filters at low environmental concentrations cannot be predicted using experiments conducted at high concentrations, at least not in any simple, physically-based way. Of course, empirical approaches may be possible, e.g., one of the chemisorption models (Elovich equation) may be used with empirical equations that predict necessary model parameters (a, b, k) on the basis of experimental results, or purely empirical models might be used. However, such approaches are not altogether satisfactory as they are not mechanistically derived. Furthermore, they are subject to a number of flaws in application, e.g., extrapolations may be erroneous.

This work did demonstrate the feasibility of measuring, in a reproducible manner and within a reasonable time frame, O₃ breakthrough curves and other parameters for AC at environmentally relevant conditions. Such tests require the use of very small quantities

of AC (as low as 0.5 mg). These tests are facilitated by the use of a mixture of the AC in glass beads, which provide a means to increase the uniformity of flow and exposure conditions. Tests of mixed media might also be relevant to AC-impregnated fabric filters, which essentially surround the AC within a larger filter matrix which is likely to be largely inert with respect to O_3 removal.

3.8 Conclusion

Ozone breakthrough on activated carbon can be expedited using an AC-glass bead mixture that facilitates the use of extremely small amounts of AC. While the AC-bead mixtures showed slightly lower O_3 penetration fractions, likely due to greater uniformity of flows within the bed and not due to O_3 removal by the glass beads themselves, differences appear modest and not likely to change estimated model parameters or parameter trends.

Nonlinear relationships exist between time to breakthrough, penetration fractions, bed depth, exposure time, and O_3 concentration. For example, O_3 penetration fractions at a given exposure time decrease linearly with AC bed depth at high O_3 concentrations and long exposure times, but curvilinear relationships are seen at low O_3 concentrations or short exposure times. Rates of O_3 removal per unit mass of AC increase considerably at higher O_3 concentrations and shorter bed depths, but these rates do not scale linearly with bed depth or exposure time.

Of the four chemisorption models tested, the Elovich and Ritchie models best predicted O_3 breakthrough at both low and high concentrations. Both models require several parameters that are specific to bed depth and O_3 concentration, and possibly to other factors that may be relevant in applications and not tested in the current research,

e.g., flow velocity, humidity, temperature, soiling, and loadings of volatile organic compounds. The lack of a generalizable model means that O_3 removal on AC must be determined experimentally, and that results obtained at high O_3 concentration cannot be scaled to environmental conditions. Experimental data obtained in this study provide critical bed depths, removal capacities, and removal rates at both low (<200 ppb) and high (500 – 2000 ppb) O_3 concentrations, information useful for O_3 filtration applications.

3.9 References

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Table 3-1. Estimated critical bed masses at various concentrations. Duplicate concentrations were separate experiments.

O ₃ conc. (ppm)	No. of samples	Beads ^a	Critical bed mass (mg)	Critical bed depth (mm)
0.12	10	Yes	< 0.5	< 0.6
0.54	12	Yes	5 - 7	6.0 - 8.4
0.98	14	Yes	7 - 9	8.4 - 10.8
1.41	6	No	5 - 10	6.0 - 12.0
1.62	6	No	10 - 15	12.0 - 18.0
1.67	2	No	> 5	> 6.0
1.68	6	Yes	4 - 5	4.8 - 6.0
1.68	18	Yes	> 5	> 6.0
1.74	8	Yes ^b	15 - 20	18.0 - 24.0
1.85	10	No	10 - 15	12.0 - 18.0

^aBead mass = 65 mg.

^bFour each beads/no beads.

Table 3-2. Estimated parameters of the Elovich equation (time constant, initial rate, adsorption constant) and measured initial O₃ removal rates at O₃ concentrations of 1680 and 196 ppb.

AC Mass (mg)	Rep. no.	Elovich Equation			Measured
		k (hr)	a (wt % hr ⁻¹)	b (wt % ⁻¹)	a (wt % hr ⁻¹)
1680 ppb					
1	1	52	1.03	0.019	1.72
2	1	31	0.73	0.045	1.07
	2	52	0.67	0.029	1.43
3	1	56	0.60	0.030	1.03
	2	125	0.35	0.023	0.81
4	1	77	0.61	0.021	0.72
	2	71	0.62	0.023	0.77
5	1	150	0.37	0.018	0.60
	2	141	0.40	0.018	0.60
7	1	81	0.39	0.032	0.45
	2	86	0.43	0.027	0.45
	3	218	0.34	0.014	0.42
	4	155	0.34	0.019	0.44
9	1	65	0.36	0.043	0.35
	2	73	0.37	0.037	0.35
11	1	696	0.24	0.006	0.29
	2	226	0.46	0.010	0.27
	3	395	0.28	0.009	0.28
	1	580	0.23	0.008	0.24
13	2	326	0.25	0.012	0.24
	196 ppb				
1	1	222	0.188	0.0239	0.362
	2	47	0.195	0.1098	0.431
	1	18656	0.118	0.0005	0.203
2	2	84416	0.115	0.0001	0.181
	1	70680	0.080	0.0002	0.145
3	2	71167	0.093	0.0002	0.148
	1	572	0.078	0.0225	0.074
5	2	756	0.069	0.0192	0.079
	1	833	0.053	0.0226	0.055
7	2	866	0.056	0.0205	0.056
	1	979	0.045	0.0227	0.043
9	2	1147	0.043	0.0201	0.044
	1	1639	0.037	0.0165	0.036
11	2	1639	0.035	0.0175	0.038

Table 3-3. Observed and predicted O₃ penetration fractions estimated using the Elovich equation at an O₃ concentration of 1680 ppb. Replicates correspond to those shown in Table 3-2. Predicted penetration fractions beyond 75 hr represent extrapolated data.

Time(hr)	Penetration (Co/Ci)									
	3 mg		5 mg		7 mg		9 mg		11 mg	
	Obs	Pred	Obs	Pred	Obs	Pred	Obs	Pred	Obs	Pred
1	37.0 (6.9)	36.3 (0.0)	8.5 (1.9)	21.4 (4.2)	5.8 (6.1)	4.4 (12.2)	-0.2 (0.4)	-9.2 (13.0)	-0.2 (1.1)	-3.5 (3.2)
2	43.4 (7.4)	39.9 (0.4)	16.9 (0.3)	21.4 (4.2)	10.9 (5.7)	7.3 (10.3)	1.6 (1.6)	-6.2 (8.8)	0.4 (2.3)	-3.5 (3.6)
5	53.8 (7.7)	45.6 (0.0)	25.3 (3.3)	22.0 (4.1)	17.8 (7.5)	12.6 (11.2)	7.7 (1.1)	-1.3 (1.8)	3.9 (3.0)	-1.0 (5.1)
10	59.8 (6.2)	52.5 (0.1)	31.7 (3.4)	25.2 (3.8)	22.7 (8.0)	18.9 (10.8)	13.9 (3.0)	10.6 (2.4)	6.6 (3.6)	0.4 (7.7)
25	65.8 (4.1)	62.5 (0.0)	40.6 (2.9)	34.4 (3.1)	30.4 (6.2)	29.2 (10.2)	25.6 (3.1)	27.1 (2.4)	10.1 (4.9)	5.5 (6.7)
50	71.2 (2.8)	70.8 (0.0)	48.3 (2.4)	43.2 (2.4)	39.5 (6.4)	39.2 (11.0)	39.9 (2.3)	41.8 (3.1)	14.5 (4.9)	7.9 (8.9)
75	75.9 (2.3)	72.7 (0.0)	57.1 (2.4)	47.9 (2.0)	45.2 (5.3)	41.6 (9.6)	43.0 (3.8)	44.3 (3.3)		10.2 (7.5)
100		78.6 (0.0)		54.1 (1.6)		49.0 (10.6)		52.1 (0.8)		14.0 (8.1)
150		83.8 (0.0)		61.9 (1.2)		58.0 (10.7)		63.1 (0.9)		20.8 (9.0)
200		86.9 (0.0)		67.4 (0.9)		64.2 (10.3)		70.0 (0.9)		26.5 (9.6)
250		89.1 (0.0)		71.5 (0.7)		68.8 (9.8)		74.7 (0.8)		31.4 (10.0)

Figure 3-1. Schematic of the ozone exposure system. Four sampling ports were omitted from the drawing for simplicity. (R = flow rotameter, A = adsorption tube, S = solenoid valve.)

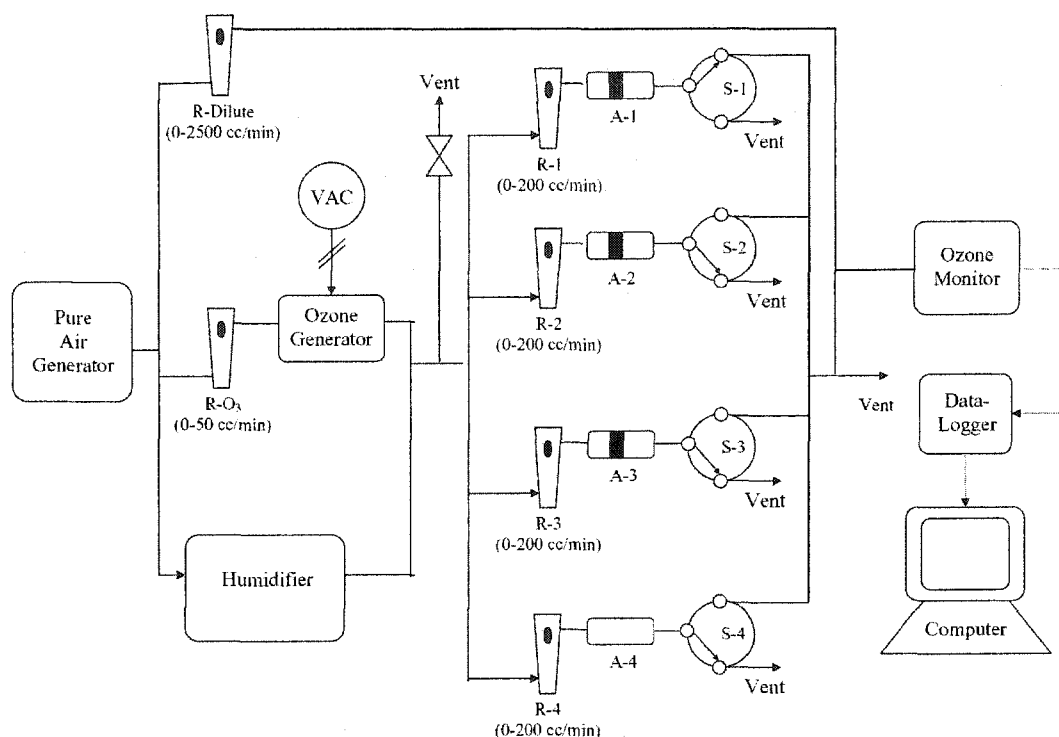


Figure 3-2. Typical set of ozone breakthrough curves (with error bars) at an O_3 concentration of 1680 ppb. Penetration fractions (C_t/C_0) represent averages of two replicate samples.

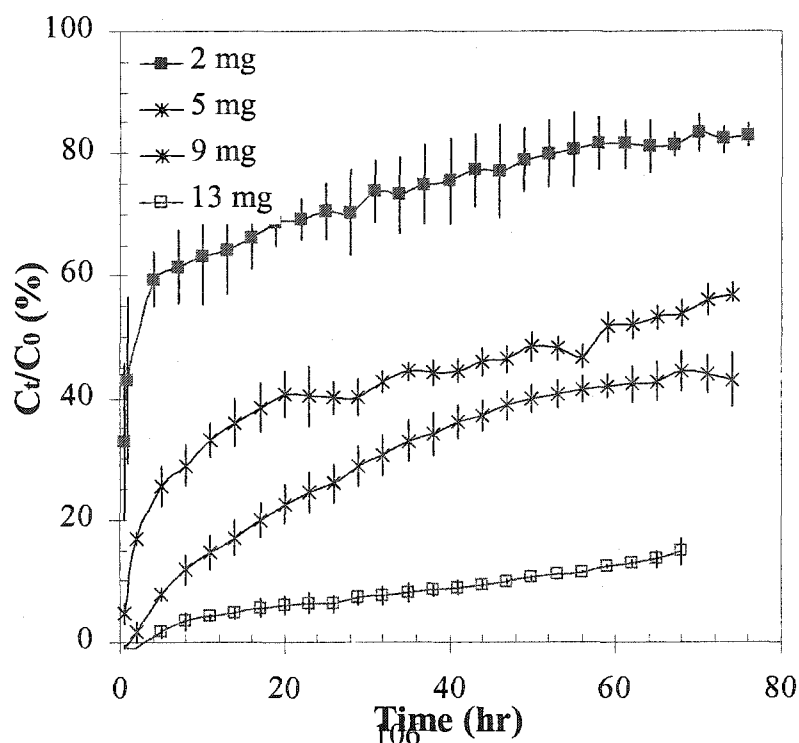


Figure 3-3. Comparison of O₃ penetration fractions of virgin AC samples with samples containing mixtures of AC (5 and 10 mg, left panel; 15 and 20 mg, right panel) and glass beads (130 mg) at an O₃ concentration of 1740 ppb.

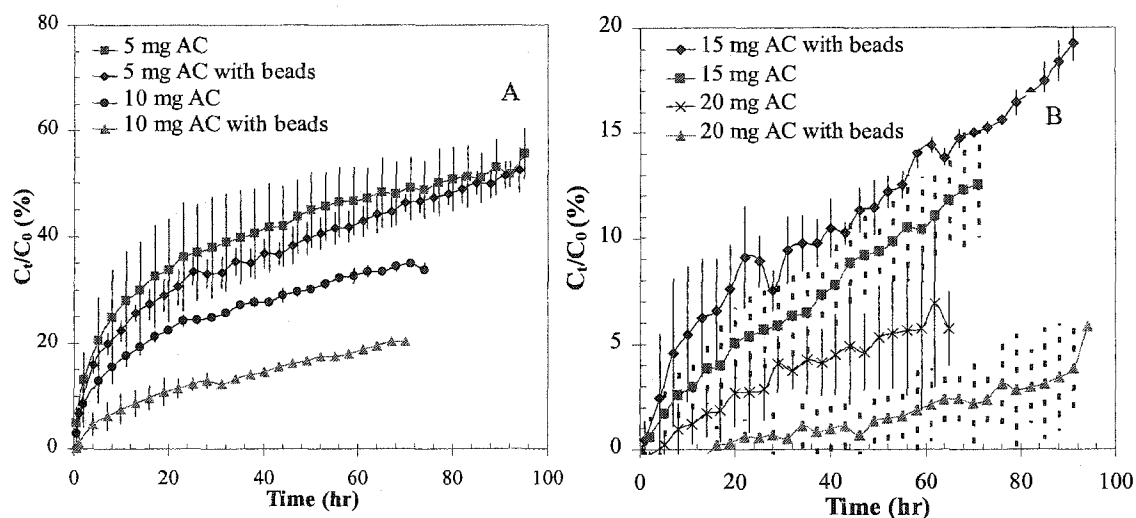


Figure 3-4. Time to breakthrough versus bed mass for various penetration fractions at an O₃ concentration of 1680 ppb. Predictive equations: $t_{25\%} = 6.6(M_B - 6.4)^{1.5}$, $t_{20\%} = 4.1(M_B - 6.5)^{1.7}$, $t_{10\%} = 1.6(M_B - 6.5)^{1.8}$.

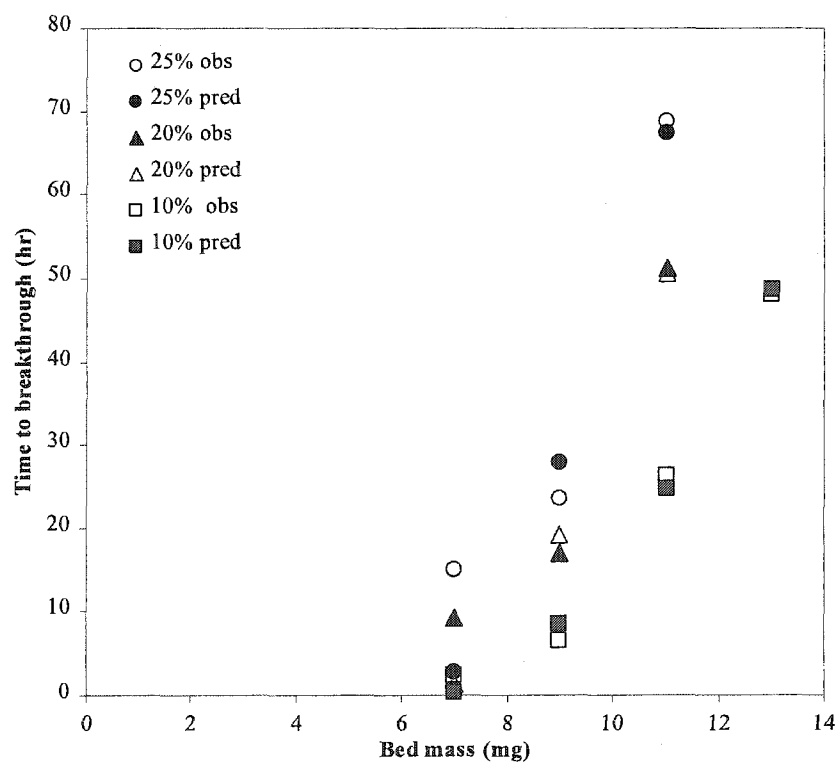


Figure 3-5. O₃ penetration fraction versus bed mass for various exposure times at an O₃ concentration of 1680 ppb (left panel) and 196 ppb (right panel). Data points are averages of replicate samples.

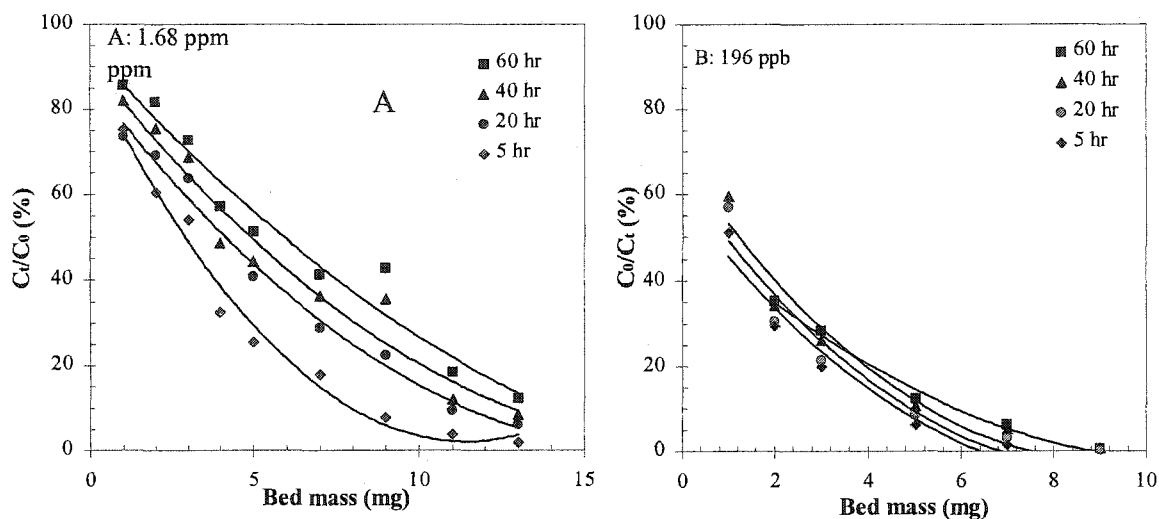


Figure 3-6. O₃ penetration fraction versus bed mass for three O₃ concentrations and an exposure time of 20 hr. Data points are averages of replicate samples.

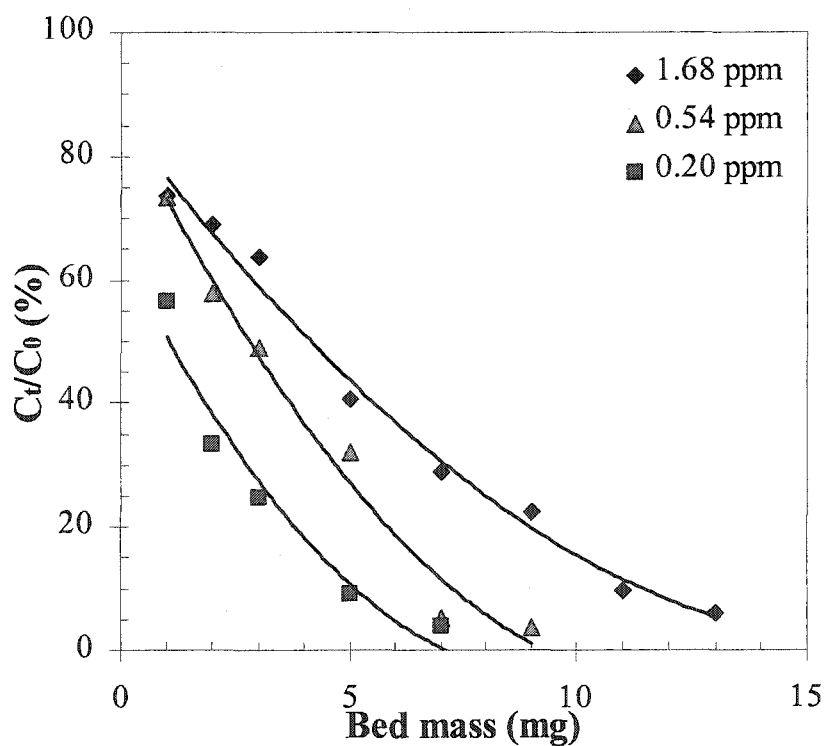


Figure 3-7. O_3 removal rates per g of AC for selected samples at low (196 ppb, left panel) and high (1680 ppb, right panel) O_3 concentrations.

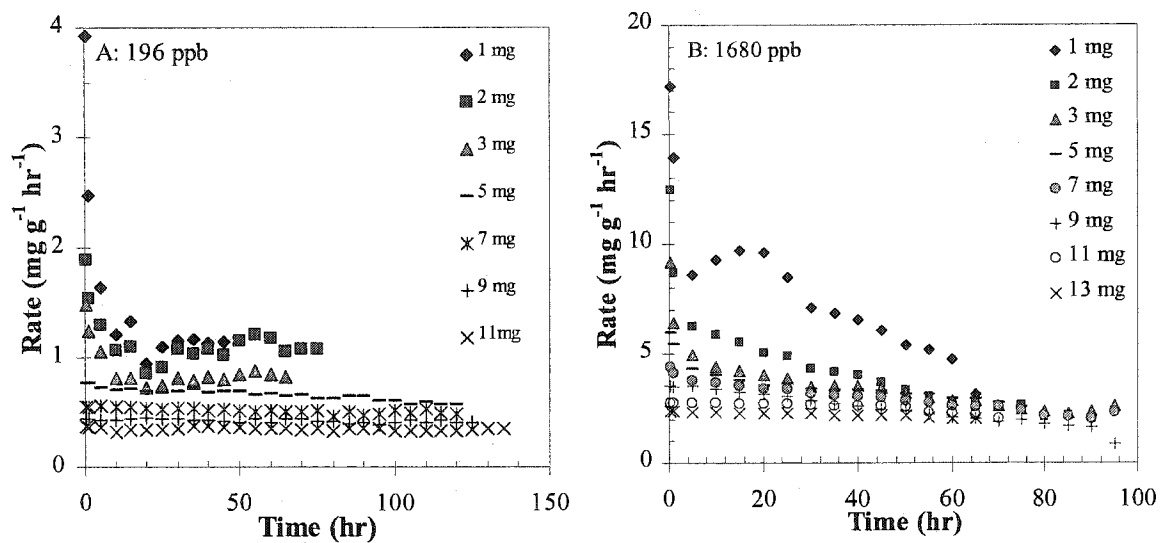


Figure 3-8. Chemisorption of 1680 ppb O_3 on 2 mg and 11 mg of AC modeled using pseudo-first order kinetics. A. Shows fit to model structure. B. Shows model predictions (solid lines) and observations (dashed lines) for O_3 penetration fractions.

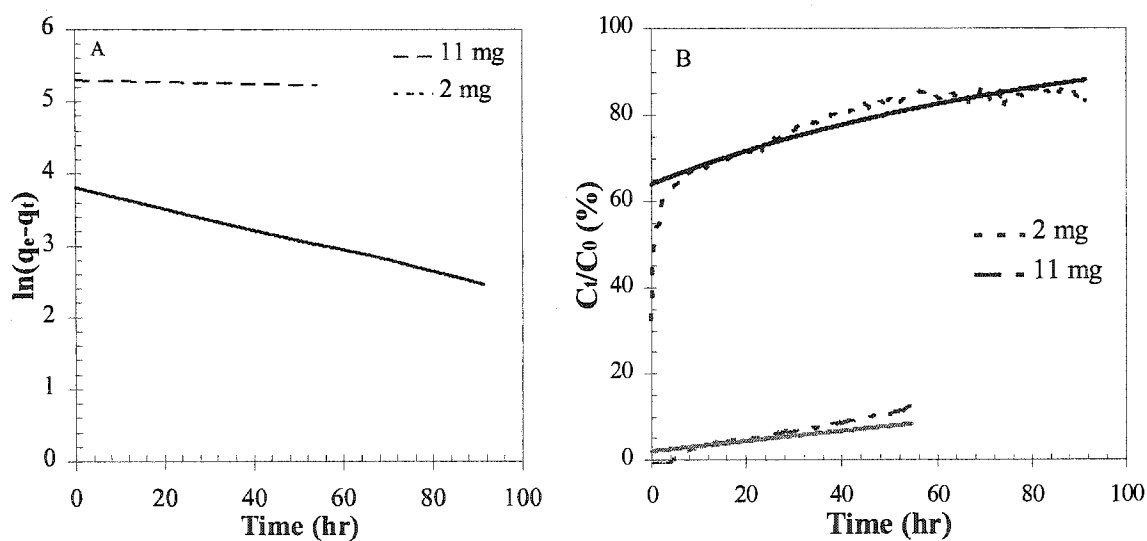


Figure 3-9. Chemisorption of 1680 ppb O_3 on 2 mg or 11 mg of AC modeled using pseudo-second order kinetics. A. Shows fit to model structure. B. Shows model predictions (solid lines) and observations (dashed lines) for O_3 penetration fractions.

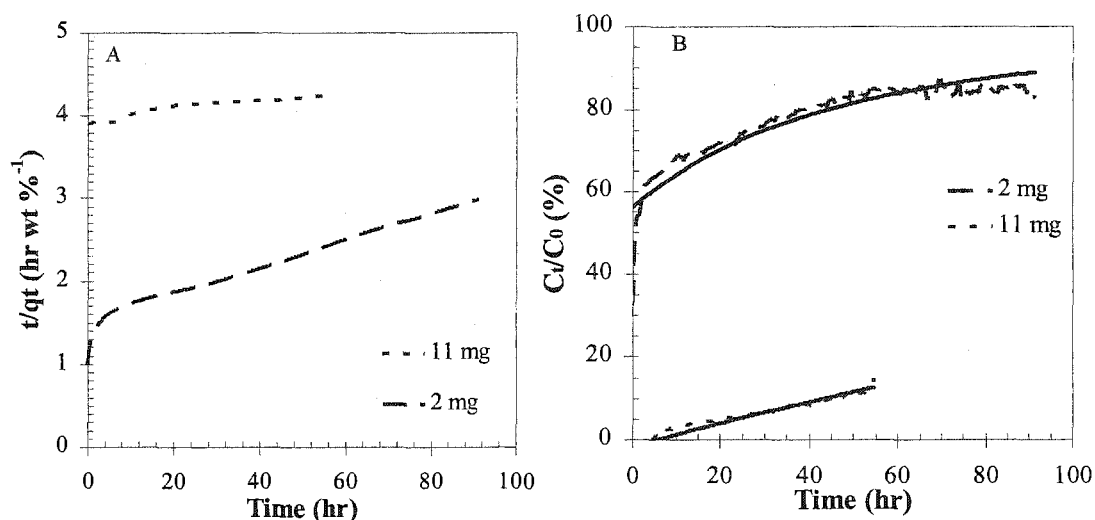


Figure 3-10. Chemisorption of 1680 ppb O_3 on 2 and 11 mg AC modeled using the Elovich equation. A. Shows fit to model structure. B. Shows model predictions (solid lines) and observations (dashed lines) for O_3 penetration fractions.

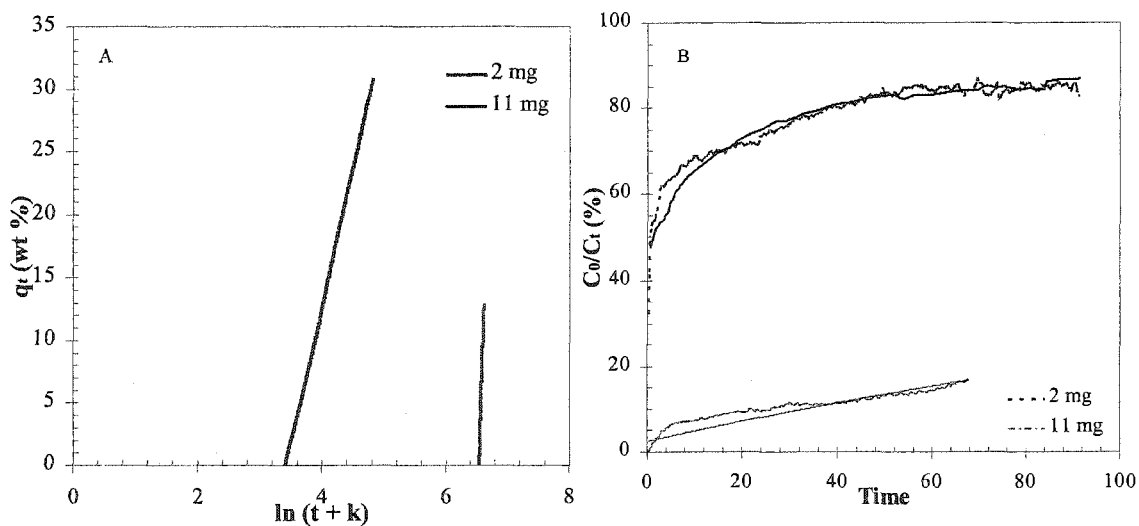
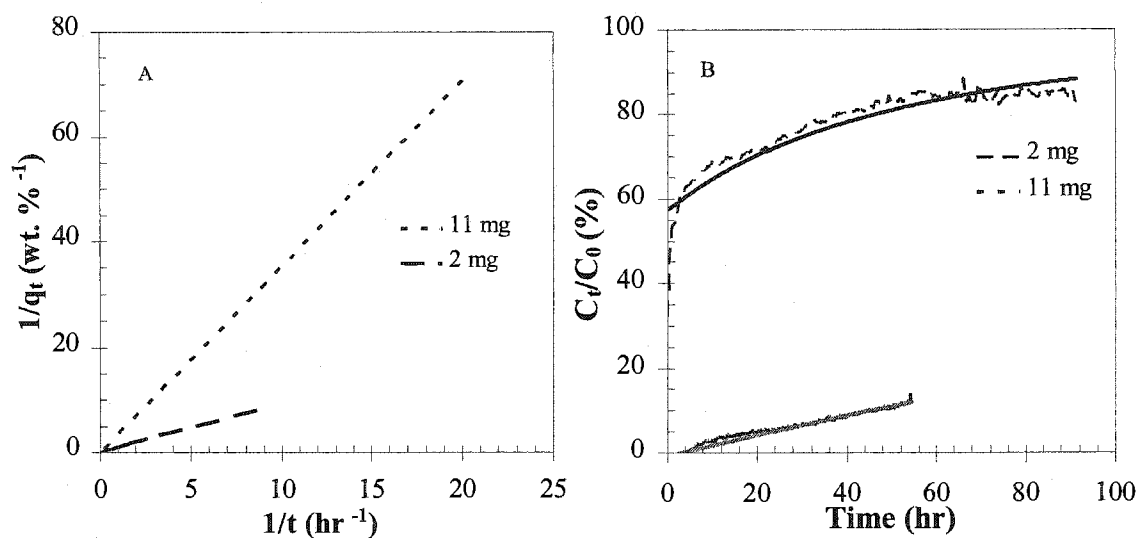


Figure 3-11. Chemisorption of 1680 ppb O_3 on AC (2 mg or 11 mg) modeled using the Ritchie equation. A. Shows fit to model structure. B. Shows model predictions (solid lines) and observations (dashed lines) for O_3 penetration fractions.



CHAPTER 4. EFFECT OF VOC-LOADING ON THE OZONE REMOVAL EFFICIENCY OF ACTIVATED CARBON FILTERS IN INDOOR AIR

4.1 Abstract

Activated carbon (AC) filters are used widely in air cleaning applications to remove volatile organic compounds (VOCs) and ozone (O_3). This chapter investigates the O_3 removal efficiency of AC filters after previous exposure to VOCs. Filter performance was tested in laboratory simulations using conventional coconut shell AC and two common indoor VOCs, toluene and *d*-limonene, representing low and high reactivities with O_3 . Small (10 mg) AC samples dosed with low, medium and high loadings (28 to 100% of capacity) of VOCs were exposed to humidified (50% RH) and ozonated (1.13 – 1.15 ppm) air at a typical filter velocity (14.7 cm s^{-1}). O_3 breakthrough curves were measured, from which O_3 removal capacity and parameters of the Elovich chemisorption equation were determined. VOC-loaded filters differed in breakthrough behavior and were less efficient at removing O_3 than the unloaded (virgin) filters. Toluene-loaded filters showed especially rapid breakthrough of O_3 . After 80 hrs of exposure at O_3 concentrations, VOC-loaded AC samples exhibited 75 to 95% of the O_3 removal capacity of corresponding virgin samples. In most cases, O_3 breakthrough and removal capacity were not influenced by the VOC loading rate. Toluene loadings are demonstrated to poison the AC, while pseudo-poisoning (initially higher O_3 adsorption

rates that rapidly decrease) is suggested for limonene loadings. Overall, results show an overall reduction in chemisorption rate, a modest reduction in O₃ removal capacity, and sometimes dramatic changes in breakthrough behavior.

4.2 Keywords

Activated carbon, efficiency, filter, ozone, poisoning, VOCs.

4.3 Introduction

Activated carbon (AC) filters have been used for volatile organic compound (VOC) removal and odor control for many years and in many applications. Ozone (O₃) removal by these filters is an added benefit. O₃ is harmful to human health, plants and materials even at low concentrations (EPA, 1996). Not only does O₃ directly affect indoor air quality (IAQ), it can also react with unsaturated VOCs, such as monoterpenes, commonly found in citrus and pine oils, to produce secondary pollutants that are eye and respiratory irritants (Wolkoff et al., 1997).

Much of the O₃ found indoors originates outdoors. Outdoors, O₃ production and destruction occurs through a complex set of chemical reactions involving volatile organic compounds (VOCs), nitrogen oxides, carbon monoxide, and sunlight (EPA, 1996). While most indoor O₃ is due to exchange and infiltration of outdoor air, additional (and generally small) contributions are made by several indoor sources, e.g., laser printers, photocopy machines, and electrostatic air cleaners (Weschler, 2000). Because source elimination is often impractical, AC filters can be used to help reduce indoor O₃ concentrations to acceptable levels. While the absorption of VOCs on AC and, to a lesser

extent, on O₃-treated AC is reasonably well understood, little information exists regarding effects of VOC loadings on O₃ removal.

4.4 Study aims

The purpose of this study is to determine the effect of adsorbed VOCs on the O₃ removal efficiency of AC. O₃ removal and breakthrough were measured in laboratory tests after loading AC with toluene and *d*-limonene, two VOCs that represent common constituents in indoor air that have widely different reactivities, e.g., limonene readily reacts with O₃ due to its unsaturated structure and forms secondary reaction products, while toluene is relatively nonreactive. An improved understanding of O₃ removal by AC and other filter types will help in the design and use of filters, especially in areas where the levels of VOCs and O₃ are high.

4.5 Background

4.5.1 O₃ removal by AC

Ozone removal by AC is a chemisorption process. Many studies have attempted to elucidate the AC/O₃ reaction mechanism and/or resultant structural changes in the AC (Donnet and Ehrburger, 1970; Dietz and Bitner, 1972; Ellis and Tometz, 1972; Dietz and Bitner, 1973; Stephens et al., 1986; Atyaksheva and Emel'yanova, 1989; Takeuchi and Itoh, 1993; Gomez-Serrano et al., 2002; Valdes et al., 2002). O₃ oxidation leads to the formation of hydroxyl, carbonyl, -C-O-, and -COOH surface functional groups (You et al., 1994; Mawhinney and Yates, 2001; Chiang et al., 2002). O₃ also changes the structure of AC by enlarging pores and creating new ones. During the first stage of ozonation, surface area slightly increases because of a slight increase in the carbon's

porosity. As exposure time increases, the surface area is reduced due to gasification and destruction of pore walls (Valdez et al., 2002). Gasification occurs when the AC surface is oxidized by O₃ forming CO₂, which then exits the carbon surface and creates new micropores (You et al., 1994).

Important parameters for filtration applications include efficiency (E), critical bed depth, and O₃ removal capacity. Filter efficiency E (%) may be defined as:

$$E = \frac{(C_i - C_e) \times 100\%}{C_i} \quad (4-1)$$

where C_i and C_e = the influent and effluent O₃ concentrations (ppb), respectively. Filter efficiency generally decreases as a function of time. The critical bed depth is the minimum length (thickness) of AC measured along the mean air flow path that is required to contain the O₃ mass transfer zone. If the bed depth is less than the critical bed depth, O₃ will immediately appear in the effluent air stream (ASTM, 1998).

The specific O₃ removal capacity, q (wt %) may be represented as

$$q = M^{-1} \int_t C_{i,t} E_t Q_t dt \quad (4-2)$$

where M is the AC bed mass (μg), C_{i,t} is the influent concentration (μg m³), E_t is the O₃ removal efficiency, and Q_t is the flow rate through the filter (m³ min⁻¹). Note that eq. (4-2) gives the general case in which filter conditions may vary over time. In laboratory tests, the influent concentration and filter flow rate are normally held constant.

Most studies examining O₃ and AC filters have focused on reaction mechanisms or changes in the carbon structure due to ozonation, and relatively few laboratory studies have examined the removal efficiencies. Ellis and Tometz (1972) tested the O₃ removal

efficiency of 35 materials, e.g., charcoal, metals and metal oxides, and found that coconut shell charcoal was the most efficient, removing 90 – 100% of O₃ (250 ppb) over a 15 min test period. Using a much higher O₃ concentration (5 ppm), Johnston et al. (1989) measured O₃ removal capacities of welding fume respirators containing AC filters and found them to be acceptable for protection against low levels of O₃ (<10 times the permissible exposure limit). Lee and Davidson (1999) tested ten commercial filters (8 AC, 1 AC fiber, 1 O₃ catalyst) at an O₃ concentration of 120 ppb and found that O₃ removal efficiency and pressure drop generally increased with carbon surface area. A few field studies have been described in the literature, and AC filters have been found to effectively reduce indoor O₃ concentrations in buildings with mechanical ventilation systems. In a 3-yr study conducted in the Los Angeles area, an auxiliary filtration system utilizing nine pre-filters and nine AC filters used intermittently (~ 1200 hr yr⁻¹) removed 95, 80 and 50% of O₃ after 1, 2 and 3 years, respectively (Shair, 1981). O₃ removal efficiencies of commercial AC filters located in a test plenum, in an air handler providing outside air to a clean room, and in a plenum downstream of an air handler providing outside air to another clean room, were tested over 37 months (Weschler et al., 1994). At the conclusion of the test periods, AC filters servicing the test plenum (37 mo.), first clean room (37 mo.), and second clean room (24 mo.) had O₃ removal efficiencies of 90, 60 and 95%, respectively. Additional data from this study published subsequently indicated that adequately-sized AC filters have very long service lives for O₃ removal as long as they are not excessively soiled by submicron particles, which contributes to a faster decrease in O₃ removal efficiency (Shields et al., 1999). Salmon et al. (2000) determined that the National Museum of Poland's AC filtration system averaged an O₃

removal efficiency of 77% over a 33-day measurement period. All of these studies employed substantial bed depths of AC, not the very thin carbon impregnated filters sold to remove both odors and particulate matter. For example, AC filters in the Weschler et al. (1994) study employed filter panels (61 cm by 74 cm by 2.5 cm); total AC mass ranged from 20 kg to 41 kg depending on the number of panels. (Filter dimensions were not given in the other field studies.)

4.5.2 Effect of VOCs on O₃ removal

Other than soiling by fine particulate matter, little is known about how VOCs and other substances in indoor air affect the O₃ removal by AC. Only two peer-reviewed studies were found that measured the effect of VOC loading on O₃ penetration, and both focused on use of advanced oxidants (O₃, OH·, HO₂, etc.) and the regeneration of spent carbon. Dusenbury and Cannon (1996) saturated granulated coconut shell AC (GAC) beds (32 mm thick, 3.8 cm dia) with methyl isobutyl ketone, acetone, benzene or 2,3-dimethyl-2-butane, which was then exposed to moderate concentrations of O₃ (250-350 ppm). O₃ penetration for the first 2 hrs depended on the VOC. Benzene, among the least reactive of the VOCs tested, allowed the most O₃ to penetrate the AC bed. In contrast, 2,3-dimethyl-2-butene, the most reactive VOC, allowed no penetration. After 24 hr, O₃ penetration was similar to that of virgin AC, with the exception of methyl isobutyl ketone (MIBK) in that O₃ penetration increased continuously with time, attributed to the presence of MIBK and its partial oxidation products that protected the GAC surface from further oxidation. In the second study, Cannon et al. (1996) loaded GAC beds (3.8 cm dia x 15.2 cm depth) with MIBK that were then exposed to advanced oxidants for 24 hr. Oxidant regeneration was most effective in the first 2.5 cm of the GAC bed, with most of the MIBK desorbed or destroyed, and ~25% of the initial MIBK mass was removed in

the remainder of the bed. Only 10-15% of the MIBK was converted into reaction products. Cannon et al. (1996) suggest that the oxidants penetrated only 2-3 cm into the GAC bed, displacing the MIBK.

Weschler et al. (1994) measured O₃ removal efficiency over a 3-yr period for three GAC filters with a bed depth of 2.5 cm (installed in test plenum, air handler providing outside air to a clean room, and a plenum located downstream of an air handler providing outside air to a different clean room). In a discussion section following the article, VOC loadings were stated to have little effect on O₃ removal efficiency. VOC loadings for filters servicing the two clean rooms (not reported in the article itself) were close to the expected saturation levels (4.7 and 3.6 wt %), yet the filters continued to remove O₃ with efficiencies of 60 and 90%, respectively. No further information was given regarding VOC loadings, and no experiments were conducted to determine the O₃ removal efficiency relative to virgin AC. No other peer-reviewed articles were found regarding the effect of VOC loading on O₃ removal efficiency at low concentrations.

4.5.3 Effect of O₃ exposure on VOC removal

Several studies have focused on VOC adsorption properties of O₃-treated AC. In a field study, Cannon et al. (1996) studied several GAC beds loaded with VOCs (alcohols, phenol, acetone, mineral spirits, etc.) and regenerated with advanced oxidants over several years. After 500 – 1000 daily loading/regeneration cycles, one GAC sample had lost 35% of its micropore volume and 17-35% of its VOC sorption capacity; a second had lost 80% of its volume and 23-63% of its sorption capacity. You et al. (1994) studied AC samples treated with O₃ and VOC removal capacity for n-hexane, methyl-ethyl-ketone and benzene, and found that O₃-treated AC had a greater affinity for polar compounds than virgin AC. Chiang et al. (2002) studied ozonation of AC and its effects

on the adsorption of methyl ethyl ketone (MEK) and benzene and found that the adsorption capacity of benzene was smaller on O₃-treated AC compared to virgin AC. However, the MEK adsorption capacity was greater on O₃-treated AC compared to virgin AC when the influent relative vapor pressure of MEK exceeded 0.008, attributed to the dominance of physical adsorption at higher concentrations, while chemisorption is important at lower VOC concentrations. Because MEK is a slightly polar compound, its adsorption capacity on O₃-treated AC exceeds that of virgin AC (a less polar surface). Álvarez et al. (2004) studied regeneration of GAC used for phenol removal from aqueous solutions and found that there was an optimum O₃ dose for which phenol was totally removed without decreasing the AC surface area. If too much O₃ was applied, acidic surface groups decreased GAC's sorption capacity for phenol. Masuda et al. (2001) found that the capacity of AC to remove hydrogen sulfide (H₂S) in effluent gas was diminished when VOCs were present. However, the H₂S removal capacity of AC could be restored by O₃ injection (~ 500 ppm) to remove the VOCs. Toluene, which is not very reactive with O₃, was displaced by O₃ and H₂S oxidation products; ethanol, which is easily decomposed by O₃ and is adsorbed by AC in only small amounts, was removed by O₃; and butanol compounds exhibited intermediate behavior between toluene and ethanol.

4.5.4 The Elovich equation and preadsorption phenomena

The Elovich equation has been applied successfully to some chemisorption data where the adsorbing surface is heterogeneous (Cheung et al., 2000). The Elovich equation is expressed as

$$dq_t/dt = a \exp (-b q_t) \quad (4-1)$$

where q_t = sorption capacity at time t (wt %), t = time (hr), a = initial sorption rate (wt % hr⁻¹); and b = adsorption constant (wt %⁻¹) for a given experiment (Ho and McKay, 1998). Following integration, eq. (4-1) becomes:

$$q_t = 1/b \ln (a b) + 1/b \ln (t + t_0) \quad (4-2)$$

where t_0 = time constant (hr) and is estimated by trial-and-error to achieve a linear plot of q_t versus $\ln (t + t_0)$. If the Elovich model applies, constants a and b can be calculated from the slope and intercept. If $q_t = 0$ at $t = 0$, $t_0 = 1/ab$. However, if an amount of gas is instantaneously adsorbed, the integrated form of eq. (4-1) becomes (Low, 1960):

$$q_t = 1/b \ln (a b) + 1/b \ln (t + k) \quad (4-3)$$

where k (hr) = $t_0 \exp (b q_0)$. Because of rapid initial adsorption or other kinetic processes that may displace plots, the Elovich equation may not be practical for determining values of q_t . Rather, it is most useful for determining adsorption rates and not sorption capacities (Low, 1960).

The Elovich equation may be used to determine the effects of a pre-adsorbed gas (i.e., VOC) on the sequential adsorption of another gas (i.e., O₃) (Low, 1960). Either of the parameters (a , b) of the Elovich equation may be affected by pre-adsorption assuming non-selective adsorption. (Selective adsorption occurs when the pre-adsorbate is adsorbed onto areas of the sorbent that it first contacts, creating a stratified adsorption zone [Low, 1960]). There are four basic types of pre-adsorption phenomena: 1) enhancement, in which a increases and b decreases; 2) poisoning, in which a decreases and b increases; 3) pseudo-enhancement, in which both a and b decrease; and 4) pseudo-poisoning, in which both a and b increase (Low, 1960).

4.6 Methods

Based on experimentally-determined sorption capacities, AC filter samples simulating filter beds were loaded with either toluene or *d*-limonene at levels designed to represent high, moderate, or light loads. Filter samples were then exposed to O₃ and breakthrough curves measured. Breakthrough data were used to calculate removal efficiencies and adsorption capacities. Finally, data were fit to the Elovich model and parameters *a* and *b* were used to determine the effect of VOC pre-adsorption on O₃ removal efficiency of AC.

4.6.1 AC sample assemblies

Thin beds of either virgin AC or VOC-spiked AC were prepared as follows. AC was acquired as mesh size 30-60 (Standard Coconut Shell Carbon, G55-C, PICA USA, Columbus, OH), ground using a mortar and pestle, and sieved between 50 and 60 mesh screens to obtain a particulate diameters from 250 to 300 μm, selected to minimize wall effects that could lead to short-circuiting. AC samples were packed between two fine stainless steel screens, which in turn were held in place by fine stainless steel screens retained by friction in Teflon[®] tubes (8.5-cm long, 4.8 mm ID) equipped with Swagelok[®] fittings. A small plug of unsilanized glass wool was placed in each end to trap any particles that might escape through the screens. Initially, AC beds contained 10 mg of AC, weighed to 0.1 mg using an analytical balance (Mettler Instrument Corp.;

Hightstown, NJ), corresponding to a bed depth of 1.2 mm. This bed depth was thin enough to allow for rapid breakthrough yet thick enough to maintain a uniform surface. In subsequent tests, the bed mass was increased to 15 mg (bed depth of 1.8 mm) to allow for slower breakthrough.

AC samples were carefully prepared to obtain a cylindrical bed with flat and near parallel faces as follows: A clean tube was mounted vertically on a ring stand and vacuum was applied to the bottom of the tube. A ~4 mm long spring was placed in one end of the tube, followed by a stainless screen disk that was carefully cut to the fit the tube's inner dimensions. A stainless steel rod was used to help position the components. The previously weighed AC was transferred to the tube using a disposable glass pipette as a funnel. The second screen was placed on top of the AC, followed by another spring section. The tube was then removed from the vacuum and small plugs of glass wool were placed in each end to prevent leakage.

When not in use, the AC and packed tubes were stored under vacuum in a dessicator containing Drierite[®] material to minimize aging effects.

4.6.2 Sorption capacity determination

Sorption capacity of the AC for toluene and *d*-limonene was determined in dynamic breakthrough tests. A test atmosphere of 270 ppm and 50% RH was prepared by injecting 18 μ L of neat toluene (ACS grade, Malinckrodt, Inc., Paris, KY) or *d*-limonene (97% purity, Aldrich Chemical Co., Milwaukee, WI) into a 10 L Tedlar bag filled with 9 L of humidified (50% RH) zero air. Air was humidified to simulate typical indoor air conditions. The Tedlar bag was warmed slightly with a heat lamp to facilitate volatilization. The test gas was passed through a Teflon tube containing approximately 30 ± 1 mg of AC and drawn into a photo-ionization detector (PID; Model PDM-10A,

RAE Systems Inc., Sunnyvale, CA) used to monitor effluent VOC concentrations. Flow rates, measured using an automated piston meter (DryCal DC-lite Model L, Bios International Corp., Butler, NJ), ranged from 310 to 320 ml min⁻¹. PID output was measured using a voltmeter and also recorded at 1 Hz using a data logger (Hobo H8, Onset Computer Corp., Bourne, MA). Data were downloaded to a PC using BoxCar Pro 4.3 software (Onset Computer Corp.). Replicate samples were tested for each VOC.

The sorption capacity (mg VOC/g AC) was determined by plotting the VOC concentrations (estimated as a PID voltage) versus VOC dose (VOC dose = concentration * flow rate * time), extrapolating the steepest part of the curve to the x-axis, and dividing by the AC mass.

4.6.3 VOC loading of sample beds

AC beds were loaded using a closed-loop system that recirculated the VOC through the sample tube to ensure maximum adsorption. Using a microliter syringe, 2, 1 or 0.5 µL of neat VOC, representing highly-, moderately- and lightly-loaded samples, respectively, was injected into the system. The septum area was gently heated to facilitate volatilization. Flow proceeded from the injection area to a 500 ml mixing chamber (Teflon bottle) to facilitate mixing, through the sample tube, a PID/pump (Model PDM-10A, RAE Systems Inc.), and then back to the septum area. After an equilibrium period of ~15 min., the AC tube was removed from the system, capped and stored in a dessicator containing Drierite® under vacuum until use.

4.6.4 O₃ exposure system

The exposure system depicted in Fig. 4-1 was used to deliver a test atmosphere to up to 8 AC samples at a constant O₃ concentration, temperature (24 C), relative humidity (50%) and flow rate (160 cm³ min⁻¹). The flow rate provided a superficial face velocity

of 14.7 cm s^{-1} , (884 cm min^{-1}), comparable to typical values in filter applications. A pure air generator (Model 737-12A, AADCO Instruments, Inc., Clearwater, FL) supplied hydrocarbon-free air to an UV O_3 generator (Model MZ-250, Clearwater Tech Inc., San Luis Obispo, CA). The flow was diluted with 50% RH air, obtained using temperature-controlled bubblers and the pure air generator. Using rotameters, the flow was metered into 8 identical streams: seven were used to expose media; the eighth was used to monitor the O_3 concentration. Downstream of each sample tube, a 3-way Teflon[®] solenoid valve (Cole-Parmer Instrument Co., Vernon Hills, IL) vented flows to an exhaust hood (valve off) or for measurement (valve energized) after dilution with a clean, dry air (1.50 L min^{-1}) using a continuous O_3 analyzer (400A, Advanced Pollution Instrumentation, Inc., San Diego, CA) and a continuous NO/NO_2 chemiluminescence analyzer (CLD 700 AL, Eco Physics Inc., Ann Arbor, MI). A datalogger (21X, Campbell Scientific, Inc., Logan, UT) controlled the system and collected data from the two analyzers. The datalogger was programmed to advance the solenoid valves every 2 min. The first 1 min of data was discarded to allow the O_3 analyzer and the system to stabilize. The second 1 min of data was recorded at 1 Hz and averaged to obtain a 1-min average. Thus, O_3 and NO_x concentrations were attained for each tube every 16 min.

The continuous O_3 and NO/NO_x instruments were modified to reduce response times by eliminating signal smoothing. Both instruments had low detection limits (LDLs) and large dynamic ranges. The O_3 analyzer had a performance range of 0-10 ppm and an LDL of $<0.6 \text{ ppb}$, and was calibrated using a certified transfer standard (UV photometer, 401X, Advanced Pollution Instrumentation, Inc., San Diego, CA). The NO/NO_x monitor had a performance range from 0-100 ppm and a LDL of 1 ppb.

The system provided stable O₃ concentrations (within 5.5%). The NO/NO_x data were used to monitor for presence of nitrogen oxides (NO_x), which can be produced when using an air-fed ozonator (Fendel et al., 1995). Significant amounts of NO_x would be undesirable in this study because nitric oxide (NO) readily reacts with O₃. No evidence of NO_x production was found at any time during the experiments. (In earlier experiments, a high voltage AC generator was used to generate O₃, along with unwanted NO_x. Switching to a UV generator eliminated NO_x production.)

4.6.5 O₃ removal efficiency experiments

O₃ removal was measured using low, medium, or high VOC loadings. Each experiment used 2 tubes each of limonene-loaded, toluene-loaded, and virgin AC that were simultaneously exposed to O₃. Collected data were uploaded to a computer and imported into a spreadsheet for analysis. O₃ breakthrough curves were constructed and used to calculate breakthrough times. Unless otherwise noted, 1-hr averages of replicate experiments were used. In cases, points were plotted less frequently to improve graph clarity.

The system was tested to verify that limonene did not interfere with the O₃ measurements as certain O₃ analyzers have shown positive biases at high concentrations of unsaturated VOCs (Clausen, 2001). Two 20 mg virgin AC samples were spiked with 2 µL of limonene and placed into two of the ports in the O₃-exposure system. The samples were exposed to the normal flow of humidified air for ~24 hrs. No positive interferences were noted.

4.6.6 VOC measurements

To quantify any VOCs desorbing from the AC samples, VOC concentrations were measured in the effluent air stream. In conjunction with experiments described in the

next chapter, 20 mg AC samples (30/60 mesh) were loaded with either 0, 1 or 2 μL of limonene, exposed to 5.81 ppm of O_3 for 91 hr (two replicates each), and breakthrough curves constructed. Downstream of the AC, 10-min VOC samples were collected on Tenax-GR/Carbosieve SIII sorbent tubes at exposure times of 0, 1, and 23 hr for later analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS).

To avoid possible loss of analytes and sorbent artifacts, an O_3 trap was placed upstream of the VOC sampling tube in some experiments to prevent degradation of the Tenax-GR sorbents and further reactions of any adsorbed VOCs. Traps were prepared by filling a 10 cm length of 4 mm dia. Teflon[®] tubing with crystalline potassium iodide (KI, ACS grade, Eastman Kodak Co., Rochester, NY). Tube ends were plugged with silanized glass wool to retain the KI. Traps were tested prior to use to verify that O_3 was completely removed from the sample stream by placing them in the O_3 exposure system, exposing them to humidified, ozonated air (1.1 ppm) for 24 hrs, and monitoring the effluent for O_3 . No O_3 was detected.

The stainless steel VOC sampling tubes had dimensions 10 cm length, 6 mm OD, 4 mm ID, with tapered screw threads on both ends (Scientific Instruments Services, Ringoes, NJ). Tubes were packed at the upstream (sampling) end with 3-mm silanized glass wool, 160 mg 60/80 mesh Tenax GR (polyester-phenyl ether with 23% graphitized carbon), followed by 3-mm silanized glass wool, 70 mg Carbosieve SIII (60/80 mesh), and finally 3-mm silanized glass wool at the downstream end. The adsorbent bed was positioned 1.7 cm from the tube end. Packed tubes were conditioned at 325° C in a 24-tube conditioning for 6 hr with a 25-50 ml min^{-1} reverse flow of high purity (99.999%) helium. After conditioning, the tubes were sealed with stainless steel caps with Teflon[®]

seals screwed onto both ends. The tubes were then wrapped in previously baked aluminum foil and stored in a glass jar at 4° C.

VOC sampling tubes were analyzed immediately after sample collection by thermal desorption/gas chromatography/mass spectrometry. A complete description of the method and its performance is given in Peng and Batterman (2000). Prior to analysis, tubes were spiked with 2 μL of an internal standard solution (1 $\text{ng } \mu\text{L}^{-1}$ each of fluorobenzene and p-bromofluorobenzene). After a 1 min dry purge (40 ml min^{-1} of GC carrier gas) to remove excess water, the tube was heated to 200° C and the sample was desorbed for 5 min at 10 ml min^{-1} and transferred to the GC inlet via a “short-path” 3.5-cm long stainless steel side-port needle previously screwed onto the sorbent tube. Using a split ratio of 10:1, the sample was cryofocused at the head of the column, previously cooled to -140 °C. The sample was then removed from the GC flow path and the cryotrap was rapidly heated to 250° C, providing a narrow injection band that enhanced separation and resolution of compounds. The GC program was then started. A 30 m x 0.25 mm ID column with 0.25 μm film thickness of 5% diphenyl-95%-dimethylsiloxane copolymer was used. The oven temperature started at -10° C and was ramped in 4 stages to 250° C. VOCs were quantified based on the ratios of its target ions to that of the internal standards.

To quantify the amount of limonene remaining on the AC after prolonged O_3 exposure, two 20 mg AC samples were loaded with 2 μL of limonene and exposed to 8.95 ppm of O_3 for 48 hr. Immediately following the test period, AC samples were placed in 2 mL glass vials to which 1 mL of carbon disulfide (Spectranalyzed® grade, Fisher-Scientific, Fair Lawn, NJ) was added to each. The capped vials were shaken and

allowed to stand for several hours at room temperature. Prior to analysis, internal standard was also added to the vial. Two- μ L aliquots were directly injected into the GC and analyzed using the GC/MS method described above. For comparison, 20 mg limonene-spiked samples were exposed to humidified, purified air ($160 \text{ cm}^3 \text{ min}^{-1}$) but not O_3 for 48 hr, extracted with CS_2 , and analyzed by GC/MS.

4.7 Results

4.7.1 VOC sorption capacity

The average sorption capacities for limonene and toluene were determined to be 10.8 ± 1.3 and 15.2 ± 1.0 wt %, respectively, based on VOC breakthrough curves (Figs. 4-2 and 4-3). Note that while the upper ends of these curves are limited by the response of the instrumentation (at $\sim 2 \text{ V}$), sorption capacities determined using the middle (linear) portion of the curve are unaffected.

4.7.2 O_3 breakthrough – 10 mg tests

Breakthrough curves for highly, moderately, and lightly loaded 10 mg experiments (in three experiment runs) are shown in Figs. 4-4, 4-5 and 4-6, respectively. Table 4-1 shows the degree of O_3 penetration (C_t/C_0) at selected exposure times for virgin and VOC-loaded AC samples.

The virgin (unloaded) filters containing 10 mg AC (bed depth = 1.2 mm) exceeded the critical bed depth, shown by no penetration ($C_t/C_0 = 0$) at $t = 0$. For these filters, the average (standard deviation) breakthrough time was 0.8 ± 0.4 hr for $C_t/C_0 = 1\%$. While removal efficiencies gradually decreased through the test, the virgin AC filters continued to remove most O_3 , e.g., the penetration was $24 \pm 2\%$ after 90 hr.

Toluene-loaded filters showed immediate breakthrough for 5 of 6 replicates, and the 6th replicate had very rapid (0.3 hr) breakthrough. Thus, toluene loadings diminished the initial O₃ removal capacity of the AC, and the critical bed depth was not reached at any toluene loading.

Limonene-loaded filters had variable breakthrough times, e.g., 0.9 ± 1.0 hr for $C_i/C_o = 1\%$, and breakthrough occurred immediately or within 16 min (the system resolution) for 2 of 6 replicates. Breakthrough was slower for moderate limonene loadings, as compared to low and high loadings. Thus, limonene's effect was variable, at least in the early portion of the breakthrough curves, and appeared to be dependent on the loading rate.

The variability observed for limonene was not a system artifact. Breakthrough curves were reproducible, e.g., replicates had penetrations generally within 20% at any given exposure time. Slightly larger deviations sometimes occurred initially, however, replicates tended to "catch up" with each other as time progressed. Replicate variability may result from several factors: (1) variation in tube packing, e.g., the amount and distribution of AC, bed depth and uniformity, resulting in each tube having a unique surface available for O₃ reaction; (2) differences in flow rates in the exposure and measurement system; and (3) variation in VOC loadings, e.g., possibly including the VOC losses occurring after sample preparation but before O₃ exposure.

Because challenge O₃ concentrations were very close (within 1%), data among experimental runs were pooled, and single-factor ANOVA tests were performed at selected exposure times to determine if differences existed between mean O₃ penetration fractions of different loadings. Mean O₃ penetration fractions among the three virgin

runs showed no differences, with the exception of 1 and 2 hr values (p -value = 0.03 and 0.02, respectively, Table 4-1). Mean O_3 penetration fractions also did not differ at each tested exposure time for the three loadings of both limonene and toluene, thus, loading rates did not have a significant effect. However, mean O_3 penetration fractions of VOC-loaded AC and virgin AC (no VOC loading) varied at most exposure times (except some initial points; t -tests, Table 4-1). Compared to the virgin AC samples, limonene-loaded AC samples showed greater penetration on average (though moderately loaded samples initially showed lower penetration.) Similarly, penetration through the toluene-loaded AC also exceeded that of the virgin AC, and also exceeded penetrations through limonene-loaded AC.

4.7.3 O_3 breakthrough – 15 mg tests

Additional tests were conducted using 15 mg of AC to provide greater bed depth (1.8 mm) that clearly exceeded the critical bed depth. Both moderate (52% of capacity) and high loadings (100% of capacity) of limonene were tested. Limonene-loaded samples broke through much faster (2 ± 2 hr) than the virgin AC samples (23 ± 13 hr; Fig. 4-7). As seen earlier, breakthrough behavior was not influenced by the loading rate.

A follow-up experiment was conducted using much higher O_3 concentrations (5.8 ppm) and 20 mg of the 30/60 mesh AC at two limonene loadings (39% and 78% of capacity). O_3 removals by loaded and unloaded AC samples were nearly identical for the first 12 hr, after which limonene-loaded AC provided less O_3 removal than virgin AC (Fig. 4-8). After ~25 hr of exposure, the highly-loaded samples provided slightly less O_3 removal than the moderately loaded sample, though differences were small.

To illustrate the effect of VOC-loadings on the total O_3 removal efficiency, O_3 removals were calculated at selected exposure times (Table 4-2). O_3 removals of VOC-

loaded samples were in some cases equivalent to or even slightly higher than the corresponding virgin samples. After 10 hr of O₃ exposure, however, VOC-loaded samples had diminished O₃ removals compared to virgin samples. At 80 hr, VOC-loaded samples removed from 75% to 95% the O₃ mass compared to corresponding virgin samples.

4.7.4 VOCs in air and AC

Limonene concentrations in the effluent of the 20 mg samples were measured to determine the amount of VOC desorbed from the samples. For the highly loaded AC samples, limonene concentrations were initially (first 10 min) 304 µg m⁻³, and dropped rapidly to 82 and 6 µg m⁻¹ after 1 and 23 hr, respectively. For the moderately-loaded AC, limonene concentrations were initially 87 µg m⁻³, and then below detection limit (0.06 ng) in subsequent 1 and 23-hr samples.

CS₂ extraction tests showed that even after prolonged exposure to high concentrations of O₃, most of the limonene remained adsorbed on the AC. After 48 hr of exposure (160 cm³ min⁻¹) to 8.95 ppm O₃, 58 ± 2% of the original limonene remained on the AC, compared with 84 ± 1% for AC samples exposed to non-ozonated air. These experiments used an excess of O₃ (168.3 µmol) compared to limonene (12.4 µmol). These results are conservative since experiments using lower O₃ concentrations would be expected to show higher percentages of limonene remaining.

4.7.5 Application of the Elovich equation

Application of the Elovich equation to AC/O₃ systems was demonstrated in Chapter 3. Table 4-3 shows Elovich parameters (k, a, b) and measured initial rates for each of the VOC-loaded and virgin AC samples tested. In all cases, values indicated excellent model fit (R² > 0.999). Toluene-loaded samples showed decreased *a* values and

increased b values, indicating true poisoning in which both the rate and extent of O_3 adsorption were decreased.

Limonene results using the Elovich equation were not as straightforward as for toluene. All limonene-loaded samples exhibited increased b values compared to virgin AC samples. In most cases limonene-loaded AC samples had decreased a values, though in a few cases they were similar to or even higher than the virgin AC samples (most evident in the 20 mg samples). Thus, there are two possibilities for the limonene-loaded samples: true poisoning or pseudo-poisoning. The overall effect of pseudo-poisoning is an increased initial rate followed by decreased ambient rate of adsorption, resulting in reduced adsorption capacity (Low, 1960). This was observed in several of the breakthrough curves where limonene-loaded AC samples frequently had lower O_3 penetration fractions compared to virgin AC during the first few hours of O_3 exposure, but then would surpass the virgin samples.

4.8 Discussion

Loadings of either VOC altered breakthrough behavior and diminished the AC's capacity to remove O_3 . Poisoning is suggested for toluene-loaded AC filters; pseudo-poisoning is suggested for limonene loadings. The two VOCs have very different O_3 reactivities, e.g., gas-phase rate constants for O_3 reaction with toluene and d -limonene are 3.69×10^{-12} and 5.14×10^{-6} $\text{ppb}^{-1} \text{ hr}^{-1}$, respectively (Weschler, 2000 and references therein). No consistent effect was seen for light, moderate and high loadings of VOCs, suggesting that lower VOC loadings may be sufficient to cause these effects. While the effects of VOC loadings are relatively modest when expressed in terms of O_3 removal capacity, earlier breakthrough by loadings of non-reactive VOCs, and pseudo-poisoning

by loadings of reactive VOCs, may substantially alter filter efficiency and O₃ concentrations in effluents, a potentially serious operational concern.

4.8.1 Comparison to literature

Dusenbury and Cannon (1996) found that O₃ penetration into a GAC bed was a function of VOC type during the first 2 hr of ozonation. Less reactive VOCs (e.g., benzene) allowed more O₃ to breakthrough the AC bed; more reactive VOCs (DMB) allowed no breakthrough initially. Toluene (used here) and benzene have similar structure and reactivity, e.g., benzene-O₃ gas-phase rate constant for benzene-O₃ is $1.72 \times 10^{-12} \text{ ppb}^{-1} \text{ hr}^{-1}$ (Weschler, 2000). The 10 mg samples loaded with toluene began breaking through almost immediately in every test. Although breakthrough for several limonene samples also began very quickly, several samples took up to 1.6 hr. However, limonene-loaded AC became less efficient than virgin AC after a few hr. The limonene-loaded 20 mg samples behaved similarly, initially allowing slightly less O₃ to penetrate than the virgin samples until ~12 and ~9 hr, for highly and moderately-loaded samples, respectively, after which limonene-loaded sample breakthrough surpassed that of virgin AC.

Dusenbury and Cannon (1996) also found that after prolonged O₃ exposure (6 - 24 hr at 250-350 ppm O₃), advanced oxidant penetration into VOC-laden GAC beds became similar to virgin GAC beds with the exception of MIBK, which differed from the other VOCs in that O₃ penetration increased continuously with time. These authors suggested that the presence of MIBK and its partial oxidation products protected the AC surface from further oxidation by O₃. Although limonene is not structurally similar to MIBK, it is known to react with O₃ to form several products (e.g., Calogirou et al., 1999) that might affect O₃ removal in similar manner as MIBK. In the present study, neither

limonene nor toluene-loaded samples reached a point where their O₃-removal efficiencies became similar to those of virgin AC. However, influent O₃ concentrations used here were much lower (2 – 3 orders of magnitude), and thus much longer periods would be required to reach the point where O₃-removal efficiencies of the VOC-laden and virgin AC samples become similar.

Even after prolonged exposure to high concentrations of O₃, the majority of limonene remained adsorbed on the AC. Dusenbury and Cannon (1996) found that >95% of acetone, 65% of DMB, and 75% of benzene were removed from their GAC beds after 24 hr of oxidant exposure. There are two possible ways that O₃ can remove VOCs from AC: chemical reaction or physical desorption. In both cases, Dusenbury and Cannon (1986) suggest that O₃ must penetrate the AC in the vicinity of the VOC, removal is limited by the ability of O₃ to react with either the AC or the VOC, and possibly O₃ (and other oxidants) create an unfavorable adsorption zone that increases desorption and allows more VOCs to be destroyed. The much higher retention of VOCs on the AC found here was likely a function of the much lower O₃ concentrations.

4.8.2 Mechanisms for O₃ removal

The experiments spanned a range of VOC and O₃ doses. In the low concentration tests (1.13 – 1.15 ppm O₃), AC beds were exposed to 42 - 106 µmol of O₃, compared to 3 to 16 µmol of VOC applied. O₃ doses were approximately 5 times higher in the 5.81 ppm tests. Considering only VOC-O₃ reactions, O₃ should not have been limiting if both reactants were accessible. However, this is clearly not the case. Of the VOC applied, most remained on the AC (58% after 48 hr at 8.95 ppm). As will be discussed in Chapter 5, only a small fraction of limonene formed detectable reaction products (formic acid, AMCH, limonene oxides, possibly formaldehyde), and a small amount of limonene was

desorbed and released in the effluent air. Only physical adsorption is expected for toluene.

Differences in the O₃ removal of VOC-loaded and virgin AC are likely due to VOC molecules blocking O₃ access to active adsorption sites. In the case of limonene sorbed on the AC, e.g., O₃ may react with easily accessible limonene molecules, thereby permitting less O₃ penetration through the bed. This may explain why several of the limonene-loaded samples were equally or possibly slightly more efficient in removing O₃ than the corresponding toluene-loaded or virgin AC samples during the initial exposure period. In contrast, comparable or enhanced O₃ removal was not seen for toluene, which does not readily react with O₃. As the readily accessible limonene molecules are depleted with additional O₃ exposure, limonene- and toluene-loaded samples behave similarly and VOC/O₃ interactions may become predominantly physical. VOC molecules are transferred more deeply through the bed until some are eventually desorbed into the effluent air stream. Additionally, the presence of limonene-O₃ reaction byproducts may influence the amount of O₃ able to break through the AC bed.

4.8.3 Relevance of lab studies

The laboratory tests showed that both limonene and toluene adsorbed on AC diminish O₃ removal efficiency and alter breakthrough behavior, and it seems likely that similar effects would be observed in the field, e.g., in indoor air filtration or respiratory protection applications. Although only two VOCs were tested, other VOCs would likely produce similar effects. As discussed previously, AC exposed to O₃ has demonstrated reduced VOC sorption capacity (Cannon et al., 1996; Chiang et al., 2002; Álvarez et al., 2004). Conversely, here it is shown that VOC exposure diminishes an AC filter's ability to remove O₃. Because VOCs and O₃ often coexist in indoor air (along with other

contaminants), it is important to consider how one contaminant affects a filter's ability to remove the other, especially in areas where contaminant levels are high.

4.8.4 Study limitations

This study provides insight regarding the interactions of limonene and toluene adsorbed on AC, however, additional factors must be considered to apply findings to indoor air filtration. Although two VOCs tested were common indoor air contaminants and represented a wide range of O₃ reactivities, tests should be conducted with other VOCs to see if they yield similar results. In addition, tests should be conducted with lower and potentially more realistic indoor O₃ concentrations (50-100 ppb). Other variables may also influence the manner by which VOCs affect O₃ removal, e.g., humidity, VOC concentration, temperature, AC type, bed dimensions, flow rate, other contaminants. Finally, in this study VOCs were loaded onto AC prior to O₃ exposure, which may not reflect actual (dynamic) conditions.

4.9 Conclusion

When loaded with toluene or limonene, activated carbon removes O₃ less efficiently as compared to virgin AC. Non-reactive VOC loadings (toluene) substantially shortened the time to O₃ breakthrough. Reactive VOC loadings (limonene) may demonstrate equal or possibly enhanced removal as virgin AC, likely due to reaction of O₃ with readily-available limonene. At later exposure times, however, differences between toluene and limonene-loaded samples could not be easily discerned. While no relationship between VOC loading and O₃ removal efficiency was found, the tested loadings were all fairly high (> 28% of estimated sorption capacity). The effect of VOCs

on the ability of AC filters to remove O_3 from indoor air is an important consideration in the design, placement and maintenance of AC filters relative to VOC sources.

4.10 References

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Table 4-1. O₃ penetration (%) at selected exposure times for 10 mg virgin AC, limonene-loaded AC, and toluene-loaded AC exposed to O₃.

Exposure time (hr)	Run # / O ₃ concentration (ppm)						Overall		Anova p-value ^a	t-test p-value ^b
	Run 1 / 1.13 ppm		Run 2 / 1.13 ppm		Run 3 / 1.15 ppm					
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Mean	St. Dev.		
Virgin AC										
1	2.5	2.4	0.2	1.2	0.4	0.0	1.1	1.1	0.03	
2	5.6	5.4	2.6	3.4	3.1	2.0	3.7	1.5	0.02	
5	7.9	7.5	7.0	6.8	7.3	5.6	7.0	0.8	0.34	
10	10.1	9.9	8.2	8.4	10.5	8.6	9.3	1.0	0.22	
50	14.9	18.8	17.1	18.5	23.5	19.3	18.7	2.8	0.28	
90	21.1	25.7	24.3	23.9	27.7	22.7	24.3	2.3	0.82	
Limonene-loaded AC										
	High		Moderate		Light					
1	3.4	12.1	0.0	0.0	9.6	2.8	4.6	5.1	0.29	^c
2	7.7	17.6	2.8	0.2	11.7	4.7	7.4	6.4	0.23	^c
5	13.3	24.9	6.6	3.2	16.8	9.6	12.4	7.8	0.19	0.12
10	19.2	31.2	10.5	6.2	20.4	13.1	16.8	8.9	0.14	0.07
50	35.9	46.2	26.5	19.3	34.3	26.6	31.5	9.4	0.12	0.01
90	44.4	53.1	37.3	28.6	39.6	34.5	39.6	8.5	0.12	0.002
Toluene-loaded AC										
	High		Moderate		Light					
1	6.9	4.7	14.7	2.6	24.3	7.4	10.1	8.1	0.55	^c
2	9.1	6.4	18.5	6.3	26.6	11.6	13.1	8.0	0.46	^c
5	13.1	10.2	23.7	10.5	32.5	20.4	18.4	8.8	0.28	0.010
10	18.0	14.8	27.9	14.7	35.6	28.6	23.3	8.7	0.17	0.003
50	33.0	29.3	47.3	32.5	47.1	50.2	39.9	9.2	0.15	0.0003
90	42.4	36.3	51.8	42.2	49.3	51.1	45.5	6.2	0.20	0.000013

^a Single-factor ANOVA testing whether the three experiments have equal means.

^b Two-tailed t-test comparing mean of VOC-loaded AC samples (all loadings) to virgin AC samples.

^c Not tested because ANOVA indicated a significant difference among the three experiments.

Table 4-2. O₃ removal (wt %) of virgin, limonene-, and toluene-loaded AC at selected exposure times.

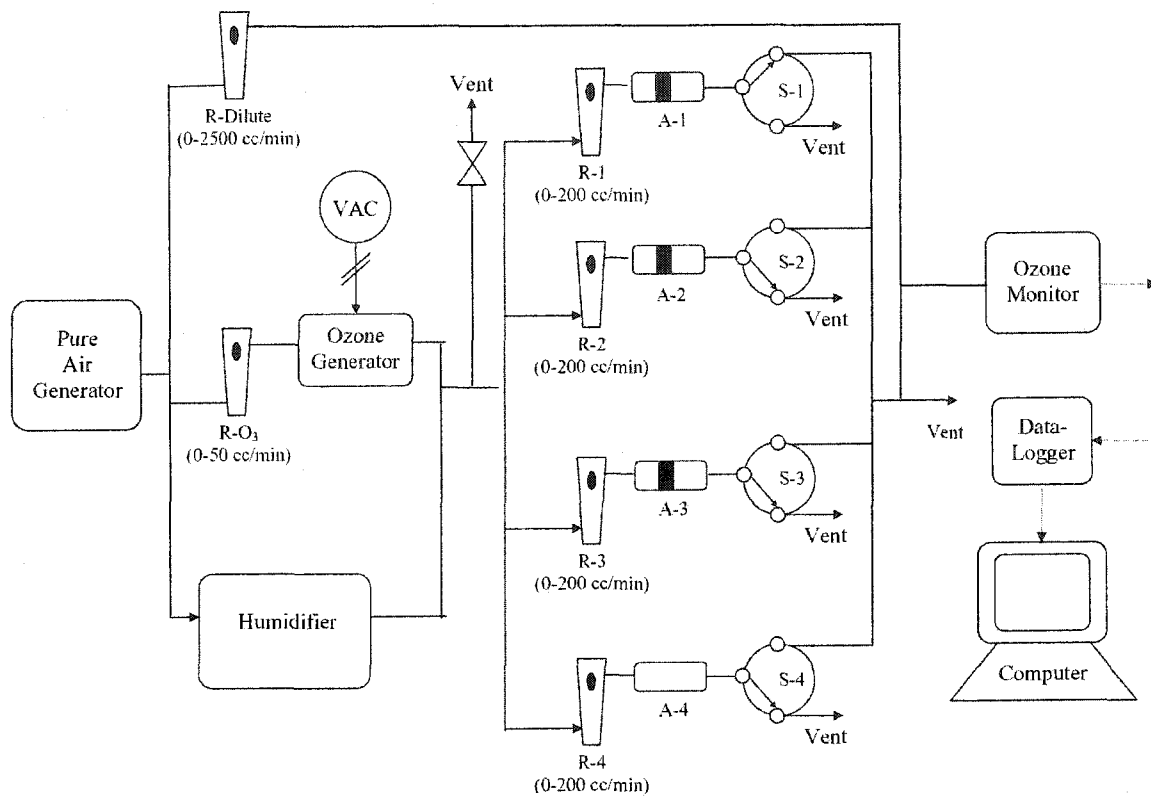
Exposure time (hr)	O ₃ concentration (ppm)						
	1.13 ^a		1.15 ^a	0.89 ^b		5.81 ^c	
	Virgin AC						
1	0.17 (0.00)	0.19 (0.05)	0.19 (0.00)	0.10 (0.00)		0.44 (0.02)	
2	0.39 (0.00)	0.39 (0.02)	0.34 (0.00)	0.22 (0.00)		1.02 (0.02)	
5	0.98 (0.00)	1.04 (0.10)	0.97 (0.01)	0.54 (0.00)		2.59 (0.00)	
10	1.98 (0.00)	2.06 (0.12)	1.90 (0.02)	1.12 (0.00)		5.15 (0.01)	
20	3.92 (0.00)	4.14 (0.24)	3.81 (0.05)	2.24 (0.01)		9.74 (0.12)	
40	7.62 (0.06)	7.95 (0.05)	7.45 (0.11)	4.43 (0.03)		17.44 (0.29)	
80	14.51 (0.30)	14.95 (0.39)	14.40 (0.39)	5.80 (0.04)		30.03 (0.65)	
	Limonene-loaded AC						
	High load	Mod. Load	Light load	High load	Mod. Load	High load	Mod. Load
1	0.18 (0.01)	0.17 (0.00)	0.18 (0.00)	0.09 (0.00)	0.10 (0.00)	0.43 (0.03)	0.45 (0.00)
2	0.39 (0.03)	0.39 (0.00)	0.35 (0.04)	0.21 (0.00)	0.20 (0.02)	1.02 (0.02)	1.03 (0.01)
5	0.92 (0.08)	1.00 (0.02)	0.91 (0.04)	0.53 (0.01)	0.54 (0.00)	2.60 (0.01)	2.60 (0.05)
10	1.77 (0.17)	2.02 (0.05)	1.80 (0.13)	1.08 (0.03)	1.08 (0.02)	5.17 (0.11)	5.15 (0.14)
20	3.27 (0.36)	3.90 (0.13)	3.52 (0.19)	2.13 (0.05)	2.12 (0.00)	9.70 (0.41)	9.61 (0.28)
40	6.04 (0.71)	7.60 (0.35)	6.79 (0.46)	4.11 (0.08)	4.07 (0.03)	16.72 (0.66)	16.83 (0.41)
80	10.86 (1.25)	14.21 (0.88)	12.91 (0.92)	5.11 (0.09)	5.06 (0.04)	26.95 (0.96)	27.68 (0.17)
	Toluene-loaded AC						
	High load	Mod. Load	Light load				
1	0.18 (0.00)	0.16 (0.01)	0.16 (0.01)				
2	0.40 (0.01)	0.36 (0.03)	0.32 (0.07)				
5	0.97 (0.02)	0.89 (0.09)	0.83 (0.14)				
10	1.91 (0.05)	1.77 (0.20)	1.64 (0.35)				
20	3.62 (0.10)	3.37 (0.39)	3.23 (0.69)				
40	6.77 (0.24)	6.37 (0.82)	6.28 (1.31)				
80	12.42 (0.49)	11.66 (1.65)	11.97 (2.55)				

^{a,b,c} AC mass = 10, 15, 20 mg, respectively.

Table 4-3. Elovich parameters (time constant, initial O₃ removal rate, adsorption constant) and measured initial rates for virgin, toluene-loaded, or limonene-loaded AC. Standard deviation in parentheses.

Sample	VOC Load	O ₃ Conc. (ppm)	AC Mass (mg)	Elovich parameters			Meas. init. rate (wt % hr ⁻¹)
				k (hr)	a (wt % hr ⁻¹)	b (wt % ⁻¹)	
Virgin AC	None	1.13	10	436 (145)	0.175 (0.003)	0.014 (0.004)	0.189 (0.000)
Toluene-loaded AC	High	1.13	10	204 (19)	0.159 (0.004)	0.031 (0.004)	0.182 (0.002)
Limonene-loaded AC	High	1.13	10	156 (7)	0.147 (0.018)	0.044 (0.004)	0.186 (0.009)
Virgin AC	None	1.13	10	303 (78)	0.211 (0.015)	0.016 (0.003)	0.222 (0.013)
Toluene-loaded AC	Mod.	1.13	10	215 (47)	0.171 (0.032)	0.028 (0.001)	0.205 (0.011)
Limonene-loaded AC	Mod.	1.13	10	210 (1)	0.210 (0.014)	0.023 (0.001)	0.213 (0.001)
Virgin AC	None	1.15	10	457 (114)	0.196 (0.001)	0.012 (0.003)	0.206 (0.000)
Toluene-loaded AC	Light	1.15	10	243 (127)	0.149 (0.011)	0.031 (0.014)	0.185 (0.022)
Limonene-loaded AC	Light	1.15	10	294 (61)	0.183 (0.018)	0.019 (0.002)	0.204 (0.005)
Virgin AC	None	0.88	15	870 (133)	0.114 (0.000)	0.010 (0.002)	0.106 (0.000)
Limonene-loaded AC	Mod.	0.88	15	262 (39)	0.110 (0.000)	0.035 (0.005)	0.108 (0.001)
Limonene-loaded AC	High	0.88	15	284 (44)	0.110 (0.003)	0.032 (0.004)	0.108 (0.000)
Virgin AC	None	5.81	20	80 (6)	0.542 (0.000)	0.023 (0.002)	0.546 (0.001)
Limonene-loaded AC	Mod.	5.81	20	52 (9)	0.577 (0.040)	0.034 (0.004)	0.546 (0.001)
Limonene-loaded AC	High	5.81	20	44 (1)	0.595 (0.027)	0.038 (0.001)	0.546 (0.000)

Figure 4-1. Ozone exposure system. Ports 5-8 omitted for simplification.



(R = flow rotameter, A = adsorption tube, S = solenoid valve)

Figure 4-2. Breakthrough curve for toluene on AC.

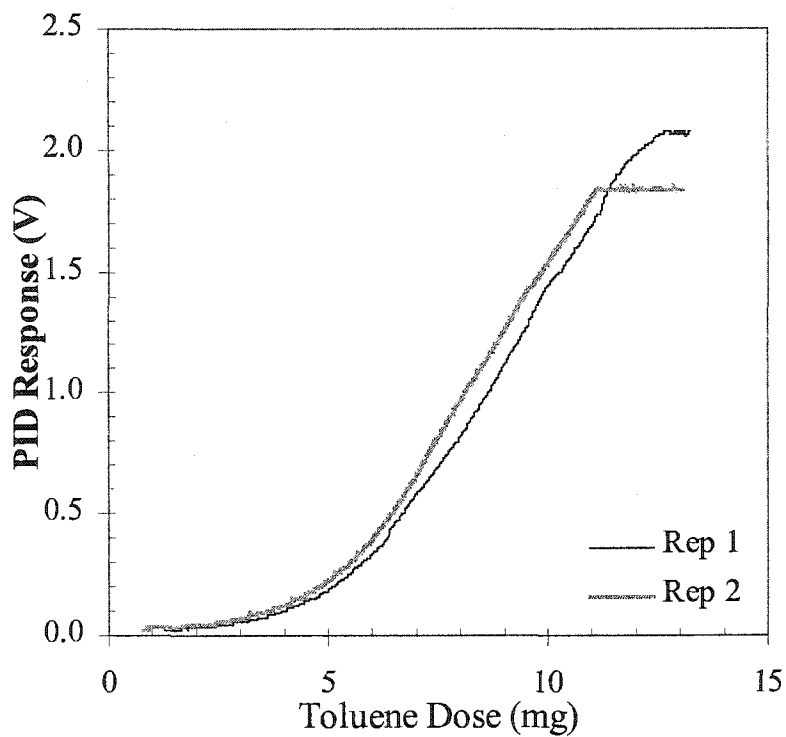


Figure 4-3. Breakthrough curve for *d*-limonene on AC.

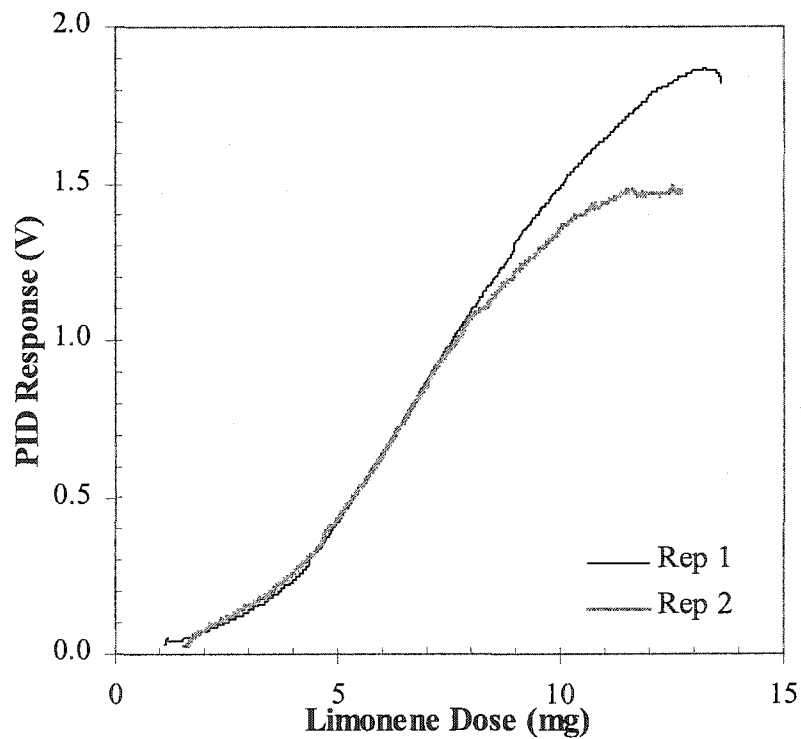


Figure 4-4. Breakthrough curves of highly-loaded (toluene or limonene) AC and virgin AC samples exposed to 1.13 ppm of O_3 . Average of replicates shown. 10 mg carbon.

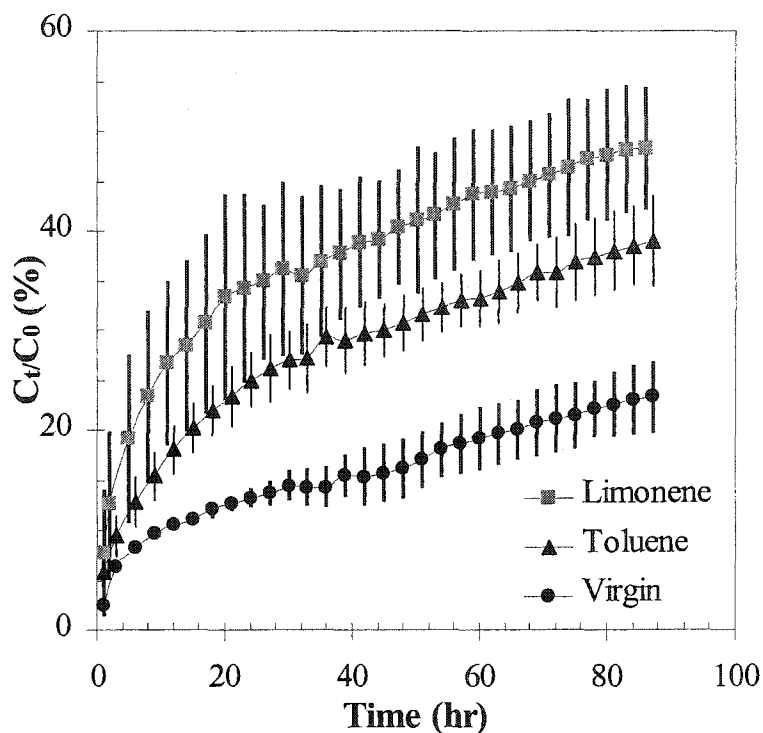


Figure 4-5. Breakthrough curves of moderately-loaded (toluene or limonene) AC and virgin AC samples exposed to 1.13 ppm of O_3 . Averages of replicates shown. 10 mg carbon.

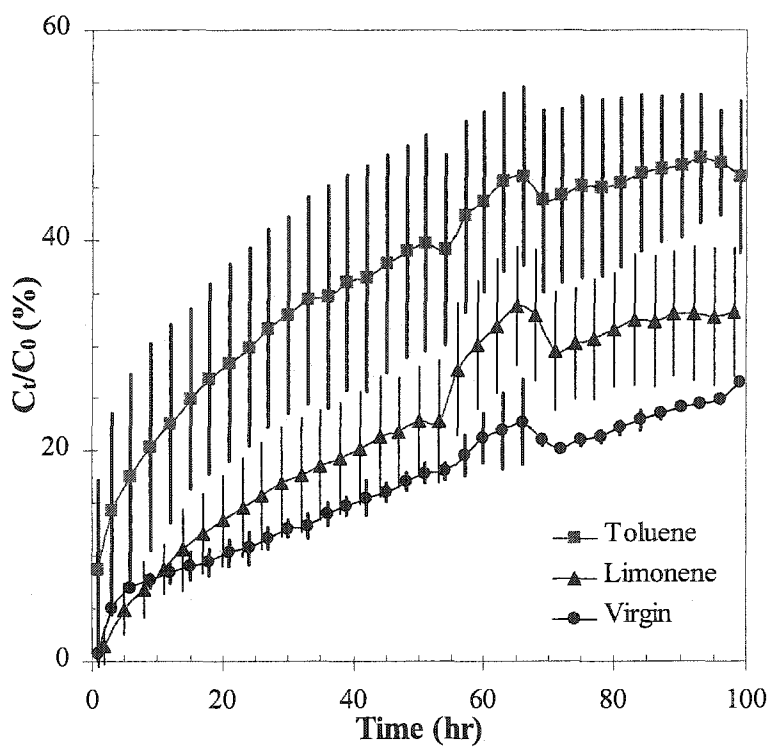


Figure 4-6. Breakthrough curves of lightly-loaded (toluene or limonene) AC and virgin AC samples exposed to 1.15 ppm of O_3 . Averages of replicates shown. 10 mg carbon.

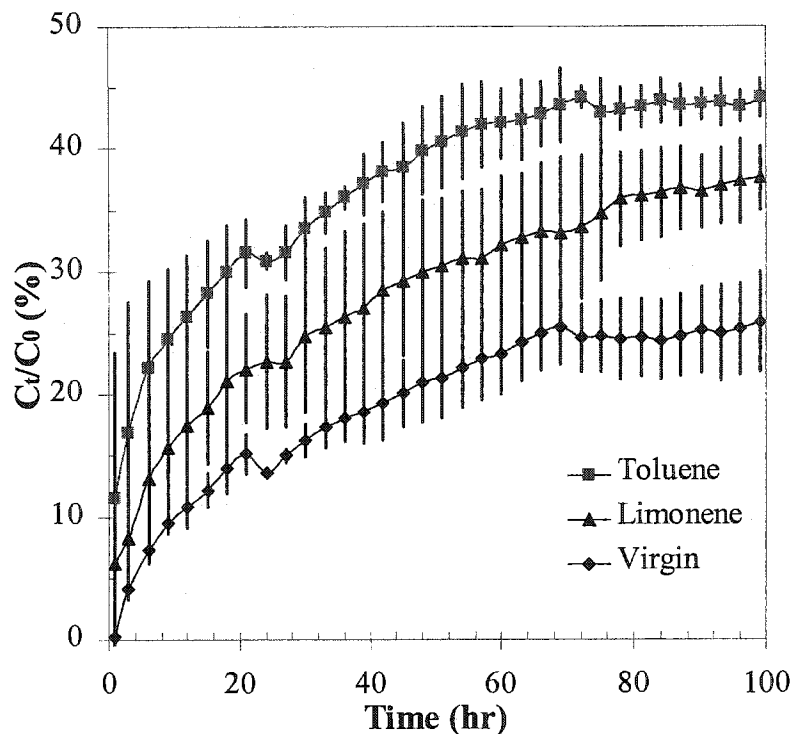


Figure 4-7. Breakthrough curves for virgin or limonene-loaded (high and moderate loads) of 15 mg AC samples exposed to 881 ppb of O_3 . Averages of replicates shown.

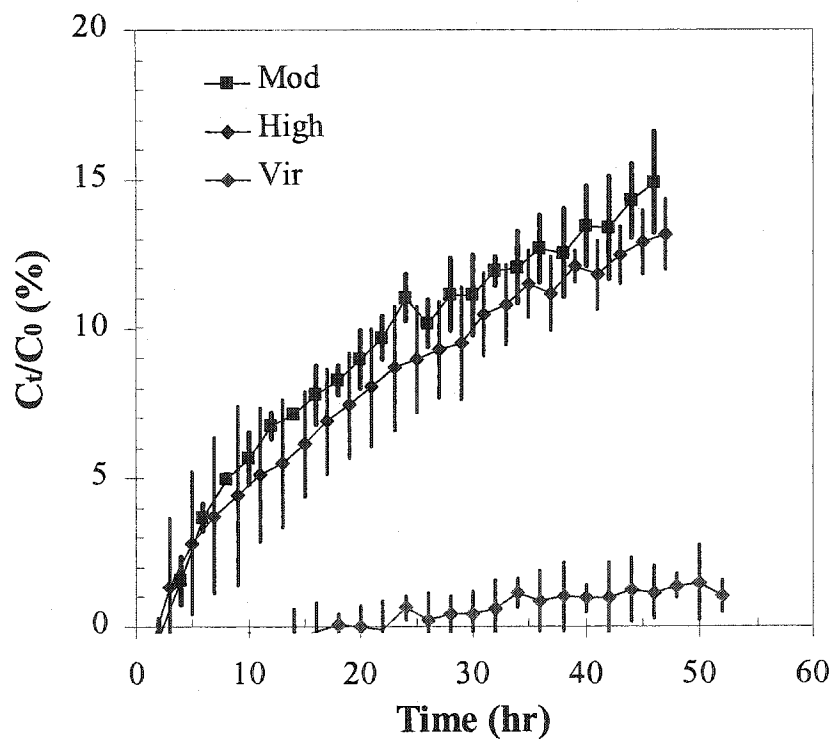
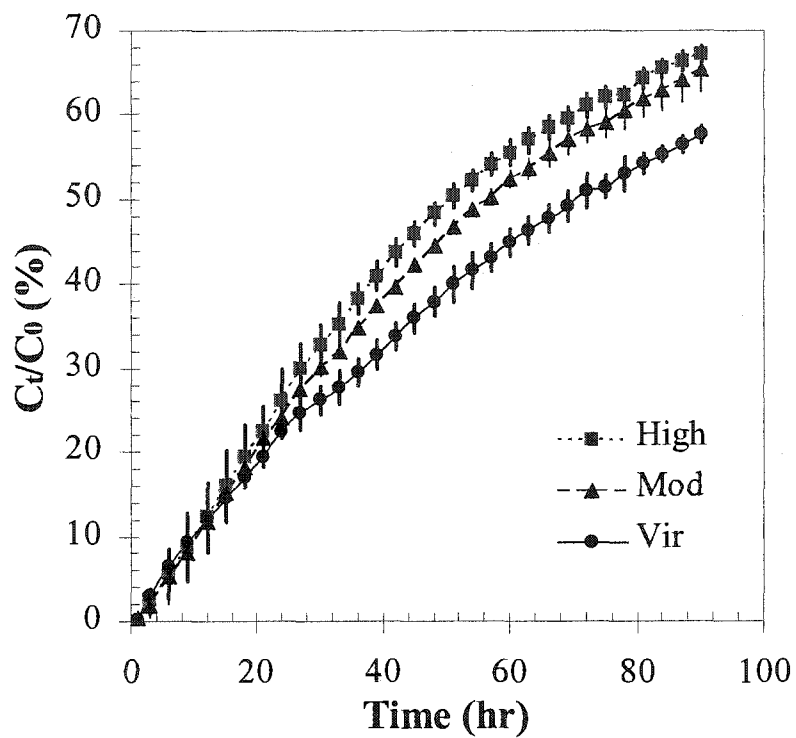


Figure 4-8. Average breakthrough curves (ave. of two replicates) for virgin AC and limonene-loaded AC (highly- or moderately-loaded) exposed to 5.8 ppm of O₃.



CHAPTER 5. HETEROGENEOUS REACTIONS OF OZONE AND VOLATILE ORGANIC COMPOUNDS ON ACTIVATED CARBON

5.1 Abstract

Products produced by reactions between ozone (O_3) and volatile organic compounds (VOCs) on the surface of activated carbon (AC), if released in significant amounts from AC filters, could negatively affect indoor air quality (IAQ). A series of experiments was conducted to investigate these heterogeneous reactions and possible gaseous and particulate products. Initially, gas-phase experiments were conducted to identify gas- and condensed-phase compounds formed in homogeneous reactions between O_3 and VOCs (toluene or *d*-limonene) and to determine yields. Toluene- O_3 mixtures did not yield significant product formation. Reaction products (and molar yields) of *d*-limonene and O_3 included formic acid (37%), 4-acetyl-1-methylcyclohexene (4%), propanoic acid (3%) and limonene oxides (3%). AC samples were then loaded with limonene, exposed to O_3 , and the effluent air analyzed by thermal desorption/gas chromatography/mass spectrometry. The major measured component in the effluent air was unreacted limonene ($501 \pm 197 \mu\text{g m}^{-3}$). Smaller amounts of 4-acetyl-1-methylcyclohexene ($20 \pm 2 \mu\text{g m}^{-3}$) and limonene oxides ($25 \pm 7 \mu\text{g m}^{-3}$) were also found. Most (58%) of the original limonene remained unreacted on the AC even after exposure to a stoichiometric excess of O_3 (8.95 ppm) for 48 hr. Thus, in addition to the known homogenous reactions, O_3 -limonene reactions occur heterogeneously on AC filters.

While additional work is necessary to investigate certain pollutants (e.g., formaldehyde, ultrafine particles) and other environmental conditions (temperature, humidity, concentrations, etc.), VOC-loaded AC air filters exposed to O₃ do not seem likely to constitute significant emission sources of secondary reaction products.

5.2 Keywords

Carbon, Heterogeneous, Limonene, Volatile Organic Compounds

5.3 Introduction

There is mounting, though indirect, evidence that chemical reactions occurring on surfaces or in the air are among the factors associated with sick building syndrome (SBS) symptoms. Reactions between oxidants such as ozone (O₃) and unsaturated volatile organic compounds (VOCs) produce chemically reactive compounds that appear more likely to cause eye and respiratory irritation than the non-reactive VOCs typically measured indoors (Wolkoff et al., 1997; 1999; 2000; Wolkoff and Nielson, 2001; Clausen et al., 2001; Rohr et al., 2002; Fan et al., 2003; Klenø and Wolkoff, 2004). Unsaturated VOCs are highly reactive due to their olefinic double bonds and hence usually have short lifetimes. In addition to playing an important role in indoor air chemistry, unsaturated VOCs are important in the formation of photochemical O₃ and secondary atmospheric organic aerosols.

5.4 Objectives

This research investigates interactions between O₃, VOCs (namely *d*-limonene and toluene) and activated carbon (AC) using laboratory experiments designed to reflect

conditions in indoor air. AC is often used in filters in order to remove pollutants from air; AC should not be a source of pollution. The overall goal of this research is to better understand the formation of reaction products occurring when AC is used to filter indoor air, and to enhance the performance and application of carbon filtration. A specific objective was to determine whether O₃ reacts heterogeneously with VOCs adsorbed on AC to form oxidation products.

5.5 Background

5.5.1 Unsaturated VOCs present indoors

The indoor environment contains many sources of unsaturated VOCs. One class of unsaturated VOCs commonly found in indoor and outdoor air is terpenes, organic compounds with structures divided into isoprene units found in oils of many citrus, pine and other plants. Monoterpenes from plant oils are ingredients in many consumer products, e.g., cleaning products, degreasers, solvents, toiletry items, and insecticides. Monoterpenes are themselves eye, mucous membrane and skin irritants as observed during inhalation exposure studies in humans and animals (Kasanen et al., 1999). Unsaturated VOCs may also be emitted from office equipment (Leovic et al., 1996; Lee et al., 2001) and wood products such as flooring and furniture (Bauman et al., 1999).

5.5.2 Reaction mechanisms

O₃ can react with certain unsaturated VOCs at a fast enough rate to affect indoor air quality (IAQ). O₃ attacks the carbon-carbon double bond to form an ozonide that quickly decomposes into one of two possible carbonyl and Criegee biradical combinations (Weschler, 2000):





where: $\bullet$ = an unpaired electron and $*$ represents an excited state. The biradicals are very energy rich and can rearrange or react by different mechanisms, which are not entirely understood (Atkinson et al., 1995). The intermediate products are highly reactive and include hydroxyl, hydroperoxyl, and alkylperoxyl radicals. Unless scavenged, hydroxyl radicals can also react with unsaturated VOCs to form secondary products. Thus, reactions involving both O_3 and hydroxyl radicals are important when studying product formation and yield. The end-result of this reaction system is the formation of stable products, e.g., carbonyls and organic acids.

Formaldehyde is one of the major products resulting from the reaction of O_3 and most unsaturated VOCs containing a terminal carbon-carbon double bond. Other stable products include aldehydes and organic acids. Reaction products can be further classified as gas-phase or aerosol species. In smog chamber experiments, Glasius et al. (2000) identified three classes of secondary aerosols from the reaction of cyclic monoterpenes with O_3 : dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids. Because carboxylic acids are highly polar and have lower vapor pressures than their corresponding aldehydes, they may play an important role in the formation of secondary organic aerosols (SOAs). O_3 -terpene reactions are a significant source of indoor sub-micron particles (Weschler and Shields, 1999; Wainman et al., 2000; Sarwar et al., 2004). Acetic and formic acids are the predominant organic acid products for most O_3 -terpene reactions. Of the higher molecular weight organic acids, dicarboxylic acids are the most abundant with yields ranging from 1-5 mol% (Koch et al., 2000). Dicarboxylic acid

yields are slightly lower when cyclohexane is used as an OH radical scavenger, indicating a small contribution by OH radicals in the formation of these acids (Koch et al., 2000).

In humidified air, water vapor can play an important role in O₃-alkene chemistry by increasing the formation of hydrogen peroxide (Sauer et al., 1999) and formic acid (Zhang et al. 1994). Humidity also influences the degree of upper airway irritation, with greater irritation reported in mice exposed to terpene-O₃ reaction mixtures at low humidity levels compared to moderate levels (Wilkins et al., 2003), suggesting that some intermediates react with water to form less irritating compounds.

Indoor reactions between O₃ and unsaturated VOCs can form hydroxyl radicals in concentrations that approach or exceed outdoor levels (Weschler and Shields, 1996). Indoor hydroxyl radical levels track non-linearly with outdoor O₃ levels, indoor alkene emission rates, and air exchange rates (Sarwar et al., 2002). These radicals can further react with other indoor pollutants and generate other radicals leading to the formation of additional stable products with one or more carbonyl, carboxylate or hydroxyl functional groups (Weschler, 2000). Reactions of O₃ with *d*-limonene, α -pinene, 2-methyl-2-butene, and α -terpinene are important sources of OH radicals indoors; reactions of OH radicals with *d*-limonene, nitrogen dioxide, ethanol, formaldehyde, carbon monoxide, and isoprene are important sinks (Weschler and Shields, 1996). Atkinson et al. (1992) suggested that OH radical formation yields depend on the location of the carbon-carbon double bond. Alkenes with internal double bonds have higher yields than those with terminal double bonds. For compounds with multiple double bonds, O₃ reactions proceed mainly at the internal double bonds.

5.5.3 *d*-Limonene

d-Limonene (4-isopropenyl-1-methyl-cyclohexene) is highly reactive with O₃ as well as nearly ubiquitous in indoor air. Limonene (referring to *d*-limonene isomer throughout the following), a monoterpene, is present in the oils of pine and citrus trees, as well as in citrus peels, dill, caraway, fennel, celery, and turpentine. It has a lemon-like odor and is used in numerous industrial and household products, e.g., foods, cleaning products, perfumes, and degreasers (Filipsson et al., 1998). Commercial dipentene solvent is a mixture of several terpenes including limonene isomers, which in recent years has been used as an environmentally-friendly alternative to chlorinated hydrocarbons and chlorofluorocarbons (Karlberg et al., 1994).

While indoor concentrations vary considerably, limonene is one of the most commonly detected VOCs in residences, offices and other buildings. For example, Batterman et al. (2004) recently found limonene in all but one of 49 single family homes tested (average concentration of 14 µg m⁻³) and in all 63 public school class rooms tested (4.4 µg m⁻³). A 1995-98 study by the U.S. EPA detected *d*-limonene in air samples in at least 81% of 56 randomly selected office buildings at levels ranging from 0.3 to 140 µg m⁻³ (Girman et al., 1999). Earlier, Wallace et al. (1991) determined the mean indoor limonene concentration in 51 Los Angeles homes to be 37 and 20 µg m⁻³ in February and July, respectively. Mean ratios of indoor to outdoor concentrations (12-h overnight) were 23 and >8 in winter and summer, respectively. Subramanian et al. (2000) suggested that indoor limonene levels could be an effective indicator of IAQ and that indoor limonene levels correlated with upper respiratory symptoms reported by office workers in the U.S. Midwest.

5.5.4 Reaction products

Atmospheric studies have generated much of the data regarding the homogeneous reactions of O_3 and limonene. A review of gas-phase terpene oxidation products identified major reaction products as limonon aldehyde (3-isopropenyl-6-oxo-heptanal), keto-limonon aldehyde (3-acetyl-6-oxo-heptanal), a decarbonylized analogue, limononic acid (3-isopropenyl-6-oxo-heptanoic acid), and keto-limononic acid (3-acetyl-6-oxo-heptanoic acid; Calogirou et al. 1999). Other reaction products include formaldehyde and 4-acetyl-1-methylcyclohexene (AMCH or called limona ketone). AMCH can itself react with O_3 or $OH^\bullet$ to eventually form low-volatility C_9 and C_{10} oxidation products or smaller carbonyls such as formaldehyde, glyoxal, and 3-oxobutanal (Grosjean et al., 1992; 1993). Other products identified following limonene- O_3 reaction include ethanol, acetone, isopropanol, octanal, nonanal, limonene oxides, decanal, acetaldehyde, acrolein, propanal, hexanal, formic acid, acetic acid, C2-C6 linear saturated aldehydes, and carvone (Grosjean et al., 1992; Clausen et al., 2001; Wolkoff et al., 2000). Calogirou et al. (1999) estimated the chemical lifetimes of limona ketone and limonon aldehyde in the troposphere ($[O_3] = 30$ ppb) to be 2.6 h and 2 d, respectively. Using reaction conditions typical of indoor air, Zhang et al. (1994) produced concentrations of $81\text{--}509\ \mu\text{g m}^{-3}$, $31\text{--}39\ \mu\text{g m}^{-3}$, and $6\text{--}58\ \mu\text{g m}^{-3}$ for formaldehyde, formic acid, and acetic acid, respectively.

Atkinson et al. (1992) obtained an OH radical formation yield for homogeneous limonene- O_3 reactions of 0.86 (uncertainty factor of ~ 1.5). Li et al. (2002) introduced O_3 and limonene into an unoccupied office and measured total hydroperoxide levels of 0.6–0.8 and 1.0–1.5 ppb at high and low air exchange rates, respectively. However, Fick et al. (2002) did not find any evidence of hydroxyl radical formation in limonene/ O_3 experiments conducted with/without an $OH^\bullet$ scavenger.

Homogeneous limonene-O₃ reactions can be a significant source of ultrafine particles. Using varying reactant concentrations and experimental conditions in limonene-O₃ chamber studies, Rohr et al. (2003) measured particle concentrations from 51-11213 µg m⁻³ and particle counts from 4.2 x 10⁵-1.6 x 10⁷ cm⁻³ with O₃ as the limiting reagent. Mean particle diameters ranged from 45-107 nm and the time to reach steady state was 21-30 min. Particle growth occurs over time due to condensation and coagulation, and rates are highest at low air exchange rates (Rohr et al., 2003; Weschler and Shields, 1999; Koch et al., 2000, Weschler and Shields, 2003). Koch et al. (2000) analyzed aerosol samples from the ozonolysis (4 x 10¹³ molecule cm⁻³ O₃) of limonene (1 x 10¹⁴ molecule cm⁻³) and estimated molar yields of 6.1% for formic acid, 6.2% for acetic acid, 1.3% for dicarboxylic acids, 0.6% for acetylcarboxylic acids, and <2% for other acids. Using reaction conditions typical of indoor air, Zhang et al. (1994) found much higher molar yields, averaging 42 ± 17% and 30 ± 15% for formic acid and acetic acid, respectively.

5.6 Methods

Tests were conducted to identify and quantify products formed in heterogeneous reactions of O₃ with VOCs (toluene or *d*-limonene) adsorbed on AC. Initially, homogeneous tests at high concentrations were performed to identify reaction products and yields. Both gas- and condensed-phase samples were analyzed. AC samples were then loaded with VOCs, exposed to O₃, and effluent air samples collected and analyzed. In addition, AC samples were chemically desorbed to determine if any reaction products remained adsorbed on the carbon. Experiments were conducted at 24 C and 50% relative humidity (RH) unless otherwise noted.

5.6.1 Ozone exposure system

An exposure system generated stable (within 5.5%) test atmospheres of O₃ in humidified air (Fig. 5-1). A controlled flow of VOC -free air was supplied by a pure air generator (Model 737-12A, AADCO Instruments, Inc., Clearwater, FL) to an O₃ generator (Model MZ-250, Clearwater Tech Inc., San Luis Obispo, CA), which was then diluted with 50% RH air, obtained using temperature-controlled bubblers filled with distilled water. The test atmosphere was simultaneously delivered to 8 ports (for concurrent breakthrough experiments), one of which was used to monitor O₃ concentrations in the influent. The flow was split into an additional 4 “accessory” ports using rotameters to supply O₃ in the homogeneous experiments and to expose AC in the heterogeneous experiments. Ozone concentrations were not monitored in these ports. All effluents were vented to an exhaust hood. The O₃ concentration was monitored using a continuous ultraviolet absorption analyzer (Model 400A, Advanced Pollution Instrumentation, Inc., San Diego, CA). Protocols, including calibration and operation, were discussed in Chapter 3. VOC effluents were exhausted directly to the hood, thus eliminating any potential for interference with O₃ measurements.

5.6.2 VOC analysis

VOCs were sampled using adsorbent tubes, and analyzed by thermal desorption, cryogenic focusing and GC-MS analysis. The stainless steel sampling tubes (Scientific Instruments Services, Ringoes, NJ) were packed at the upstream (sampling) end with 3-mm silanized glass wool, 160 mg 60/80 mesh Tenax GR (polyester-phenyl ether with 23% graphitized carbon), followed by 3-mm silanized glass wool, 70 mg Carbosieve SIII (60/80 mesh), and 3-mm silanized glass wool at the downstream end. Packed tubes were conditioned at 325° C for 6 hr with a 25-50 ml min⁻¹ reverse flow of high purity

(99.999%) helium, then sealed with stainless steel caps with Teflon[®] seals, wrapped in previously baked aluminum foil, and stored in a glass jar at 4° C.

Tubes were analyzed by a validated method (Peng and Batterman, 2000) within several days of collection. Prior to analysis, tubes were spiked with 2 μL of an internal standard solution (1 $\text{ng } \mu\text{L}^{-1}$ each of fluorobenzene and p-bromofluorobenzene). Then, up to 12 tubes were loaded in the automated thermal desorption system. After a 1 min dry purge (40 ml min^{-1} of He) to remove excess water, the tube was heated to 200° C, the sample was desorbed for 5 min at 10 ml min^{-1} , and the sample transferred to the GC inlet via a 3.5-cm long stainless steel side-port needle previously screwed onto the sorbent tube. Using a split ratio of 10:1, the sample was cryofocused at the head of the column, previously cooled to -140 °C. After 5 min desorption, the cryofocus trap was rapidly heated to 250° C, providing a narrow injection band that enhanced separation and resolution of compounds. The GC program was then started. Separation of target compounds was achieved using a 30 m x 0.25 mm ID column with 0.25 μm film thickness of 5% diphenyl-95%-dimethylsiloxane copolymer, and an oven temperature starting at -10° C and ramped in 4 stages to 250° C. Compounds were identified using target ions, qualifier ions and retention time. Quantification of 81 target compounds was based on the ratio of the target ion of the target compound to ion $M/Z = 96$ of the internal standard fluorobenzene for compounds eluting in the first 13 min, and to ion $M/Z = 174$ of p-bromofluorobenzene for compounds eluting from 13 to 38 min. Nontarget compounds were identified and their amounts estimated using either toluene or limonene equivalents.

Commercial standards for many O₃-limonene reaction products were not available. Only 4-acetyl-1-methylcyclohexene (AMCH) (Rare Chemical Library, Sigma-Aldrich, Milwaukee, WI) and (+)- limonene oxides (97% mixture of cis and trans, Acros Organics, Morris Plains, NJ) were obtained. Although the AMCH was not of guaranteed purity, it provided a means for spectral identification and an approximate calibration. AMCH co-eluted with the limonene oxides making quantification difficult, though spectra differed. Calibration solutions were prepared using equal amounts of AMCH and limonene oxides in carbon disulfide (CS₂) over a 6-point concentration range with injection quantities of 9.9 to 58.4 ng. Replicate samples were averaged. AMCH was calibrated using M/Z = 138, which had very low abundance in the limonene oxides. Good linearity ($R^2 = 0.96$) was achieved over the calibration range. The ratio of M/Z = 138 area to the total area of AMCH was 0.116, which was stable over the entire concentration range. This ratio was then used to estimate the total AMCH area in co-eluted peaks by subtracting the total AMCH area from the total peak area. Thus, for this compound, calibrations depended on the areas of the limonene oxide peaks, rather than a specific target ion. Although indirect, this method obtained good linearity ($R^2 = 0.97$) over the calibration range.

5.6.3 Homogenous experiments

Tests performed to analyze products formed during homogeneous reactions of VOCs (limonene or toluene) with O₃ were performed in 10 L Tedlar bags. Stabilities of each compound were individually tested prior to beginning ozonation experiments and impurities identified. Gas-phase samples were collected onto sorbent tubes and analyzed by TD/GC/MS. Condensed-phase samples were collected onto filters and analyzed using GC/MS. Particles were also measured using an optical particle counter.

To test the stability of limonene in the Tedlar bag and to identify impurities, 4 μL of limonene (97% purity, Aldrich Chemical Co., Milwaukee, WI) was injected into a 10 L Tedlar bag containing 9 L of nitrogen gas. The bag was warmed slightly to facilitate volatilization and 4 mL of the contents were withdrawn with a gas-tight syringe, loaded onto a sorbent tube, and analyzed by TD/GC/MS. Four samples were collected over a 40 min period.

The stability of O_3 in Tedlar bags was determined by measuring the O_3 concentration (initial concentration = 2.6 ppm) in the bag before and after a 10 min time period. Replicate tests were performed.

Limonene- O_3 mixtures were prepared by injecting 2 μL of limonene into a Tedlar bag, which was then filled with humidified, ozonated air at a flow rate of $500 \text{ cm}^3 \text{ min}^{-1}$, a process taking 20 min. Two bags were prepared with O_3 concentrations of 10.5 and 13.6 ppm. Limonene and O_3 quantities were selected to provide excess limonene, eliminating the need for an O_3 scrubber. After filling each bag, a 5 mL sample was collected with a gas-tight syringe, loaded onto a sorbent tube, and immediately analyzed by TD/GC/MS. Bags were cleaned between experiments by rinsing several times with air and then with high concentrations of ozonated air. In addition, three bags were prepared as controls (without O_3) by injecting 2 μL of limonene into 10 L of humidified, purified air.

For comparison, similar experiments were conducted using 2 μL of toluene (ACS grade, Malinckrodt, Inc., Paris, KY) and 9.19 ppm O_3 .

Particle counts and particle size distribution. Reaction mixtures were prepared by injecting 10 μL of neat VOC (toluene or limonene) into 10 L Tedlar bags filled with humidified, ozonated air (920 or 621 ppb). These concentrations provided excess VOC

(consuming most O₃) to minimize detrimental effects to the particle counter. Mixtures were allowed to react for 35 and 15 min for toluene and limonene, respectively. Blank bags filled with humidified, purified air were also prepared. At least two replicate bags were prepared for each sample type. Particle number concentrations were measured with an optical particle counter (Model GT-521, Met One Instruments, Inc., Grants Pass, OR) in several size fractions, including the instrument's smallest size range (0.3 to 0.4 μm). Data from the counter was logged and downloaded to a computer using GT-Comm software (Version 1.0.1, Met One Instruments, Inc., Grants Pass, OR). In preliminary experiments, an O₃ scrubber (discussed below) was used to protect the particle counter, but because the scrubber removed ~35% of the particles, its use was discontinued.

The particle size distribution was measured using either humidified or dry ozonated air (916 ppb) to examine the effect of humidity. Limonene-O₃ mixtures were prepared in Tedlar bags as described above except only 2 μL of limonene was used to minimize residual limonene in the bag (excess limonene was still maintained to prevent damage to the OPC). After allowing the mixtures to react for 15 min, 0.3-0.4, 0.4-0.5, 0.6-0.7, and 0.7-0.8 μm size fractions were measured. Fresh mixtures were prepared for each test (one each, humidified or dry).

Particle identification. Aerosol-phase limonene/O₃ reaction carboxylic acid products were qualitatively identified using a methyl ester derivatization method. Reaction mixtures were prepared in 10 L Tedlar bags as in the gas-phase product analyses, except an O₃ concentration of 9.6 ± 0.5 ppm was used. Particles were captured on 12 mm round filter sections (Pallflex TF40H EMFAB; Teflon bonded onto borosilicate glass microfibers, Pallflex Products Corp., Putman, CT), placed inside 13

mm Celcon[®] acetal filter holders (Gelman Sciences, Ann Arbor, MI) between Teflon washers. Filters were doubled to minimize breakthrough. For comparison, blank filters were similarly prepared. Immediately following reaction, the filter assembly was connected to the port of the Tedlar bag and its contents collected using a gentle vacuum. Five bags of reaction mixtures were prepared (50 L total) and collected on a single filter assembly with the objective of collecting ≥ 100 μg of acids. Replicate experiments were conducted. Filters (including blanks) were then placed in glass vials containing 4 ml of methylene chloride (HPLC/GC/MS grade, Fisher Scientific, Fair Lawn, NJ), capped, and stored overnight, sonicated, filters removed, and solvent evaporated under a stream of N_2 .

Four mL of boron trifluoride/methanol (14% w/v, Alltech Assoc. Inc., Deerfield, IL) was added to each of the residue-containing vials and gently warmed (~ 50 C) for about $\frac{1}{2}$ h to which 4 mL each of water and pentane were then added. The pentane layer was removed and 1 mL pipetted into a 2 mL glass vial to which the internal standard was added. Samples were then directly injected into the GC and analyzed with the GC/MS method discussed earlier except that the solvent delay was decreased to 3.5 min to accommodate the early elution time of methyl acetate. Because methyl formate (derivative of formic acid) co-eluted with pentane, it was analyzed and calibrated separately using ions $M/Z = 60$ (target) and $M/Z = 44$ (qualifier) in the selected ion mode (SIM) with a solvent delay of 1 min.

5.6.4 Heterogeneous experiments

Heterogeneous reactions of AC, O_3 , and *d*-limonene were studied using samples containing either virgin AC or limonene-spiked AC exposed to a flow of either pure air or ozonated air. Air samples were collected on sorbent tubes during the first few min of ozonation and then analyzed by GC/MS. Following ozonation, the limonene-spiked AC

samples were extracted with CS₂ and analyzed by GC/MS. To determine background levels, unexposed virgin and limonene-spiked AC samples were extracted using CS₂ and analyzed by GC/MS. Additionally, virgin AC and limonene-spiked AC samples were subjected to long-term tests in which samples were either exposed to a flow of humidified, purified air or humidified, ozonated air for 48 h. Effluent O₃ concentrations were measured to determine breakthrough. VOCs were extracted from AC samples using CS₂ and analyzed using GC/MS, and results were compared to those of the short-term tests.

AC sample assemblies. Sample tubes containing either virgin AC or limonene-spiked AC were prepared. Unless otherwise noted, each sample contained 20 mg of AC, corresponding to a bed depth of 2.4 mm. This depth allowed for rapid breakthrough yet was thick enough to maintain a uniform surface. The AC grain size was selected to minimize wall effects that could lead to short-circuiting. AC was acquired as mesh size 30-60 (Standard Coconut Shell Carbon, G55-C, PICA USA, Columbus, OH). Unless noted otherwise, 30/60 mesh AC was used. In several initial experiments, the AC was ground using a mortar and pestle, and sieved between 50 and 60 mesh screens to obtain grain size of 250-300 µm (as used in experiments discussed in the previous chapter).

AC samples were packed between two fine stainless steel screens, which in turn were held in place by fine stainless steel springs retained in Teflon[®] tubes (8.5-cm long, 4 mm ID) equipped with Swagelok[®] fittings. A small plug of unsilanized glass wool was placed in each end to trap any particles that might escape through the screens. Tubes were carefully prepared to obtain a cylindrical bed with flat and near parallel faces as follows: A clean tube was mounted vertically on a ring stand and a slight vacuum was

applied to the bottom of the tube. A ~4 mm long spring was placed in one end of the tube, followed by a stainless screen disk that matched the tube's inner dia. A stainless steel rod was used to help position the components. The previously weighed AC was transferred to the tube using a disposable glass pipette as a funnel. The second screen was placed on top of the AC, followed by another spring section. The tube was then removed from the vacuum and small plugs of glass wool were placed in each end to prevent leakage. When not in use, the AC and packed tubes were stored under vacuum in a dessicator containing Drierite[®] material to minimize aging effects.

AC sample tubes were loaded with 2 μL of *d*-limonene using a closed-loop system that recirculated the VOC to ensure maximum adsorption. The AC was highly loaded, based on the experimentally determined sorption capacity ($10.8 \pm 1.3\%$) discussed in the previous chapter. Using a microliter syringe, neat limonene was injected into a septum, which was gently heated to facilitate volatilization. The VOC then flowed into a 500 ml Teflon bottle to facilitate mixing, and then to a photo ionization detection (PID) transmitter (Model PDM-10A, RAE Systems Inc., Sunnyvale, CA) used to monitor the system's VOC concentration. Using the PID's internal pump, the VOC circulated through the system until voltage from the PID equilibrated, indicating that the AC was saturated. The AC tube was then removed and capped.

The system was tested to verify that limonene did not interfere with the O_3 monitoring. Problems with positive interference from certain types of O_3 analyzers have been reported (Clausen, 2001). Two 20 mg AC samples spiked with 2 μL of limonene were placed into the O_3 -exposure system and exposed to a flow ($160 \text{ cm}^3 \text{ min}^{-1}$) of humidified, purified air for ~24 hrs. No positive interferences were noted.

O₃ scrubber. An O₃ scrubber was used in some experiments to prevent degradation of the sorbents and further reactions of VOCs adsorbed in the sampling tubes. Scrubbers were prepared by filling a 8.5 cm length of a 4 mm dia Teflon[®] tube with crystalline potassium iodide (KI, ACS grade, Eastman Kodak Co., Rochester, NY). Tube ends were plugged with silanized glass wool to retain the KI. The scrubber was placed immediately upstream of the sampling tubes. Scrubbers were tested prior to use by placing them in the O₃ exposure system and exposing them to humidified, ozonated air (1.1 ppm) for 24 h. The effluent O₃ concentration was monitored to ensure that breakthrough did not occur.

Analyte stability. The stability of AMCH and limonene oxides on Tenax was tested by spiking 8 sorbent tubes with 52 ng of each compound. Spiked tubes were immediately placed in a freezer and analyzed by TD/GC/MS at 0 hr, 4 hr, 1 day, and 3 days. For comparison, replicate samples of the same solution were directly injected into the GC and analyzed. Recoveries were calculated for each compound.

AMCH and limonene oxide stability/recovery. Average recoveries of AMCH and limonene oxide from spiked sorbent tubes were $57 \pm 18\%$ and $29 \pm 12\%$, respectively (n=8; Table 5-1). These low-to-moderate recoveries indicate that Tenax is not an ideal sorbent for these compounds; polar compounds are generally not well-retained on nonpolar sorbents such as Tenax (Stanetzek et al., 1996). There did not appear to be a trend indicating diminished storage stability over the 3-day test period. As a precaution, most samples reported below were analyzed on the day of collection. Also, AMCH and limonene oxide concentrations measured using sorbent tubes were adjusted for recovery to make them comparable with concentrations from directly-injected samples.

Short-term tests. Virgin and limonene-spiked AC samples were prepared and extracted with CS₂ to determine background levels of VOCs. AC samples were placed in 2 mL glass vials to which 1 mL of carbon disulfide (Spectranalyzed[®] grade, Fisher-Scientific, Fair Lawn, NJ) was added. The capped vials were shaken and allowed to stand for several hours at room temperature. After adding an internal standard to each vial, 2 µL aliquots were withdrawn and analyzed by GC/MS. Benzene concentrations were adjusted to reflect peaks present in the CS₂ blanks. Replicate analyses were performed for each sample. Limonene-spiked samples were prepared and analyzed in a similar manner, except 2 µL of limonene was added to the AC samples (two samples, 10.3 mg each). The vial was capped, shaken well, and uncapped to allow any unadsorbed limonene to volatilize prior to adding the CS₂. Two 50/60 mesh virgin AC samples (9.9 mg each) initially tested were found to have considerable VOC background. Tests were repeated using two 30/60 mesh AC samples (19.5 and 20.6 mg) with the same AC except it had not been ground and had been stored in a different container that was less exposed to air contaminants.

Virgin AC and limonene-spiked AC samples were exposed to flows (160 cm³ min⁻¹) of either humidified, pure air (controls) or humidified, ozonated air (5.8 ppm) and effluent air samples collected. AC samples (two of each type) were prepared using tube packing and limonene-spiking methods described above. A sorbent tube was connected downstream of the sample tube. KI scrubbers were not used as previous tests indicated that O₃ breakthrough would not be significant during the first several minutes of ozonation with the AC mass and O₃ concentration used. AC sample assemblies were

placed onto the 4 accessory ports and exposed to either pure air or ozonated air for the desired test period. Breakthrough tests were conducted concurrently in the other 8 ports.

The first effluent air sample, collected from a virgin AC sample during the initial 30 min of ozonation, revealed the presence of possible O₃-Tenax artifacts, e.g., benzaldehyde, straight-chain aldehydes, cresols, and acetophenone. Thus, a second 30-min air sample was collected from the same AC sample (beginning at t = 31 min) with the expectation that if these compounds were indeed Tenax artifacts, concentrations would increase on the second tube since more O₃ breakthrough would have occurred. Because of the possibility of O₃ breakthrough leading to analyte loss on the sorbent tubes, subsequent tests using limonene-spiked AC samples were limited to 10-min sampling periods starting when ozonation started (t = 0). To keep experimental conditions the same, controls (purified air, no O₃) utilized the same sampling periods. Samples were analyzed with GC/MS on the same day. Limonene-spiked AC samples (both purified air and ozonated) were extracted with CS₂ immediately following the test period and analyzed with GC/MS.

Long-term tests. Virgin- and limonene-spiked AC samples (20 mg each) were exposed to 0, 1.08, or 8.95 ppm O₃ for 48 hrs. Duplicate samples of each type were exposed at each concentration level using ports that allowed for O₃ monitoring. O₃ penetration fractions were calculated at 48 hrs. Immediately following the tests, AC samples were extracted with CS₂ and analyzed by GC/MS.

A 97-hr test using 50/60 mesh AC was also performed in conjunction with an efficiency experiment discussed in the previous chapter. The test was similar as the 48 hr

test except 15 mg AC samples (two virgin and two spiked with 2 μL of limonene) were exposed to 773 ppb of O_3 for 97 hr. Replicate analyses were performed on each sample.

To determine the amount of VOCs desorbing from the AC samples over time, VOC concentrations were measured in the effluent air stream. Two 20 mg AC samples (30/60 mesh) loaded with either 1 or 2 μL of limonene (representing moderate and high VOC loads) were exposed to 5.8 ppm of O_3 for 24 hr, and breakthrough curves constructed. Downstream of the AC, 10-min VOC samples were collected on sorbent tubes at exposure times of 0, 1, and 23 hr for analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). A KI O_3 scrubber was used in these tests to minimize any O_3 /Tenax artifacts.

Particle analyses. Tests were conducted to quantify particles in the effluent of limonene-spiked AC exposed to O_3 . A 20 mg AC sample was spiked with 2 μL of limonene and exposed to a flow of humidified, ozonated air ($160 \text{ cm}^3 \text{ min}^{-1}$). Effluent air samples were collected in 10 L Tedlar bags for ~ 1 h. Tedlar bags were used rather than directly connecting the effluent to the OPC to minimize damage to the counter. The first sample for each replicate was collected immediately upon O_3 exposure; 5 additional samples were collected throughout a 1 d exposure period. Two size fractions were counted with the OPC: $0.3\text{-}0.4 \mu\text{m}$ and $>0.4 \mu\text{m}$, based on results of the homogeneous experiments. The initial O_3 concentration was 3.6 ppm. However, since no particles were found in the early stages of the experiment, the O_3 concentration was increased to 9.7 ppm.

5.7 Results and Discussion

5.7.1 Homogenous experiments

Limonene and O₃ stability/recovery. Tests using individual compounds (limonene and O₃) showed good stability in Tedlar bags. Limonene concentrations remained stable over 40 min, e.g., final concentrations (2 sample average) decreased by only 1.6% from initial values (Table 5-2). O₃ losses were higher, $10.5 \pm 3.3\%$ after 10 min, but still acceptable for the 20 min experiments. To minimize the effects of any losses, subsequent experiments first added limonene to the bag, after which the bag was filled with O₃ at $500 \text{ cm}^3 \text{ min}^{-1}$. This process, which took 20 min., allowed a continuous supply of fresh O₃ to come in contact with the limonene.

Impurities. Several impurities were detected in the limonene samples. Toluene was found in two samples, but this was likely a lab or bag contaminant rather than a limonene impurity. Other impurities represented $1.7 \pm 0.4\%$ of the total mass, of which p-isopropyltoluene was the most abundant, constituting $42 \pm 1\%$ of the total impurity mass. Four other compounds, most likely other terpenes based on Clausen et al. (2001) who detected α -pinene, β -myrcene, Δ -3-carene, α -terpinolene, and two unidentified terpenes in 98% purity limonene, were detected consistently. These compounds could not be positively identified using the MS library. Quantities were estimated using limonene equivalents. No limonene auto-oxidation products, e.g., limonene oxides, were detected.

Reaction products. Homogeneous limonene-O₃ experiments performed in Tedlar bags used initial O₃ concentrations of 0, 10.5 or 13.6 ppm, limonene concentrations of 25 ppm (142 mg m^{-3}), and a 20 min exposure period. O₃ exposure caused several significant

changes (Table 5-3): 8 to 18% of limonene was lost; AMCH was formed and detected at a concentration of 366-426 ppb; and a mixture of mixture of cis and trans limonene oxides were found at a concentration of 321-358 ppb. These tests showed similar impurities as found in the limonene stability tests.

Molar yields, estimated as the percentage of the reacted O₃ molar mass, averaged $3.6 \pm 0.8\%$ for AMCH and $3.1 \pm 0.6\%$ for limonene oxides (Table 5-4). The 10.5 ppm test yielded slightly higher molar yields than the 13.6 ppm test, possibly a result of experimental error or a concentration effect. The AMCH molar yield agrees with the 2% estimate by Grosjean et al. (1993) and the 3-4% estimate by Clausen et al. (2001), respectively. The total limonene oxides yield is also close to the 1-3% (cis) and 1-2% (trans) found by Clausen et al. (2001). Yields here were calculated assuming no O₃ losses due to wall decomposition and 1:1 stoichiometry between O₃ and limonene, which may not be the case. Zhang et al. (1994) found that formaldehyde yields ($125 \pm 28\%$) depended on initial reactant concentrations and >1:1 stoichiometry, indicating additional reactions involving Criegee biradicals. Some product formation due to secondary reactions with hydroxyl or other radicals is likely.

Assuming 1:1 stoichiometry between O₃ and limonene, identified gas-phase products accounted for only ~6% of the reacted O₃. This may be explained by several reasons: (1) Several compounds are not detected by the techniques used during this experiment; (2) Low sampling efficiency and recovery by the Tenax GR and Carbosieve III adsorbents (though corrections were made for partial recovery); (3) Some product may remain in particulate phase and not be effectively captured using adsorbents

designed for gases and vapors, and; (4) Reaction products may have short lifetimes and undergo secondary reactions before samples were collected and/or analyzed.

The O₃-toluene experiments, which used O₃ at 9.2 ppm and toluene at 40.6 ppm, did not yield any of the expected or target compounds (Table 5-5). With ozonation, toluene concentrations decreased by ~20%, but this difference was not statistically significant ($p = 0.20$). Several contaminants were detected at low levels, i.e., limonene in the non-ozonated samples, probably from the syringe used; and benzene in all samples, a known toluene contaminant. However, no O₃-toluene reaction products were identified. These results are not remarkable considering that the O₃-toluene reaction is much slower than the O₃-limonene reaction (rate constants are 3.69×10^{-12} and 5.14×10^{-6} ppb⁻¹ hr⁻¹, respectively; Weschler, 2000 and references therein).

Particle experiments. High numbers of small particles were found as O₃-limonene products (Table 5-6), most of which were in the smallest (0.3-0.4 μm dia) size range measurable by the optical particle counter. The counts measured in this range represent the instrument's maximum reading, thus, actual counts are higher. This experiment provides strong but qualitative evidence of particle formation by the O₃-limonene mixture. In contrast, few particles were found in the O₃-toluene mixture or in the blank controls.

Other studies also have shown that O₃-limonene reactions produce significant quantities of small particles (Rohr et al., 2003; Weschler and Shields, 1999; Koch et al., 2000; Clausen et al., 2001; Zhang et al., 1994). Most particles will be considerably smaller than the instrument's resolution of 0.3 μm, e.g., as mentioned, Rohr et al. (2003) found mean particle diameters of 45 to 107 nm for O₃-limonene products.

To approximate the particulate mass from the measured number concentrations, the following assumptions were made: spherical particles = 0.3 μm dia; particle density = 1.5 g cm^{-3} ; and particle number concentration = 650,000 Counts L^{-1} . These assumptions yield a mass concentration of 0.014 $\mu\text{g L}^{-1}$, equivalent to 0.14 μg of particles in the 10 L bag. For particles at the upper size range, 0.5 μm dia, the concentration is 0.064 $\mu\text{g L}^{-1}$ and 0.64 μg of particles were formed. For comparison, the initial O_3 mass was 12.2 μg (621 ppb), and the initial limonene mass was 8410 μg . A mass balance cannot be estimated since the true particle size distribution is unknown, most particles were <0.3 μm dia and could not be detected, and because the instrument was overrange. Possibly compensating to a degree, however, larger particles account for a disproportionate mass fraction. These calculations likely significantly underestimate the mass concentration. Particle yields in the literature vary widely depending on reaction conditions and the quantification method. For example, Rohr et al (2003) calculated mass-based yields for limonene- O_3 systems ranging from 27.8% (at 184 $\mu\text{g m}^{-3}$ O_3) to 183% (at $\mu\text{g m}^{-3}$ O_3), corresponding to calculated (not measured gravimetrically) mass concentrations of 0.041 to 11 $\mu\text{g L}^{-1}$. It should be noted that several studies have listed total molar yields but interpretation can be tricky because different molecular weights were used or only identified products are included. For example, Rohr et al (2003) gave yields of 7.4 mol% (94 ppb O_3) to 48.9 mol % (2550 ppb O_3) using an average molecular weight of 180, while Koch et al. (2000) estimated 16 mol% on the basis of total measured carboxylic acids. Because particle yields from limonene/ O_3 systems track nonlinearly with O_3 concentration (Rohr et al., 2003), particle yields would be expected to be even smaller using O_3 concentrations typically found in indoor air (< 100 ppb).

Particulate size distributions forming in dry and humidified (RH = 50%) air after 15 min between O₃ (916 ppb) and an excess of limonene (151 ppm) are compared in Fig. 5-2. In both cases, most particles were <0.6 µm dia. The humidified experiments formed more (by 37%) and smaller particles, e.g., 89% ≤0.4 µm, compared with only 32% ≤0.4 µm in dry experiments. These experiments also formed smaller numbers of 0.3 – 0.4 µm dia particles than earlier tests using higher (151 ppm) limonene concentrations (Table 5-6). While coagulation might explain the shift to larger particles, the ability to differentiate differences in particulate size distributions is hampered by several factors. The optical measurements sensed only the extreme right tail of the particle size distribution. Settling and deposition rates in the Tedlar bag will differ by particle size. The sensing instrument may differentially detect particles formed in the presence and absence of water. Finally, experimental variability is present.

Particles consisted mainly of formic acid with a molar yield (based on available O₃) of 37 ± 2%, with small amounts of propanoic acid with a molar yield of ~2% (Table 5-7). No unidentified methyl esters (derivatives of other carboxylic acids) were found. Since some O₃ was lost over the course of the experiments, molar yields may be slightly underestimated. However, estimated formic acid yields are comparable to those found elsewhere, i.e., 6 to 42% (Koch et al., 2000; Clausen et al., 2001; Zhang et al., 1994). Acetic acid was not detected, though this acid previously has been found along with formic acid with molar yields of 6 to 30% (Koch et al., 2000; Clausen et al., 2001; Zhang et al., 1994). Koch et al. (2000) also identified small quantities of dicarboxylic acids (1.3 mol %), acetylcarboxylic acids (0.6 mol %), and other acids (< 2 mol %) in aerosol samples from the O₃-limonene reactions, but none were found here. Although similar

analytical methods were used (BF₃-methanol, GCMS, though a different column), it is always possible that these compounds may not have been separated, detected or identified.

5.7.2 Impurities on AC

Virgin AC samples, used as controls, showed 8 VOCs after extraction with CS₂, the most abundant of which were cyclohexane and n-hexane in the 50/60 and 30/60 mesh samples, respectively (Table 5-8). Cyclohexane is of interest due to its ability to act as a hydroxyl radical scavenger leading to the formation of cyclohexanone and cyclohexanol (Atkinson et al., 1992; Grosjean et al., 1993). With the exception of the xylenes, 30/60 mesh AC samples were cleaner than 50/60 mesh, which received more handling. Total VOC concentrations were 8.6 ± 1.1 and 3.7 ± 0.3 µg per mg of AC for the 50/60 and 30/60 mesh AC samples, respectively. Table 5-8 also shows the VOC composition of limonene-spiked AC samples extracted with CS₂. Limonene averaged 8.4 ± 0.9 wt %, slightly lower than that experimentally-determined (10.8 ± 1.3 wt %) discussed in the previous chapter. Small amounts of p-isopropyltoluene were found, likely a limonene impurity as determined in the homogeneous experiments. In addition, the same 8 compounds found in the virgin AC samples were detected.

5.7.3 Heterogeneous experiments - short exposure times

AC + O₃ effluents. Effluent concentrations of AC samples exposed to humidified air for 30 min showed only hexane and styrene (Table 5-9, leftmost columns), two VOCs previously detected as AC impurities in the virgin AC (Table 5-8). The effluent of the ozonated AC samples contained several additional compounds, including benzene and toluene (previously detected as AC impurities), limonene (likely a system contaminant), as well as chloroform, tetrahydrofuran, methyl isobutyl ketone, phenol, 1,2,4-

trimethylbenzene, cresols, decane, undecane, acetophenone, benzaldehyde, and straight-chain aldehydes. These compounds may have been impurities in the AC that were not detected due to the lower sensitivity of the CS₂-extraction method compared to thermal desorption. Possibly, O₃ may have displaced these compounds from the AC, if present, assuming competitive sorption processes. Tests of 2 dry and 2 humidified pure air samples (5 L each) did not show these compounds, thus the test gas generation system was ruled out as a contaminant source. O₃ may have reacted with the AC, impurities in the AC, or other constituents in the exposure system and test gas (like residual chlorine) to form these compounds, though this seems unlikely. It is also possible that several of these compounds are O₃-Tenax artifacts (Helmig, 1997). Klenø et al. (2002) identified benzaldehyde, phenol, acetophenone, nonanal and decanal as artifacts from O₃ degradation of Tenax TA. Benzaldehyde was also found by (Zhang et al., 1994). Although styrene was present at low concentrations in several of the virgin AC samples used, it is not likely to be a significant source of benzaldehyde. Additional samples were collected and analyzed after further ozonation of the AC samples, to investigate whether VOC levels increased, consistent with the artifact hypothesis. Surprisingly, fewer VOCs were detected in samples in the second 30 min (starting at t = 31 min; Table 5-9).

The samples described in Table 5-9 were collected without an O₃ scrubber (e.g., KI) since previous experiments at higher O₃ concentrations indicated that little if any O₃ breakthrough would occur during the first 30 min of ozonation. O₃ concentrations in the effluent for this test's conditions (O₃ at 5.81 ppm) were measured for two tubes (Table 5-10). (These runs were performed in conjunction with breakthrough experiments conducted concurrently, as discussed in Chapter 4.) After 30 min, O₃ concentration

reached 16 ppb in 1 tube; the second tube required ~60 min to reach this level. These tests indicate that some, though relatively low, O₃ exposure on the Tenax is expected, thus O₃-Tenax artifacts are a possibility.

Clausen and Wolkoff (1997) have suggested that artifact products could be used to calibrate the O₃-Tenax reaction. However, Pellizzari et al. (1984) found that Tenax GC aging (between the first and fifth use) decreased artifact yield (benzaldehyde, acetophenone, and phenol) by an order of magnitude. The unexpected relationship between O₃ exposure time and artifact production might be explained by the age variation of sorbent tubes used in this study.

AC + O₃ + limonene effluents. While only low O₃ concentrations were attained during the sampling period, as a precaution against O₃-Tenax artifact formation, subsequent samples of limonene-spiked AC effluent were collected for only the initial 10 min of ozonation. Effluent samples from these tests showed a large number of compounds (Table 5-9, rightmost columns).

Without O₃, the limonene-spiked AC effluent contained the spiked compound, limonene and its impurities (p-isopropyltoluene); VOCs previously detected in extracted virgin AC samples (tetrachloroethylene, xylenes, cyclohexane, and methylcyclohexane which was detected in subsequent tests discussed later); VOCs not detected in the exposed virgin samples (chloroform and tetrahydrofuran), and three unidentified compounds including two that were detected in homogeneous tests (Table 5-2). These compounds may have been AC impurities not detected in previous tests due to the lower sensitivity of the CS₂-extraction method compared to thermal desorption. Further, limonene may have displaced these compounds from the AC, if present and assuming

competitive sorption processes. The unidentified compounds are likely limonene impurities, as discussed previously. The presence of these VOCs again suggests that impurities in the AC that may be liberated by saturating the AC with limonene and detected with considerable sensitivity. Importantly, these VOCs represent only trace level contaminants in the AC, e.g. the TVOC concentration of $542 \mu\text{g m}^{-3}$ represents only $2.7 \mu\text{g}$ of mass (5 L air sample), and only 0.03% of the AC mass (10.3 mg AC sample).

Effluent from the O_3 -exposed limonene-loaded AC samples showed several new VOCs (Table 5-9) including: AMCH and limonene oxides, representing expected limonene- O_3 reaction products; octane, which was previously found in extracted virgin AC samples; α -pinene, likely a limonene impurity; and 1,1,1-trichlorobenzene and ethylbenzene. As seen with the virgin AC, ozonation increased concentrations of many VOCs in the effluent. A number of straight-chain aldehydes were detected in one replicate. Eight unidentified peaks were detected, including 4 not found previously. These samples showed no acetophenone, cresols or phenol, and much less benzaldehyde compared to ozonated AC samples collected at 0 hr. Although duplicate precision was fairly good for many compounds, the second replicate had much higher limonene concentrations (640 vs $361 \mu\text{g m}^{-3}$), but lower (or undetected) levels of straight-chain aldehydes, AMCH and limonene oxides. Possibly limonene on the first replicate had undergone greater reactions with O_3 , but the small sample size precludes firm conclusions. Some differences may result from variation in sample loadings, however, the pattern is irregular, e.g., some VOC concentrations are higher in the first sample and others are higher in the second sample. As discussed earlier, the formation of Tenax degradation products is another possible source for several of the compounds

(benzaldehyde, straight-chain aldehydes) detected in the O₃-limonene-AC effluent. The appearance of straight-chain aldehydes is more difficult to explain. As mentioned, they are possibly O₃-Tenax artifacts. However, decanal and nonanal were also found in subsequent experiments utilizing the KI scrubber. Nonanal and decanal (and other carbonyl compounds) could also be artifacts formed from the reaction of O₃ with human skin lipids containing squalene as Fruekilde et al. (1998) suggested, although care was taken not to touch AC or O₃ contact surfaces. Clausen et al. (2001) also detected octanal, nonanal, and decanal in homogeneous limonene/O₃ experiments and could not explain their formation. Zhang et al. (1994) suggested that long-chain aldehydes could be formed as the result of ozonation and opening of the unsaturated bond in limonene's cyclohexene ring, but were unable to measure these products with their analytical method. Another possibility is that these aldehydes were formed from the reaction of O₃ with AC rather than limonene.

In summary, limonene-loaded AC and O₃+limonene-loaded AC samples yielded higher VOC concentrations in effluent air, compared to unexposed AC. A number of mechanisms have been suggested, including VOC formation, competitive sorption, AC impurities, limonene impurities, and Tenax-O₃ measurement artifacts. Results indicate that O₃ exposure increases releases of a number of VOCs from AC, thus, AC filters exposed to high O₃ concentrations could potentially contribute to poor IAQ. These results are based on short-term laboratory tests that used high VOC loadings (8.4 wt %) and high (5.8 ppm) O₃ concentrations. The relevance of these results to concentrations found indoors has yet to be determined.

VOCs extracted from AC samples. The same limonene-spiked AC samples used in the effluent air tests discussed above were immediately extracted with CS₂ following collection of the 10-min effluent air samples. Ozonation substantially decreased (by 55 ± 13%) limonene weight fractions (Table 5-11). Weight fractions of limonene remaining among replicates varied over a large range (27 - 44 µg mg⁻¹, n=2). AMCH and limonene oxides were only found in the replicate with the lower limonene content, suggesting more reaction had occurred compared to the other replicate. As reported, this replicate also yielded 14% more AMCH and 49% more limonene oxides in its effluent compared to the other replicate. Weight fractions of other VOCs were not statistically different from those found without the O₃ exposure.

Mass balance. After ozonation, 42 ± 14% of the limonene remained on the AC. Of the depleted limonene, measured reaction products (on both the AC and in effluent air) account for only ~4.4 mol %, and (unreacted) limonene in the effluent air accounted for only 0.08% of the depleted limonene. Thus, the fate of 95% of the depleted limonene was not measured. Some limonene may have been lost through physical desorption, both before and after the test period. More limonene is likely to have reacted to form products not detectable with the analytical methods used, e.g., acid particles, formaldehyde, and CO₂. For the identified reaction products, nearly all of the mass remained on the AC surface, e.g., gas-phase products in effluent air for total AMCH and limonene oxides represented only 1.2 and 1.5% of the total AMCH and limonene oxides, respectively. The fate of products that are more volatile or not readily adsorbed on AC, e.g., formaldehyde, may differ.

Because O_3 was the limiting reagent during this experiment ($0.38 \mu\text{mol } O_3$ versus $12.35 \mu\text{mol}$ of limonene), product yields were estimated relative to O_3 . Using the total (sorbed and gas phase) AMCH and limonene oxides formed, the yields are 4.5 and 4.9 mol % , respectively. These are not yields in the conventional sense since much of the O_3 was likely lost due to chemisorption on the AC, and this quantity cannot be separated from the O_3 that reacted with limonene. Moreover, limonene-loaded AC demonstrated faster breakthrough of O_3 than unloaded (virgin) AC, and chemisorption and reaction kinetics likely affect product formation in even short-term experiments. While the complex fate of O_3 on VOC-loaded AC makes a detailed mass/molar balance difficult to describe, it is clear that a substantial fraction of the limonene remained unreacted on the AC, and that only a small percentage of limonene loss was attributable to reaction with O_3 (including secondary reactions with radicals). This applies even in long-term tests where is a large stoichiometric excess of O_3 (see below). Of the identified oxidation products, ~99% of the total mass remained adsorbed on the AC rather than desorbed into the effluent air stream. However, it remains possible that low molecular weight or other compounds that are not strongly retained by AC may be emitted from the AC bed. Finally, unlike the homogeneous tests, effluent air from the heterogeneous reaction of limonene and O_3 on AC do not appear to be a significant source of submicron particles.

5.7.4 Heterogeneous experiments – long exposure times

VOC weight fractions in virgin AC exposed to 0, 1.08, and 8.95 ppm of O_3 for a 48 hr exposure period are presented in Table 5-12. O_3 had broken through the AC bed by the end of the exposure period with penetration fractions (C_t/C_0) of 5.2 ± 2.6 and $50.0 \pm 0.3\%$ for the 1.08 and 8.95 ppm tests, respectively. While trends are difficult to establish given the small sample size, weight fractions of hexane, benzene and toluene remaining

in the AC did not change with increasing O₃ levels; weight fractions of tetrachloroethylene, xylenes, styrene and octane increased. Note that these experiments should not be compared to short duration experiments, since they were conducted on different days and different background levels in the starting media might affect weight fractions.

Table 5-12 also shows the VOC weight fractions for limonene-spiked AC exposed to pure air or ozonated air. These samples had slightly greater O₃ penetration than the virgin AC samples; penetration fractions were 9.1 ± 0.0 and $54.4 \pm 0.1\%$ for the 1.08 and 8.95 ppm test, respectively. Again, it is difficult to establish trends, except in the case of limonene where concentrations are clearly decreased with greater O₃ exposure, as expected given its reactivity with O₃. However, 58% of the initial limonene remained after 48 hr of exposure to 8.95 ppm of O₃. These experiments used an excess of O₃ (equal to 20.3 and 168.3 μmol in the 1.08 and 8.95 ppm tests, respectively, compared to 12.4 μmol of limonene). Tests with non-ozonated air indicated that ~ 2 μmol of limonene was desorbed during the 48 hr test. With ozonated air, 2.5 and 5.2 μmol of limonene were depleted for O₃ levels of 1.08 and 8.95 ppm tests, respectively. Assuming that limonene desorption losses do not differ for purified and ozonated air (though some differences are likely), 0.7 and 4.5 μmol of the original limonene (equivalent to 4 and 26%) were depleted by reaction in the 1.08 and 8.95 ppm tests, respectively. Thus, most O₃ in these experiments was either chemisorbed on the AC or penetrated the AC, and only a small fraction reacted with limonene. While most of the limonene was retained in the AC, limonene reaction products AMCH and limonene oxides were detected in the limonene-spiked AC samples, though O₃ concentrations appeared to make little

difference in the amounts formed. Based on the short duration experiments presented earlier, small amounts of these compounds were likely emitted into the effluent flow. Due to the excess O₃ levels and likely problems of O₃-Tenax artifacts, gas-phase effluents were not measured in these tests.

A longer (97 hr) O₃ exposure (773 ppb) test was conducted to compare AC (50/60 mesh) with and without limonene (Table 5-13). At the test's conclusion, O₃ had broken through both virgin and limonene-spiked AC samples with penetration fractions averaging 2.4 ± 0.4 and $17.5 \pm 0.5\%$, respectively. As seen in earlier tests, small amounts of AMCH and limonene oxides were detected, and limonene loadings increased O₃ penetrations. However, even after 97 hr of O₃ exposure, ~74% of the original limonene was recovered on the AC.

VOC concentrations in the effluent air samples collected over the course of a day for limonene-loaded AC samples exposed to 5.81 ppm of O₃ show rapid decreases in VOC concentrations (Table 14). As seen with the previous effluent samples, limonene was the major identified VOC. VOC concentrations collected at the same time were greater in the highly-loaded samples ($84 \mu\text{g mg}^{-1}$) compared to the moderately loaded ($42 \mu\text{g mg}^{-1}$) samples. VOC emission rates decreased rapidly. No limonene oxidation products were detected, though small amounts of nonanal and decanal were found in the effluent air samples of the highly-loaded samples collected at early times. Possibly the O₃ scrubber used to minimize O₃-Tenax artifacts removed some VOCs, though Fick et al. (2001) reported recoveries >95% for selected terpenes and terpene oxidation products (including AMCH) with KI scrubbers.

5.7.5 Particle analysis

Few particles were found during ozonation of limonene loaded-AC (Table 15), in contrast to the homogenous experiments. Measured concentrations gradually increased with increasing time, reaching a concentration of 1100 Counts L⁻¹ after 24 hr, and most particles were in the 0.3-0.4 µm size range. As mentioned, particles below 0.3 µm dia were not counted. Some or perhaps all of the particles may have formed homogeneously by reaction between residual limonene and O₃ that escaped the AC bed and collected in the Tedlar bag. While the formation and/or removal mechanisms are unclear, the low particle concentrations suggest that heterogeneous reactions occurring on AC between O₃ and limonene are not significant sources of particles. In future experiments, a high efficiency filter following the AC bed might be used to separate particles formed in the AC bed effluent (following the filter) from those formed heterogeneously (before the bed total minus effluent).

5.7.6 Limitations

This study provides insight into O₃-limonene reactions and the extent of product formation in a laboratory setting; however, additional factors must be considered to apply findings to IAQ filtration and other applications. Tests should be conducted with realistic indoor O₃ concentrations (~100 ppb). Evaluations should address other variables that may influence results, e.g., humidity, intermittent O₃ exposure, limonene concentration, temperature, AC type, bed dimensions, flow rate, other contaminants. Another limitation of this study is that VOCs were preloaded onto AC prior to O₃ exposure, which does not realistically reflect dynamic VOC filtration conditions. The possibility that O₃ increases desorption of adsorbed VOCs should also be explored. Finally, tests capable of identifying a broader range of oxidation products, especially low molecular weight

carbonyls, and the use of instrumentation capable of detecting much smaller particles, should be considered.

5.8 Conclusion

Homogeneous reaction experiments between O_3 and limonene showed the formation of formic acid, with an average molar yield of 37%, two gas-phase oxidation products, AMCH and limonene oxides, with molar yields of 3% each, and the production of a significant amount of small ($<0.5 \mu m$) particles. Heterogenous reaction experiments involving the same reactants on activated carbon also showed AMCH and limonene oxides products, as well as straight-chain aldehydes, and many unidentified peaks that were likely terpene impurities, e.g., other monoterpenes. Although O_3 -limonene products were detected, most of the limonene remained unreacted on the AC samples even after long exposures to a stoichiometric excess of O_3 . The bulk of reaction products remained on the AC, and few particles or VOC reaction products were measured in the effluent from the AC bed. Thus, in addition to the known homogenous reactions, O_3 -limonene reactions occur heterogeneously on AC filters. While additional work is necessary to investigate certain pollutants (e.g., formaldehyde, ultrafine particles) and other environmental conditions (temperature, humidity, concentrations, etc.), the results suggest that VOC-loaded AC air filters exposed to O_3 are not likely to emit significant amounts of secondary pollutants. However, further work is necessary to investigate secondary pollutants formed homogeneously by the desorption of VOCs from filters at O_3 concentrations typical of indoor air, which is enhanced by O_3 exposure. .

5.9 References

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Table 5-1. Recoveries (ng) of AMCH and limonene oxides at various analysis times.

Sample Type	Time (hr)	Recoveries (ng)					
		AMCH			Limonene oxides		
		Rep 1	Rep 2	Ave.	Rep 1	Rep 2	Ave.
Direct injection	0	59.8	52.5	56.2	58.5	58.5	58.5
Sorbent	0	35.4	22.2	28.8	28.2	19.7	24.0
Sorbent	4	40.2	33.7	37.0	19.0	12.0	15.5
Sorbent	23	17.3	23.5	20.4	6.9	12.1	9.5
Sorbent	71	45.1	39.7	42.4	20.1	13.8	16.9

Table 5-2. VOC concentrations (mg m^{-3}) in the limonene stability test.

Compounds	VOC concentration (mg m^{-3})			
	0 min	3 min	33 min	40 min
Toluene	-	13.7	0.6	-
p-Isopropyltoluene	2.8	2.3	2.2	1.6
Limonene	304.2	308.0	313.1	289.1
Unidentified peaks ^a	4.0	3.2	3.2	2.1
Total	311.0	327.2	319.1	292.7

^a Estimated using limonene equivalents.Table 5-3. VOC mass loads (μg) of limonene blanks (no O_3) and (with O_3) in the O_3 -limonene homogeneous experiment after 20 min.

Compounds	VOC mass load (μg)							
	Lim				Lim/ O_3			
	Rep 1	Rep 2	Rep 3	Ave.	Rep 1 ^a	Rep 2 ^a	Rep 3 ^b	Ave.
Toluene	-	-	1.9	1.9	-	-	8.4	8.4
p-Isopropyltoluene	13.0	8.1	4.9	8.6 (4.0)	13.3	26.0	5.3	14.9 (10.5)
Limonene	1066.8	1322.0	1023.4	1137.4 (161.3)	1045.3	1055.9	938.9	1013.4 (64.7)
AMCH	-	-	-	-	24.7	23.6	20.8	23.1 (2.0)
Limonene oxides	-	-	-	-	22.1	22.6	20.1	21.6 (1.3)
Unidentified peaks ^c	34.8	19.7	32.7	29.1 (8.2)	27.5	56.0	22.8	35.4 (17.9)
Total	1114.6	1349.7	1062.9	1175.7 (152.9)	1132.9	1184.2	1016.4	1111.2 (86.0)

^a $[\text{O}_3] = 10.5 \text{ ppm}$.^b $[\text{O}_3] = 13.6 \text{ ppm}$.^c Limonene equivalents.

Table 5-4. Amounts (μmol) of O_3 , limonene, and reaction products in the O_3 -limonene homogeneous experiment.

Compound	Bag 1					Bag 2		
	Initial (μmol)	Final (μmol)		Yield ^a (%)		Initial (μmol)	Final (μmol)	Yield ^a (%)
		Rep 1	Rep 2	Rep 1	Rep 2		Rep 1	Rep 1
Ozone	4.3	-	-	-	-	5.5	-	-
Limonene	8.3	7.7	7.8	-	-	8.3	6.9	-
AMCH	-	0.2	0.2	4.2	4.0	-	0.2	2.7
Limonene oxides	-	0.1	0.1	3.4	3.5	-	0.1	2.4

^aMolar yield based on reacted O_3 .

Table 5-5. VOC loadings (μg) in the O_3 -toluene homogeneous tests. Each 10-L Tedlar bag contained 2 μL of toluene, which was exposed to either humidified, pure air or humidified, ozonated air (9.19 ppm) for 20 min.

Compounds	VOC mass load (μg)					
	Toluene			Toluene/ O_3		
	Rep 1	Rep2	Ave.	Rep 1	Rep2	Ave.
Benzene	0.6	4.5	2.6 (3)	1.6	0.7	1.2 (1)
Toluene	1379.0	1704.3	1541.6 (230)	1252.9	1203.8	1228.3 (35)
Limonene	23.4	17.2	20.3 (4)	-	-	-
Total	1392.1	1714.9	1553.5 (228)	1254.5	1204.5	1229.5 (35)

Table 5-6. Average particle counts (Counts L^{-1}) in two size fractions (0.3-0.4 μm and $>0.4 \mu\text{m}$) in O_3 -limonene homogeneous experiments.

Sample	Ozone conc. (ppb)	Reaction time (min)	No. of reps.	0.3-0.4 micron	>0.4 micron
				Ave.	Ave.
				(Counts L^{-1})	(Counts L^{-1})
Pure air	0	0	2	66 (22)	5 (4)
Toluene	920	35	2	318 (117)	14 (3)
Limonene	621	15	3	670788 (12796)	2768 (3037)

* OPC is over range, thus actual counts are higher.

Table 5-7. Mass loads and molar yields of particles collected on filters in the homogeneous experiment (total volume = 50 L each).

Compound	Filter 1				Filter 2			
	Mass		Molar yield		Mass		Molar yield	
	(μg)		(%) ^a		(μg)		(%) ^a	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Formic acid	63.6	NA	35.2	NA	68.3	NA	37.8	NA
Propanoic acid ^b	-	6.7	-	2.3	7.6	7.3	2.6	2.5
Total	63.6	NA	35.2	NA	75.9	NA	40.4	NA

^a Based on moles of O₃.

^b Toluene equivalents.

Table 5-8. VOC weight fractions in virgin and VOC-loaded activated carbon samples without O₃ exposure (μg VOC/mg AC). Asterisk "*" denotes nontarget compounds that are quantified as toluene equivalents.

Compounds	Virgin AC						Limonene/AC		
	50/60 mesh			30/60 mesh			50/60 mesh		
	AC mass	No. of reps.	Conc.	AC mass	No. of reps.	Conc.	AC mass	No. of reps.	Conc.
	(mg)		(μg mg ⁻¹)	(mg)		(μg mg ⁻¹)	(mg)		(μg mg ⁻¹)
Hexane	9.9	4	2.48 (0.06)	20.0	4	2.21 (0.13)	10.3	2	2.94 (0.11)
Benzene			0.32 (0.01)			0.13 (0.01)			1.50 (0.37)
Toluene			0.49 (0.05)			0.15 (0.08)			2.10 (2.08)
Tetrachloroethylene			0.53 (0.08)			0.08 (0.07)			0.62 (0.56)
p-Xylene, m-xylene			0.29 (0.01)			0.51 (0.05)			0.25 (0.02)
Styrene			- -			0.06 (0.00)			1.06 -
p-Isopropyltoluene			- -			- -			0.10 (0.01)
Limonene			- -			- -			83.97 (0.92)
Cyclohexane			4.44 (1.01)			0.41 (0.12)			1.61 (0.17)
Octane*			- -			0.14 (0.07)			0.02 (0.02)
Total			8.55 (1.09)			3.70 (0.26)			94.17 (3.12)

* Toluene equivalents.

Table 5-9. Summary of VOC concentrations ($\mu\text{g m}^{-3}$) in effluent air samples from the pure air-exposed and O_3 -exposed heterogeneous experiments.

Compound	AC ^a				AC/Limonene ^b			
	Pure air		Ozone		Pure air		Ozone	
	0 min ^c	31 min ^d	0 min ^c	31 min ^d	0 min ^c		0 min ^c	
	Rep 1	Rep 1	Rep 1	Rep 1	Rep 1	Rep 2	Rep 1	Rep 2
Hexane	1.8	1.2	4.3	-	54.3	118.5	145.4	23.0
Chloroform	-	-	1.4	0.5	13.5	18.7	15.6	4.3
Tetrahydrofuran	-	-	1.2	0.7	13.6	20.7	22.4	2.1
1,1,1-Trichloroethane	-	-	-	-	-	-	0.7	-
Benzene	-	-	0.9	-	11.7	14.2	18.0	4.1
Methyl isobutyl ketone	-	-	4.2	-	-	0.0	0.9	0.5
Toluene	-	-	0.2	-	24.6	10.9	21.6	3.1
Tetrachloroethylene	-	-	-	-	10.3	5.3	8.6	0.0
Ethylbenzene	-	-	-	-	-	-	0.1	-
p-Xylene, m-xylene	-	-	-	-	0.5	-	0.4	0.1
Styrene	-	0.0	0.3	-	0.1	0.5	5.6	-
α -Pinene	-	-	-	-	-	-	0.8	-
Phenol	-	-	75.9	-	-	-	-	-
1,2,4-Trimethylbenzene	-	-	0.1	-	-	-	-	-
p-Isopropyltoluene	-	-	-	-	5.9	2.4	15.4	15.8
Limonene	-	-	2.7	-	441.6	235.7	500.8	197.5
p-Cresol, m-cresol	-	-	2.0	-	-	-	-	-
AMCH	-	-	-	-	-	-	20.1	1.9
Limonene oxides	-	-	-	-	-	-	24.9	6.9
Cyclohexane	-	-	-	-	12.2	11.8	53.3	48.3
Methylcyclohexane	-	-	-	-	37.1	19.7	29.0	2.3
Decane	-	-	5.5	0.6	-	-	-	-
Undecane	-	-	6.7	0.6	-	-	-	-
Acetophenone ^e	-	-	0.7	0.1	-	-	-	-
Benzaldehyde ^e	-	-	18.1	1.2	-	-	1.6	-
Decanal ^e	-	-	-	0.1	-	-	13.7	-
Hexanal ^e	-	-	5.1	5.8	-	-	9.1	-
Nonanal ^e	-	-	3.1	3.5	-	-	27.3	-
Octanal ^e	-	-	3.0	-	-	-	2.8	-
Octane ^e	-	-	-	-	-	-	2.9	-
Unidentified compounds ^f	-	-	-	-	16.6	7.5	57.9	51.4
Total	1.8	1.2	135.3	13.1	641.9	466.0	998.9	361.4

^{a,b} Sample volume = 4.8 and 1.6 L, respectively.

^c Sample start-time = 0 min.

^d Sample start-time = 31 min.

^e Nontarget compounds, estimated using toluene equivalents.

^f Estimated using limonene equivalents.

Table 5-10. Measured O₃ concentrations (ppb) in effluent air for virgin and limonene-spiked AC exposed to humidified, ozonated air (5.81 ppm). Samples were tested concurrently with samples shown in Tables 9 and 11.

Exposure time	O ₃ penetration (ppb)			
	AC		AC/Limonene	
	Rep 1	Rep 2	Rep 1	Rep 2
10 min.	4	0	0	0
30 min.	16	0	0	0
60 min.	47	16	0	10

Table 5-11. VOC weight fractions in limonene-spiked AC exposed to purified or ozonated air for 10 min (µg VOC/mg AC). Samples correspond to the effluent air samples shown in Table 9.

Compound	VOC concentration (µg mg ⁻¹) ^a				t-test p-value ^b
	Pure air		5.81 ppm O ₃		
	0	0	0	0	
	Rep 1	Rep 2	Rep 1	Rep 2	
Hexane	3.27	3.00	2.06	2.51	0.09
Chloroform	0.02	0.02	0.01	0.02	0.48
Tetrahydrofuran	0.02	0.01	0.01	0.02	0.53
Benzene	0.28	0.31	0.25	0.22	0.10
Toluene	1.39	0.74	1.20	0.95	0.98
Tetrachloroethylene	0.46	0.43	0.43	0.35	0.29
Ethylbenzene	0.06	-	0.11	-	-
p-Xylene, m-xylene	0.19	0.76	0.28	0.65	0.98
Styrene	0.78	0.45	1.22	0.42	0.69
p-Isopropyltoluene	0.45	0.46	0.17	0.28	0.05
Limonene	75.21	81.88	27.05	43.95	0.04
AMCH	-	-	0.24	-	-
Limonene oxides	-	-	0.26	-	-
Cyclohexane	0.69	0.88	0.62	0.65	0.26
Methylcyclohexane	0.97	0.71	0.90	1.01	0.50
Decane	-	-	0.06	-	-
Undecane	-	-	0.09	-	-
Octane ^c	-	0.16	-	0.28	-
Total	83.78	89.81	34.93	51.29	0.04

^a AC mass = 20 mg.

^b Two-tailed test comparing mean VOC concentrations of nonozonated and ozon

^c Nontarget compound, estimated using toluene equivalents.

Table 5-12. VOC weight fractions ($\mu\text{g VOC/mg AC}$) on virgin AC (20 mg) or limonene-loaded AC exposed to pure air or ozonated air for 48 hr.

Compounds	VOC concentration ($\mu\text{g mg}^{-1}$) ^a					
	AC			AC/limonene		
	0 ppm	1.08 ppm	8.95 ppm	0 ppm	1.08 ppm	8.95 ppm
Hexane	2.72 (0.20)	2.93 (0.25)	2.22 (0.27)	2.67 (0.35)	2.22 (0.51)	1.85 (0.02)
Benzene	0.14 (0.02)	0.17 (0.02)	0.16 (0.05)	0.21 (0.06)	0.14 (0.05)	0.17 (0.08)
Toluene	0.25 (0.12)	0.22 (0.05)	0.21 (0.01)	0.44 (0.20)	0.25 (0.02)	0.34 (0.27)
Tetrachloroethylene	0.11 (0.09)	0.17 (0.01)	0.19 (0.02)	0.27 (0.16)	0.18 (0.09)	0.37 (0.34)
p-Xylene, m-xylene	0.22 (0.11)	0.37 (0.20)	0.57 (0.03)	0.53 (0.21)	0.21 (0.10)	0.22 (0.02)
Styrene	--	0.14 (0.18)	0.20 (0.12)	0.20 (0.03)	0.03 (0.04)	0.15 (0.15)
p-Isopropyltoluene	--	--	--	0.39 (0.03)	0.41 (0.01)	0.33 (0.02)
Limonene	--	--	--	71.75 (2.13)	67.12 (2.02)	48.89 (1.72)
AMCH	--	--	--	--	0.89 (0.06)	0.85 (0.04)
Limonene oxides	--	--	--	--	0.47 (0.08)	0.38 (0.02)
Cyclohexane	0.32 (0.17)	0.79 (0.14)	0.73 (0.23)	0.91 (0.35)	0.55 (0.02)	1.01 (0.63)
Methylcyclohexane	--	1.85 (2.28)	0.92 (0.28)	0.81 (0.23)	0.36 -	0.53 (0.35)
Octane ^b	0.01 (0.01)	0.05 (0.07)	0.11 (0.02)	0.09 (0.05)	0.02 -	--
Total	3.78 (0.48)	6.69 (2.57)	5.32 (0.91)	78.27 (2.23)	72.84 (2.29)	55.10 (0.02)

^a AC mass = 20 mg, two replicates at each O₃ concentration.

^b Nontarget compound, estimated with toluene equivalents.

Table 5-13. VOC weight fractions ($\mu\text{g mg}^{-1}$ of AC) of virgin and limonene-spiked AC samples exposed to humidified, ozonated air (773 ppb) for 97 hr.

Compounds	VOC concentration ($\mu\text{g mg}^{-1}$) ^a	
	AC ^b	AC/limonene ^c
Hexane	2.15 (0.13)	2.01 (0.13)
Benzene	0.12 (0.02)	0.15 (0.01)
Toluene	0.21 (0.09)	0.17 (0.03)
Tetrachloroethylene	0.16 (0.06)	0.15 (0.02)
p-Xylene, m-xylene	0.35 (0.15)	0.37 (0.09)
Styrene	0.01 -	--
p-Isopropyltoluene	--	0.07 (0.00)
Limonene	--	62.15 (4.27)
AMCH	--	0.97 (0.10)
Limonene oxides	--	1.15 (0.08)
Cyclohexane	0.65 (0.20)	0.52 (0.11)
Octane ^d	0.02 (0.01)	0.02 (0.03)
Unidentified peaks ^e	--	0.35 (0.13)
Total	3.68 (0.35)	68.10 (4.18)

^a Four replicates for each sample type.

^{b,c} Average sample mass = 15.3 and 15.0, respectively.

^d Nontarget compound estimated using toluene equivalents.

^e Estimated using limonene equivalents.

Table 5-14. VOC concentrations ($\mu\text{g m}^{-3}$) of effluent air samples from AC samples highly ($84 \mu\text{g mg}^{-1}$) or moderately ($42 \mu\text{g mg}^{-1}$) loaded with limonene and exposed to 5.81 ppm of O_3 . (Due to a GC/MS problem, no data was available for the moderately-loaded sample collected at one hr.)

Compounds	Highly loaded						Moderately loaded			
	0 hr		1 hr		23 hr		0 hr		23 hr	
	$\text{O}_3 \text{ C}_i/\text{C}_0$	VOC conc.	$\text{O}_3 \text{ C}_i/\text{C}_0$	VOC conc.	$\text{O}_3 \text{ C}_i/\text{C}_0$	VOC conc.	$\text{O}_3 \text{ C}_i/\text{C}_0$	VOC conc.	$\text{O}_3 \text{ C}_i/\text{C}_0$	VOC conc.
	(%)	($\mu\text{g m}^{-3}$)	(%)	($\mu\text{g m}^{-3}$)	(%)	($\mu\text{g m}^{-3}$)	(%)	($\mu\text{g m}^{-3}$)	(%)	($\mu\text{g m}^{-3}$)
	0		0		25		0		24	
Hexane		141.75		30.48		24.01		80.28		-
Chloroform		18.16		6.83		-		12.28		-
Tetrahydrofuran		26.73		7.88		-		20.44		-
Benzene		16.41		7.21		0.92		10.14		-
Toluene		23.53		8.80		1.75		9.01		2.97
Tetrachloroethylene		7.86		3.03		-		4.40		0.12
Ethylbenzene		0.33		-		-		-		-
p-Xylene, m-xylene		0.03		-		-		-		-
Styrene		2.27		1.03		0.04		0.87		-
p-Isopropyltoluene		3.02		0.43		-		0.98		-
Limonene		304.05		82.52		6.26		86.45		-
Methylcyclohexane		47.93		19.35		1.00		24.57		0.98
Decanal ^a		3.26		3.02		-		-		-
Nonanal ^a		0.62		1.07		-		-		-
Total		597.23		172.88		35.24		250.68		5.32

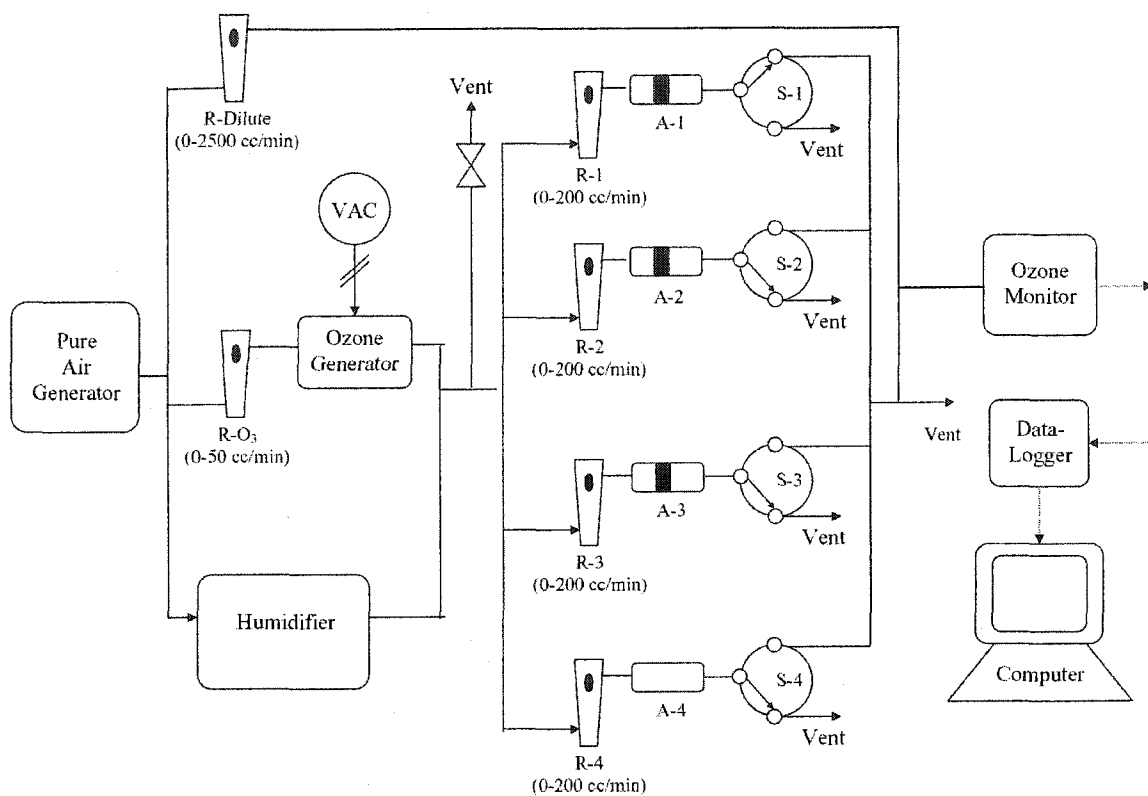
^aNontarget compounds, estimated with toluene equivalents.

Table 5-15. Particle counts (Counts L⁻¹) for two size fractions in the heterogeneous experiments. AC mass = 20 mg, and limonene dose = 2 µL (1.68 mg). O₃ concentrations were measured using the O₃ exposure measurement system.

Time (hr)	O ₃ conc. (ppm)	Cum. O ₃ dose (µg)	0.3-0.4 µm	>0.4 µm
			Particle counts ^a (Counts L ⁻¹)	Particle counts ^a (Counts L ⁻¹)
0.0	0.0	0	66 (22)	5 (4)
1.1	3.6	50	242 (58)	22 (13)
2.4	7.2	197	129 (16)	7 (3)
3.6	9.4	375	302 (27)	17 (8)
4.8	9.7	621	744 (69)	27 (8)
23.6	9.6	4092	1095 (51)	46 (7)

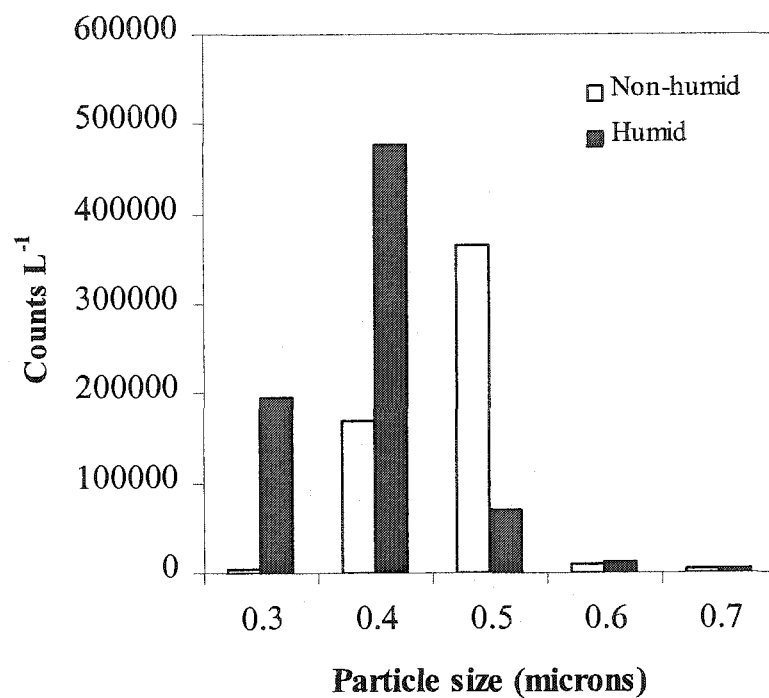
^a Average of 6 - 7 10 sec. readings.

Figure 5-1. Ozone exposure measurement system. Ports 5-8 omitted for simplification.



(R = flow rotameter, A = adsorption tube, S = solenoid valve)

Figure 5-2. Size fractions for particles formed after 15 min. reaction of O₃ (916 ppb) with limonene in dry (RH = 0%) or humidified (RH = 50%) air.



CHAPTER 6. Ozone Removal by Diesel Particulate Matter

6.1 Abstract

The most significant removal mechanisms for tropospheric ozone (O_3) include dry deposition, photolysis, and photochemical reactions. This study examines another mechanism potentially important in urban areas: sorption and removal on diesel particulate matter (DPM). Tests were performed to determine O_3 breakthrough and the amount of O_3 removed by DPM generated by a heavy-duty diesel engine. Teflon filters loaded with 1.8 mg of DPM were exposed to a test atmosphere of humidified and ozonated air designed to represent realistic ambient air conditions. In addition, soot samples with the organic fraction removed were tested to determine whether the organic or elemental fraction contributed to O_3 removal. For comparison purposes, activated carbon (AC) samples were tested. The DPM-loaded filters removed 5.6 ± 1.8 wt % of O_3 , while the organic-fraction of DPM removed 31 ± 4 wt %. Removal capacities of DPM were small relative to AC, which removed $>38 \pm 3$ wt % of O_3 in comparable tests. Of the Lagergren pseudo-first order, pseudo-second order, Elovich, and Ritchie chemisorption models tested, the Ritchie model provided the best fit to the breakthrough data. Preliminary estimates drawn from laboratory results suggest that diesel soot present at typical urban levels will remove only a small portion of O_3 from urban/tropospheric

air. In air cleaning applications, DPM-loaded filters similarly are also expected to remove only a small portion of indoor O_3 .

6.2 Keywords

Air pollution, diesel, filter, ozone, particulate matter, soot

6.3 Introduction

Tropospheric ozone (O_3) is the most widespread air pollutant in the US and in many other countries. Ambient O_3 concentrations in many areas exceed standards (120 ppb, 1-hr average; 80 ppb, 8-hr average in the US), and it has proven exceedingly difficult to reduce O_3 concentrations. In urban areas, high concentrations of O_3 often co-exist with other air pollutants, including particulate matter ($PM_{2.5}$, PM_{10}). O_3 removal mechanisms include a number of homogeneous and heterogeneous mechanisms, the most significant being deposition on dry surfaces or water, photolysis by UV radiation, and photochemical reactions involving the HO_2 radical (Paluch et al., 1995).

This research examines O_3 removal by particulate matter, specifically, diesel particulate matter (DPM), often called 'soot'. DPM itself is of interest since it is associated with adverse health and visibility impacts, and because it is an important component of $PM_{2.5}$ and PM_{10} . An assessment of O_3 removal capacity by DPM is relevant to understanding interactions between DPM and ambient O_3 , as well as effects of DPM collected on ventilation filters and other surfaces that may affect O_3 levels in indoor or personal air. This study also demonstrates a laboratory system that allows relatively rapid tests of O_3 removal capacity of DPM and other types of particulate matter.

6.4 Background

Soot is a by-product of diesel fuel combustion and consists of both elemental carbon (EC) and organic carbon (OC) fractions as well as up to 10 mol % of hydrogen and other trace elements (Seinfeld and Pandis, 1998). The US EPA (1996) estimated EC emission rates of 0.1-0.2 g km⁻¹ and 0.5-1.2 g km⁻¹ for light and heavy-duty diesel vehicles, respectively. Greater than 90 wt % of the EC emitted by diesel engines is in the submicron range with mean volume diameters from 50 to 250 nm (Seinfeld and Pandis, 1998). Braun et al. (2004) characterized diesel particulate matter into three size ranges: fractal aggregates (70-100 nm); primary particulates (10-20 nm); and particulate subunits (~ 2 nm). Soot particles can adsorb a significant amount of organic vapors as the combustion products cool. Although soot particles have unique chemical and physical properties, aging processes such as coagulation and condensation cause them to become mixed with other types of atmospheric PM, thereby becoming more similar to other particles in the atmosphere (Seinfeld and Pandis, 1998).

Due to its large surface area, the graphitic structure of soot particles provides an ideal surface for heterogeneous chemical reactions. For fuel combustion soots, specific surface areas typically range from 60-150 m² g⁻¹ and track linearly with increasing air/fuel combustion ratio (Chughtai et al., 2002). Reactions of O₃ and other oxidants can affect the structure and properties of soot and other carbonaceous particles. Whether atmospheric O₃/soot reactions are significant depend both on soot concentration and its structure and properties, which in turn depend on the fuel composition, combustion conditions, and aging processes (Pöschl et al., 2001; Wei et al., 2001; Chughtai et al., 2002; Seinfeld and Pandis, 1998). Atmospheric soot chemistry may also be affected by

the presence of other contaminants, such as volatile organic compounds (VOCs), inorganic compounds, and radicals, which can potentially affect soot surface reactivity or lead to indirect O₃ losses. For example, Lary et al. (1999) suggested that heterogeneous reduction of NO₂ and HNO₃ on soot could form an O₃ sink. Fan et al. (1996) found that particle-associated nitro polycyclic aromatic hydrocarbons (NPAH) and PAH are degraded by O₃, which may be the dominant loss process for these compounds at night.

O₃ loss on soot. Much of the literature regarding O₃ loss on particulate matter has focused on O₃ reactions with soot emitted by aircraft in the upper troposphere/lower stratosphere and the potential contribution to stratospheric O₃ depletion (Bekki, 1997; Gao et al., 1998; Lary et al., 1999). Generally, these reactions are believed to have a negligible effect on atmospheric O₃ concentrations (Kamm et al., 1999; Disselkamp et al., 2000; Longfellow et al., 2000; Wei et al., 2001; Chughtai et al., 2003; Lelievre et al., 2004).

A few studies have explored the potential for soot particles to act as O₃ scavengers in the lower atmosphere. While soot particles are normally hydrophobic, ozonation causes them to become more hydrophilic, potentially acting as cloud condensation nuclei (Kotzick and Niessner, 1999; Decesari et al., 2002), which in turn could also affect atmospheric residence times of particles since rain-out is a major removal mechanism for atmospheric soot aerosols. Berkowitz et al. (2001) proposed a heterogeneous reaction for aerosol particles in the lower troposphere as one explanation for O₃ depletion observed in a nighttime urban plume. O₃ removal by DPM probably occurs both day and night as sunlight does not appear to affect O₃ loss. In studying the effect of simulated sunlight irradiation on the loss of O₃ on n-hexane soot, Smith and

Chughtai (1997) found that although solar radiation shifted product formation toward gaseous CO₂, CO and H₂O rather than functional groups on the soot surface, it did not significantly affect the overall rate or quantity of O₃ loss.

The O₃ loss rate on soot aerosol appears to depend on specific surface area, reaction time, O₃ concentration, relative humidity, and temperature (Kamm et al., 1999; Chughtai et al., 2002; 2003). Current understanding is based on laboratory experiments generally using n-hexane soot as a surrogate for fuel combustion aerosols (e.g., from diesel, kerosene, JP8). Most chemical properties are similar, the main difference being the presence of trace elements or commercial additives in fuels (Chughtai et al., 2002). Still, O₃ removal mechanisms are not completely understood. Smith and Chughtai (1997) characterized O₃ loss on n-hexane soot particles by an initial rapid, catalytic decomposition stage, followed by slower stages during which surface carboxylic groups are formed, gaseous CO₂, CO, and H₂O are desorbed, and further O₃ is lost by a second-order process. During the catalytic stage, in which O₃ is converted to O₂, the soot is treated as a catalyst and is not destroyed by O₃ (Wei et al., 2001). During the non-catalytic stages, an O₃ molecule oxygenates one active site on the soot's surface, thereby inactivating or "poisoning" the site (Wei et al., 2001). "Poisoned" soot may be regenerated by further reaction with O₃ to liberate O₂ (Wei et al., 2001; Smith and Chughtai, 1997). Kamm et al. (1999) proposed a set of four equations for modeling O₃ loss on soot aerosol: rapid surface reaction resulting in a loss of a monolayer-equivalent of O₃; O₃-induced recovery of surface sites; spontaneous recovery of surface sites; and spontaneous conversion of active sites into inactive sites (passivation). The first three

equations represent a catalytic cycle that continues until either all active sites or O₃ are depleted.

The reversibility of O₃ loss on soot also remains an open question. Fendel et al. (1995) and Kamm et al. (1999) proposed that O₃ loss was irreversible, characterized by an initial adsorption process where an O atom is adsorbed and liberated as O₂. Earlier, Stephens et al. (1986) proposed that O₃ adsorption on charcoal is reversible consistent with a Langmuir isotherm, with O₃ molecules subsequently reacting heterogeneously to form oxygenated surface groups, CO and CO₂. Pöschl et al. (2001) extended this mechanism to fresh spark-discharge soot particles coated with benzo[a]pyrene, a polycyclic aromatic hydrocarbon (PAH), suggesting that gaseous O₃ loss initially proceeds via fast reversible adsorption and then continues through irreversible oxidation reactions with surface PAH or carbon leading to the formation of oxygenated surface functional groups. These functional groups can then be further oxidized to form CO, CO₂, and semi-volatile organic compounds.

Also controversial is the extent of catalytic decomposition of O₃ on soot. Pöschl et al. (2001) suggested that catalytic decomposition of O₃ may occur in parallel with oxidation reactions on the particle surface, but stated the need for more studies to determine whether decomposition was significant. While Smith and Chughtai (1997) attributed initial, rapid O₃ loss to catalytic decomposition, Stephens et al. (1986) and Disselkamp et al. (2000) stated that their results did not show any evidence of a catalytic process.

Chemisorption models. Several models have been developed to characterize the kinetics of chemisorption processes on solid surfaces, including the Elovich, Ritchie,

Lagergren pseudo-first order, and pseudo-second order equations (e.g., Ho and McKay, 1998; Cheung et al., 2000). These models have been used for a myriad of sorbents (e.g., moss, clay, fly ash) and sorbates (e.g., metal ions, dyes, VOCs). However, they have not been validated for O₃/soot reactions. The basis and form of these four models are summarized below.

The pseudo-first order Lagergren equation has been used to describe the kinetics of a variety of sorbate/sorbent systems (Ho and McKay, 1998):

$$dq_t/dt = k_1 (q_e - q_t) \quad (6-1)$$

where q_t = sorption capacity at time t ($\mu\text{g mg}^{-1}$), q_e = the equilibrium sorption capacity ($\mu\text{g mg}^{-1}$), and k_1 = pseudo-first order rate constant (hr^{-1}). Eq. 6-1 can be integrated to:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6-2)$$

Plots of $\ln(q_e - q_t)$ vs. t should be linear if pseudo-first order kinetics apply. Since q_e is rarely known and is generally impractical to measure, the data can be extrapolated to $t = \infty$ or q_e can be determined by trial-and-error. Pseudo-first order kinetics often only apply to the first 20 – 30 minutes in many sorbate/sorbent systems.

Pseudo-second order kinetics may be represented by the following equation (Ho and McKay, 1998):

$$dq_t/dt = k (q_e - q_t)^2 \quad (6-3)$$

which following integration and rearrangement becomes:

$$t/q_t = 1/h + t/q_e \quad (6-4)$$

where h = initial sorption rate as $q_t/t \rightarrow 0$ ($\mu\text{g mg}^{-1} \text{ hr}^{-1}$). Thus, a plot of t/q_t vs. t should yield a straight line from which q_e , k , and h can be directly determined from the regression coefficients if pseudo-second order kinetics apply. Unlike the pseudo-first

order model, there is no need for extrapolation or solving by trial-and-error to obtain q_e . Also, if applicable, this model has the advantage of fitting the entire range of data rather than just the first few minutes of chemisorption.

The Elovich equation has been applied successfully to some chemisorption data where the adsorbing surface is heterogeneous (Cheung et al., 2000). The Elovich equation uses additional terms,

$$dq_t/dt = a \exp(-b q_t) \quad (6-5)$$

where a = initial sorption rate ($\mu\text{g mg}^{-1} \text{ hr}^{-1}$), and b = adsorption constant ($\text{mg } \mu\text{g}^{-1}$) for a given experiment (Ho and McKay, 1998). Following integration, eq. (6-5) becomes:

$$q_t = 1/b \ln(a b) + 1/b \ln(t + t_0) \quad (6-6)$$

where t_0 = time constant (hr) and is estimated by trial-and-error to achieve a linear plot of q_t versus $\ln(t + t_0)$. If the Elovich model applies, the constants a and b can then be calculated from the slope and intercept. If $q_t = 0$ at $t = 0$, $t_0 = 1/ab$. However, if an amount of gas is instantaneously adsorbed, the integrated form of eq. (6-5) becomes:

$$q_t = 1/b \ln(a b) + 1/b \ln(t + k) \quad (6-7)$$

where $k \text{ (hr)} = t_0 \exp(b q_0)$ (Low, 1960). Because of rapid initial adsorption or other kinetic processes that may displace plots, the Elovich equation is not practical for determining values of q_t . Rather, it is most useful for determining adsorption rates and not sorption capacities (Low, 1960).

The Ritchie equation was originally proposed for modeling chemisorption of gases on carbon and has since been applied to the adsorption of cadmium ions on bone char in aqueous solutions (Cheung et al., 2000). The differential form is:

$$d\theta/dt = k (1 - \theta)^n \quad (6-8)$$

where θ = fraction of surface sites occupied by the adsorbed gas, k = rate constant ($\text{mg } \mu\text{g}^{-1} \text{ hr}^{-1}$), and n = number of surface sites occupied by each gas molecule. At time, t , $\theta = q_t/q_e$. Assuming second-order kinetics and that $\theta = 0$ at $t = 0$, eq. (6-8) can be integrated, simplified and rearranged to a linear form,

$$1/q_t = 1/(k q_e t) + 1/q_e \quad (6-9)$$

from which q_e and k can be determined from the regression of $1/q_t$ vs. $1/t$.

6.5 Methods

A series of laboratory tests was performed to determine the amount of O_3 removed by DPM collected on Teflon filters. DPM samples with varying soot loadings were exposed to a test atmosphere of humidified and ozonated air designed to represent realistic ambient air conditions. In addition, DPM samples with the organic fraction removed were tested to determine whether the organic or elemental fraction contributed to O_3 removal. For comparison purposes, activated carbon and blank samples were tested. The four chemisorption models previously described were tested to determine their applicability to the O_3 /soot system.

6.5.1 Diesel PM generation and collection

DPM was generated using a heavy-duty diesel engine (1995 Detroit Diesel Series-60) burning AMOCO Premium Diesel fuel (sulfur content of ~ 300 ppm). The 6 cylinder inline engine has a displacement of 12.7 L, 4 valves/cylinder, 130 mm bore, 160 mm stroke, a compression ratio of 15, and is capable of 1575 ft-lb (217.8 kg-s) at 1200 rpm (max torque) and 450 HP at 2100 rpm (max power). The engine had been upgraded with exhaust gas recirculation (EGR), a variable geometry turbocharger (VGT), EGR cooler and charge air after-cooler, DDEC-IV ECM control module, and upgraded fuel injectors.

Conditions used in most tests were high speed (2100 RPM), low load (30%), and steady-state conditions (all engine parameters were maintained constant for at least 30 min before taking samples). The highest engine speed was selected as PM mass is known to increase with engine speed (at the same load). In addition, the fuel injection timing was retarded to 8° BTDC (from 13) to increase PM emissions. For these conditions, the air flow, fuel flow, and exhaust flow rates were estimated as 27.6 kg/min, 0.311 kg/min, and 22,600 L/min, respectively. One test was conducted in which PM was collected under engine startup conditions.

DPM was collected using a mini-dilution tunnel manufactured in-house in collaboration with Electro Mechanical Associates (Ann Arbor, MI). The mini-dilution tunnel was 102 cm long and 8 cm in diameter. A transfer line (53 cm long x 0.46 cm ID) sampled exhaust approximately 290 cm from the VGT outlet using a constant volume sampling system (up to 50 L/min). The dilution ratio (DR) capability was 3-200 and was measured using NDIR CO₂ analyzers. Dilution air was HEPA-filtered to remove entrained oil and water. The sample was maintained at 45 C. For these tests, the DR=13.5, the filter flow rate 45 L min⁻¹, and the tunnel residence time (RT) for these conditions was ~0.4 s. Typical NO_x and CO₂ concentrations were 183 ppm and 2.48 vol %, respectively.

Particles were captured on 47 mm filters (Pallflex TF40H EMFAB; Teflon bonded onto borosilicate glass microfibers, Pallflex Products Corp., Putman, CT) using isokinetic sampling and a sampling period of 40 min. Filters were conditioned at 22 C and 45% RH and weighed prior and after loading with a microbalance (Mettler) with 1 µg accuracy in a Class 100 clean room. The particulate load ranged from 0.730 to 1.808 mg

per filter. After loading, filters were carefully cut into four 12 mm dia circular sections using a cork boring tool. Sections were taken in a radially symmetric manner near the center of the filter where the PM was most evenly distributed. These sections were then placed inside 13 mm Celcon[®] acetal filter holders (Gelman Sciences, Ann Arbor, MI) containing a Teflon washer. For comparison, blank filters were sectioned and similarly prepared. Two types of blanks were tested: clean (unused) filters; and filters mounted in the dilution tunnel that had the same volume of air passed through as samples, but without diesel exhaust.

O₃ removal capacities of DPM and activated carbon (AC) were compared using similar procedures. An AC powder (Mallinckrodt, Paris, KY) was further ground using a mortar and pestle, sieved between 140 and 325 mesh screens (Soiltest, Inc., Lake Bluff, IL) to obtain particle sizes from 45 to 106 μm , and then suspended and loaded onto pre-weighed 47 mm dia filters (Pallflex TF40H EMFAB) mounted in a filter holder under a moderate air flow until a loading comparable to the DPM samples was achieved. After a second weighing to determine the AC mass, the filters were sectioned into 12 mm samples as described above. These AC filter samples, as well as the diesel PM and blank samples, were tested in the exposure system described below.

6.5.2 O₃ exposure measurement system

Each filter sample was exposed to a constant ($\pm 7\%$) O₃ concentration at a controlled temperature (24 C), relative humidity (50%) and flow rate (160 cm³ min⁻¹). The exposure system (Fig. 6-1) consisted of a pure air generator (Model 737-12A, Addco Instruments, Inc., Clearwater, FL) that supplied hydrocarbon-free air to an O₃ generator (Model MZ-250, Clearwater Tech Inc., San Luis Obispo, CA). The flow was diluted with 50% RH air, obtained using temperature-controlled bubblers and the pure air

generator, then split into eight identical streams by rotameters, of which seven were used to expose samples. The eighth stream was used to monitor the O₃ concentration. Downstream of each sample was a 2-way Teflon[®] solenoid valve (Cole-Parmer Instrument Co., Vernon Hills, IL). In the normally-opened position, flow was vented to an exhaust hood. If the solenoid valve was energized, the flow was diluted with a clean, dry air (1.5 L min⁻¹) for measurement with a continuous O₃ analyzer (Model 400A, Advanced Pollution Instrumentation, Inc., San Diego, CA). A datalogger (Model 21X, Campbell Scientific, Inc., Logan Utah) controlled the solenoid valves and recorded data from the O₃ analyzer.

The O₃ analyzer's data processing was modified to improve response time by eliminating signal smoothing. Analyzer specifications include a performance range of 0 to 10 ppm, and detection limit below 0.6 ppb. The O₃ analyzer was calibrated using a certified, portable transfer standard (UV photometer, Model 401X, Advanced Pollution Instrumentation, Inc., San Diego, CA).

6.5.3 Data analysis

O₃ concentrations exiting each of 7 sample tubes and the blank were measured every 16 min. The datalogger was programmed to advance the solenoid valves every 2 min. The first min of data for each filter was discarded to allow the O₃ analyzer and the system to stabilize. In the second min, O₃ concentrations were measured at 1 s intervals and averaged.

Collected data were uploaded to a computer and imported into a spreadsheet for analysis. Raw data were processed to 1-hr block averages and then exponentially smoothed using a damping factor of 0.2. O₃ breakthrough curves were constructed for each sample by trending the penetration, expressed as C_t/C_0 (%) where C_t is the O₃

concentration measured at time t downstream of the filter, and C_0 is the (constant) upstream concentration. The removal capacity of soot or carbon was expressed as a wt % based on the removed mass of O_3 estimated using sample flow rate, and O_3 concentrations up- and down-stream of the filter over the sampling period, divided by the mass loading on the filter.

6.5.4 Ozone exposure experiments

The following filters were tested: 1) three filters with soot collected with the engine in the high speed, low load nominal condition (denoted filters S-115, S-116, and S-117); 2) soot with the organic fraction removed but otherwise under the same conditions just mentioned (I); 3) soot collected during engine startup (S-114); 4) soot collected during a shorter (20 min) sampling period (S-118); and 5) activated carbon (AC). Filters were exposed to O_3 concentrations from 94 to 166 ppb and exposure times from 19 to 63 hr. Two to four replicates of each filter were tested. Blank samples were also tested and showed negligible O_3 removal. Experimental conditions are summarized in Table 6-1.

6.5.5 Determination of soluble organic fraction

To determine the soluble organic fraction (SOF) of the DPM, Soxhlet extractions were carried out using 150 mL of solvent (mixture of 70% dichloromethane and 30% benzene), 300-350 cycles, and ~40 hr percolation time. Filters were dried overnight at 50 C, stored one day in a dessicator containing Drierite, reconditioned in the conditioning chamber, and weighed. Extracts were evaporated to approximately 10 mL at 40 C with a turbo evaporator (Zymark Turbovap II concentrator), transferred into test tubes and dried under a N_2 flow until constant weight was achieved. The loss in filter weight was comparable (within 10%) to the increase of weight of the organic solvent extract.

A screening level analysis was performed to identify the major organic fractions in the diesel soot. The dried SOF was dissolved in 1 mL of benzene, cleaned by thin layer chromatography (TLC) on alumina plates, and analyzed using a GC/MS (Hewlett-Packard 5990 GC with 5971 Mass Selective Detector, and a 30 m x 0.25 mm (i.d.) 5 μ m film DB-5ms column (J&W Scientific). The GC temperature program was started at 50 C, ramped 25 C min⁻¹ to 150 C, ramped 6 C min⁻¹ to 200 C, and 15 C min⁻¹ to 300 C. Other parameters included: He carrier gas at 35 cm/sec, splitless injections, detector temperature at 250 C, and MSD and transfer line temperatures at 325 C.

6.6 Results

6.6.1 Breakthrough curves

O₃ breakthrough curves for 4 replicates of sample S-117 (DPM loading of 139 ± 3 μ g) are typical results, e.g., showing rapid and near complete breakthrough (85-90%) within 15 hr of O₃ exposure (Fig. 6-2). Replicate precisions in each experiment were generally good, e.g., penetrations (C_t/C_0) were within 5% at a given time. Fig. 6-2 also shows breakthrough curves for 2 replicates of clean (unloaded) filters, used as controls. The controls show essentially no O₃ removal over the 18-hr test period, e.g., O₃ penetrations averaged $98 \pm 3\%$ and $103 \pm 3\%$ for the replicates.

Breakthrough curves for several conditions are shown in Fig. 6-3: three different DPM-loaded filters (samples S-115, S-116, S-117), the inorganic fraction of the DPM (sample I), and activated carbon (AC). For each condition, replicate samples were averaged. The times required for selected penetrations are shown in Table 6-2. As seen in Fig. 6-2, the DPM filters show rapid breakthrough, typically reaching near 100% penetration after 5 to 14 hr of O₃ exposure (mean of 9.7 ± 3.3 hr). As expected, the filter

with reduced mass load (75.9 μg , S-118) reached 100% penetration more rapidly (3.1 ± 1.5 hr). The sample collected during engine startup (S-114) also reached 100% penetration rapidly (2.2 ± 0.6 hr), probably due to its reduced mass load (82.8 μg) though possible differences in composition may have made a difference. The inorganic fraction of the DPM (Filter I) had much slower breakthrough than the unaltered DPM, requiring an average of 28 hr to reach 100% penetration, even though these samples had the lightest loadings (58 μg) of all filters tested. The AC filter efficiently removed all O_3 at the beginning of the experiment, and continued to remove about 29% at the end of the experiment (after 43 hr).

Over the exposure period, the soot samples collected under high speed conditions (D-115, 116, 117) removed an average of 5.6 ± 1.8 wt % of O_3 . Removals by DPM collected during startup (S-114) or reduced mass loads (S-118) were comparable, 4.4 and 5.9 wt %, respectively. In contrast, much more O_3 , 31.4 wt %, was removed by the inorganic fraction of the DPM (I), and still more, 38.3 wt %, by the AC (Table 6-3). For the AC, the removal capacity is underestimated as it includes only the O_3 removal reached by the conclusion of the experiment, which is only a fraction of the O_3 that can be removed by the AC had the experiment continued. Over the 63-hr experiment, the DPM removed only 14% of the O_3 removed by the AC, while the inorganic diesel sample removed 82%, nearly as much as that removed by the AC.

6.6.2 Organic fraction

The soluble organic fraction (SOF) of the DPM averaged $46 \pm 13\%$ by weight ($n = 23$). Other studies have found DPM SOFs ranging from 10 to 65% (Watson and Valberg, 2001 and references therein). The organic fraction did not appear to vary by engine load or start-up condition, though sample sizes were small and variability may

have obscured differences. In contrast, Fraser et al. (2002) tested DPM emissions from four different diesel vehicles (two tractor-trailer trucks, city bus, school bus) and found that ratios of elemental carbon to total carbon (EC/TC) increased considerably for three of the four vehicles under load compared to idle conditions; average EC/TC ratios under idle conditions were 0.16 ± 0.05 , while EC/TC ratios ranged from 0.18 to 0.94 under load. We identified in the organic fraction extract, among other compounds, acenaphthylene, acenaphthene, anthracene, fluoranthene, fluorene, naphthalene, phenanthrene, pyrene and the following group of carcinogenic PAHs: benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, and dibenz[a,h]anthracene. Fraser et al. (2002) identified 36 different compounds from the four different diesel vehicles discussed above including 14 n-alkanes, 9 petroleum biomarkers, 2 oxygenated PAHs, and 11 PAHs.

6.6.3 Testing of chemisorption models

Fig. 6-4 shows chemisorption of O_3 on three AC samples (S-115, S-116, S-117) plotted using the pseudo-first order model. Since q_e was known, it was not necessary to solve by trial-and-error. A linear fit ($R^2 > 0.99$) was achieved only for about the first hour of ozonation, after which the plot became curvilinear, suggesting other kinetic processes. Pseudo-first order rate constants, k_1 , estimated over the first 1.5 hr of exposure, were 0.41, 0.13, and 0.35 hr^{-1} for samples S-115, S-116, and S-117, respectively. O_3 chemisorption of one of the DPM samples (S-115) appeared to fit the pseudo-second order model ($R^2 > 0.999$, Fig. 6-5) and regression estimates of q_e , 3.5 wt %, closely agreed with the experimentally measured value (3.4 wt %). However, the other two DPM samples (S-116 and S-117) did not fit this model (Fig. 6-5). Other than experimental variability, it is unclear why sample S-115 behaved differently than the

other two samples. Samples S-115 and S-116 were collected on the same day under identical engine conditions, and these samples were analyzed simultaneously (S-117 was collected and analyzed on a different day). Overall, the pseudo-second order model does not appear to fit the experimental results.

The fit of the three DPM samples to the Elovich equation is shown in Fig. 6-6. Although this equation provided a very high fit ($R^2 > 0.99$) for all replicates, some deviation from linearity was noted, especially during early exposure times. Table 6-4 shows a summary of the absorption constants (k , a , and b), R^2 values, and measured initial rates obtained for all replicates of samples S-115, S-116, and S-117. The averaged values of k , a , and b were 1.9 ± 1.4 hr, 1.6 ± 1.1 wt % hr^{-1} , and 0.66 ± 0.30 wt % $^{-1}$, respectively. The average initial rate was 1.4 ± 0.2 wt % hr^{-1} , which was likely underestimated due to limitations of the O_3 exposure measurement system (i.e., measurements taken in 16 min increments).

The Ritchie equation provided a very high fit ($R^2 > 0.99$) for all replicates (Fig. 6-7). Predicted values of q_e and k , calculated from regression coefficients, are summarized in Table 6-5, along with measured values of q_e for comparison. The average predicted value of q_e was 5.3 ± 1.3 wt %, in close agreement with the measured value of $5.6 \pm 1.8\%$. The average predicted k was 0.28 ± 0.08 wt % $^{-1}$ hr^{-1} . Considering individual samples, better agreement was obtained between predicted and measured values of S-115 and S-117 (within 7%) compared to S-116 (within 16-18%). The S-116 replicates also had higher measured O_3 uptakes compared to the other DPM samples.

Of the four chemisorption models tested, the Ritchie model provided the best fit. Sample S-116 showed some differences from the other two samples, though it was

collected and analyzed under identical experimental conditions. As mentioned, O_3 removal by DPM is not thoroughly understood and likely consists of multiple kinetic processes. Also, because of the heterogeneous nature of DPM, other surface interactions other than simple chemisorption may occur. As such, it is difficult to describe the entire range of O_3 uptake data using simple chemisorption models. In particular, the pseudo-first order and pseudo-second order models fail due to the assumption of a single kinetic order. The Elovich equation, which has wide applicability to sorbate/sorbent systems exhibiting slow chemisorption (Low, 1960), also did not fit the entire data range well using a single set of parameter values, also suggesting the complexity of the O_3 uptake process.

6.7 Discussion

6.7.1 O_3 removal mechanisms

O_3 removal on DPM is complex and likely dependent on factors that include particle characteristics, e.g., presence and composition of surface complexes, functional groups, active metals, and particle surface area; particle bed characteristics, e.g., depth and coverage; and the flow regime, e.g., O_3 concentration, face velocity, temperature and RH. While this study was not intended to identify or confirm specific removal mechanisms, it is interesting to note that the removal of the organic fraction of the DPM greatly increased (by 18 times) the O_3 removal capacity. Removing the organic fraction may have freed up additional graphitic surfaces, thus increasing O_3 removal by chemisorption and/or other mechanisms.

No significant differences between O₃ removal capacities for DPM collected in high speed/low load and startup conditions were seen, though only preliminary tests were run in the latter condition. Increased engine load may affect particle size distribution and particle structure, e.g., Virtanen et al. (2004) found that an increase in diesel engine load changed the shape of the soot particle size distribution and decreased the particles' fractal dimension. In contrast, Braun et al. (2004) did not find differences in aggregate particle size between diesel fuel soot samples collected under idle and load conditions, although oxygenated diesel samples did differ significantly.

6.7.2 Comparison of studies

Lelièvre et al. (2004) suggested that the number of O₃ molecules taken on soot equals the number of O₃-active sites on the soot's surface, assuming the reaction is non-catalytic and one O₃ molecule is lost per active site. Using these assumptions and soot saturation data, O₃ uptake on toluene and kerosene soot was calculated as 1.2×10^{18} and 1.1×10^{18} sites mg⁻¹, respectively. Applying these assumptions to our DPM O₃ uptake measurements, an average value of $7.0 \pm 2.3 \times 10^{17}$ sites mg⁻¹ is obtained for the three DPM samples, a similar value. Lelièvre et al. (2004) also expressed O₃ uptake in terms of BET surface area, obtaining 7×10^{14} and 9×10^{14} sites cm⁻² for toluene and kerosene soot, respectively. These values are comparable to estimates by Kamm et al. (1999) and Pöschl (2001) for spark-discharge soot, 5.6×10^{14} and 6.5×10^{14} sites cm⁻², respectively. Using a specific surface area estimate of 60 to 150 m² g⁻¹ for fuel combustion soots (Chughtai et al., 2002), 4.6×10^{14} to 1.1×10^{15} sites cm⁻² was calculated for the DPM samples in this study, again comparable to the other soot studies.

6.7.3 *O₃ removal by diesel particulate in ambient air*

To provide a preliminary estimate of the significance of ambient O₃ removal by diesel particulate, several strong assumptions were made, foremost of which is that that laboratory-determined O₃ removal capacity of 5.6 wt % applies to DPM in ambient air. The amount of DPM in urban air is site-specific, but 1 to 5 µg m⁻³ is a reasonable range; here the upper value was used. The test O₃ concentration of 100 ppb (196 µg m⁻³), which is above the 8-hr standard (80 ppb) that is commonly experienced in a number of O₃ non-attainment areas, is used. Finally, it was assumed that the atmospheric lifetime of O₃ and DPM is similar, in which case the 5 µg m⁻³ of DPM comes into contact with 196 µg m⁻³ of O₃. With these assumptions, DPM has the capability to lower O₃ concentration by 0.28 µg m⁻³, equivalent to 0.15 ppb or 0.15% of the initial O₃ concentration. Effects will be small even if the soot lifetime is 10 times greater than that of O₃. These small values suggest that anticipated decreases in diesel PM due to upcoming emission limits will not cause an observable change in ambient O₃ concentrations.

As mentioned, extrapolating laboratory findings to field settings involves many strong assumptions. For example, very fresh and aged DPM have different size distributions, chemical characteristics, and likely varying O₃ removal potentials. When collected onto filters, the DPM characteristics may not be representative of DPM in urban air. For example, Bekki (1997) estimated that the specific surface area of atmospheric soot particles was 30 times greater than that measured in the laboratory. Smith and Chughtai (1996) found both different rates and rate laws for reactions of aged *n*-hexane soot with O₃ compared to fresh soot, in part attributed to the adsorption of molecular oxygen, a participant in the O₃-soot reaction. Soot particles from aircraft emissions may become immediately coated with a film of aqueous sulfuric acid, which is one possible

explanation for the negligible O₃ uptake values compared to fresh laboratory soot (Gao et al., 1998). Additionally, DPM in ambient air may affect UV intensity, be associated with other pollutants (especially NO_x) involved in O₃ chemistry, and its distribution and dispersion may differ significantly from that of O₃. Further work is necessary, possibly using chamber experiments, to investigate the role of DPM in O₃ scavenging.

6.7.4 Importance of O₃ removal by loaded air filters

DPM collected on a filter, such as those used in heating, ventilating and air conditioning systems or room air filters, is expected to remove some O₃ from air entering indoor spaces. The DPM loading on the filter will depend on the DPM concentration in air (C), volumetric flow rate (Q), and filter efficiency (E). To estimate the O₃ removal on a loaded air filters, the following were assumed: a high DPM concentration, $C = 10 \mu\text{g m}^{-3}$; O₃ concentration = 100 ppb; flow rate $Q = 0.94 \text{ m}^3 \text{ s}^{-1}$; and particle collection efficiency $E = 75\%$. Under these (constant) conditions, the filter will collect 17 g month^{-1} of DPM. Using the average O₃ removal capacity found, 5.6 wt %, $969 \text{ mg month}^{-1}$ of O₃ would be removed by the DPM on the filter, equivalent to only 0.2 wt % of the total O₃ mass passing through the filter. Therefore, it is unlikely that DPM (and possibly other PM) collected on air filters plays a significant role in O₃ removal under most conditions. Only in very contaminated environments would the PM loading on filters be high enough to remove significant amounts of O₃.

6.7.5 Limitations and experimental errors

While the experimental system proved precise and stable (once the desired O₃ concentration was achieved), several sources of error caused differences among replicates. The largest error sources were: variations in flow rates between the channels, which result in concentration errors when O₃ measurements are adjusted for dilutions in

each channel; potentially non-homogeneous distribution of DPM particles collected on filters, which resulted in different loadings on replicates; and approximate or incomplete capture of breakthrough curves due to limited time resolution of the O₃ measurements (especially at the beginning of some runs) and termination of the run before complete breakthrough was achieved.

6.8 Conclusion

In flow-through experiments, the O₃ removal capacity of fresh diesel soot particles collected on filters was found to be 5.6 wt %. The amount of O₃ removed depends on the filter loading, and more heavily loaded filters removed considerable more O₃. Of four chemisorption models tested, the Ritchie model provided the best fit to experimental data. Removing the organic portion (~ 46% of the total mass) from the diesel soot considerably increased the O₃ removal capacity of the remainder, perhaps due to additional surface area. However, the O₃ removal capacity of diesel soot is small, more than an order of magnitude below that of activated carbon. Estimates derived from lab data indicated that that diesel soot is expected to remove only a small portion of O₃ from urban/tropospheric and indoor air.

6.9 References

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Table 6-1. Summary of experimental conditions (AC = activated carbon, I = inorganic fraction only, DPM = diesel particulate matter).

	AC		DPM				
	Inorg. fraction	Start -up	High Speed/Low Load				
			1	2	3	4	
Filter designation	AC	I	S-114 ^a	S-115	S-116	S-117	S-118 ^a
Mass (µg)	94.7	56.9	82.8	135.7	140.0	140.8	75.9
O ₃ conc. (ppb)	94	113	85	166	166	108	118
Test duration (hr)	43	63	67	47	47	19	19
Exhaust DPM conc. (µg m ⁻³)	-	-	591	968	998	1004	1083
Number of replicates	4	4	4	3	2	4	3

^aReduced filter load (collection time = 20 min.).

Table 6-2. Breakthrough times (min) at given O₃ penetrations.

Sample Type	Replicate Number	O ₃ penetration fraction (%)									
		10	20	30	40	50	60	70	80	90	100
AC	1	189	477	685	877	1085	1709	2157	2541	-	-
	2	509	733	1037	1229	1373	2061	2525	-	-	-
	3	669	925	1085	1245	1469	1773	2397	2573	-	-
	4	493	813	877	1277	1581	2029	2509	-	-	-
I	1	-	9	*	*	41	25	57	201	137	1049
	2	9	*	*	*	25	41	153	121	537	1097
	3	-	-	5	*	21	37	101	133	485	1061
	4	-	-	-	-	21	53	149	133	837	3445
S-114	1	-	-	-	-	12	*	44	28	108	172
	2	-	6	*	*	*	22	*	54	70	214
	3	-	-	-	-	12	*	28	60	44	76
	4	-	-	-	-	-	-	7	39	23	55
S-115	1	-	-	-	11	*	*	27	59	139	299
	2	-	11	*	*	27	43	91	75	123	443
	3	-	-	10	*	*	26	58	90	122	618
S-116	1	-	-	-	8	*	40	24	88	152	680
	2	-	-	-	10	*	26	58	90	154	874
S-117	1	-	-	-	-	25	41	57	105	137	505
	2	-	-	-	23	39	55	103	167	199	359
	3	-	6	*	22	38	*	54	102	198	614
	4	-	-	-	21	53	69	101	181	357	837
S-118	1	-	-	14	*	*	30	142	46	94	206
	2	59	*	*	*	*	75	155	171	187	267
	3	-	-	-	10	74	26	122	42	106	90

* Could not be determined given 16 min resolution of system.

Table 6-3. Ozone removal capacity (wt %) for particulate samples.

Filter Sample	Replicate				Ave.	St. Dev.
	1	2	3	4		
AC*	33.9	39.4	39.8	40.0	38.3	2.9
I	27.1	30.8	30.2	37.6	31.4	4.4
S-114	2.5	4.8	3.7	6.6	4.4	1.7
S-115	3.6	5.7	6.8	-	5.4	1.6
S-116	8.4	7.8	-	-	8.1	0.4
S-117	3.7	4.8	3.8	5.8	4.5	1.0
S-118	3.1	8.9	5.6	-	5.9	2.9

*Breakthrough capacity at conclusion of test.

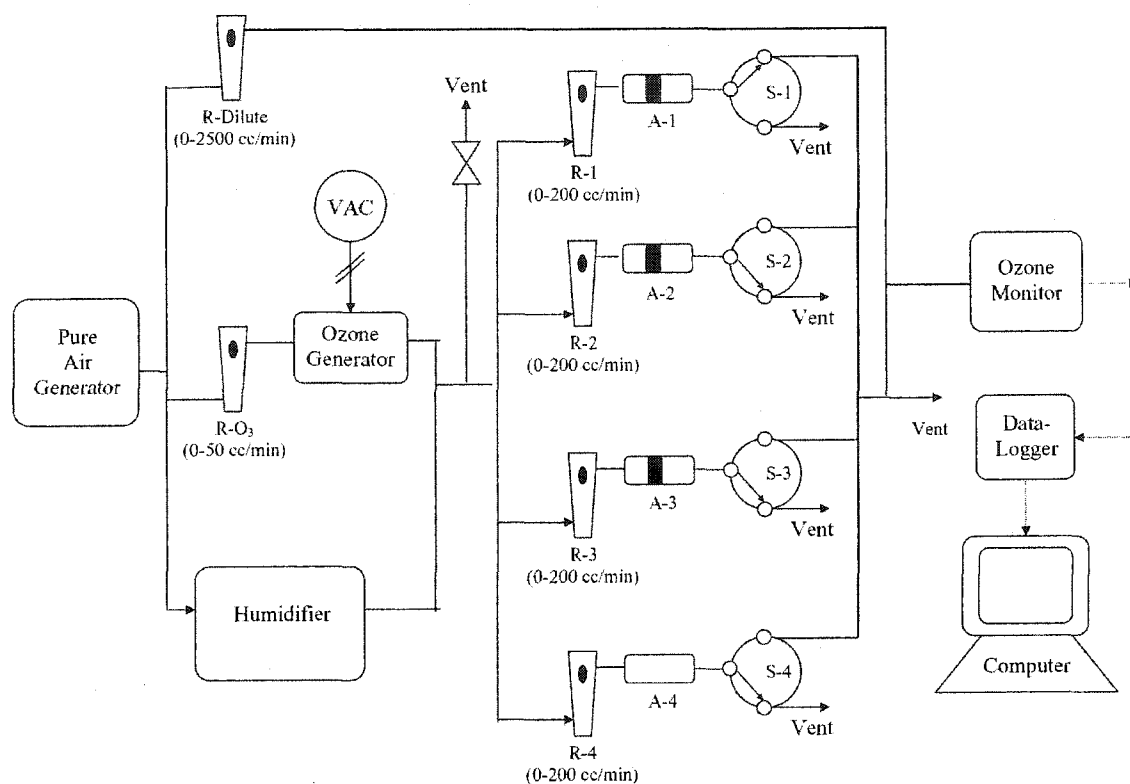
Table 6-4. Predicted time constants (k), initial sorption rates (a), adsorption constants (b), R^2 , and measured initial rates for O_3 removal on DPM using the Elovich equation.

Filter Sample	Replicate	k	a	b	R^2	Meas. Init. Rate
		(hr)	(wt % hr ⁻¹)	(wt % ⁻¹)		(wt % hr ⁻¹)
S-115	1	0.10	3.40	1.30	0.997	1.35
	2	0.21	3.74	0.85	0.999	1.83
	3	1.42	1.49	0.53	0.997	1.53
S-116	1	3.08	0.89	0.41	0.996	1.17
	2	2.34	0.99	0.49	0.996	1.16
S-117	1	1.13	1.30	0.84	0.992	1.33
	2	2.54	0.96	0.47	0.996	1.30
	3	1.61	0.98	0.70	0.997	1.07
	4	4.35	0.80	0.33	0.993	1.39

Table 6-5. Predicted O₃ removal capacities (q_e), rate constants (k), and R² for O₃ removal on DPM using the Ritchie equation. Measured O₃ removal capacities provided for comparison.

Filter Sample	Replicate Number	Ritchie Equation			R ²
		q _e measured (wt %)	q _e predicted (wt %)	k predicted (wt % ⁻¹ hr ⁻¹)	
S-115	1	3.6	3.8	0.39	0.998
	2	5.7	5.6	0.35	0.997
	3	6.8	6.3	0.25	0.995
S-116	1	8.4	7.1	0.17	0.996
	2	7.8	6.6	0.18	0.993
S-117	1	3.7	3.7	0.38	0.997
	2	4.8	4.9	0.27	0.999
	3	3.8	4.0	0.28	0.999
	4	5.8	5.4	0.26	0.999

Figure 6-1. Ozone exposure measurement system. Ports 5-8 omitted for simplification.



(R = flow rotameter, A = adsorption tube, S = solenoid valve)

Figure 6-2. Breakthrough curves for four DPM sample replicates (S-117) and two clean filter blanks.

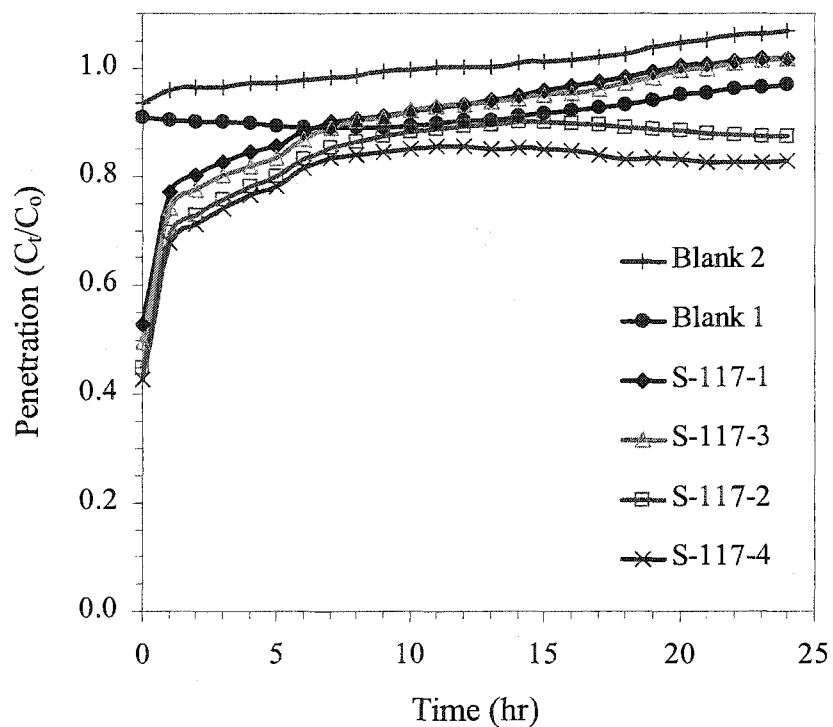


Figure 6-3. Breakthrough curves for three diesel particulate loaded filters, inorganic fraction (I), and activated carbon (AC) samples.

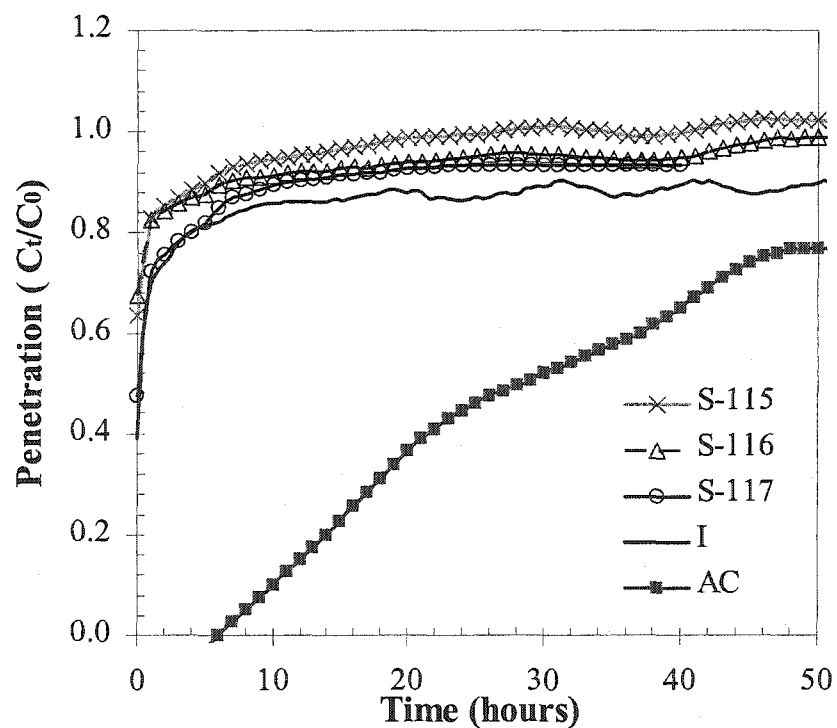


Figure 6-4. Chemisorption of O_3 on three DPM samples modeled using pseudo-first order kinetics.

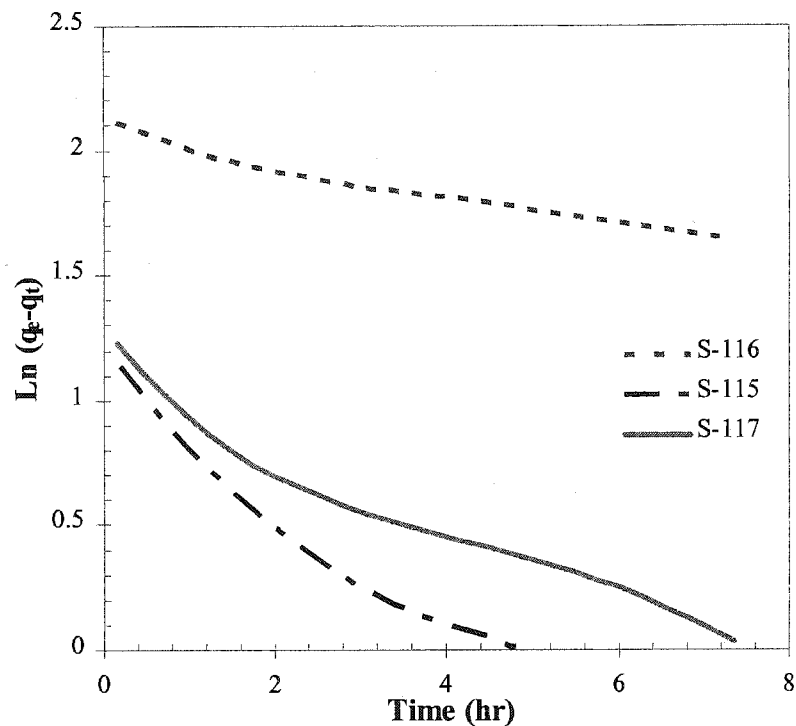


Figure 6-5. Chemisorption of O_3 on three DPM samples modeled using pseudo-second order kinetics.

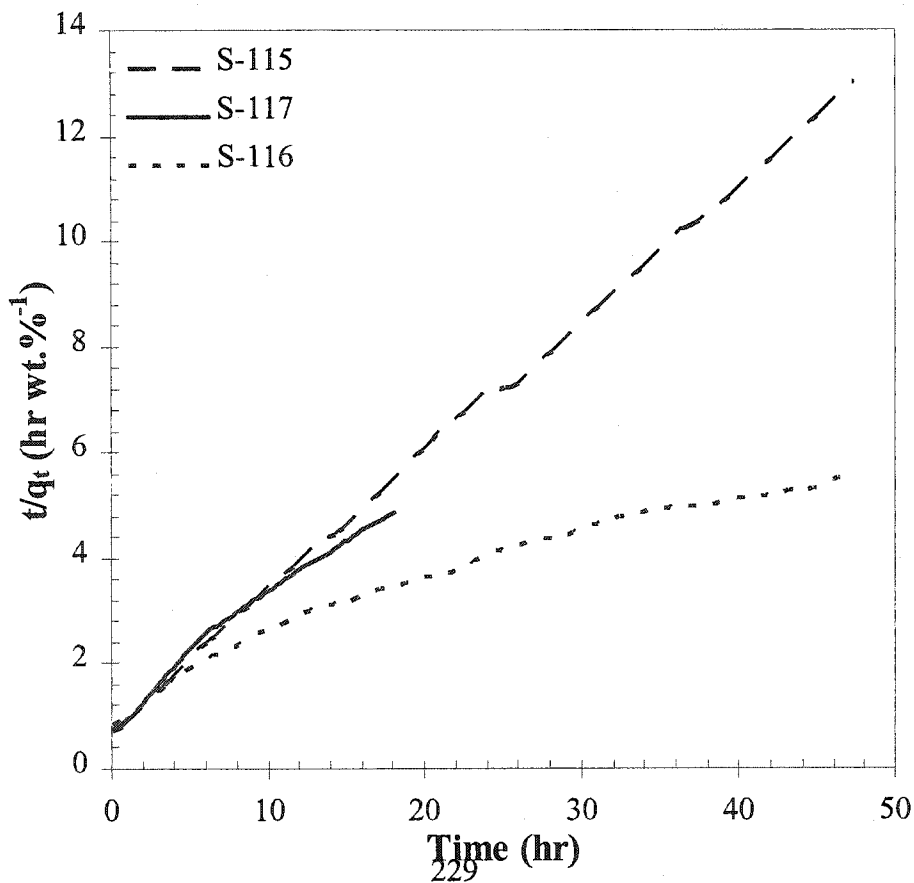


Figure 6-6. Chemisorption of O_3 on three DPM samples modeled using the Elovich equation.

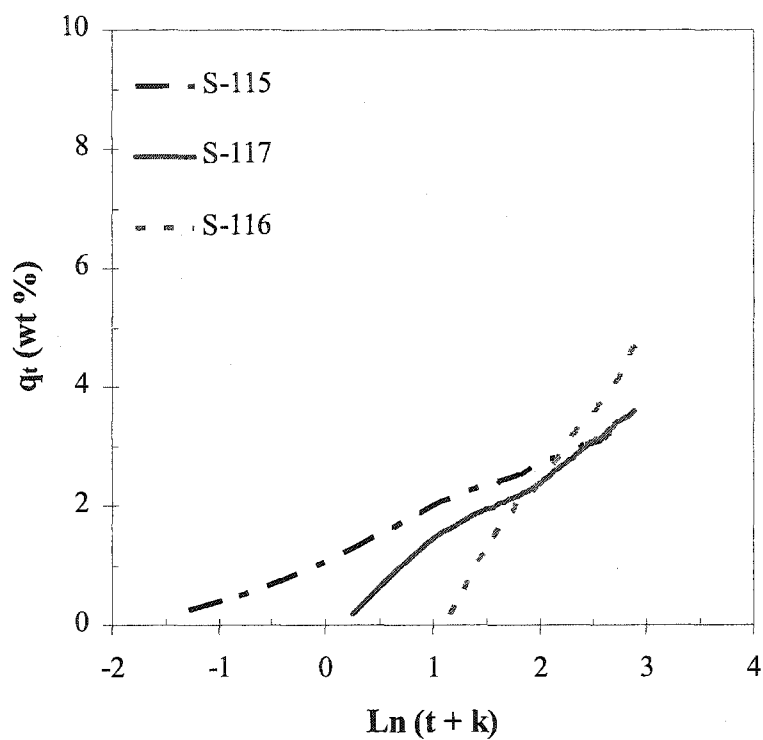
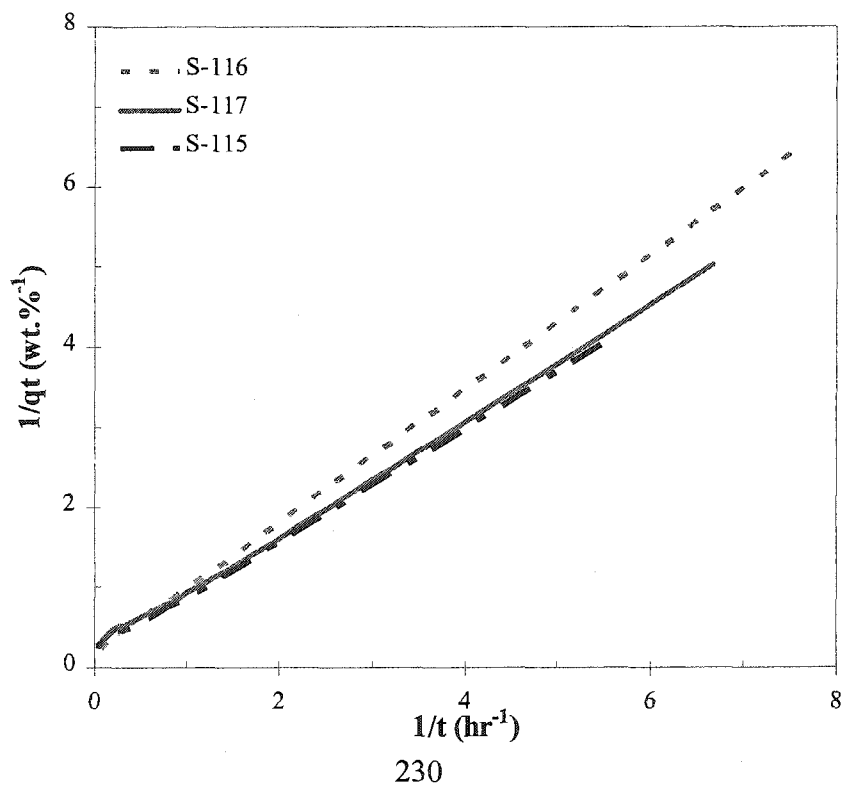


Figure 6-7. Chemisorption of O_3 on three DPM samples modeled using the Ritchie equation.



CHAPTER 7. CONCLUSION

This research explored O₃ uptake on carbonaceous materials, specifically activated carbon (AC) and diesel particulate matter (DPM or soot). It also explored the effects of preloading AC with VOCs (toluene and *d*-limonene) on O₃ removal efficiency and the formation of secondary reaction products. The following summarizes some of the key findings and implications resulting from this research, after which recommendations for further research are made.

7.1 Key findings and implications

7.1.1 Ozone breakthrough on activated carbon (Chapter 3)

Ozone-AC breakthrough tests can be expedited by using an AC-glass bead mixture that facilitates the use of extremely small amounts of AC. While the AC-bead mixtures showed slightly lower O₃ penetration fractions, likely due to greater uniformity of flows within the bed and not due to O₃ removal by the glass beads themselves, differences appear modest and not likely to change estimated model parameters or parameter trends.

The relationships between time to breakthrough, penetration fractions, bed depth, exposure time, and O₃ concentration were complex, making it difficult to develop a predictive model encompassing a wide range of exposure times. For example, O₃ penetration fractions at a given exposure time decrease linearly with AC bed depth at high O₃ concentrations and long exposure times, but curvilinear relationships are seen at

low O₃ concentrations or short exposure times. Rates of O₃ removal per unit mass of AC increase considerably at higher O₃ concentrations and shorter bed depths, but these rates do not scale linearly with bed depth or exposure time.

Elovich and Ritchie chemisorption models provided a reasonable fit to O₃ breakthrough at both low and high concentrations. These models require several parameters that are specific to bed depth and O₃ concentration, and possibly to other factors, e.g., flow velocity, humidity, temperature, soiling, and loadings of volatile organic compounds. The lack of a generalizable model means that O₃ removal on AC must be determined experimentally, and that results obtained at high O₃ concentration cannot be scaled to environmental conditions. Experimental data obtained in this study provides critical bed depths, removal capacities, and removal rates at both low (<200 ppb) and high (500 – 2000 ppb) O₃ concentrations, information useful for O₃ filtration applications.

7.1.2 Effects of VOC loadings (Chapter 4)

In typical indoor air filtration applications where a mixture of pollutants is encountered, AC becomes loaded with volatile organic compounds. While several studies have shown the effect of previous O₃ exposure on AC characteristics and VOC adsorption, the effect of VOC loadings on O₃ removal by AC has not been previously determined.

Experiments show that when loaded with toluene or limonene, two VOCs found at relatively high concentrations indoors, AC removed O₃ less efficiently than virgin (unloaded) AC. Exceptions may occur during early exposure times with reactive VOCs (limonene), which demonstrated equal or possibly enhanced removal, likely due to reaction of O₃ with readily available limonene (so-called pseudo-poisoning). AC loaded

with nonreactive VOCs (toluene) demonstrated more typical poisoning behavior. At later exposure times, however, differences between toluene- and limonene-loaded samples were small. In general, O₃ removal efficiency did not depend on the loading rate, although all of the tested loadings were fairly high (>28% of estimated sorption capacity). VOC loadings can greatly reduce O₃ breakthrough times, though reductions in O₃ removal capacities were modest (5 – 25%).

The effect of VOCs on the ability of AC filters to remove O₃ from indoor air is an important consideration in the design and placement of AC filters relative to VOC sources. In areas where O₃ co-exists with high VOC levels, filters with thicker bed depths should be considered or filters may have to be changed more frequently.

7.1.3 Homogeneous and heterogeneous formation of O₃-VOC products (Chapter 5)

O₃-VOC reactions form both particulate and gaseous products known or suspected to be irritating and thus of concern for indoor air quality. Homogeneous reaction experiments between O₃ and limonene showed the formation of formic acid, with an average molar yield of 37%, two gas-phase oxidation products, AMCH and limonene oxides, with molar yields of 3% each, and the production of a significant amount of small (<0.5 µm) particles. Heterogeneous reaction experiments involving the same reactants on activated carbon also showed AMCH, limonene oxides, and straight-chain aldehydes, all reaction products, as well as many unidentified peaks that were likely terpene impurities, e.g., other monoterpenes. Although O₃-limonene products were detected, most of the limonene remained unreacted on the AC samples even after long exposures to a stoichiometric excess of O₃. The bulk of reaction products remained on the AC, and few particles or VOC reaction products were measured in the effluent from

the AC bed. Thus, in addition to the known homogenous reactions, O₃-limonene reactions occur heterogeneously on AC filters.

While additional work is necessary to investigate certain pollutants (e.g., formaldehyde, ultrafine particles) and other environmental conditions (temperature, humidity, concentrations, etc.), results suggest that VOC-loaded AC air filters exposed to O₃ are not likely to emit significant amounts of secondary pollutants. However, further work is necessary to investigate secondary pollutants formed homogeneously by the desorption of VOCs from filters, which is enhanced by O₃ exposure.

7.1.4 O₃ removal by diesel particulate matter (Chapter 6)

Diesel particulate matter (DPM or “soot”) is a major carbonaceous component in ambient and sometimes in indoor air. DPM collects on air filters and thus O₃ might be removed fortuitously by DPM-loaded filters. Using flow-through experiments, the O₃ removal capacity of fresh diesel soot particles collected on filters was found to be 5.6 wt % at an O₃ concentration of 140 ppb. The amount of O₃ removed depends on the filter loading, and more heavily loaded filters removed considerably more O₃. Of the four chemisorption models tested, the Ritchie model provided the best fit to experimental data. Removing the organic portion (~46% of the total mass) from the diesel soot considerably increased the O₃ removal capacity of the remainder, likely due to additional surface area. However, the O₃ removal capacity of DPM is small, over an order of magnitude below that of activated carbon. Estimates derived from lab data indicate that that diesel soot is expected to remove only a small portion of O₃ from urban/tropospheric and indoor air. This appears to be the first study examining O₃ removal on actual DPM; previous studies were aimed at soots formed in the upper troposphere and lower stratosphere from jet exhaust.

7.2 Limitations and recommendations for further study

Although this research provides insight into O₃ removal by AC and DPM, additional research is needed to better understand the complex interactions between O₃, VOCs, and carbonaceous materials.

While this study contributed to a better understanding of O₃ removal by AC, additional information is needed to fully extend results to the testing of indoor air filters. Although the several chemisorption models (e.g., Elovich equation) appeared to fit the experimental data, long-term tests are needed to avoid excessive extrapolation, i.e., how long must a filter be tested in order to reasonably predict a given O₃ penetration fraction? In addition, experiments here employed a small set of conditions (humidity, bed dimensions, temperature). Further experiments using O₃ concentrations typical of indoor air (50 – 100 ppb) and varying other conditions should be conducted.

This study provides insight regarding the interactions of limonene and toluene adsorbed on AC and how O₃ removal efficiency is affected, however, additional factors should be considered to apply findings to indoor air filtration. Although the two VOCs tested were common indoor air contaminants and represented a wide range of O₃ reactivities, other VOCs should be tested to see if similar results are obtained. In addition, tests should be conducted with lower and potentially more realistic indoor O₃ concentrations (50-100 ppb). Other variables may also influence the manner VOCs affect O₃ removal, e.g., humidity, VOC concentration, temperature, AC type, bed dimensions, flow rate, other contaminants. Finally, in this study VOCs were loaded onto AC prior to O₃ exposure, which may not reflect actual (dynamic) conditions.

Findings on O₃-limonene reactions and the extent of product formation both homogeneously and heterogeneously were conducted in a laboratory setting. Again, additional factors should be considered to apply findings to IAQ filtration and other applications. Tests should be conducted with realistic indoor O₃ concentrations (~100 ppb). Evaluations should address other variables that may influence results, e.g., humidity, intermittent O₃ exposure, limonene concentration, temperature, AC type, bed dimensions, flow rate, other contaminants. Another limitation of this study is that VOCs were preloaded onto AC prior to O₃ exposure, which does not realistically reflect dynamic VOC filtration conditions. The possibility that O₃ increases desorption of adsorbed VOCs should also be explored. Ideally, tests would identify a broader range of oxidation products, especially low molecular weight carbonyls, and employ instrumentation capable of detecting much smaller particles.

While the experimental system used in the DPM experiments proved precise and stable (once the desired O₃ concentration was achieved), several sources of error caused differences among replicates. The largest error sources were: variations in flow rates between the channels, which result in concentration errors when O₃ measurements were adjusted for dilutions in each channel; potentially non-homogeneous distribution of DPM particles collected on filters, which resulted in different loadings on replicates; and approximate or incomplete capture of breakthrough curves due to limited time resolution of the O₃ measurements (especially at the beginning of some runs) and termination of the run before complete breakthrough was achieved.