# UNDERSTANDING THE GREAT INDOORS: A REVIEW ON CHEMICAL AND PHYSICAL TRANSFORMATIONS THAT OCCUR IN INDOOR ENVIRONMENTS

by

YOHANNA JENICE B. WHITE

(Under the Direction of Geoffrey Smith)

## ABSTRACT

Many of the reaction mechanisms that occur outdoors, such as radical chemistry, photolysis, and interfacial chemistry, also frequently occur in an indoor atmosphere. Though they share similar chemical processes, they are far from identical. Unlike the outdoors, pollutants accumulate indoors due to poor ventilation. They may also be transported through air exchange with outdoor ambient air. Although 90% of a human's life is spent indoors, few regulations exist to control critical levels of hazardous compounds. Thus, understanding the chemical processes that form hazardous emissions will help us promote better indoor air quality. This review will approach the study of air pollutants from the perspective of the indoor environment. We will explore how common indoor environmental conditions and physicochemical properties transform the indoor domain into a world that is radically different from chemical compositions that make up the outdoor atmosphere.

INDEX WORDS: indoor chemistry, ambient air, gas, particle, equilibrium, partitioning, SVOCs, oxidation, surface chemistry, atmosphere

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The University of Georgia
May 2020

# DEDICATION

To my parents

# ACKNOWLEDGEMENTS

I am here today because of the tremendous support that I have received from my family, friends, professors, and community. I would first like to acknowledge the people who have supported my academic transformation, from pre-school to graduate school. I would especially like to thank Mrs. Miya, who helped me process my feelings at an early age when my best friend moved, to Mr. Sanchez; though I was not in your class, thanks for teaching me good citizenship by picking up trash (even if we were rewarded with air heads candy). To Ms. Bell, who was an excellent and strict teacher, who taught the class not only reading and math, but also table manners and generally good manners. I am amazed by how you kept our fourth grade class obedient and engaged without raising your voice. To Mrs. Coffey, who taught eighth grade history in an unconventional way that I enjoyed. I can even still remember some of the history lessons. To Mr. Ireland, who also taught eighth grade science in an unconventional way. Though we had some classic science projects like making paper-mached volcanoes and blew them up with baking soda and vinegar, you also took us on orienteering adventures. You claimed that you were teaching us vital life skills by learning to read the Thomas Guide (maps of California that were popular in the 90's) and by learning to use a compass. Yes, these have been vital life skills for me. I use them all the time when I go backpacking. To Ms. McNulty who made calculus fun and engaging. I especially appreciated the encouraging "Great job!" comments on bad test exams, and reassured us that we were all doing great. It was a good introduction to what undergraduate education would be like. To Mr. Smith, who made chemistry fun and exciting, and is the reason why I decided to study chemistry. Thank you for staying many days before the

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# CHAPTER 1

# ATMOSPHERIC CHEMISTRY 101

## *1.1 Introduction*

Atmospheric chemistry has historically been synonymous with outdoor chemistry. Atmospheric emissions from industrial processes, vehicular exhaust, vegetation are just a few examples of outdoor pollutant sources. As a result of our thriving worldly population and of our increased reliance on manufacturing products since the industrial revolution, poor air quality has caused mass tragic deaths. Donora, Pennsylvania in 1948 had 14,000 residents suffering from severe respiratory problems that led to nearly 40 deaths over a period of five days. In 1952, London experienced a similar tragedy and was coined as the Great Smog of London. The impact of air pollution was detrimental; it had caused almost 4,000 deaths over a period of five days. The culprit of the two events were the accumulated air pollutants that had reached critical amounts.

Regulation of air pollutants has made humans recognize that most global environmental challenges are influenced by human activities. Realizing the destructible nature of CFCs released into the atmosphere is one example that demonstrates how knowledge of an underlying cause of a problem has instigated the development of responsible policies to protect humanity and the environment from harm.

Although 90% of a human's life is spent indoors, many existing pollutants have yet to be studied for its implications on human health. Many have experienced sick building syndrome (SBS), a common unpleasant experience people feel indoors, which is a direct effect of poor air quality. Air quality is aggravated by poor ventilation and by the diverse classes of organic aerosols (OA) present. Thus, protecting indoor air quality is equally as important as outdoor (atmospheric) air quality.

This review will commence with a brief overview on important atmospheric chemistry topics that are relevant to our understanding of indoor processes. In this review, we will explore current knowledge on indoor chemistry, determine the gaps in our understanding, and speculate how working towards comprehension will allow us to assess potential inter-relationships between different chemical and physical processes. We aim to understand how chemical and environmental conditions synergistically influence chemical dynamics in the great indoors.

### *1.2 Aerosol Chemistry*

Aerosols and their changing properties are largely influenced by their atmospheric conditions. Aerosols are a cluster of fine solid or liquid particulates that are suspended in a gas, and in our case, suspended in air. Aerosols are emitted through biomass burning, combustion, sea spray mist, and living organisms such as bacteria. Important types of aerosols found in the atmosphere include black carbon (BC), organic aerosols (OA) which includes volatile organic compounds (VOCs) with varying volatility properties.

Aerosols come in a wide distribution of sizes, shapes, and chemical heterogeneity. Their size distribution spans over three orders of magnitude, which, for most instrumentation, are incapable of capturing the upper and lower limits simultaneously. They are continuously evolving with time, making their chemical and physical state transient. Characterization and classification are not trivial tasks. Oftentimes, physical and chemical properties are not enough to understand their impact on the climate, .which is one reason why many studies combine multiple data sets to acquire new information about their properties [1, 2 3, 4]. These properties are important to climate scientists for several reasons. One, their attributes may significantly alter their radiative forcing properties [5]. Both single particle and bulk aerosol measurements are critical to our understanding of their properties. There are many internal parameters that affect a particle's behavior, such as its hygroscopic ability, particle size, its mixing state, morphology, and optical properties. Understanding how such characteristics influence each other to alter optical properties will give a better understanding of how these particulates transform our environment. These properties require the atmospheric chemistry community to develop methods for probing these features.

The challenge of classifying aerosols lies in simplifying the complexity of aerosols. For example, a particle's mixing state was first described in 1973. Winkler et al. first noted the variability in chemical composition of aerosols [6], and described that aerosols can be classified to have an internal or external mixing-state. An internally mixed sample will contain homogeneous particles that have the exact same chemical composition across all particles. Externally mixed compositions will be composed of a mixture of heterogeneous particles, where the chemical composition may not be elementally the same. But as pointed out by several studies [7-9], classification by internal versus external are idealized assumptions, and that real aerosols lie in a spectrum within these two extremes. An aerosol can contain both internal and external particles, and can be coated heterogeneously [10-13] or homogeneous coatings [14]. Aerosols may be composed of inorganics and organics; many different organic matter such as simple alkanes and alkenes, carboxylic acids, aromatics, etc [15]. Nonetheless, their classification is transient because of their dynamic environment. Even the introduction of water may redistribute the gas-particle partitioning of semi-volatile organic compounds (SVOCs) or affect an aerosol's solubility. Such changes may influence their optical properties. To summarize the nature of aerosols, their ultimate influence on radiative forcing is sensitive to many different parameters. It is more likely that multiple factors result in a change of a property. The complexity of aerosol studies lies in pinpointing factors that cause a change. This is the goal of understanding both outdoor and indoor aerosols.

### *1.3 Aerosol Formation*

The size of an aerosol particle can range anywhere from the nm to the micrometer range in diameter. This large range of sizes impacts their physical properties. Ultrafine particles that are less than 10 nm may condense to form new particles by nucleation. Nucleation is a thermodynamically driven process through which aerosols form from gaseous nanoparticles[16]. In the atmosphere, the most common sources are usually from photo-oxidation processes such as the breakdown of VOCs to SVOCs, or the formation of sulfuric acid from sulfur dioxide, and ion clusters [17]. The volatility and surface area of the particle where the nanoparticles condense impacts the partitioning of the molecule to the gas or particle phase. Nanoparticles can either create new aerosols, or they may coagulate with existing aerosols, which is dictated by the concentration of nucleating species and the size of the emerging particle. During nucleation, nanoparticles will randomly aggregate and disassociate when large concentrations of the chemical species is available, allowing them to grow by condensation and forming secondary organic aerosols[18]. As they grow, less surface area is exposed, thus decreasing the vapor pressure of the particle. As nanoparticles grow by condensation, the energetic barrier to form new particles increases. The molar concentration available for nucleation also influences particle formation. As the chemical species is increased, the vapor pressure decreases, thereby inhibiting nucleation. The nanoparticles may also coagulate with other aerosols, which provides an alternate sink for the ultra-fine particulates. Due to diverse heterogeneous chemistry that can occur between the interface, there is much debate on how heterogeneous reaction kinetics activate growth [17, 19, 20]. However, it is known that organic acids do activate nucleation.[21-25] Sulfuric acid is an example of a common agent for nucleation due to its low volatility and the presence of high concentrations of organic acids in the atmosphere [21, 26].

As the aerosol continues to grow in size, particles may also change in size and characteristics with aging due to winds, diffusion, and the condensation of organic compounds. Gas-particle partitioning between the aerosol surface and will occur, and an aerosol's fate in partitioning will depend on its volatility. A traveling aerosol will no doubt experience changes in relative humidity (RH). RH greater than 100% will encourage further cloud formation, but they will eventually be removed by wet deposition. If the RH is oscillating between high and low, then a particle may continuously transition between wetting (condensation) and drying (evaporation) conditions. This process often leaves residues that coat the particle. The process of condensation and evaporation is described as the accumulation mode for particles within the 100 - 2000 nm range. Larger particles belong in the coarse mode and are usually primary sources that have physically degraded. Such particles may include salt, dust, and pollen.

The introduction of water to a particle creates an aqueous environment that may redistribute the gas-particle partitioning of semi-volatile organic compounds (SVOCs). Aerosols may also change by interacting with organic vapors such as with sulfuric acid, amines, and nitrates. A high concentration of these vapors will induce condensation and adhere to the surface of a particle. If other gases are present, gas phase chemical reactions with organic vapors may also occur and condense onto the particle. This process allows for gas-particle partitioning, where thermodynamics can also influence the state of the particle. Aerosols may be in any of these modes throughout their chemical aging. These processes demonstrate the possible fates of aerosols and the chemical influences on the particle through its journey.

# CHAPTER 2

# UNIQUE FEATURES OF THE INDOOR ENVIRONMENT

## *2.1 Physical Features*

The indoor and outdoor environments share similar reaction mechanisms. One reason is because similar compounds are found in both environments. VOCs, tropospheric ozone ($O_3$), $NO_x$, and $HO_x$ are still major players in driving indoor air composition and air quality. Gas-phase reactions, multi-phase chemistry, photolysis, and oxidation occurs indoors. There are, however, many differences in how indoor species evolve due to differences in sources and sinks, initial concentrations, and due to conditions unique to the indoors. Indoor air is less regulated than outdoor air. The U.S. Environmental Protection Agency (EPA) monitors and regulates the concentration of particulates below 2.5 µm, more commonly known as particulate matter ($PM_{2.5}$) because they are known to be harmful to human health. Previous studies have shown that these particulates infiltrate the indoors, but, the interior atmosphere does not have restrictive regulations for particles like the outdoors. This is unfortunate because people spend 90% of their time indoors, which potentially exposes people to harmful chemical concentrations. Understanding the dynamics of the indoor environment may lead to similar policies that improve indoor air quality.

The physical features of indoor environments play a big role in the chemical processes that occur. Buildings and homes are confined, and floor plans differ between apartment homes, single-family homes, large ranch style homes, and public spaces affect diffusion and chemical concentrations. Databases provide a snapshot of variations on chemical composition in residential homes. The Relationship Between Indoor, Outdoor and Personal Air (RIOPA) was a comprehensive study that monitored VOCs, carbonyls, and fine particulates near an emission source to determine how outdoor air toxins influenced indoor air quality [27]. Many parameters were documented such as information on air exchange, relative humidity, and distance from the toxin site. This database is an effective resource for chemical modelers and experimentalists alike. Information from databases manifests degree of commonalities between homes, even when homes are dissimilar across the U.S. Databases allow chamber studies, reference homes, and computational models such as chemical transport to be designed with some realism.

The interior atmosphere is far from being self-contained. Outdoor chemical species permeate through building materials and wall barriers, thereby influencing indoor air composition [28]. As a result of outdoor air transport, studies often compare and contrast indoor air composition in different locations, such as conducting studies in both rural and urban areas. Moreover, attached homes like apartments and condominiums will have additional mass transport from their neighbors. The average lifetime of interior air is about one to two hours before the air is exchanged. Air exchange rate (AER) is a unique indoor feature that does not apply to outdoor conditions. It is important to compare a species' residence time with the AER, which may free the species even before the end of its lifetime. For example, $O_3$ reaction rates with other species are often very slow except with unsaturated compounds. Thus, $O_3$ will be removed by air exchange before it can react with other compounds. One caveat about AER is that it generally does not affect surface reactions. This implies that if $O_3$ was adsorbed instead of remaining in the gas phase, it will now be able to partake in slower reactions. AER also changes as a function of season; the average for the spring was found to be 0.74 +/- 0.24/hour and the average for the fall/winer was 0.65 +/- 0.36/hour. The average AER determined from studying about 3,000 residential homes around the U.S. show that the average AER inside the home is roughly 0.5 per hour, but with a a high standard deviation of 0.9 per hour [29]. The high standard deviation and sensitivity of chemical composition to AER is problematic for characterization.

Aside from opening windows and doors and transient movement by the indoor population, the indoor environment is relatively stable compared to the outdoors. Temperature and humidity conditions much more stable, and wet deposition happens at a smaller scale, and is for the most part limited to bathrooms and kitchens. Wet deposition is not a significant sink for species like the outdoors. Nevertheless, water is not insignificant indoors. In fact, water has a greater role in aqueous chemical processes, which affect solubilities and influence gas-particle partitioning, and other processes such as acid-base reactions are becoming more prominent areas of study. Water is involved in almost every reaction whether it be the reactant, the matrix, or act as the solvent. On surfaces, adsorbed water may facilitate acid-base chemistry and change the adsorbing properties of the substrate material. $CO_2$ and $NH_3$ will be readily dissolved, thus changing the pH of the film. A change of pH may offset equilibrium and control the concentrations of the adsorbed and desorbed compounds.

Most gas-particle partitioning occurs on aerosol surfaces in the outdoor atmospheric conditions. Indoor environments are markedly different in this respect, due to the much larger surface area to volume ratio (S/V), which has an average ratio of at least 3 $m^{-1}$ . To put this vastness in perspective, outdoor S/V are estimated to be $10^{-3}$ $m^{-1}$ to $10^{-2}$ $m^{-1}$ [30]. Most species will settle on surfaces, in addition to particle surfaces. Interfacial chemistry plays a huge role in indoor processes. They act as reservoirs of chemical compounds, and the interaction between the surface and air impact the chemical partitioning of semi-volatile organic compounds (SVOCs). As a general trend observed, the reaction uptake of compounds will be faster on cleaner surfaces than dirty surfaces. On soiled surfaces, the surface characteristics is less influential on chemical uptake and different material types will have similar uptake rates. Morrison et al.’s findings showed no distinction between partition coefficient (K) values for clean and soiled clothing for the uptake of methamphetamine [31]. This demonstrates that surface films have an aging effect.

Photolysis still occurs indoors but is limited by the amount of light penetration through windows. For natural light transmission, a location in a room will experience light in varying degrees of intensity depending on its distance relative to a window source. Intensity drops significantly with distance [32]. Indoor lights expend much less photon fluxes than natural light and offer little UV light[33] , but weakened photolysis is a common chemical process that occurs indoors as well. One study demonstrates that the type of lightbulbs (flourescent, incandescent, LEDs, etc) affect photolysis reactions[34]. Figure 2.1.1 demonstrates the light intensity of different light systems and the absorption cross sections of a few chemical species. These figures are interesting to compare the ranges at which certain species can absorb, and relate it to the actinic flux in that wavelength region. The spectra demonstrate that some species are decomposed in artificial light. Nitrous acid (HONO) is shown to be broadly absorbing over a wide wavelength range and is an important source of OH. Figure 2.1.1 shows that although weak, some photon flux is available. HONO is the most studied because it absorbs broadly in the 300-400 nm range. $O_3$ is not photolyzed indoors, but $NO_2$ may be photolyzed when near sunlight. Photolysis creates chemical heterogeneity indoors, and chemical compositions are spatially localized. This is because actinic flux decreases exponentially as a function of distance. It is not uncommon for there to be a high concentration of reactive species near a window, but nearly zero even as little as 3 feet away before it begins to diffuse. Consequently, different rooms in a home will have different chemical compositions. Figure2.1.2 shows how light transmission varies per room and emphasizes the clear distinction between atmospheric radiation and radiation transmitted through windows. The amount of photolysis is spatially dependent both indoors and outdoors. Rooms facing the window will have higher photon fluxes, and even a distance of a few feet away from the windows depletes the amount of flux available for reactions. Even light sources such as light-emitting diodes (LEDs), fluorescent, and incandescent lights have varying photon fluxes as shown in Figure2.1.1 [32, 35, 36]. Thus, homes are further diversified in chemical composition depending on preferred light sources.

This will create great heterogeneity indoors—even within the same room. Moreover, photolysis is also geographically dependent and is affected by typical weather patterns of a region. However, even homes within a neighborhood may be exposed to differing amounts of photon fluxes that may vary due to window positioning relative to the sun.

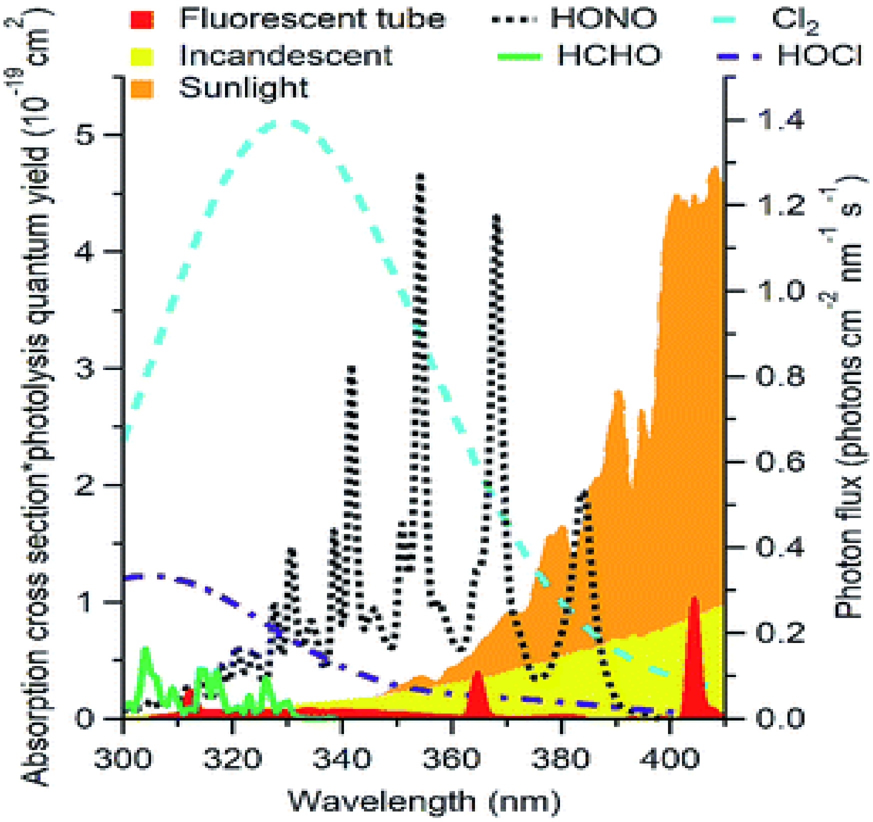


Figure 2.1.1. Comparing the photon flux of the sun with common indoor light sources. The absorption cross sections of a few key species are that are known to absorb in this region is also depicted. Figure reproduced from Young et al. [34].

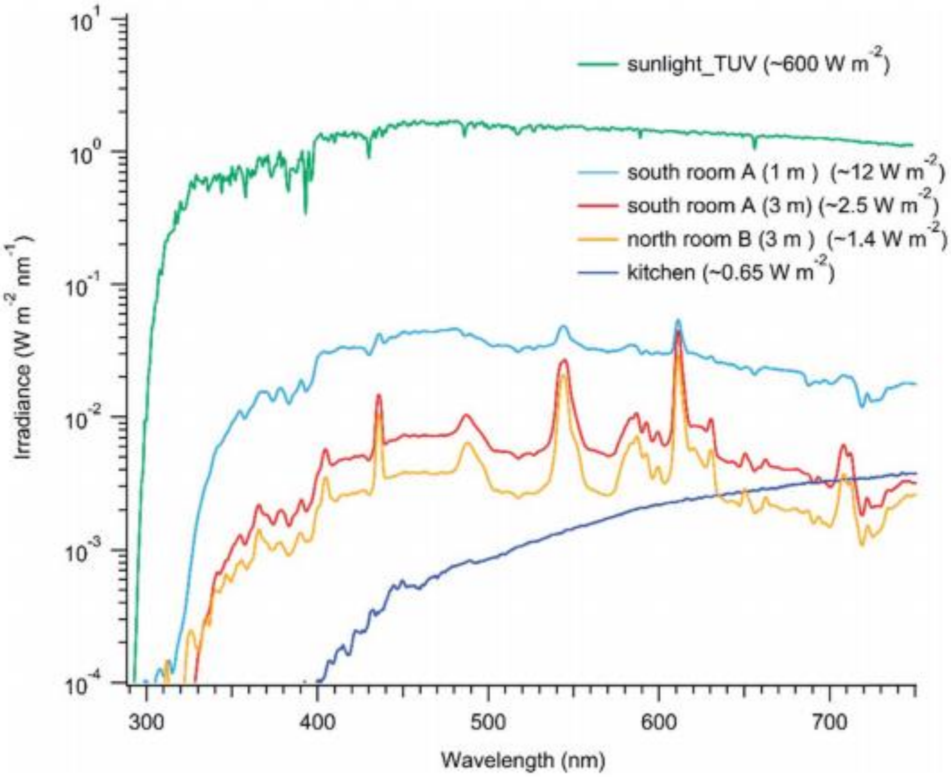


Figure 2.1.2. Displaying the varied light attenuation that occurs in indoor environments. Two measurements were made for room A at two different distances from a window. Room B's irradiance was measured at 4pm with a 3 m distance from the window. Reproduced from Abbatt et al. [30].

Outdoor air penetration through building materials will influence the types of processes that occur indoors. The transported $O_3$ mixing ratios, for example, may be different in suburban vs. urban environments, which will thus influence the chemical balance within. Other sources of air pollutants are from cooking, cleaning, and household synthetic products heavily impacts indoor air quality. Humans and animals also emit sources, and hence population is another factor to consider. Almost everything inside the home emits VOCs, such as furniture, carpets, and wall coatings [37]. In fact, VOC concentrations and diversity may be much higher than the troposphere [38]. Numerous synthetic emissions (such as hairspray, air fresheners, etc.), exacerbate the VOC concentration and lead to a wider range of secondary organic aerosols (SOA). Even materials such as vinyls, wood, and carpets release formaldehyde. Surface reactions with $NO_2$ and $O_3$ also ultimately end with oxidized VOCs. VOCs are difficult to classify due to their functional diversity and low-barrier chemical reactions that it can participate in. The release of both natural and synthetic compounds indoors and its containment inside further diversifies chemical species. There is much more diversity of organic compounds indoors compared to the troposphere, making the study of indoor chemistry inherently complex

Homes have an average surface area to volume ratio (S/V) of 3 $m^{-1}$. This is much more pronounced than S/V ratios of the tropospheric boundary layer, which may have values between $10^{-3}$ to $10^{-2}$ $m^{-1}$. Surface chemistry is an integral part of understanding the indoors, which will will be discussed in further detail in Chapter 4. High S/V ratios are one of the most influential factors that sets the indoor environment apart from the outdoor atmosphere. Surfaces, such as tables, countertops, etc. are often coated with organic films, and sometimes acting as permanent reservoirs of compounds. Surfaces will also have their own physical properties (such as their texture, thickness of film coating, etc.) that influence reaction uptakes.

### *2.2 Role of Databases*

Most research on indoor environments are examined through chamber studies, building model homes that simulate typical household conditions, and computation modeling. These types of observational require experimental measurements in the real household environment in order to achieve accurate model results. The Relationship of Indoor, Outdoor and Personal Air (RIOPA) is often consulted in simulation studies. The goal of this study was to understand the direct effect of outdoor pollutants to indoor populations. More specifically, it aimed to identify VOCs and PM 2.5 found indoors that originated from outdoor pollution sources. RIOPA is a compilation of information about indoor air quality in real residences, which provides baseline measurements for typical environmental factors within the home and outside the home. Concentrations of outdoor pollutants and AER between outdoor and indoor environments were important metrics, and the relationship between the two can help predict indoor concentrations. Measurements of VOCs, PM 2.5, AER, RH, occupancy within a home, and other factors. These studies were conducted in New Jersey, Texas, and California, with a sample size of 100 non-smoking residences in each state with seasonal measurements in each. An interesting addition to this study was the use of personal air monitoring devices, which were passive samplers worn by residents to measure the VOCs of ambient air within their breathing radius.

Many studies have taken advantage of the RIOPA study and other similar databases. Many questions can be posed and answered through analyzing data sets. For example, a study was conducted to compare AER between homes, and to determine whether geographical location had any effects on AER. The intent of this study was to provide parameters to chemical exposure modeling [39].

Databases are crucial for the progress of indoor air science. For example, Hodas et al. utilizes RIOPA data to improve chemical transport models that involve outdoor air infiltration [40]. Many models and studies make the assumption that the concentrations of indoor and outdoor $PM_{2.5}$ are interchangeable, but there are many factors that affect air penetration. The building's material and structure, weather conditions, outdoor and indoor temperatures have all been shown to affect infiltration [41-44]. By taking these factors into consideration, the RIOPA database was utilized to obtain reference measurements of air exchange rates (AER), meteorological conditions, and other housing characteristics aimed at improving the modeling of chemical transport between the outdoor and indoor air for inert particles. Improved models have the potential to influence regulatory policies by determining key species that penetrate through buildings.

The study's aim was to enhance a transport model by utilizing RIOPA data to parametrize the penetration of $PM_{2.5}$, which are obtain pollutant concentrations dictated by a species' production and loss rates. Hodas et al. developed a functional form to describe a pollutant's mass transport by assuming that changing indoor concentrations are motivated by the concentrations of entering and exiting particles. These models were compared to RIOPA measurements. Interestingly, the correlation between the measured and modeled cases varied depending on the type of aerosols studied.

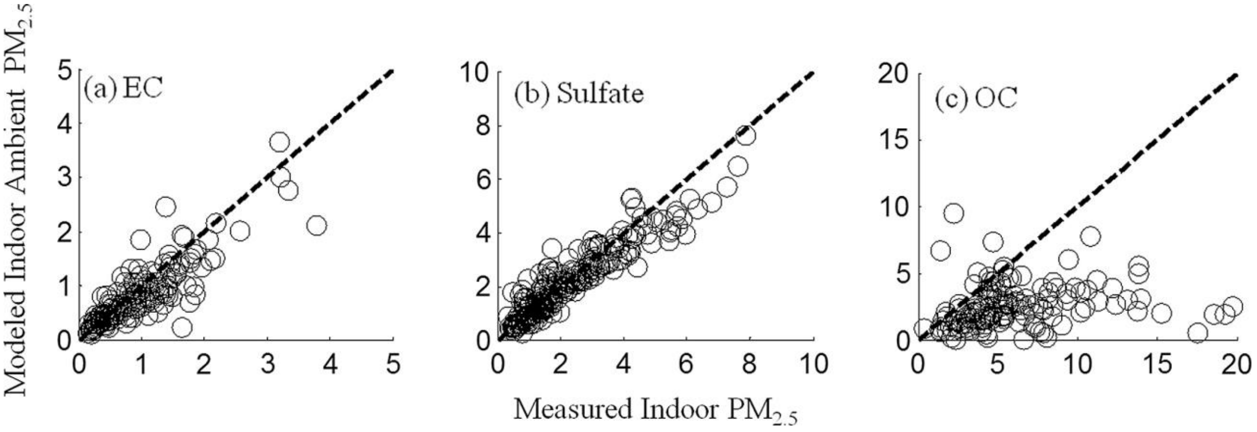


Figure 2.2.1. Comparison of $PM_{2.5}$ concentrations (µg $m^{-3}$) between RIOPA measurements and model results for (a) elemental carbon (EC), (b) sulfate, and (c) organic carbon (OC). The circles represent RIOPA measurements and the dashed lines are the 1:1 correlation line. Reproduced from Hodas et al.[40].

Figures 2.2.1a and 2.2.1b show that the modeled $PM_{2.5}$ concentrations for sulfate and EC correlate with RIOPA measurements. . Elemental carbon and sulfate show correlations between the modeled ambient air to the measured indoor air, but organic carbon largely deviates from a 1:1 correlation and underestimates concentrations. For all models, there tends to be more agreement for smaller concentrations relative to larger concentrations. EC and sulfates are also known to be dominantly exported through walls [43]. This study exemplifies the utility of such databases. This comparison between modeled and measured data demonstrates the vulnerability of computational methods that may result if parameterization is not carefully considered for different species types. RIOPA and other similar compilations of large data, are essential for creating accurate conditions both for physical and computational models.  Thus, databases are essential and many studies rely on RIOPA and other databases.

# CHAPTER 3

# INDOOR OXIDATION AND THEIR EFFECTS ON CHEMICAL COMPOSITION

## *3.1 Coupling behavior Between* $NO_x$ *and* $O_3$ *in Indoor Oxidation*

Although radical chemistry is less prevalent indoors due to weakened radiation, it is still a crucial mechanism that is responsible for many chemical compounds that worsen air quality. Many of the produced secondary products have the potential to affect chemical composition. For example, SVOCs may be created and will settle onto surfaces, possibly transforming into a permanent reservoir of chemical contaminants. Another fate of oxidized compounds is that they may be converted to radicals themselves, thereby propagating radical reactions. Products formed through oxidation often increase the number density of $PM_{2.5}$.

$O_3$ is primarily sourced from the outdoors via penetration through buildings [45, 46]. Although a small fraction of $O_3$ can be formed from printers and copy machines, indoor $O_3$ formation is less efficient compared to outdoor rates because of radiative energy [34]. Thus, indoor concentrations of $O_3$ are also dependent on outdoor concentrations. Since outdoor concentrations may vary by region, time of day, or season, $O_3$ levels indoors will also vary between different geographical locations, and even differ between rooms [45, 47].

$O_3$ concentrations are significantly lower than outdoor concentrations because of weakened photolysis rates, but more predominantly, $O_3$ is removed by the ever-present surfaces that act as sinks. Indoor to outdoor concentration ratios (I/O) is a common metric used to quantify human exposure to $O_3$ [48, 49]. Lee et al. developed a model that calculated predicted I/O ratios based on data obtained about housing and environmental characteristics, such as regional climate and indoor activity[50]. I/O measurements or having a fractional penetration parameter are two strategies that are used to recognize influences from the indoors to the outdoors.

Lioy et al. reported that simultaneous measurements of ratios of indoor to outdoor (I/O) concentrations varied from 0.22 +/- 0.09 to 0.62 +/- 0.11 in residential homes[51] . Indoor to $O_3$ levels were generally higher in the spring than the winter[52-55] Indoors, $O_3$ itself is not the dominant pollutant. Byproducts from $O_3$ removal, however, require more scrutiny.$O_3$ is removed by reacting with typical indoor VOCs include benzene-containing compounds, aldehydes, and unsaturated compounds such as fatty acids and terpenoids. These compounds require reactive species such as $O_3$ and $NO_2$ to produce SOA. Many have argued that secondary pollutants are more hazardous than $O_3$ and primary pollutants[56, 57].

Since the majority of indoor $O_3$ is from outdoor penetration, transient movement such as opening doors and windows will abruptly influence $O_3$ concentrations, as shown in Figure 3.1.1. The highlighted green region reveals that $O_3$ levels increased as soon as the doors were opened in a home.

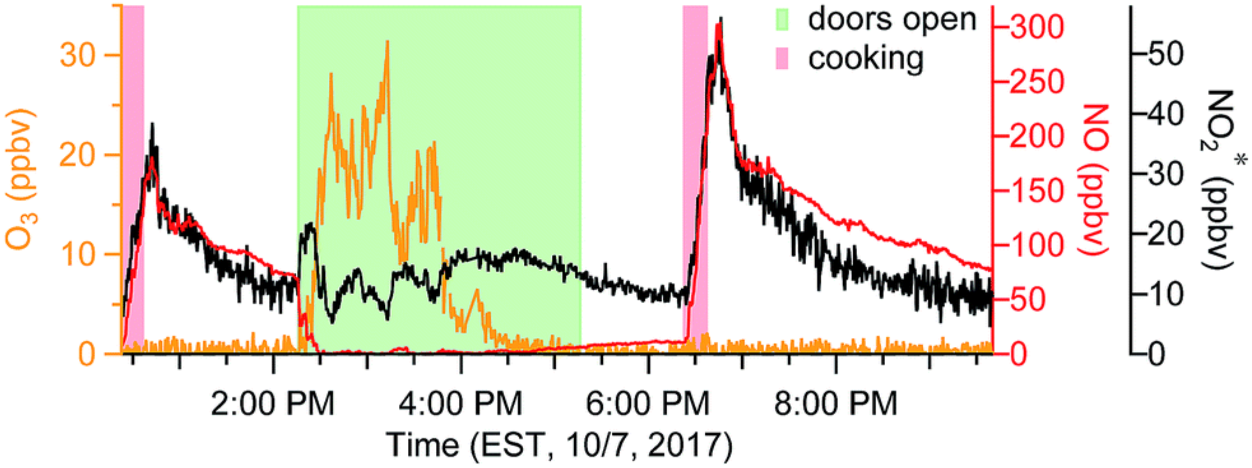


Figure 3.1.1. Time evolution of $O_3$, $NO_2$, and NO concentraions. Reproduced from Zhou et al.[52]

The outdoors has higher levels of $O_3$ than the indoors, which is why an influx of tropospheric $O_3$ was expected. The simultaneous measurements of $NO_2$ and NO along $O_3$ measurements pose an additional possibility for the rise in $O_3$. The data suggests that $NO_x$ is also partially responsible for indoor $O_3$ concentrations. In Figure 3.1.1., at the moment the door opens, NO concentrations abruptly drop. As the door remains open, measurements reveal that around 2:30 pm, $NO_2$ and $O_3$ are inversely related; peaks in $NO_2$ roughly coincide with $O_3$ levels at a minimum and vice versa. The relationship between the three suggests that $NO_2$ photolysis may lead to $O_3$ production, which is a plausible reaction that may occur in sunlit rooms [35].

Similar results were obtained when no ventilation was provided, as shown in Fig. 3.1.2. Home measurements were also compared to unventilated lab measurements. Figure 3.1.2a shows that cooking increased $NO_x$ levels and declined with time once cooking stopped. Figure 3.1.2b shows the O3 and $NO_x$ mixing ratios in a lab setting. $O_3$ levels were much higher than the home setting. A sharp increase in $NO_2$ occurs at 8, and a smaller increase occurs between 16:00 to 20:00 hours that is most likely from elevated $NO_2$ levels due to traffic. Though no ventilation was provided, species may permeate through building materials.

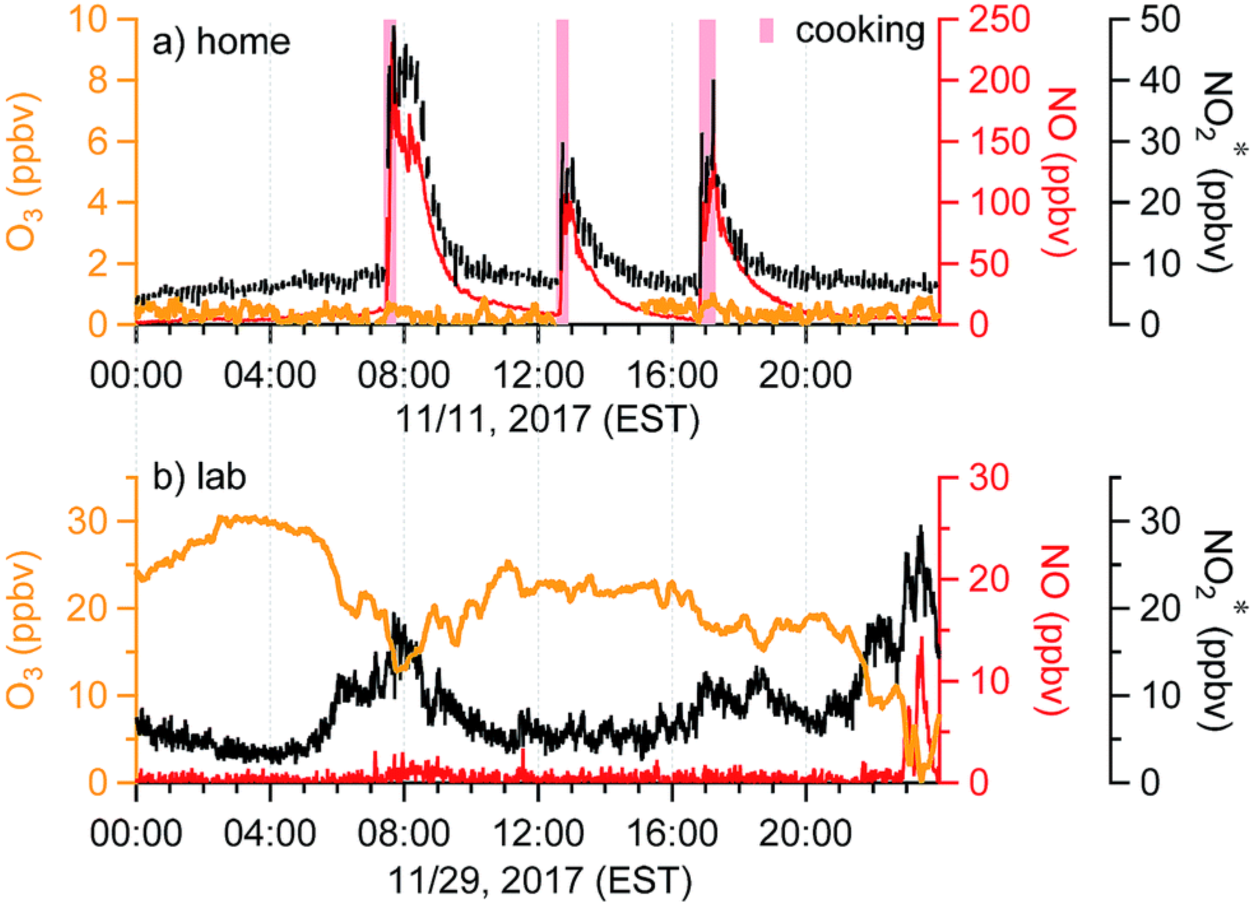


Figure 3.1.2. Resulting concentrations of $NO_x$ and $O_3$ indoors over a 24-hour period with no ventilation at two different settings, the home (a) a lab setting (b). (a) shows rises in NO during cooking times (red regions). Reproduced from Zhou et al.[52]

NO and $NO_2$ were further examined by monitoring how mixing ratios present indoors and outdoors were influenced by opening doors. Figure 3.1.3 demonstrates the effects of ventilation on $NO_x$. If $NO_x$ does not participate in any reactions, it is expected that mass transport will dilute concentration both indoors and outdoors, and that the $NO_x$ levels will be within the minimum and maximum concentrations of initial indoor and outdoor mixing ratios. However, $NO_2$ surpassed indoor concentrations by about 1.7 ppbv while NO depleted to about 0.67 ppbv post door opening, which is much less than the outdoor concentration of 1.5 ppb.

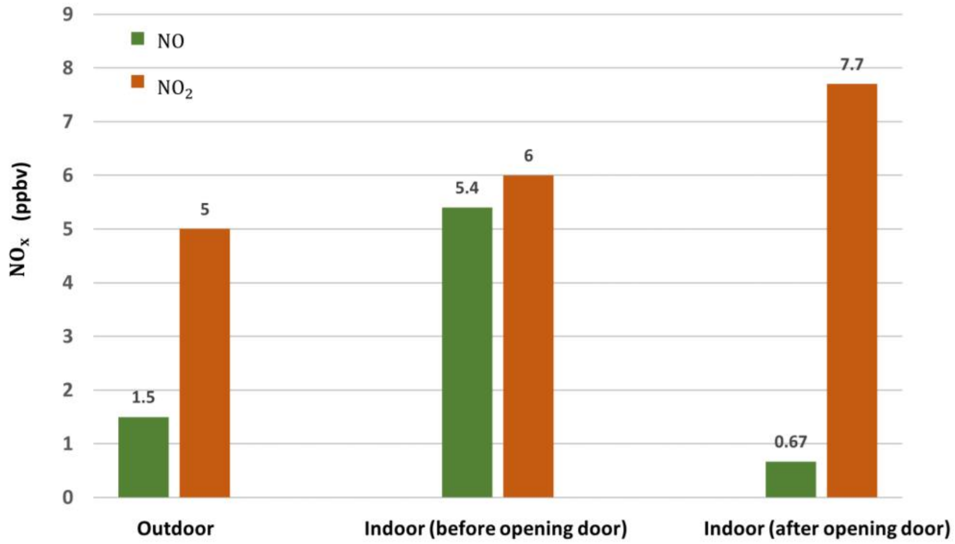


Figure 3.1.3. $NO_x$ levels before and after allowing ventilation. The outdoor concentrations before ventilation for NO and $NO_2$ were 1.5 (+/- 3.7) and 5.0 (+/- 3.4) ppbv, respectively. The indoor concentrations before ventilation for NO and $NO_2$ were 5.4 (+/- 3.2) and 6.0 (+/- 1.4) ppbv. The indoor concentrations after ventilation for NO and $NO_2$ were 0.67 (+/- 1.7) and 7.7 ppbv, respectively [27].

Combining the results from Figure 3.1.2 and 3.1.3 infer that $NO_2$ is a secondary product. produced by imported $O_3$ and NO. This explains the immediate dip in NO concentrations in Figure 3.1.1. The produced $NO_2$ may undergo photolysis even in low photon flux cases, which re-forms NO concentrations. Figure 3.1.4 depicts the codependent relationship between $NO_x$ and $O_3$.

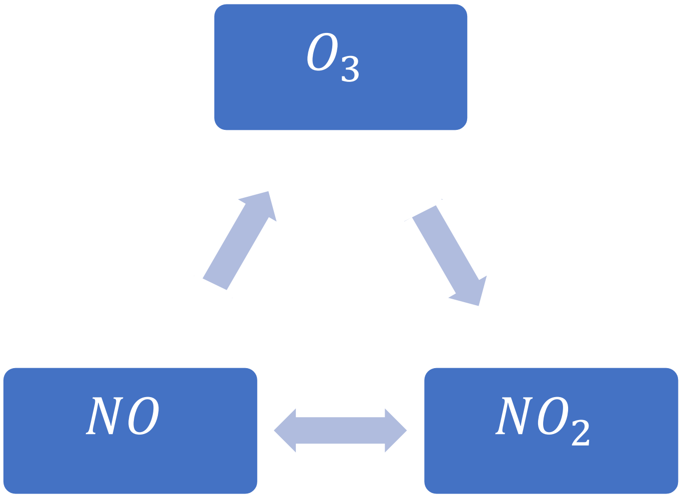


Figure 3.1.4. Illustration of how $O_3$ and $NO_x$ influence each other when $O_3$ enters the indoor environment.

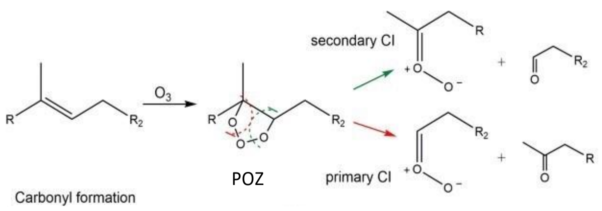
### *3.2 Oxidation via Ozonolysis*

Ozonolysis is an important chemical pathway for SOA formation, especially indoors, where surface ozonolysis is abundant. One of the most common ozonolysis reactions involve terpenoids, such as limonene and pinene. These common compounds are found outdoors and indoors and are reactive compounds with $O_3$. Limonene is primarily emitted from fruit trees, especially citrus plants, and pinene is released from resins. Indoors, these compounds originate from fragrances from air fresheners and perfumes, essential oils, and cleaning products. Indoor limonene concentrations can accumulate to as much as 50 ppb in two days [27]. Many studies have demonstrated ozonolysis as a source for new particle generation, especially its reactions with terpenoids [58, 59].

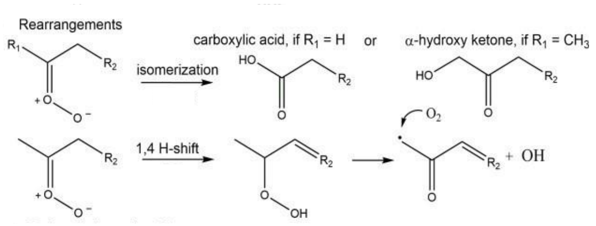
Characterizing SOA formation is a difficult task. Oftentimes, ozonolysis is dictated by many environmental conditions, such as temperature, volume size of the room, initial concentrations of ozone and the reactive organic, RH, AER, and even the number of people occupying a home [60, 61]. These parameters often influence gas-surface partitioning, which inevitably modifies the chemical composition of the ambient air. For example, the number of occupants in a room will influence ozone concentrations by uptaking $O_3$ through clothing and skin. Skin oils, such as squalene have been found to be important sinks for $O_3$. The mechanistic pathways that lead to SOA are mostly undiscovered, although many organic products share similar constituents such as carbonyl, alkenes, and phenols [62]. The reaction rate of these common functional groups are often characterized, which allows us to predict their reactivity. Highly reactive components such as alkenes may contribute to aerosol formation at a faster rate than less reactive organic compounds. For example, alkenes tend to form SOA in less than an hour, whereas aromatics often take six hours or more[63]. It is common to quantify the potential of SOA production by measuring its SOA yield, which is also known as the fractional aerosol coefficient. This ratio compares the amount of SOA mass produced to the initial amount of organic material that reacted [18, 63]. This gives an estimate of the potency of the reaction between $O_3$ and the reactive compound.

SOA yield is a general method for determining species that are influential, but does not explain any chemical transformations, which thus ignores the effects of minor and intermediate products produced along the reaction pathway. Ideally, the reaction mechanism is desired because it allows us to trace major and minor products created through the process of ozonolysis. Ozonolysis results in intermediate products that may induce ozonolysis for a different set of reactive species or may undergo other side reactions.

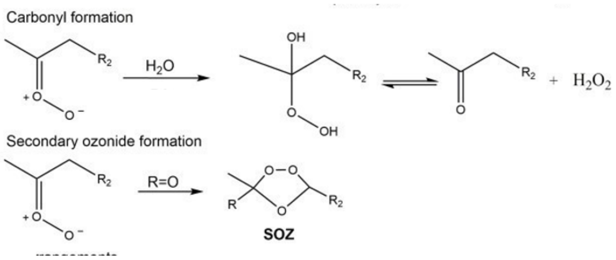
Unsaturated compounds are very susceptible to ozonolysis. Eqns. 3.1 -3.4 summarizes the reaction mechanism of ozonolysis. Ozone attacks the alkene causing electrons to be displaced to one of the oxygen atoms in $O_3$, which leads to the formation of an ozonide (Eqn. 3.1). The ozonide easily decomposes into two Criegee intermediates (CI) that have several fates: they can be transformed to carboxylic acid via isomerization (Eqn. 3.2), they can react with carboxylic acid to form a hydroperoxide, or they can react with water and produce an aldehyde and hydrogen peroxide (Eqn. 3.3), or they can react with a ketone and produce a secondary ozonide (Eqn. 3.4), which will reiterate Eqns. 3.1-3.4. These are the reaction steps for one of the CI compounds. The second CI compound will also follow the same steps. For compounds that are highly unsaturated, ozonolysis will occur on any or multiple double bonds. The continuous propagation of ozonolysis that lead to formation of intermediate products is one reason why ozonolysis is a master creator for SOA. where many products will be produced and have potential secondary reactions that contribute to the growing concentration of SOA. This will lead to an array of products with varying vapor pressures and partition coefficients. A simplified visualization of ozonolysis is also displayed in Figures 3.2.1.



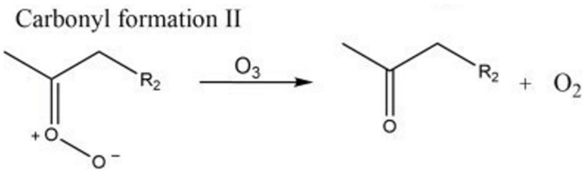
Eqn. 3.1



Eqn. 3.2



Eqn. 3.3



Eqn. 3.4

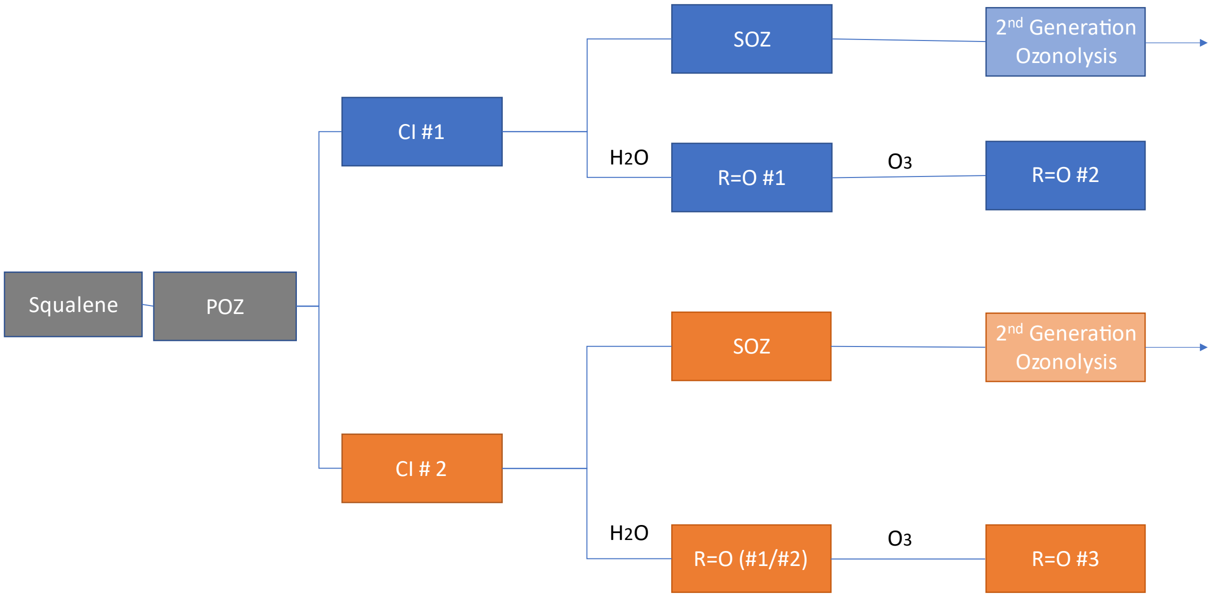


Figure 3.2.1. A visual guide of the ozonolysis process.

For compounds that are high in unsaturation, a variety of SVOCs will be produced that may develop into organic films. Typically, these low-volatility compounds are immune from being easily wiped away by air exchange, which further encourages surface ozonolysis. Squalene, a commonly emitted compound from human skin oils, is one such example of a complex unsaturated molecule. It has six double bonds, thus making it an ideal candidate for SOA product diversity. Although squalene has been studied numerous times[64-70], there is large variability in reported ozonolysis uptake coefficients [69, 71-75]. One reason for this variability is that many findings demonstrate that environmental factors such as AER, RH, temperature, size of room, and the number of occupants, to name a few, influence the reaction pathways taken by chemical species.

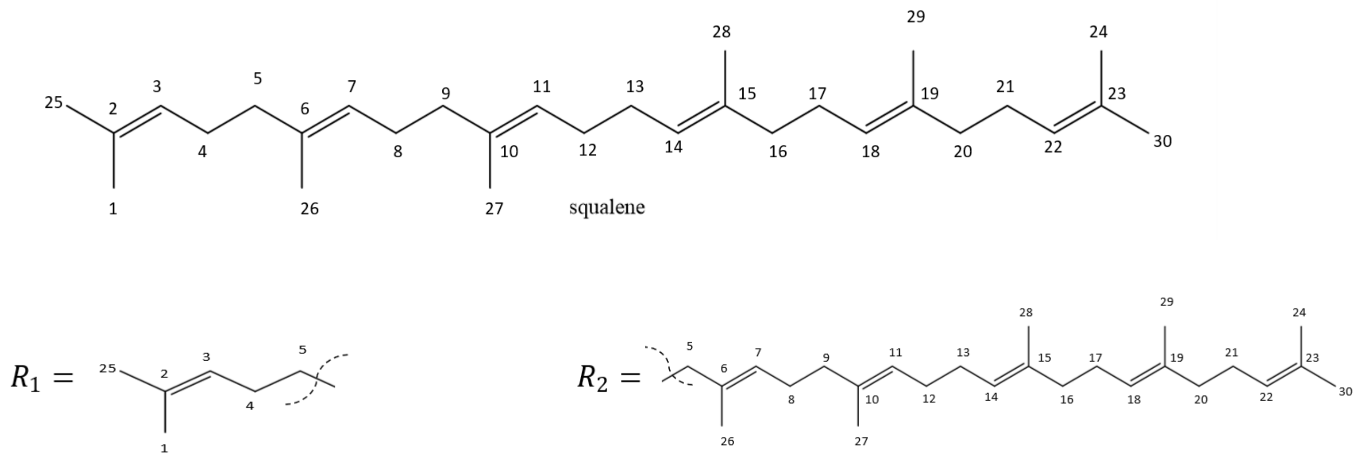


Figure 3.2.2. An example of a pair of substituents that can be formed during the first step of squalene ozonolysis.

The complexity of large molecules such as squalene can undergo several generations of ozonolysis. Squalene has three possible primary reaction pathways due to its symmetry. Figure 3.2.2. shows the structure of squalene, and one of the possible ways that we can separate the molecule into substituents that can be applied to the general equations given in Eqns. 3.1 – 3.4. With each combination of substituent pairs, the ozonolysis byproducts will largely depend on the decomposition of the primary ozonide, which will dictate the structures of the 2 CI that will drive the rest of the reaction pathways. This example of ozonolysis demonstrates that numerous possible organic compounds may be released into the air, but their chemical identities remain unknown. This makes it challenging to assess how the reactive organic compounds influence the chemical composition of ambient air.

As with most indoor chemical reactions, ozonolysis is not immune to the influence of environmental conditions. Eqn. 3.3 infers that RH may play a significant role in the resulting chemical composition as well. Houle et al. examined the decrease in squalene with increasing exposure rates to $O_3$ as a function of RH as seen in Figure 3.2.3. The data shows negligible dependence of the decay of squalene with RH. However, a closer look at reaction products in Figure 3.2.4b and 3.2.4c reveals that RH has a significant influence in controlling the composition of secondary products [76].

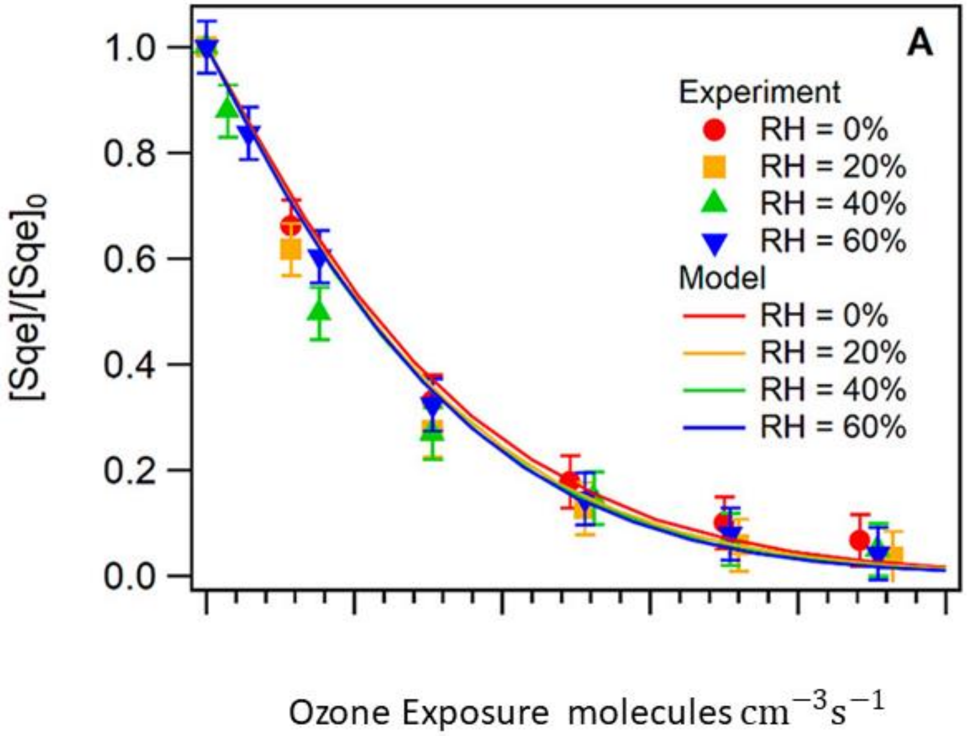


Figure 3.2.3. Measurements of 300 nm size-selected particles of squalene and byproduct as a function of RH after ozonolysis for (a) with increased $O_3$ exposure. Solid lines indicate model results. These are compared to their corresponding colored experimental data points. Reproduced from Heine al.[76] .

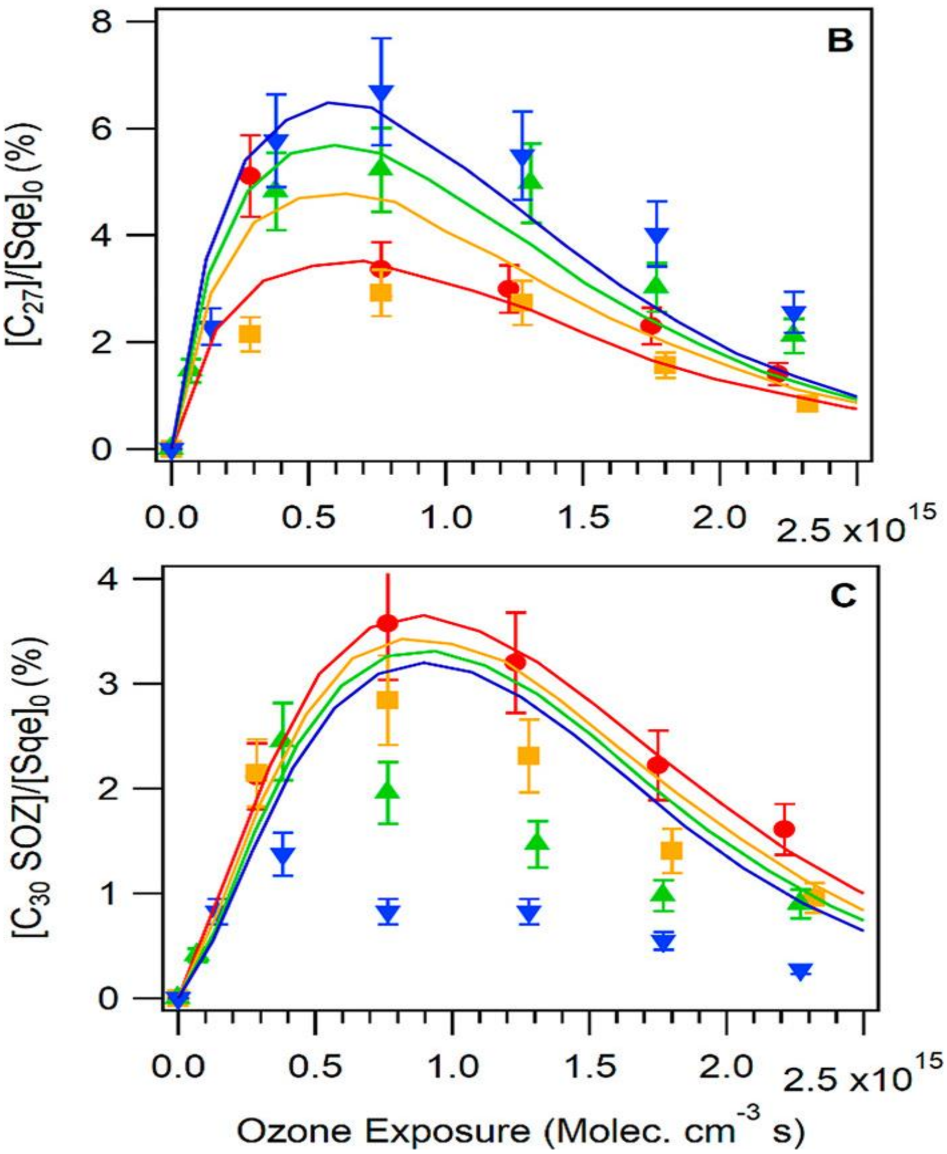


Figure 3.2.4 Measurements of 300 nm size-selected particles of squalene and byproduct as a function of RH after ozonolysis for (b) ketone products cleaved at C27 (c) secondary ozonides as a function of RH.  with increased $O_3$ exposure. solid lines indicate model results. These are compared to their corresponding colored data points. Reproduced from Heine et al.[76].

A closer look at the reaction mechanism of squalene shows that there are three possible sites for $O_3$ to intervene (at carbon numbers 27, 22, and 17). Figure 3.2.2 shows one possible cleavage of squalene. Each set of reactions will yield distinctive primary and secondary CI intermediates and carbonyl compounds. Houle and coworkers explained that more ketones are produced with increasing RH because water will compete with one of the primary carbonyl compounds produced from the first ozonide decomposition. When less water is present, secondary ozonide is more likely to be produced. The latter will increase SOA concentration and diversity as the secondary ozonides produced continue their chemical propagation. Higher concentrations of water will produce more carbonyl compounds, and less water will yield higher secondary ozonides as expected. This trend is seen for Figure 3.2.4c, but it was also observed that with increased RH, experimental results start to deviate from model results, implying that additional reaction pathways may be into effect, but is not being accounted for in the model. It was proposed that the deviation was a result of water encapsulating the chemical species. Within the solvent, the competing reactions of water and carbonyl group still applies, but with the additional competition with mass transport. If the analytes diffuse out of the water unreacted, then the probability of secondary ozonides increase. But if the species react within the water molecules before it is able to diffuse out, then the probability of secondary ozonides is decreased. Since the modeled results only consider ozonolysis as the only reaction pathway possible, the divergence from experimental results at higher RH may be due to water encapsulation effects that are not accounted for in this modeling study. This example demonstrates that ozonolysis is a baffling reaction process to study. It demonstrated the possibility of other reaction mechanisms that may be unknown to us. Houle and coworkers justified their results by proposing that water encapsulation may be an additional pathway. Thus, it is beneficial to study ozonolysis reactions as a function of different environmental variables.

This section looked at how mass-transported $O_3$ influence air quality. Although the incoming $O_3$ concentrations may be small, they are easily consumed and produced in the presence of $NO_x$. We then discussed $O_3$'s role in ozonolysis to demonstrate their potential to produce large amounts of SOA that pollute the indoor environment. Though gas phase ozonolysis also occurs, surface abundance makes surface ozonolysis a common indoor reaction. A case study of ozonolysis with squalene was demonstrated to recognize that there are many plausible reaction mechanisms that lead to a diverse ambient air organic composition. The study implied that the decomposition of the primary ozonide leads to deterministic SOA compositions. Unfortunately, monitoring the multi-step process of ozonolysis is variable to many environmental conditions. Due to this challenge, prediction of compound distribution from ozonolysis is undetermined, which exemplifies the difficulty in pinpointing the identities of relative concentration distributions within SOA. This uncertainty in most reaction mechanisms inspired the use of the SOA yield as a metric to measure the reaction's potency to produce SOA.

### *3.3* $NO_x$*, The Attenuator of Ozonolysis*

This section will discuss how $NO_x$ concentrations influence ozonolysis by acting as an additional sink for $O_3$, thereby decreasing SOA production. From Section 3.1, we learned that the presence of $NO_x$ and $O_3$ influences each other. This also means that there are consequences for high and low $NO_x$ levels on ozonolysis.

Presto et al [77] looked at SOA yield in the presence of high and low $NO_x$ concentrations on the reaction of $O_3$ and α-pinene. It was found that in the presence of high $NO_x$, SOA yields were suppressed, as shown in Figure 3.3.1. Mid to low levels of $NO_x$ did not influence SOA yield. This implies that high $NO_x$ levels allow $NO_3$ to be produced. While $NO_3$ reacts readily with α-pinene, unlike $O_3$ reactions, it does not produce significant concentrations of SOA [78, 79]. Thus, at high $NO_x$ levels, particle generation is suppressed by $NO_3$. Moderate to low levels of $NO_x$ did not inhibit SOA formation.

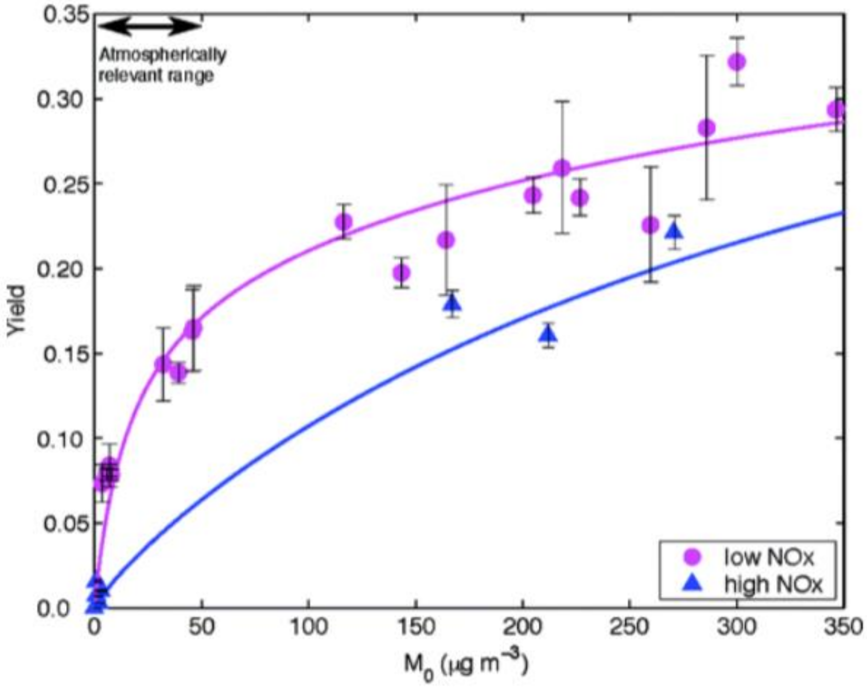


Figure 3.3.1. A comparison of SOA yields at high and low $NO_x$ concentrations. SOA yield as a function of total organic aerosol mass concentration in the presence of high and low $NO_x$. Data points represent experimental measurements obtained. The solid line represents the predicted SOA yields. Reproduced from Presto et al. [80]

Liu and coworkers [81] further analyzed the role of $NO_x$ by conducting experiments with initial ratios of 1, 0.5, and 2 of NO and $O_3$ ($NO/O_3$) in the presence of α-pinene. The $NO_x$ and $O_3$ levels were remeasured after ozonolysis reached steady-state. At equal parts of $NO/O_3$, NO reacted with $O_3$ to produce $NO_2$, as shown in Eqn. 3.1. $O_3$ residuals reacted with α-pinene, which is kinetically favored over NO reacting with α-pinene. For this case, SOA is decreased due to the titration of $O_3$ with NO. When the ratio was 0.5, NO will continue to produce $NO_2$. $NO_2$ concentrations accumulates because $NO_2$ forms faster than forming $NO_3$, as shown in Eqns.3.1-3.2. $NO_2$ will either be consumed by $O_3$ to form $NO_3$ (Eqn. 3.3) or react with $NO_3$ to produce $N_2O_5$ (Eqn.3.4). In this case, SOA concentrations are actively produced when α-pinene reacts with either $NO_3$ or $O_3$. Like the previous study, SOA yield was found to be lower than if $NO_x$ had been absent. $NO_3$ may also be converted to $N_2O_5$. When NO was twice that of $O_3$, all $O_3$ was converted to $NO_2$ and only Eqn. 3.1 occurs. No significant particle generation was observed. This study demonstrated the effects of low, high and medium levels of NO. In all cases, the presence of $NO_x$ during ozonolysis hinders new particle formation.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(Eqn. 3.1)}$$

$$NO_2 + O_3 \rightarrow NO_3 \qquad \text{(Eqn. 3.2)}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad \text{(Eqn. 3.3)}$$

These two case studies demonstrate how $NO_x$ influences SOA yields. In Presto et al's work, they also suggested that organonitrates formed from $NO_3$ which may also contribute to SOA levels. Although $NO_3$ may not be an efficient source of SOA, other studies report that $NO_3$ does lead to new particles when reacting with terpenoids [79, 82]. Thus, this section indicates that $NO_x$ can efficiently suppress SOA production.

### *3.2 Nitrous Acid (HONO), an Elusive Secondary Oxidizer*

OH in the troposphere is produced via ozone photolysis. The absence of strong actinic flux indoors, however, prevents $O_3$ photolysis from occurring indoors. This led earlier studies to believe that OH radicals were limited to small concentrations and that the dominant sink for $O_3$ was through ozonolysis [83, 84]. The expected concentrations of OH were $10^4 – 10^5$ molecules/cm$^3$ if this were true. Alvarez and coworkers, who proved otherwise, saw that OH concentrations as high as $2 \times 10^6$ molecules cm$^{-3}$ were possible indoors, which are concentrations within the range of outdoor levels [85, 86]. This led to more investigations about nitrous acid (HONO), which is a precursor to OH.

Gligorovski performed a chamber study where HONO, a weak acid, was measured at varying light intensities. It was discovered that HONO is capable of being photolyzed with standard lighting [87] and decomposes into OH and NO, thereby challenging the notion that strong photolysis was necessary for OH production. HONO became the leading culprit for OH radicals. Main sources for HONO is from $NO_2$ emissions from cooking, fireplaces, and candles, tobacco smoke, and outdoor transport [88]. In the gas phase, $NO_2$ reacts with $H_2O$ to form HONO, as shown in Eqn. 3.5. Though typical gas phase reactions of water and $NO_2$ are slow, $NO_2$ surface reactions readily form HONO, which promotes SOA formation [89]. Reaction rates compiled from previous studies is displayed in Figure 3.3.2. All studies saw an increase in $NO_x$ production with increasing S/V, thus showing that surface $NO_2$ hydrolysis is favored. The byproducts of HONO are often very hazardous, such as nitrosamines. Nitrosamines are a class of organic compounds that are formed from HONO reacting with nicotine residuals in a process coined “third-hand smoke”. Its potential hazard has been documented, and HONO has been seen to increase nitrosamine levels by a factor of 10 when HONO reacted with nicotine [90].

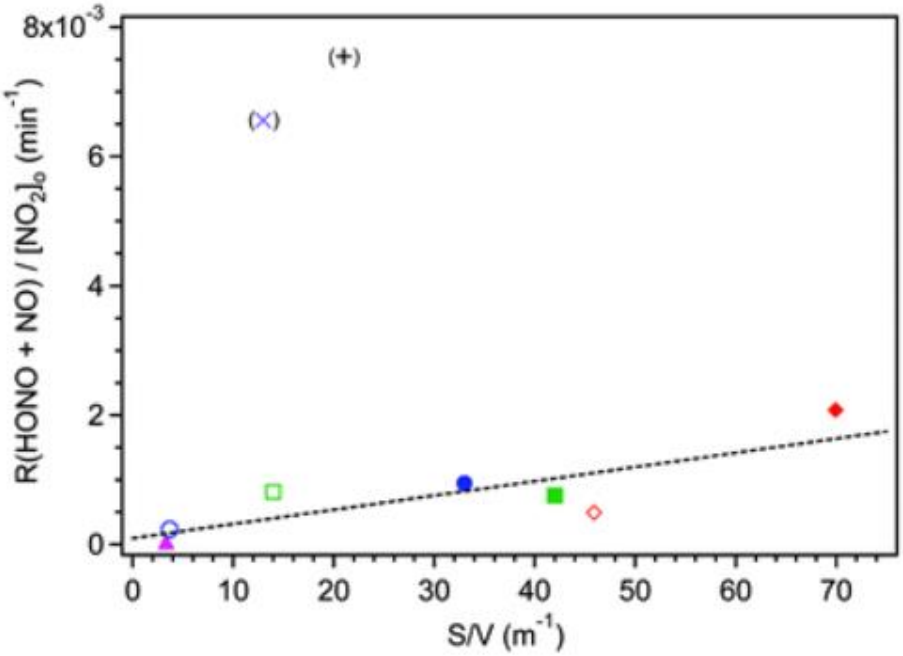


Figure 3.3.2. Demonstrating the increase in total reaction rate of HONO and NO with increasing S/V. Reproduced from[91] . Data points are from Pitts et al, Sakamaki et al, Svensson et al., Wiesen et al.shows [92-96].

The average HONO concentrations indoors and outdoors are roughly 5 ppb and 1 ppb, respectively [97]. Surprisingly, indoor HONO concentrations have been seen in much higher concentrations, sometimes 30-50 ppb, and sometimes even reaching 100 ppb [88, 98, 99]. Direct correlations between high HONO concentrations and pollution has been established for outdoor ambient air [100-102]. Hence, indoor characteristics such as poor ventilation and high S/V ratio provide a highly conducive environment to facilitate HONO formation. Nevertheless, very few studies quantify indoor OH mixing ratios contributed by HONO, even though HONO may be the driving force of oxidative chemistry. OH can generate peroxy radicals that may continue to replenish OH concentrations. Yet, the balance between HONO sources and sinks, causes and effects, are not yet completely understood. Figure 3.3.3 summarizes key mechanisms that affect HONO levels. This knowledge gap in indoor oxidative chemistry has several implications: we will not be able to effectively control HONO sources, which has been shown to aggravate respiratory functioning [103]. We will not understand its influence on relative contribution to $NO_x$ and $O_3$ levels, which will underestimate the role of HONO. Current modeling studies suffer from incomplete HONO parameterization. Until a complete understanding of HONO mechanisms are understood, its influence on $HO_x$, $NO_x$, and $O_3$, and thereby its effect on indoor air composition, is largely unknown.

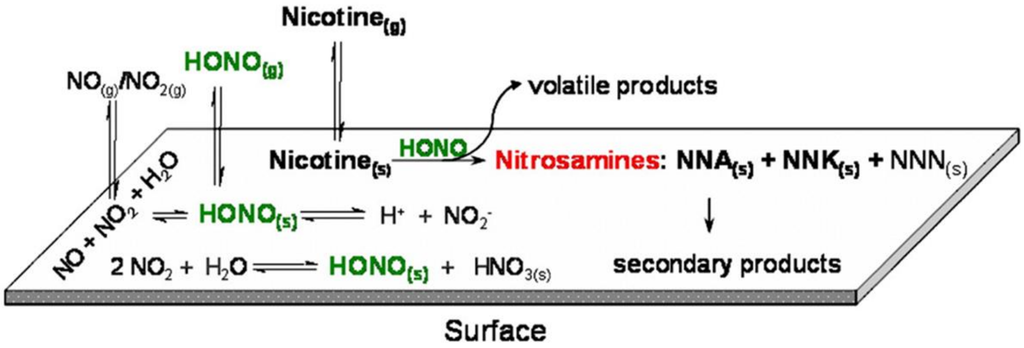


Figure 3.3.3. Surface reaction pathways of HONO. Interactions between gaseous and sorbed species produce hazardous byproducts such as nitrosamines. Reproduced from Sleiman et al. [90].

The potency of indoor HONO is only recently being realized and is currently an active area of study. Several studies proposed the following possible relationships between $NO_2$ , water, and surfaces, as demonstrated in Eqns. 3.5-3.8 [104-108]. Numerous studies confirm that Eqn. 3.5 is the dominant reaction for HONO formation. Figure 3.3.4 validates that $NO_2$ hydrolysis on surfaces is preferred. A linear relationship (R^2 = 0.87) was determined between HONO measurements and increasing water levels, suggests that water mediates surface chemistry.

$2NO_2 + H_2O$ (surface) → HONO + $HNO_3$ (Eqn. 3.5)

$NO_2$ + reduced surface → HONO + oxidized surface (Eqn. 3.6)

NO + $NO_2$ + H20 (surface) → 2 HONO (Eqn. 3.7)

NO + $HNO_3$ (surface) → $NO_2$ + HONO (Eqn. 3.8)

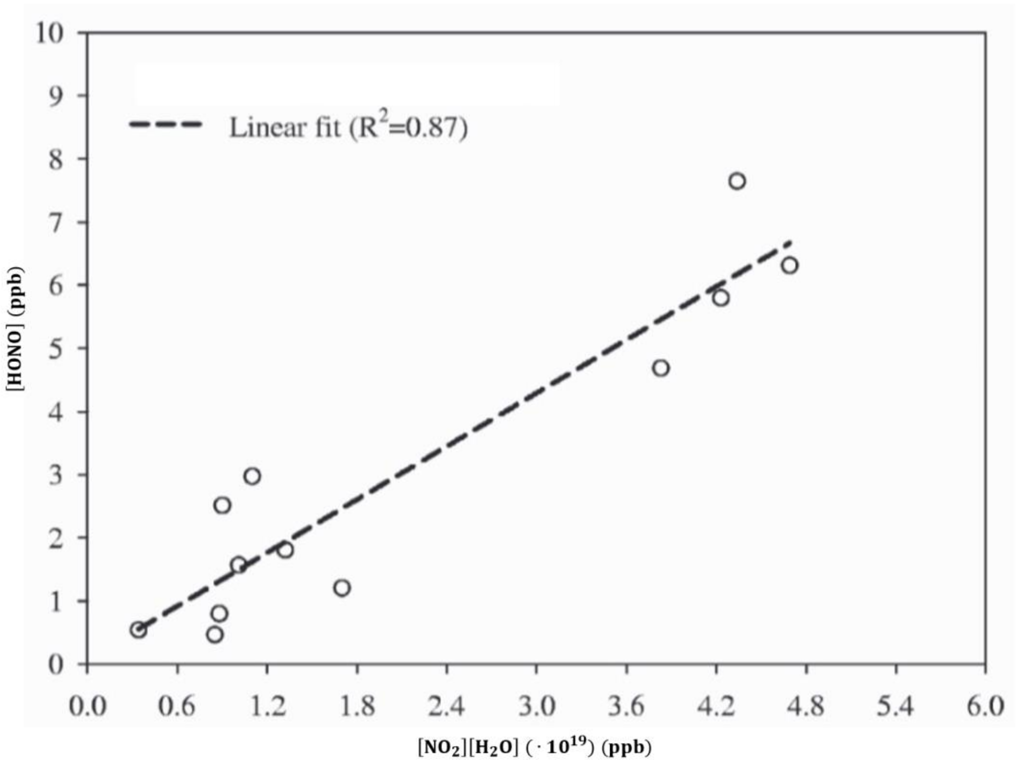


Figure 3.3.4. Correlation between HONO concentrations with increasing water amounts. Water vapor was calculated by RH. Reproduced from Concentration of HONO as a result of hydrolysis [108].

The coupling between indoor HONO and $NO_2$ has been investigated by determining the enhancement of HONO in the presence of $NO_2$. This is quantified by taking the ratio HONO/$NO_2$ [88, 108-116]. Typical values of HONO/$NO_2$ range inside buildings range from 0.1-0.3, but ratios of 0.04- 0.15 were found to be more typical for chamber studies where $NO_2$ was solely emitted. This distinction implies that surfaces play a significant role in elevating HONO mixing ratios, unlike chamber studies, which have minimal surface reactions compared to buildings.. In terms of chemical lifetimes, HONO and NO have relatively long lifetimes (about a few hours), whereas $HNO_3$ has a lifetime of 30 minutes. $NO_2$ was in the middle of the two extremes with a lifetime of about 1 hour. The shorter lifetime of $NO_2$ suggests that HONO was being replenished.

$NO_2$ originates from outdoor transmission and indoor combustion. Park and Cho analyzed the relationships between HONO, NO, and $NO_2$ with in-situ measurements in an apartment and discovered that night concentrations accumulate due to less actinic flux. The study was furthered by simultaneously monitoring HONO, NO, and $NO_2$ as a function of ventilation. Figure 3.3.6 shows that unvented rooms contained higher levels of $NO_2$ levels than strongly ventilated rooms. Although HONO levels decreased with increasing ventilation, the amount of HONO produced was significantly less than $NO_x$ amounts. Their results also show consistent HONO/$NO_2$ ratios for the different ventilation rates. Ratios were 0.05-0.09, 0.05–0.11, and 0.05–0.09 for the unvented, weakly ventilated, and strongly ventilated, respectively and the time evolution of HONO, NO, and $NO_2$ are displayed in Figure 3.3.7 demonstrates the time evolution for each ventilation condition. The unvented case shows that $NO_x$ increased as soon as combustion was initiated, and decreased immediately after eliminating the combustion source. HONO continued to form after the source was turned off, and its peak is offset from $NO_x$. This experiment HONO pollutants can be readily reduced by ventilation.

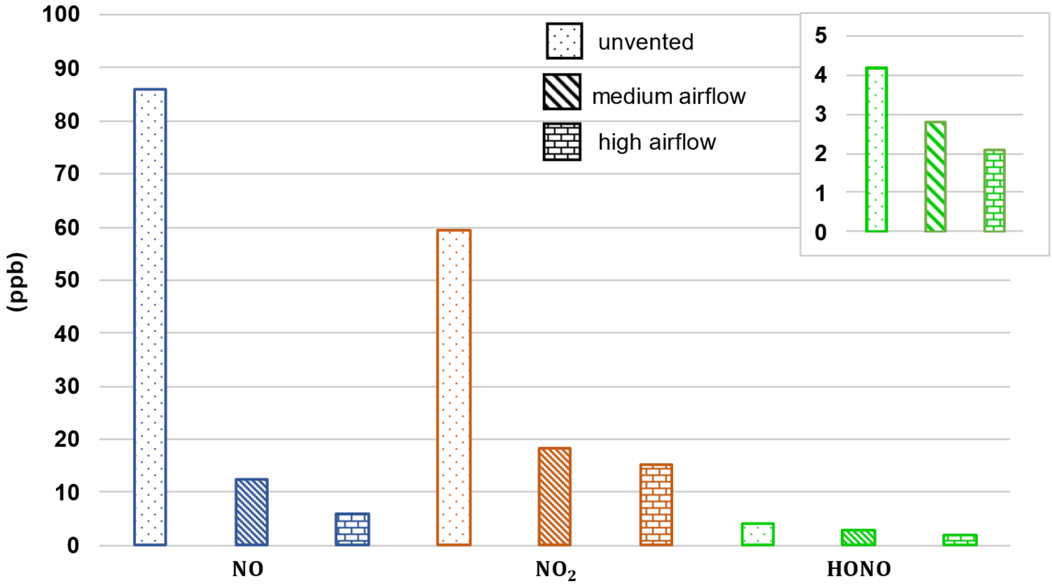


Figure 3.3.6. Representative averages for NO, $NO_2$, and HONO during a 30-minute combustion period in an unventilated, fairly ventilated (340 $m^3$ $hr^{-1}$), and highly ventilated (510 $m^3$ $hr^{-1}$) room. The combustion source was a gas burner. The burning rate was set to 50%. Data available from Park et al. [108]

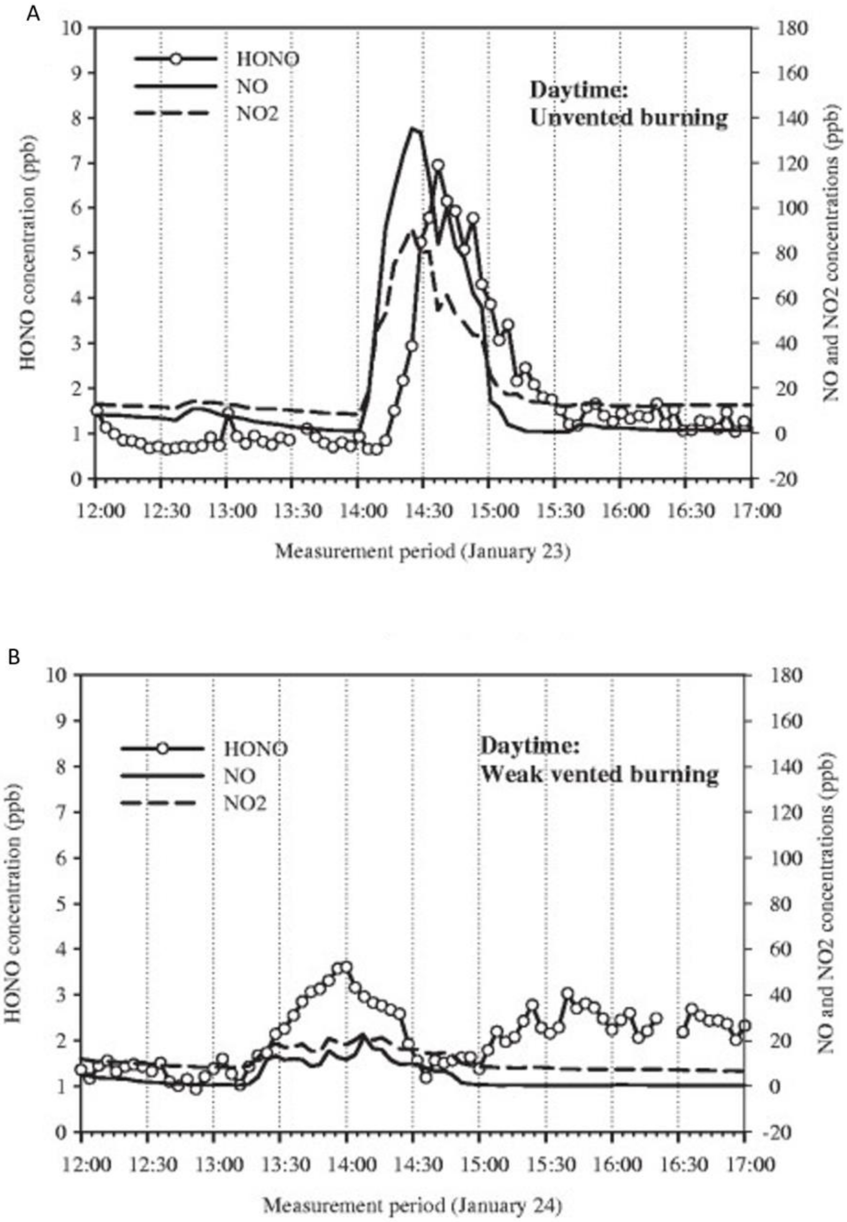


Figure 3.3.7. Monitoring the time evolution of NO, $NO_2$ and HONO at 4-min time intervals. (a) No ventilation (b) weakly vented at 340 $m^3 hr^{-1}$ (c) strongly vented at 510 $m^3 hr^{-1}$. Combustion started a little before 1:30 pm until 2:00 pm. Reproduced from Park et al. [108]

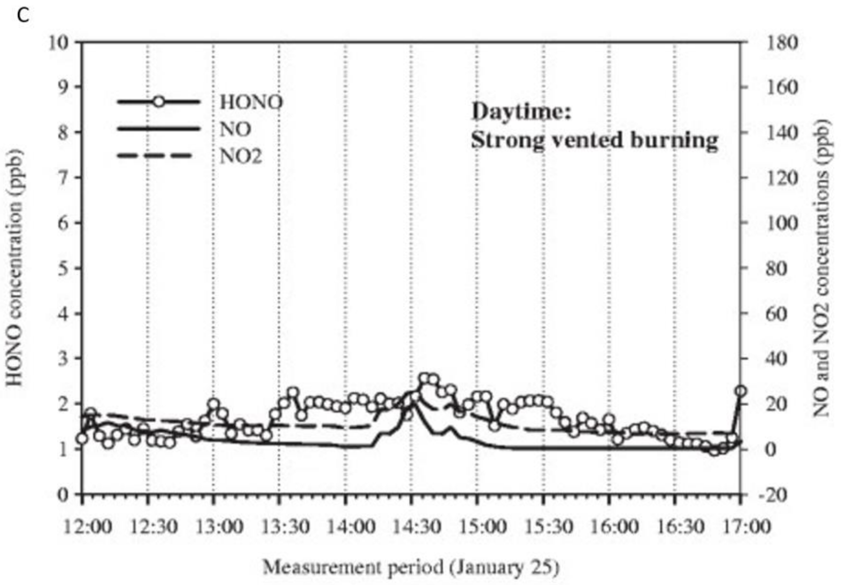


Figure 3.3.7 cont. Monitoring the time evolution of NO, $NO_2$ and HONO at 4-min time intervals. (a) No ventilation (b) weakly vented at 340 $m^3\,hr^{-1}$ (c) strongly vented at 510 m3/hr. Combustion started a little before 1:30 pm until 2:00 pm. Reproduced from Park et al. [108]

In this section, we explored the sources of HONO and its significance as an oxidizing agent. Its predicted OH contribution in the troposphere lies between 30-60% [117-119]. With increased surface area available indoors, these contributions can bear more weight. In order to understand the $HO_x$ budget indoors, surface-$NO_2$ studies must be characterized so that we can identify strong mediators of HONO production. Our understanding of indoor $HO_x$ mechanisms is significantly lower than our knowledge  about indoor $NO_x$ and $O_3$ processes. OH's influence is also likely to be very different from the outdoors due to surface abundance and filtering of UV rays. To compensate for the lack of experimental studies, many modeling studies have proposed plausible reaction mechanisms for HONO formation [91]. But until we can understand its processes, we can only speculate on possibilities.

# CHAPTER 4

# GAS-PARTICLE-SURFACE PARTITIONING OF SEMIVOLATILE ORGANIC COMPOUNDS (SVOCs)

## *4.1 Properties and Partitioning of SVOCs*

In the troposphere, particles such as soot, ice, dust, and water droplets act as agents for surface reactions. The deposition of organic compounds onto surfaces can modify their optical properties or chemical reactions may take place that change the chemical composition of the aerosol, or they may produce new products. SVOCs have low volatility, and easily adsorb onto surfaces. In fact, upper tropospheric aerosols contain large amounts of carboxylic acids, alcohols, and amines. The boundary between a particle and the air that surrounds it is a unique layer where SVOCs may partition between the gas and particle phases. Adsorption of organics onto a particle surface will create an organic film. Consequently, optical properties of the aerosol may be altered or chemical reactions may change its chemical properties. These modifications can have serious effects on radiative forcing and atmospheric chemical composition.

Indoor environments undergo similar partitioning patterns as outdoor gas-particle partitioning However, in addition to gas-particle partitioning, the indoor environment also undergoes surface partitioning. Kitchen countertops, walls, flooring, and fabric are just a few sites available for surface reactions. Ambient SVOCs may exist in the gas or particle form, coat ambient aerosols, which may settle onto surfaces and dust. SVOCs are often secondary products formed from oxidized VOCs. There are several major indoor pollutants that are considered SVOCs, which includes but are not limited to: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), and halogenated flame retardants (NFRs). These SVOCs originate from building materials, furniture, etc. Some other common SVOCs include phthalates and phenols. . These compounds are known to be hazardous to our endocrine system. SVOCs characteristically have high octanol-water ($K_{ow}$) and octanol-air partition ($K_{oa}$) coefficients, have low solubility, and have relatively low volatility which are all properties that make it more likely for SVOCs to adsorb to surface films. The main concern of interfacial processes is that surfaces serve as large reservoirs of species that have virtually little to no sinks. Surface-adsorbed compounds may exist for longer periods than when they are in the gas-phase, where reactions are limited by air exchange. The everlasting reservoir of hazardous compounds may be transferred to humans. This is a major health concern and one motivation to study and characterize SVOCs.

The impact of SVOCs on air quality is still in its preliminary research stages because of immense analytical challenges faced. For one, it is much easier to measure gas phase processes than partitioning processes. Identifying the chemical compositions that make up a surface film will reveal organics that are collected with time. A few health studies have investigated the toxicological properties of highly concentrated films[120]. Surfaces allow organics with low volatility to settle and eventually blanket a surface with a thin organic film, which is also known as the “grime layer”. Most indoor surfaces will have this thin film. In order to understand how SVOCs impact air quality, we must investigate the sources of SVOCs, the likelihood of partitioning in one state over another, strength of uptake coefficients, and the causes and effects of partitioning on the environment.  Figure 4.1.1 demonstrates the many possible partitioning pathways for a chemical compound, highlighting the ubiquity of possible SVOC partitioning.

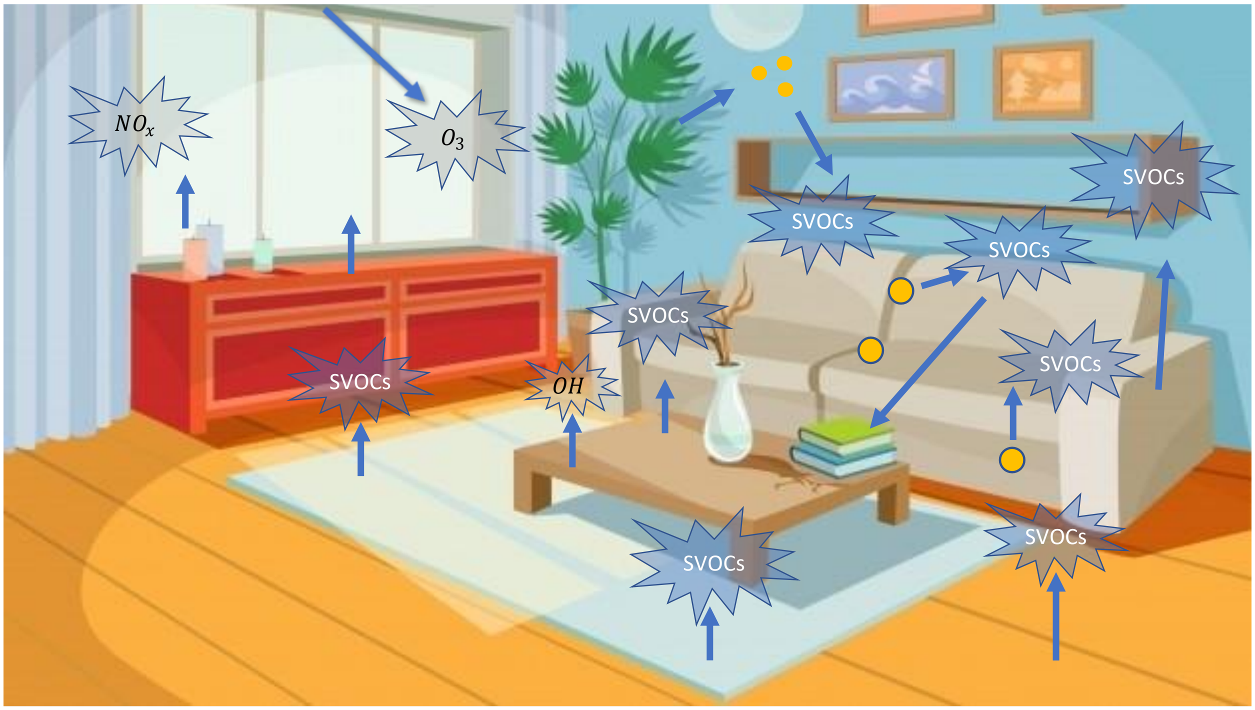


Figure 4.1.1. Representation of sources of some pollutants and the different types of SVOCs released from typical household items. Note that unique and localized SVOCs released in each marked area is due to different environmental factors, and material properties.   The small orange dots represent VOCs that are in the atmosphere. Bigger dots represent aerosols that have been coated with SVOCs and partitioning between gas-particle phases. SVOCs may partition on any surfaces or particles.

Chemical equilibrium is an important parameter to partitioning studies. In the troposphere, chemical equilibrium is defined by gas-particle interactions. The standard method for assuming an achieved equilibrium is by having constant rates of adsorption and desorption at an interfacial layer between the particle and gas-phase species. The definition of equilibrium in indoor partitioning is viewed with a slightly different perspective. Indoor environments are in constant flux. Cooking, cleaning, and turning on the air conditioner are just some examples that contribute to the highly diversified and localized chemical composition. Even the presence of a human is enough to disrupt equilibrium—a person sitting on a couch will exert heat, which will cause some portion of SVOCs to volatilize. Indoor settings complicate the equilibrium between the surface and particle by having additional sinks that disrupt surface equilibrium. These sinks may include but are not limited to the rate at which the compound is ventilated, and the rate at which the molecule will partition onto other aerosols. As a result, chemical equilibrium is rarely achieved. Instead, species may reach steady state. A steady-state condition implies that though molecules are not in equilibrium, the sums of the rates of production and removal of the compound is constant. This means that when tracking the partitioning of a species indoors, the sources will include the rate of species that are released from all surfaces in the system. This will be how we will view chemical equilibria indoors.

Measurements of octanol-water partition coefficients ($K_{ow}$) and octanol-air partition coefficients ($K_{oa}$) are often used to characterize partitioning. These coefficients represent the balance of a species in the gas phase and film phase. Many studies rely on these values to assess its phase propensities under the assumption that octanol and organic surfaces have similar affinities for SVOCs [121, 122]. Some studies argue that utilizing partition coefficients is a flawed strategy for assessing indoor equilibria because many studies are conducted at 25 °C [123], and that temperature may influence partitioning [124, 125]. But it has also been argued that temperature dependence is inconsequential [125, 126].

Improvements in utilizing K have been adopted by several groups. Liu et al. developed strategies for measuring solid-phase diffusion coefficient to supplement K coefficients [127]. This will improve the accuracy of its partitioning measurements by relying on parameters other than K for assessment. Cousins and Mackay developed a quantitative structure-activity relationship (Q-SAR) correlation plots to characterize partitioning of phthalates[128]. Their philosophy included that partitioning was influenced by water solubility of a species and vapor pressure, in addition to partition coefficients. Like Liu's study, the development of this method was inspired by the lack of "measurement resolution" when partitioning is not a one-dimensional simple process. The wide range of physicochemical and partitioning properties of phthalates from literature were compiled by Staples and coworkers. It was clear from this compilation that physicochemical data varied by as much as few orders of magnitude. This variability in data prompted a thorough examination of past results in the literature, and assessed the data's credibility. In this method, a phthalate's solubility in air $C^s_{al}$ water $C^s_{wl}$ , and octanol $C^s_{ol}$ were determined and correlated with their chosen molecular descriptor, the Le Bas molar volume. $C^s_{al}$ is essentially equal to the vapor pressure of the compound. There were no measurements for the $C^s_{ol}$ of the phthalates, but it was estimated that $C^s_{ol}$ was the product of $C^s_{wl}$ and $K_{ow}$. $K_{ow}$ values are found in the literature. Figure 4.1.2 shows the correlation plots between the ($C^s_{ol}$) and and $C^s_{al}$ as a function of its LeBas molar volume ($cm^3$ $mol^{-1}$). The hollowed markers represent data points deemed unreliable due to challenges in measuring low quantities (< 1 L $\mu g^{-1}$) and low pressures (< 1 μPa). These points were exempted from the obtained linear equations. The ratio of the three solubilities can be used to determine $K_{aw}$ (air-water), $K_{ow}$ and $K_{oa}$ as shown in Eqns. 4.1 – 4.3. Taking the log of both sides allows extraction of data from the linear relationship identified, which is shown in Eqns. 4.4 - 4.6.

$$K_{ow} = \frac{C_{ol}^{s}}{C_{wl}^{s}} \qquad K_{aw} = \frac{C_{al}^{s}}{C_{wl}^{s}} \qquad K_{aw} = \frac{C_{ol}^{s}}{C_{al}^{s}} \qquad \text{(Eqn. 4.1-4.3)}$$

$$\log K_{ow} = \log C_{ol}^{s} - \log C_{wl}^{s} \qquad \text{(Eqn. 4.4)}$$

$$\log K_{aw} = \log C_{al}^{s} - \log C_{wl}^{s} \qquad \text{(Eqn. 4.5)}$$

$$\log K_{oa} = \log C_{ol}^{s} - \log C_{al}^{s} \qquad \text{(Eqn. 4.6)}$$

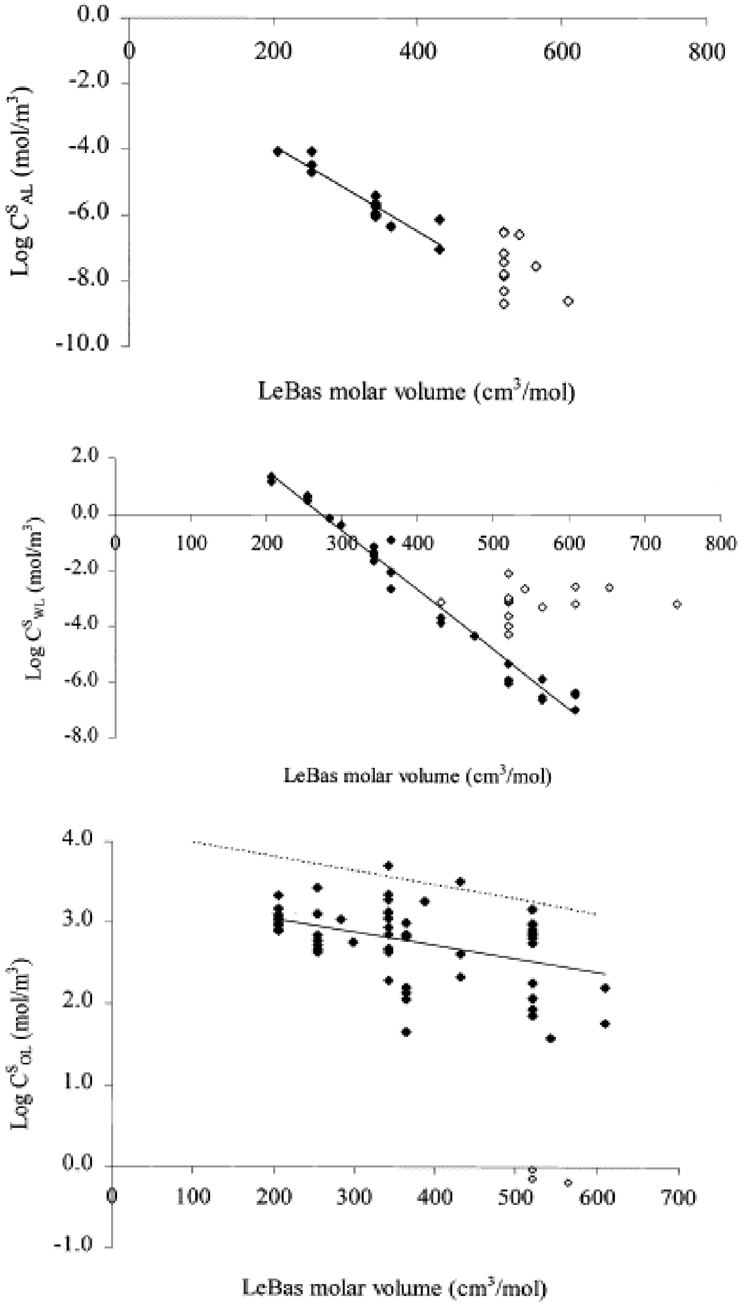


Figure 4.1.2. Correlation plots for (a) $C^{s}_{wl}$, (b) $C^{s}_{al}$ and (c) $C^{s}_{ol}$. The hollowed dots in (a) and (b) are data points that were not included in the linear regression. The dotted line in (c) represents the ideal behavior and the solid line is the linear equation that represents the correlation. Reproduced from Cousins et al.[129].

Figure 4.1.2c reveals that the phthalates deviate from ideal behavior and have a wide spread of measurements at each molar volume that $C^s_{ol}$ was measured. The predicted relationship not only deviated from ideal behavior, but the line was shifted downward by about one log unit. This variance was attributed to the flexibility of long carbon chains. Long chains will agglomerate which will have a lower solubility than their straight-chain counterpart. To summarize partitioning studies, there is large disagreement between acceptable ways to measure partitioning behavior. Liu assessed partitioning behavior by additionally measuring diffusion coefficients. Cousins and Mackay developed a quantitative method of deducing K values.

In Figure 4.1.3, Weschler et al. presents a simple hypothetical scenario to illustrate equilibrium partitioning[130]. Assuming that a gaseous phase molecule may only partition onto indoor surfaces and particulates, as $K_{oa}$ increases, the fraction that is present in the gas phase decreases. The figure also shows that film thickness also influences partitioning, and that an increase in thickness will cause more SVOC sorption onto the film. On the secondary axis, the persistence was also calculated, which is the time it takes to remove SVOC sorbed onto surfaces and air particulates if ventilation were the only possible sink. The divergent lines indicate the calculated upper and lower bounds possible. The upper bound case models partitioning if 100% of the gas species adsorbed onto surfaces only. The lower bound represents the case when the gas species are sorbed solely onto particles. The shaded region indicates the possible persistence of the compound. Most SVOCs that are of interest to us have log($K_{oa}$) values between 10-13, which lies between the upper and lower limit and the region where airborne concentrations are more ambiguous. This scenario does not apply to very high $K_{oa}$'s, where virtually no concentration remains in the gas phase.

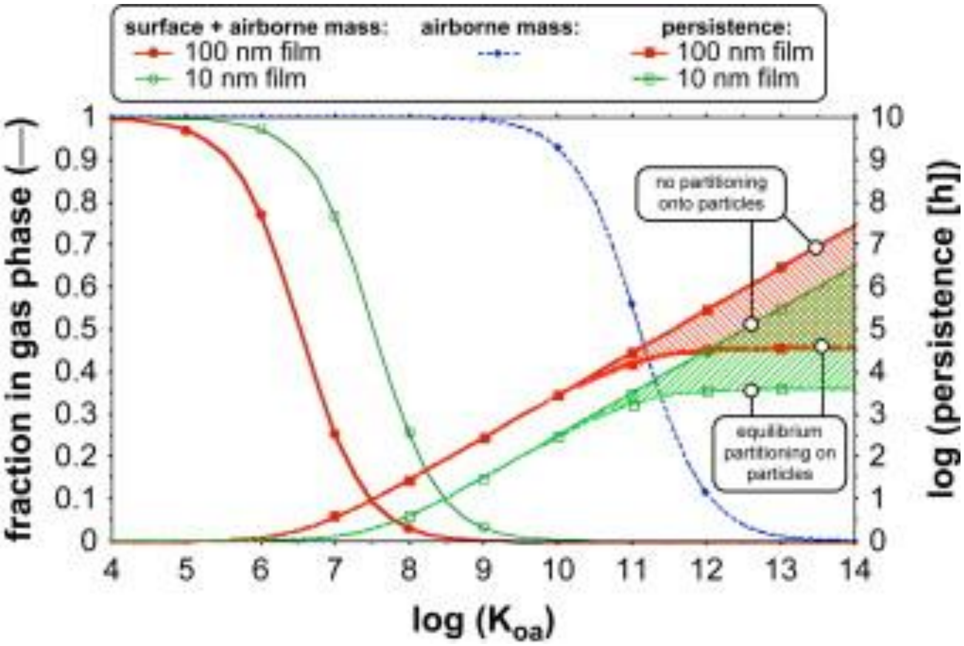


Figure 4.1.3. A Model of Partitioning Distribution of particles on a 10 nm (green) 100 nm (red) film, and their persistence to remain as an active source. Reproduced from Weschler et al. [130].

### *4.2 Physical Characteristics of Surfaces and Surface Films*

The physical characteristics of surfaces such as its texture, will impact SVOC transport, and thus, the chemical makeup of the surface film[131, 132]. Wu and coworkers examined the effect of roughness on the partitioning of phthalates on different indoor materials, such as aluminum, stainless steel, glass, and acrylic. It was, in fact, discovered that the roughness factor modified the K coefficient by increasing its surface area. The glass and stainless steel samples showed an increase in K when their true surface area were also increased. A complete list of tested materials is reported in Table 4.2.1. The roughness factor was defined as the true surface area divided by the area of the footprint. The true surface area accounts for the fact that surfaces are not completely smooth, but will have tiny crevices and indentations that increase surface area. From their findings, a positive correlation between partitioning coefficient and roughness was found. However, most partitioning studies do not include the effects of texture. It is instead approximated that the surface is flat. To understand the partitioning process, texture of material may be an important factor to also consider in future studies. Figure 4.2.1 reveals that the rate of mass deposition initially increases, but quickly plateaus as a function of time for similar materials that have differing surface morphologies. The results show that for low adsorption materials (surfaces with less than 500 ng of mass deposited onto them) such as aluminum, acrylic, and polished glass will reach equilibrium faster than the high adsorption materials. It was calculated that the difference in this example between low vs. high uptake is 300 hours and greater than 2000 hours, respectively. This trend of increased time for more mass deposition agrees with the persistence calculations shown in Figure 4.1.3. Figure 4.1.3 demonstrates that when more species are deposited onto surfaces, their persistence will be much longer.

| **Material** | **True Surface Area** $(\mu m^2)$ | **roughness factor** | **K (m)** |
|---|---|---|---|
| aluminum | 25.6 | 1.03 | 6.00E+02 |
| stainless steel #1 | 27.5 | 1.1 | 1.20E+03 |
| stainless steel #2 | 30.6 | 1.23 | 1.30E+03 |
| steel | 53.1 | 2.13 | 1.00E+04 |
| polished glass | 25.6 | 1.03 | 6.00E+02 |
| ground glass | 44.7 | 1.8 | 4.20E+03 |
| acrylic | 27.9 | 1.12 | 5.00E+02 |

Table 4.2.1. The area footprint was 24.9 µm$^2$. K is the partitioning coefficient and is described as the mass adsorbed per unit surface area divided by the concentration in air [131].

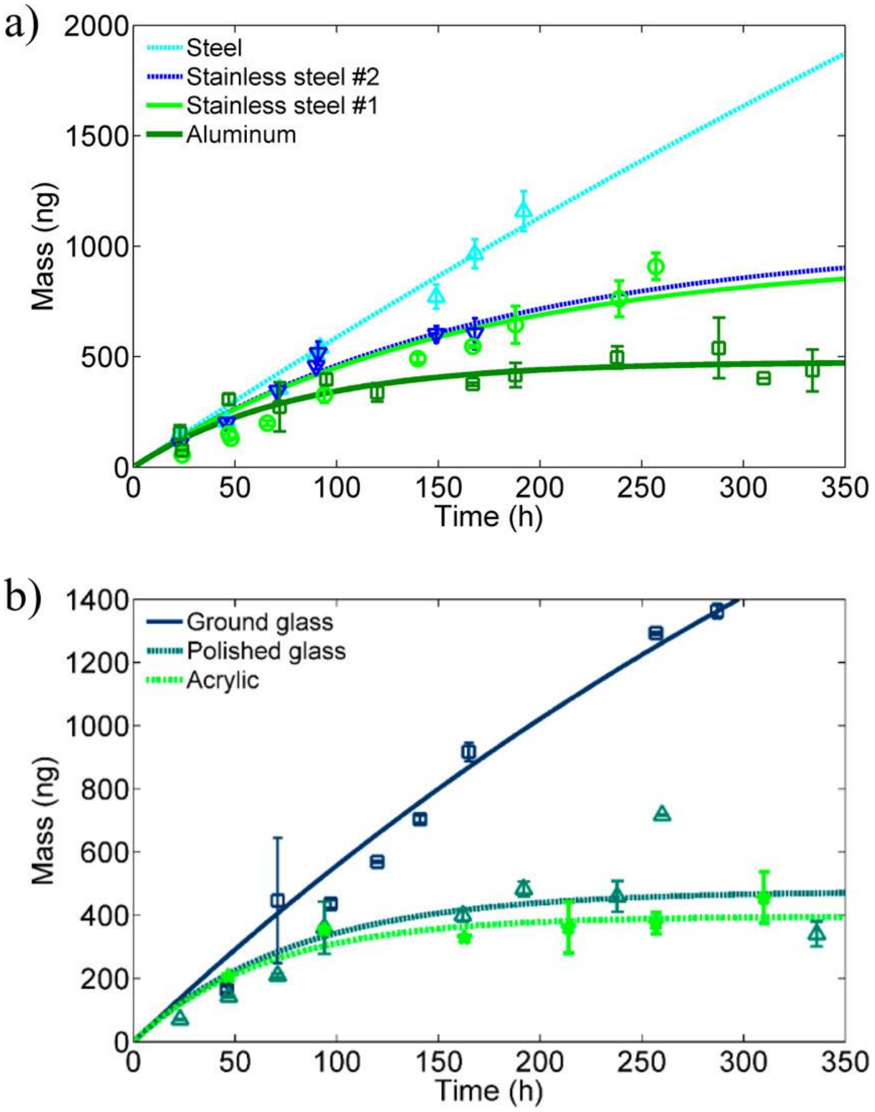


Figure 4.2.1. The mass deposition as a function of time onto different materials. (a) Shows the deposition for three different kinds of steel and aluminum. (b) Deposition for glassy materials. Reproduced from Wu et al.[131].

Once clean surfaces develop into surface films, the films thicken and the chemical composition and partitioning equilibrium are modified. Surfaces will have higher concentrations of SVOCs. In the same study, it was found that for a variety of soiled surfaces K coefficients are nearly identical. Other studies have also observed similar aging effects with time [31, 133-135]. This commonality suggests that films strongly influence partitioning, while the importance of properties of the surfaces start to decline.

The environmental conditions of local spaces are another factor that influences mass deposition onto films. It is evident from Or and coworkers' work that the ambient chemical composition may modify the surface's texture, as shown in Figure 4.2.2 [136].

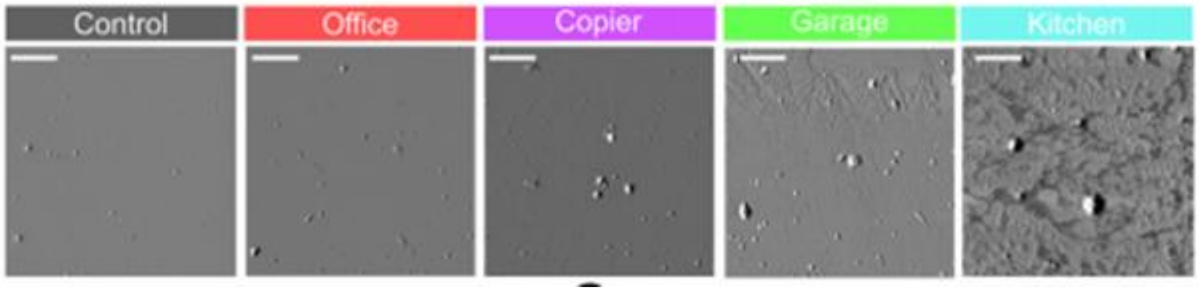


Figure 4.2.2. Deposition of ambient particles onto a glass surface. Images were taken using an atomic force microscopy–photothermal infrared (AFM–PTIR)  Reproduced from Or et al. [136]

The study analyzed glass samples placed in a copier room, office, kitchen, and garage to target a diversity of pollutants. The samples were analyzed 6 months after they were placed in their respective fields. It was determined that the glass sample from the kitchen area had the most film coverage over all the samples. The images show that particle deposition may also influence roughness. Consequently, both the material properties and the chemical composition impact partitioning because both will contribute to its roughness factor. The two case studies presented display that both the surface and the local chemical composition dictate surface-air partitioning. Consequently, characterizing surface chemistry is far more intricate than determining uptake coefficients of materials, and numerous combinations of surfaces and compounds will have to be tested to be characterized.

### *4.3 Total Deposition Velocities of Surface and Species*

The previous section showed that both the material and compound will influence each other's behavior. One method for characterizing reaction pairs is by measurements of the total dry deposition velocity ($\nu_d$), which includes velocities influenced by the mass-transport from gas to surface, and the surface uptake. The mass-transport velocity, also called the transport-limited velocity ($\nu_t$), is a measure of the amount of resistance that a compound will feel due to probable gas-phase reactions and gas transport from the surface. In other words, a falling particle will have an opposing force that limits $\nu_{t.}$ $\nu_t$ is influenced by airflow conditions that vary as a function of RH, unlike the surface velocity ($\nu_s$), which depends on the uptake due to the surface material but is independent of flow rate. The inverse of $\nu_d$ is equal to the total resistance due to transport and surface uptake resistance. Thus, deposition velocities can also be written in terms of its resistance, as seen in Eqn. 4.1. Deposition velocities allows quantification of the relative contribution of kinetic and dynamic processes indirectly, and interfacial reactions may be described as transport-limited or reaction-limited deposition. Transport-limited reactions are affected by fluid dynamics at the air-surface interface. Reaction-limited deposition is measured by calculating its reaction probability, which is the determined by comparing the removal rate of ozone to the surface collision rate, or the amount of ozone adsorbed onto the surface.

$$v_d = \left(\frac{1}{v_s} + \frac{1}{v_t}\right)^{-1} \qquad \text{(Eqn. 4.1)}$$

Cano-Ruiz et al. defined $\nu_d$ as the sum of its mass-transport velocity and surface reaction velocity.

Ozonolysis on surfaces is the most studied oxidative surface chemistry. Many have analyzed deposition velocities of $O_3$ onto common surfaces, such as glass, wool, brick, gypsum board, wood, vinyl, and many more. Aside from these materials, many surfaces are coated with paints and other materials, which will further influence deposition velocities due to inhibited reaction sites[137-139]. Figure 4.3.1 visually describes measured deposition velocities in previous studies. Figure 4.3.2 compares the obtained $\nu_d$ for carpet in various studies. This figure for ozonolysis on carpet shows that most deposition velocities for the same type of material fall within a range of $\nu_d$ values but with a variable $\nu_t$. This figure accentuates the large variability and ranges $\nu_t$ may be. The effect of $\nu_t$ on $\nu_d$, however, is generally negligible, except for the $\nu_d$ reported from Coleman et al. Figure 4.3.2 shows that for a few different materials, $\nu_d$ is within a tighter range of values than that of $\nu_t$. With the exception of Coleman et al., this suggests that air flow control is not the dominant factor in surface chemistry, and that comparisons with other studies are comparable even if different experimental conditions were used.

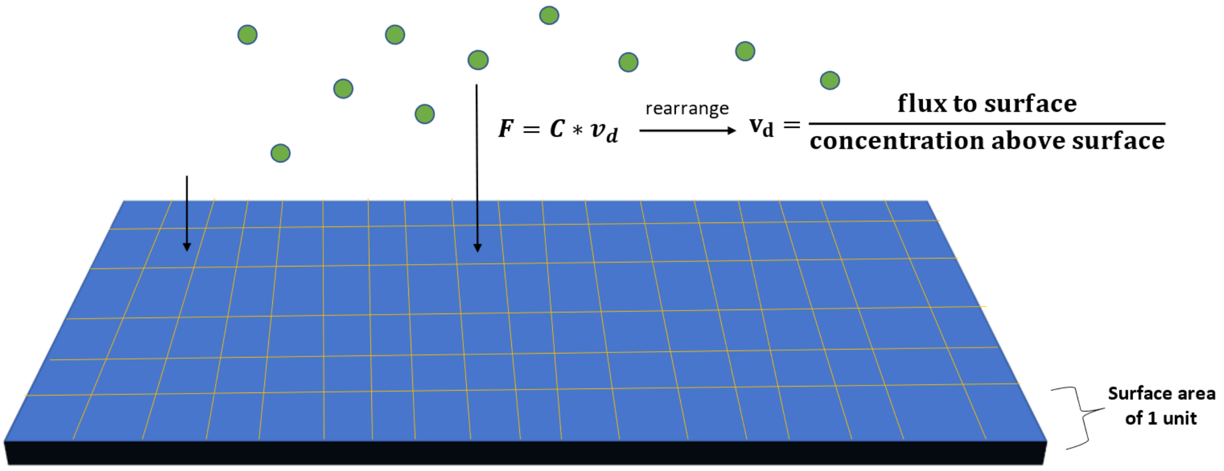


Figure 4.3.1. A visual model of how to calculate the total deposition velocity.

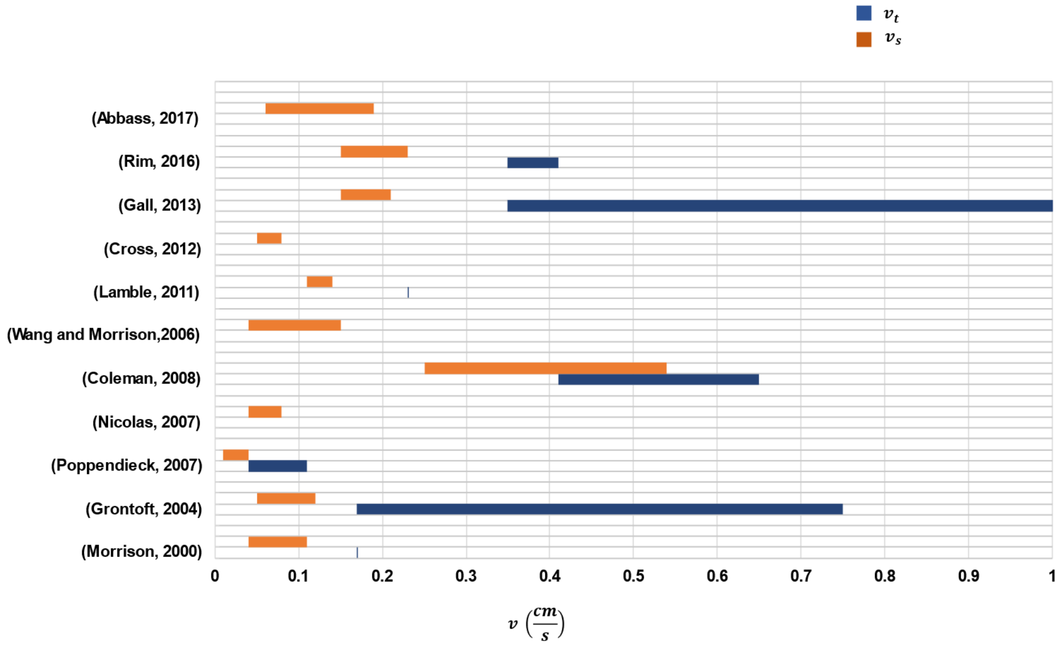


Figure 4.3.2. A compilation of measured total deposition rates. Mass-transport velocities were calculated indirectly and their ranges of $v_s$ and $v_t$ [65, 139-147]

# CHAPTER 5

# CONCLUSIONS AND FUTURE WORK

## *5.1 Challenges of the Future*

Although the field of indoor chemistry is mostly unexplored, much progress has been made in our understanding of reaction processes that influence indoor air quality. In the 90s, many pioneering studies on radical chemistry were published. Much has been learned about the relationships between $O_3$ and $NO_x$, ozonolysis, nitrate radicals, and chemical pollutants since then. These seminal studies have led to other interesting discoveries, such as the important role that HONO plays in reactive chemistry. From measuring reactive species, HONO's role in oxidative chemistry was discovered. HONO was also realized to be a dangerous compound that are precursors to nitrosamines. Surface reactions of compounds with different materials were also being explored, and many modeling studies were developed to simulate the boundary between the air and surface. By the early 2000s until the present, research was starting to include the impact that human beings make on the environment. As an example, more studies regarding occupancy, reactions of skin oils, hair, and clothing with $O_3$, and comparisons between home and office spaces are of interest.

We are progressing incrementally in understanding our environment, but many questions are still unanswered. There are few studies examining the role of hydrolysis in surface reactions, and the consequences of RH on surface-sorbed are largely unknown. Sorbed water may facilitate acid-base chemistry, another topic that is understudied. Such studies can further our understanding and enhance observations such as when studying HONO. Very few facts are known about the formation of HONO. We know that water enhances HONO formation, and that it plays an active role in forming carcinogens from nicotine residuals. With the many reactive organic compounds, the role of water must certainly be influencing acid-base equilibria. Weak photolysis reactions are another topic that deserves more attention, but research on the implications of low actinic flux are sparse. Pursuing this avenue may lead to more discoveries on how the interior atmosphere is different from the exterior one. Furthermore, the resulting chemical consequences will further inform us on our chosen light sources.

Indoor chemistry is an active field of study, and this review barely scratches the surface of what is currently being studied. Though we are progressing in our understanding, challenges persist because measurement techniques are not appropriate for indoor studies. Although many instrumentation that were used for the outdoors have been adapted for indoor use, there are some specifications that are especially important for making indoor measurements. Firstly, instruments must be able to keep up with any chemical changes due to environmental factors that perturb the indoor atmosphere. The indoor atmosphere is constantly being disrupted by the opening of doors, people walking, and the temporary release of $NO_x$ from cooking, are just a few examples of abrupt disruptions. This unpredictable environment is very different from the troposphere, where changes generally occur more slowly and have predictable patterns. Thus, instrumentation must have fast response times to capture any chemical changes. Collaborations through field campaigns and measurement comparisons are also needed. Figure 5.1.1 exemplifies collaborative measurements of HONO during a field campaign.

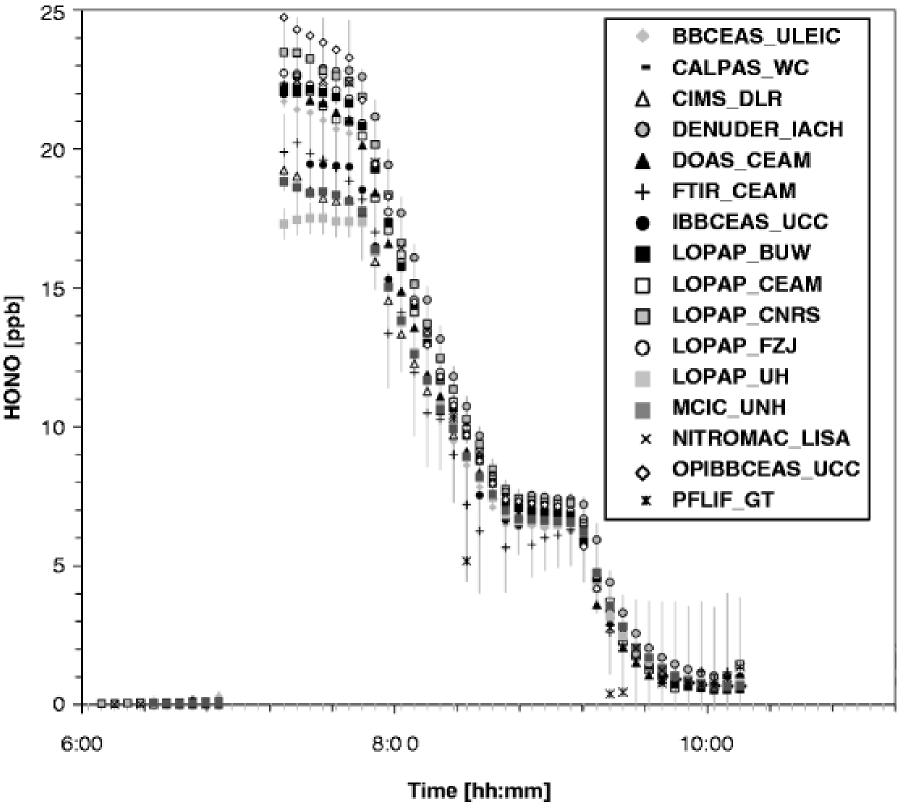


Figure 5.1.1. A Comparison of HONO Measurements. Reproduced from[148].

Another challenge we are currently investigating is the impacts of interfacial chemistry. Though indoor processes may parallel tropospheric interactions between aerosol and organics, the consequences of indoor surface chemistry and film formations may be vastly different from outdoor implications. Indoor surfaces provide reaction sites that can be a permanent reservoir of a chemical source, one that can last from days to years. Processes like these will have different consequences from outdoor surface processes. More research is needed for studying the reactions between surfaces and gaseous molecules and particulates. Many of these measurements suffer from interferences. For example, ozonolysis is a series of consecutive reactions occurring, resulting in numerous byproducts. These byproducts and secondary products that result from them have a high chance of interfering with measurements.

This review highlighted some studies from the largely undiscovered domain of indoor chemistry. Core concepts such as oxidative reactions gas-surface partitioning were discussed in terms of their influence on air composition. Many of the chemical processes discussed may parallel outdoor chemical processes, but its influence on the indoor world pose very different challenges that have very different implications on indoor air quality.

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