Kinetic Modeling Study of Organic Aerosol Formation and Processing

by

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This is to certify that I have examined the above PhD thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made

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- To all the stars in the universe -
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Kinetic Modeling Study of Organic Aerosol Formation and Processing

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Abstract

Organic matter contributes substantially to the atmospheric particulate matters in earth’s atmosphere. A wide range of techniques aiming at measuring the physical and chemical properties of particulate matters have revealed remarkable insights about the formation and evolution of particulate organic matters. Kinetic models provide a unique perspective and unravel information that is difficult or impossible to obtain otherwise. In this dissertation, kinetic models are utilized to probe some key aspects regarding the formation and evolution of organic aerosols in different atmospheric systems, and with some focus on Hong Kong, a densely populated region in the south of China. Secondary organic formation (SOA) from widely identified volatile organic precursors (isoprene, monoterpenes and aromatics) are modeled and evaluated using tracer-based measurements, and the sensitivities (e.g. on NOx and VOCs) are examined. Located in the tropical latitude, Hong Kong is feather with high humidity all year around and the ambient aerosols are expected to be rich in liquid water content. The aqueous-particle processes are unique and quite different from cloud processes. The potential contribution of aqueous-particle processes in SOA formation in ambient Hong Kong is investigated using an observation-based model, based on most updated aqueous-phase mechanism that is relevant to aqueous-particle conditions. Glyoxal, emitted by a wide range of anthropogenic and natural processes, are highly water-soluble yet its behavior in aqueous-particles remain highly uncertain. Controlled chamber experiments (PSI, Switzerland) combined with a kinetic model were conducted to investigate the reactive uptake of glyoxal on ammonium seeds and the kinetic behavior in the aerosol system under humid conditions.
Finally, a method has been developed to estimate the effective degradation of particulate semi-volatile organic compounds using ambient data, and the application of this method to estimate the effective degradation of hopanes in ambient Hong Kong.
CHAPTER 1. Introduction

1.1. Overview

Earth’s atmosphere primarily consists of N₂, O₂ and Ar, as well as trace amount of gaseous and aerosol constituents representing typically less than 1% of the atmosphere. These trace constituents greatly affect the physical and chemical properties of the atmosphere. For example, ultraviolet (UV) light in the solar radiation strikes O₂ in the stratosphere forming oxygen atoms, which recombines with O₂ to form O₃. Together with halogen- and nitrogen-containing compounds a thin layer of O₃ forms in the stratosphere. If compressed to the sea level air pressure, it would be only a few millimeters thick, yet the this thin O₃ layer screens out most of the UV radiation from the sunlight, making earth a potential habitable environment.

A variety of physical and chemical measurement techniques have established the fundamentals of the science of the atmosphere. Again take O₃ as an example – the ground-based measurements of stratospheric O₃ can be dated back in 1920s when British physicist G.M.B Dobson built the spectrophotometer based on differential absorption techniques. Nowadays stratospheric O₃ is probed using an array of ground-based, airborne and space-borne techniques. To this day observations still hold the potential of breakthroughs in the field of atmospheric science, and are also the final “touchstones” of all our understandings – with which the theories, principles or even new measurement techniques must be evaluated.

The atmosphere is a highly complex, non-linear system, in which numerous physical and chemical processes occur simultaneously. Understandings of individual processes mostly do not give implications for the system as a whole. Observations only give “snapshot” of a particular aspect at a particular time and location and hence have limitations. First off, temporally – it is difficult (and mostly impossible) to obtain the direct measurements “in the past”, and there is so far no practical way to obtain the measurements “in the future”. Secondly, spatially – not all measurement techniques can be easily deployed in locations of interests. Last but not least, not all measurements of interests can be (easily) obtained at the times of interests. As a result, lots of questions of great importance are at least practically or financially impossible to answer by looking solely at observations, for instance, what would the planet earth be like in 100 years if from now on no greenhouse gas emission controls were to carry out at all?
Mathematical models provide a unique alternative. Atmospheric models essentially are mathematical frameworks integrating our understanding of individual processes and can be used to explore their interactions and the implications. Large-scale atmospheric model developments since 1960s have been evaluated extensively with various observation and are proved to be skillful in general, not only in global mean, but also in regional patterns. However many key processes still remain poorly understood and highly uncertain to this day. Of which one of the most important is how organic aerosols are formed in the atmosphere, and how these organic aerosols interact with the other processes.

Organic matters make up a substantial fraction (20~90% by mass) of aerosol particles in earth’s atmosphere, from densely populated urban, to remote locations. Natural or anthropogenic, organic aerosols originate from either primary emissions (primary organic aerosol, POA) or secondary formation from gaseous precursors (secondary organic aerosol, SOA). Aerosols affect the earth’s radiative balance via both direct (e.g. scattering the solar radiation) and indirect forcing (mainly by effects on cloud properties). The total negative forcing of aerosols is highly uncertain and – based on the most recent evaluations – holds the great potential to offset the warming effect of greenhouse gases. Meanwhile aerosol particle related pollutions have negative impacts on human health. A better understanding the emissions, formation and the evolution of atmospheric organic aerosols is required to reduce the uncertainties in climate evaluations as well as improve air quality.

In general, SOA can be formed by condensation of low-volatility compounds emitted or photochemically formed in the atmosphere. Most “bottom-up” models use parameterizations of laboratory experiments to predict the concentrations and degree of oxidation of SOA. Despite recent progresses on SOA chemistry, current models are still facing challenges in predicting the magnitude and the evolution of atmospheric SOA. We herein summarize the major aspects and recent progress in SOA formation.

1.2. SOA Formation from Volatile Organic Compounds (VOCs)

Both laboratory and field studies indicate that the VOCs contribute substantially to atmospheric organic aerosols. An array of products with lower volatilities formed from oxidation of precursors subsequently partition into the condensed-phase. Of which the most intensively studied include isoprene, terpenes and aromatics.
1.2.1. Isoprene and terpenes

Isoprene has the largest global atmospheric emissions of all VOCs. Isoprene is highly reactive and its atmospheric lifetime is typically $10^1 \sim 10^2$ minutes. Isoprene in the atmosphere reacts with a number of oxidants, of which hydroxyl radicals (OH) is of greater importance. The OH oxidation mechanism depends on ambient NOx level. The initial OH attack forms alkyl radicals which are rapidly quenched by O2 molecules forming alkylperoxy radicals (RO2). Under low NOx condition, hydroxyhydroperoxide compounds are formed with large yields (>70%) by RO2+HO2 reaction. Other products include methacrolein (MACR), methyl vinyl ketone (MVK). Hydroxyhydroperoxides are further oxidized and structurally rearranged to form dihydroxyepoxide (IEPOX) compounds with yields exceeding 75%. Such 3-member-ring-bearing IEPOX compounds are expected to be extremely water-soluble – further IEPOX processes might be greatly affected by atmospheric waters. After partitioning into the aerosol-phase, IEPOX compounds undergo acid-catalyzed ring opening reaction and followed by the nucleophilic reaction with H2O, sulfate or even nitrate, forming a number of multi-functional group compounds such as 2-methyltrtrols, C5-alkene triols, organosulfates, methylfuran compounds, as well as oligomers. Chamber derived total SOA yield of IEPOX compounds reach ~12%. Other gas-phase products such as MACR and MVK may also partition into the aerosol-phase and contribute to SOA. In the presence of high level of NOx, RO2 radicals may react with NOx which is competing with the RO2+HO2 channel, forming ethacryloylperoxynitrate (MPAN). In addition MPAN may also be formed from MACR, a 1st generation product of isoprene oxidation. MPAN can be further oxidized by OH radicals forming an array of compounds including another epoxide compound – methacrylic acid epoxide (MAE) with a molar yield of 18%~32%. Reactive uptake of MAE onto acidified aerosols yields substantial SOA mass, including a widely used isoprene-SOA tracer 2-methylglyceric acid, while uptake onto neutral seeds is negligible. Analyze of synthesized epoxide compounds as well as the above isoprene tracers by aerosol mass spectrometry suggest that they contribute to a unique factor that can be resolved by positive matrix factorization (PMF) analysis of organic aerosol spectra, in good agreement with laboratory-generated SOA.

Terpenes are another class of VOCs emitted primarily by biogenic sources. Types of terpene species, emission strength usually vary with vegetation types, seasons and locations. Terpene species in the atmosphere can also be oxidized and subsequently contribute to SOA. Chamber studies reported total SOA mass yield ranges from 7 to 46% for α-pinene OH.
oxidation, depends also on NO\textsubscript{x} level\textsuperscript{22}. Besides the OH oxidation, O\textsubscript{3} in the ambient air can attack the endocyclic double bonds of monoterpenes species (ozonolysis) and lead to the formation of multi-functional group species with low volatilities\textsuperscript{23}. Total SOA yield up to 25% has been reported in chamber experiments\textsuperscript{23}. A number of tracer compounds are also identified in both chamber and ambient samples which are from monoterpenes oxidation, including a series of carbolic acids\textsuperscript{24} as well as organosulfates\textsuperscript{25-27}.

1.2.2. Aromatics

Aromatic compounds in the atmosphere are mostly associated with human activities, and are usually among the most abundant VOC species in the ambient air especially urban locations\textsuperscript{7,28,29}. In this section we take toluene as an example. In the atmosphere toluene mainly react with OH radicals. OH can attack on the methyl group and eventually result in the formation of benzaldehyde, the branching ratio of OH attack on the methyl group is minor (<10%). Alternatively, OH can add to the aromatic ring and form methyl hydroxy cyclohexadienyl radicals, and subsequently form cresol, 2-methyl-2,4-hexendien-dial or a bicyclic peroxy radical. This bicyclic peroxy radical can then undergo a ring-opening reaction to form a number of carbonyl compounds such as glyoxal, methyl glyoxal\textsuperscript{30,31}. SOA formation from toluene also depends on NO\textsubscript{x} level. Ng \textit{et al} reported a 30% SOA mass yield under low NO\textsubscript{x} conditions, and lower yield 8% to 13% when NO\textsubscript{x} level is high\textsuperscript{32}. Another more recent chamber study reported a slightly lower SOA yield under low NO\textsubscript{x} level, but a factor of ~2 higher yield under high NO\textsubscript{x} conditions, primarily because of the different experiment settings as well as the data treatment (e.g. condensation of organic vapors onto chamber walls were not corrected in Ng \textit{et al}\textsuperscript{33}). SOA formations from other aromatic compounds are also reported in Ng \textit{et al}\textsuperscript{32}. Chamber studies also identified tracer compound specific for aromatics, 2,3-dihydroxy-4-oxopentanoic acid, which has been reported in ambient samples as well\textsuperscript{24,34,35}. In addition, it has been reported that a substantial fraction of chamber SOA formed from photooxidation of aromatic compounds is composed of polymers\textsuperscript{36}, yet this mechanism has not been incorporated into chemical transport models until recently\textsuperscript{37}.

1.3. SOA Formation in Atmospheric Waters

A substantial fraction of our understanding about SOA formation is based on chamber experiments. Due to the difficulties in controlling relative humidity (RH) and the possible complications the moisture might bring to the experiments, most of previous chamber experiments were conducted under very dry conditions. How would moisture in the air affect the SOA formation? Seinfeld \textit{et al}\textsuperscript{38} examined the effect of RH on the partitioning of semi-
volatile organic compounds and indicated that the presence of aerosol water will decrease the mean molecular weight of the organic-phase and hence lead to a lower gas-to-particle partitioning of semi-volatile compounds. This is generally consistent with a few experiments under low-mid RH or very high organic-to-water ratio conditions. However other chamber experiments conducted under high RH conditions reported greatly enhanced SOA formation beyond the scope of “traditional” SOA formation theory. Many aerosol components are hygroscopic, e.g. sulfate, nitrate, ammonium. Even RH is low there may still be little amount of surficial water. When RH is sufficiently high the aerosol may absorb water and form liquid or metastable liquid. If further increase RH (e.g. supersaturation) the aerosol may even be activated and form droplets (e.g. cloud, fog). The condense water-phase may serve as a potential reactor for aqueous-phase processes – this pathway is clearly not captured by most previous “dry” chamber experiments.

Cloud chemistry has been found to be responsible for the majority of oxalic acid formation, the single most abundant di-carboxylic acid identified in atmospheric aerosols. However, although not entirely clear, the role of cloud chemistry on the SOA formation is perhaps limited, as (1) the further stage of cloud processing would be dominated by fragmentation and lead to organic mass reduction; and (2) photochemical cloud processing is limited by the availability of OH radicals and no (currently known) aqueous-phase OH sources can overcome this limitation. Fog processing is chemically similar to cloud but often leads to effective removal of aerosols due to the high deposition velocity of fog droplets at near ground level. Impacts of cloud and fog processing are summarized by Blando et al. Aqueous aerosols, however, could be quite different. Although the liquid water content (LWC) is much lower compared with cloud droplets, water soluble compounds usually exist in rather high concentration and hence the chemical scheme on wet aerosols are quite different. Meanwhile the aqueous-phase OH-limitation in aqueous aerosol systems might be “feasible.” Glyoxal is one major player on wet aerosols due to its potentially large source and high water-solubility and the potential to contribute to SOA mass. Bulk aqueous-phase experiments conducted under concentrated conditions (e.g. aqueous aerosol relevant) using glyoxal and other water-soluble organic compounds suggest that the aqueous-particle processes can be a potential pathway for SOA formation in the ambient environment, leading to the formation of a series of products, such as di-carboxylic acids, oligomers, organosulfates, and many of these compounds have been long identified in ambient aerosol samples. Glyoxal and aqueous particle processes have been examined in models as well as a limited
number of ambient studies\textsuperscript{68–70}. The impacts of the aqueous-particle processes show quite large variations and heavily depend on conditions. What is clear is that the aqueous-particle processes form highly oxidized products (e.g. di-carboxylid acids, organosulfates) and hence will help shorten the model-measurement discrepancies.

1.4. Recent Updates: Rethinking of Some Key Aspects of SOA

1.4.1. Wall Loss of Organic Vapors in Chamber Studies

The aforementioned VOCs have been identified as major SOA precursors and have received much attention in the past two decades or so. Parameterizations (e.g. SOA yields, atomic O/C ratio – an indicator of the oxidation state of particulate organics) based on these experiments have been extensively used in chemical transport models.

Wall loss is an issue for all chamber facilities, especially for those “smaller” chambers. Particle wall loss has been routinely accounted for. However, semi-volatile organic vapors may also loss onto chamber walls or establish equilibrium with wall-deposited organics\textsuperscript{71}. Vapor wall loss has not been accounted for in most previous chamber experiments. Zhang et al\textsuperscript{72} examined the organic vapor wall loss in earlier experiments and evaluated the effects on SOA yields – it has been demonstrated that the vapor loss can lead to substantially underestimation of SOA formation up to a factor of 4. Future applications of chamber parameterizations must take these effects into consideration and it holds great potential to shorten the model-measurement discrepancies.

1.4.2. Kinetic Behavior

Many previous chamber experiments focused more on the total SOA mass and the atomic O/C ratio, while the microphysical properties (e.g. kinetic limitations) have not been widely / closely examined, partly because of the lack of molecule-leveled understanding about the formation and evolution of SOA, not to mention that we already have enough troubles in predicting simple total SOA mass and atomic O/C ratio. Therefore in most cases it seems rational to ignore the microphysical aspects of aerosol systems. However a recent study closely examined the particle size distribution dynamics in chamber experiments revealed insights of the how SOA is formed. Using a multi-layer kinetic model, the size distribution dynamics of dodecane SOA system can only be explained by a reactive surface uptake, which accounted for more than 50\% of the SOA mass\textsuperscript{73}. Further experiments confirmed that the surface uptake can be explained by the heterogeneous reaction of aldehydes (from the photooxidation) with organic hydroperoxides forming peroxyhemiacetals\textsuperscript{73}. Aerosol particles under atmospherically relevant conditions may exist in amorphous solid state (“glassy”)\textsuperscript{74,75}. Even aqueous aerosols,
due to the low LWC / high concentrations of soluble components, the aerosol liquid water might be more “sticky” than cloud / fog droplets. Therefore diffusion in the bulk particle could be much slower compared with a liquid particle or dilution droplets / solutions, leading to a considerable reduction of the surface-to-bulk mass transport as well as the bulk reactions. Therefore the organic vapors (as well as other molecules such as OH, O$_3$) may accumulate on the surface and hence trigger the surface reactions. The combination of kinetic models with chamber experiments leads to a better understanding of the aerosol chemistry and physics as a whole.

1.4.3. Semi-/Intermediate-VOCs

“Traditional” SOA formation theory assumes the partition of condensable gases occurs between the gas-phase and the particulate organic-phase. A substantially fraction of particulate organics originates from primary emissions, a.k.a. POA, and POA was once assumed to be stable (particle-phase reactions are mostly specific to certain species such as those may trigger oligomerizations and the extent of such reactions are limited). Such assumptions are often expanded in further applications. For example, source apportionment techniques such as Chemical Mass Balance (CMB) model requires a number of tracers for each individual source, and these tracer compounds need to be chemically stable. Certain organic molecules found in aerosol particles are associated with specific sources, such as levoglucosan for biomass burning, hopanes and sterane for motor vehicles, cholesterol for meat cooking, etc. These particulate organic molecular markers were assumed to be protected in the particle-phase and hence “chemically stable”, until recent studies indicated unambiguously that these particle-phase marker compounds may as well undergo degradation that is rapid enough to result in considerable uncertainties in the CMB applications. Heterogeneous and bulk particle-phase reactions are unlikely to explain such degradation, yet it is plausible that the semi-volatile nature of these compounds determines that a substantial fraction of them exist in the gas-phase and subsequently undergo gas-phase oxidation processes, leading to an effective degradation. This hypothesis is supported by the volatility measurements of these molecular markers.

The semi-volatile nature of these particulate organic markers draws the attention in the application of them in CMB. Moreover, it leads to the rethinking of POA – what if a substantial fraction of POA is semi-/intermediate- volatile? Or, what if sources emit semi-/intermediate-volatile organics in the gas-phase as well? Chamber experiments combined with thermodynamic measurements with motor vehicle emissions and biomass burning emissions revealed remarkable insights – primary emissions were mapped into volatility bins (VBS:
Volatile Basis Set) and the evolution of these bins are parameterized. Earlier VBS-based SOA formation modeling works have been evaluated in a few field campaigns, and still face challenges in predicting total SOA mass or atomic O/C ratio\cite{68,85}. Further attempts introduced another dimension – oxidation state (e.g. atomic O/C ratio) – in addition to the volatilities (e.g. 2D-VBS) and reveal insights about how the aging processes (especially OH oxidation in the gas-phase) alter the volatilities and the oxidation states of the products\cite{86,87,88}. These works establish a framework that is more advanced than traditional SOA formation schemes in many ways: (1) S/I-VOCs are clearly missed in traditional SOA formation schemes; (2) aging of aerosols under atmospheric conditions alter both the volatilities and the oxidation states of products, while the aging processes are either missed or highly parameterized (and inaccurate) in traditional SOA formation schemes.

1.5. Scope of This Work

This work explores SOA formation from VOCs and S/I-VOCs, as well as the potential impacts of aqueous-phase processes. Chapter 1 (this chapter) serves as an introduction, reviews recent findings about the formation and evolution of organic aerosols. Chapter 2 investigated the relative contributions of major SOA precursors, isoprene, terpenes and aromatics, in Hong Kong and Pearl River Delta (PRD) region, China, based on updated emission inventories\cite{89}. The results are compared with tracer-based SOA estimates. Chapter 3 explores the potential contribution of aqueous-particle processes in SOA formation in ambient Hong Kong, an all-year-round humid and sulfate rich environment, using most updated aqueous-phase mechanism that is relevant to aqueous-particle conditions. Chapter 4 combines controlled chamber experiments (PSI, Switzerland) with a kinetic model to investigate the reactive uptake of glyoxal on ammonium seeds and the kinetic behavior in the aerosol system under humid conditions. Chapter 5 develops a method to estimate the effective degradation of particulate semi-volatile organic compounds using ambient data, and the application of this method to estimate the effective degradation of hopanes in ambient Hong Kong. In general, Chapter 2 and Chapter 5 examines SOA formation and aging from VOCs and S/I-VOCs, while Chapter 3 and Chapter 4 focused on the independent aqueous-phase processes. Small-scale kinetic models are utilized in this work to interpret the observations, with focus shifting between chemistry (e.g. Chapter 2) and microphysics (Chapter 3). Lastly Chapter 6 is conclusions and implications.
CHAPTER 2. Relative Contribution of Biogenic and Anthropogenic Precursors to Secondary Organic Formation (SOA) in Hong Kong and the Pearl River Delta Region, China

2.1. Overview

Secondary organic aerosols (SOA) formed from the atmospheric reactions of anthropogenic and biogenic volatile organic compounds (VOCs) account for a large portion of organic particulate matter. Numerous chamber studies have demonstrated that toluene, xylenes, isoprene, and terpenes are important VOC precursors for SOA formation. Field measurements of their SOA tracers spanning a range of environments also suggest these species contribute a significant fraction of identified SOA components. Current air quality models largely under-predict organic aerosol, strongly suggesting that there are missing potential pathways of SOA formation and/or missing SOA precursors in the SOA formation mechanisms, which has been demonstrated through recent smog chamber studies. In the recent years, works have been done in the modeling community to include additional SOA sources in models, as well as in explaining the lack of closure between measured and modeled SOA.

A number of approaches are available to estimate SOA formation in the ambient environment. Among them, a SOA tracer-based approach uses the relationship between certain VOC precursors and their SOA tracers derived from laboratory experiments, thereby providing the possibility of tracking SOA formation from specific SOA precursors. Although this method has its uncertainties rooted in over-simplifying the complicated SOA formation processes with a single chamber-derived tracer “yield”, it has the unique advantage in revealing the direct linkage between SOA formation and major precursors. Tracers derived from the oxidation of common VOC precursors including toluene, xylenes, isoprene and monoterpenes have been used to estimate SOA formation from these VOCs in a number of studies.

Alternatively, emission/source-based approaches have been widely used in model simulations, in which SOA formation is estimated through simulating oxidation kinetics of SOA precursors and partitioning of condensable oxidation products into aerosol-phase. The treatment of partitioning has evolved over time from simply assuming a sufficiently low vapor pressure of 2 ppt for each condensable product species to absorption partitioning equilibrium in an organic aerosol phase and more recently to reformulation of the Pankow
theory by replacing the partitioning coefficient with an effective saturation concentration \( (C^*) \) that is a function of \(^{87}\). In this work, we use the approach by \textit{Strader et al} \(^{102}\) in that the partitioning is approximated by a pseudo-ideal solution. \( C_{a,i} \), the aerosol-phase concentrations of species \( i \) in \( \mu \text{g/m}^3 \) is calculated using the equation below:

\[
C_{a,i} = C_{\text{total},i} - \frac{C_{a,i}}{MW_i} \sum_{j=1}^{a} \frac{C_{a,j}}{MW_j} + \frac{C_0}{MW_0} \times C^*_i
\]

Eq.2.1

where \( C_{\text{total},i} \) is the total concentration of condensable gas \( i \), \( C_0 \) is the organic loading, and \( MW \) is the molecular weight of different components. \( C^*_i \), the effective saturation concentration of pure organic compound \( i \), determines the potential of an individual condensable product partitioning into aerosol-phase. \( C^*_i \) is either experimentally determined or derived from theoretical work, and its temperature dependency is described by Clausius-Clapeyron equation.

This approach has been integrated into various models along with a choice of certain gas-phase chemical mechanism (e.g., CB4, CB05, SAPRC99, SAPRC07) to simulate the SOA formation \(^{102}\). This modeling approach also provides the capability of tracking the contributions of individual VOC precursors to SOA formation.

The Pearl River Delta (PRD), an economically more developed region in China, features in large anthropogenic VOC and NO\(_x\) emissions and heavy ozone episodes \(^{104}\). Due to the highly concentrated industrial activities, high levels of aromatics have been frequently observed in PRD, significantly higher than the ambient measurements in many other locations around the world. Large contributions from gasoline exhaust, coating/painting and oil refinery industry make toluene the most abundant ambient VOC in many PRD cities \(^{105,106}\). For instance, measurements using an in-situ online GC-FID in the PRD region show that in 13 out of 19 days the daily maximum toluene exceeded 20 ppbv in Guangzhou (GZ), a densely populated city. In the same period in a rural site in PRD, Xin Ken, daily peak toluene exceeded 20 ppbv in 9 out of 16 measurement days \(^{107}\). The maximum toluene measured using canister-GC/MS is reported to be 36.91 and 54.61 ppbv in GZ and Xin Ken, respectively \(^{29}\).
Table 2.1. Ambient VOC measurements in Hong Kong and in the PRD region. Results are given in average ± standard deviation unless specified otherwise.

<table>
<thead>
<tr>
<th>Location</th>
<th>Ethane</th>
<th>Ethene</th>
<th>Isoprene</th>
<th>Monoterpenes</th>
<th>Toluene</th>
<th>Xylenes</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient measurements in Hong Kong (Unit: ppbv)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Tap Mun (TM, Rural) a</td>
<td>1.15±0.71</td>
<td>0.91±1.53</td>
<td>0.58±0.45</td>
<td>N.A. j</td>
<td>1.25±1.36</td>
<td>0.43±0.91</td>
<td>UCI j</td>
</tr>
<tr>
<td>Central West (CW, Urban) a</td>
<td>1.24±0.74</td>
<td>1.41±0.70</td>
<td>0.19±0.17</td>
<td>N.A.</td>
<td>1.96±1.76</td>
<td>0.60±0.71</td>
<td>UCI</td>
</tr>
<tr>
<td>Tung Chung (TC, Urban) a</td>
<td>1.06±0.72</td>
<td>1.03±0.75</td>
<td>0.34±0.26</td>
<td>N.A.</td>
<td>1.40±1.91</td>
<td>0.44±0.88</td>
<td>UCI</td>
</tr>
<tr>
<td>Yuen Long (YL, Urban) a</td>
<td>1.38±0.74</td>
<td>2.14±0.98</td>
<td>0.26±0.11</td>
<td>N.A.</td>
<td>2.65±2.91</td>
<td>0.78±0.86</td>
<td>UCI</td>
</tr>
<tr>
<td>Tsuen Wan (TW, Urban) b</td>
<td>1.20±0.54</td>
<td>1.74±0.31</td>
<td>0.59±0.25</td>
<td>0.03±0.02</td>
<td>4.30±1.99</td>
<td>0.91±0.28</td>
<td>UCI</td>
</tr>
<tr>
<td>Poly Univ. (PU, Roadside) c</td>
<td>2.93±0.85</td>
<td>8.56±1.12</td>
<td>0.56±0.13</td>
<td>0.10±0.05</td>
<td>12.10±3.46</td>
<td>3.40±0.47</td>
<td>UCI</td>
</tr>
<tr>
<td>Mong Kok (MK, Roadside) c</td>
<td>3.33±0.65</td>
<td>8.47±0.83</td>
<td>0.27±0.12</td>
<td>0.06±0.02</td>
<td>6.93±1.87</td>
<td>2.27±0.80</td>
<td>UCI</td>
</tr>
<tr>
<td>Tunnel (HK) d</td>
<td>3.16±0.85</td>
<td>25.90±2.84</td>
<td>0.53±0.39</td>
<td>0.04±0.02</td>
<td>11.2±3.46</td>
<td>3.63±4.37</td>
<td>UCI</td>
</tr>
<tr>
<td>Ambient measurements in the PRD region (Unit: ppbv)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guangzhou (GZ, Urban) e</td>
<td>5.58±3.34</td>
<td>6.55±4.82</td>
<td>0.22±0.17</td>
<td>0.18±0.18</td>
<td>7.01±7.33</td>
<td>1.98±1.92</td>
<td>PKU j</td>
</tr>
<tr>
<td>Xin Ken (XK, Rural) e</td>
<td>3.07±1.26</td>
<td>2.68±2.19</td>
<td>0.17±0.15</td>
<td>0.17±0.22</td>
<td>8.46±9.94</td>
<td>2.65±3.97</td>
<td>PKU</td>
</tr>
<tr>
<td>Guangzhou (GZ, Urban) f</td>
<td>1.89±0.10</td>
<td>3.97±0.42</td>
<td>1.63±0.18</td>
<td>0.16±0.10</td>
<td>5.87±0.74</td>
<td>2.11±0.69</td>
<td>UCI</td>
</tr>
<tr>
<td>Dongguan (DG, Urban) f</td>
<td>1.60±0.06</td>
<td>3.07±0.27</td>
<td>0.68±0.16</td>
<td>0.14±0.02</td>
<td>6.13±0.81</td>
<td>2.00±0.17</td>
<td>UCI</td>
</tr>
<tr>
<td>Industrial Areas (PRD) g</td>
<td>2.3±1.3</td>
<td>5.1±3.8</td>
<td>0.6±0.3</td>
<td>N.A.</td>
<td>13.5±11.8</td>
<td>6.1±7.1</td>
<td>UCI</td>
</tr>
<tr>
<td>Industrial-Urban (PRD) h</td>
<td>1.8±0.6</td>
<td>2.6±1.3</td>
<td>0.4±0.2</td>
<td>N.A.</td>
<td>11.5±11.6</td>
<td>3.4±2.2</td>
<td>UCI</td>
</tr>
<tr>
<td>Suburban (PRD) i</td>
<td>1.4±0.6</td>
<td>2.0±1.1</td>
<td>0.5±0.7</td>
<td>N.A.</td>
<td>7.3±5.4</td>
<td>2.2±2.1</td>
<td>UCI</td>
</tr>
</tbody>
</table>

a Summer & autumn measurements in various sites in Hong Kong from 2006 to 2008, n = 95 / 108;
b Ambient measurements at Tsuen Wan air quality station, a urban background station in Hong Kong, n = 7 / 109;
c Roadside measurements at Hong Kong Polytechnic University and Mong Kok in Hong Kong, n = 10 / 109;
d Averaged from Shing Mun Tunnel and Tsuen Kwan Tunnel experiments in Hong Kong, n = 29 / 109;
e Ambient measurements in Guangzhou (urban) and Xin Ken (rural), about 90 samples each / 29;
f Ambient measurement in Guangzhou (urban), n = 42 samples and Dongguan (urban, 48 samples) / 110;
g Sampling near a significant industrial point source or an industrial complex (industrial) in PRD, n = 15;
h Sampling in an area (away from any known point sources) with mixed industrial and urban sources (industrial-urban) in PRD, n = 25;
i Sampling in an area (away from any known point sources) with mixed industrial and suburban/rural sources (industrial-suburban) in PRD, n = 38 samples;
j See / 111 for detailed descriptions;
k Within this table, monoterpene represent the sum of α-pinene and β-pinene;
l Xylenes are the sum of m-, p-, and o-xylene.
m N.A. = Not analyzed; UCI = University of California, Irvine, U.S.; PKU = Peking University, China (Herein blind intercomparison of 55 major NMHCs had been conducted with UCI, see Liu et al. 105)
Hong Kong (HK) is a highly urbanized city, taking up a land mass area of 1,104 km². HK, at the mouth of PRD, is frequently affected by pollution transported from the PRD to the north but its local anthropogenic VOC sources are significantly less intense. In comparison with locations in the PRD, the ambient levels of aromatics in non-roadside environments in HK are much lower. For example, a one-year measurement project in HK indicates the average toluene is 1.03 – 4.34 ppbv in typical urban and rural locations; another 2-year measurements in HK (Table 2.1) show similar results, and the maximum toluene is 14.56 ppbv. The typical levels of anthropogenic VOCs in major PRD cities are comparable to those observed in roadside environments of HK with heavy traffic influence. Table 2.1 lists more ambient measurements, consistently illustrating the spatial gradient of these major anthropogenic VOCs between HK and the PRD.

Located in the subtropics, HK and the PRD feature large coverage of vegetation, implying significant biogenic VOC emissions, e.g., isoprene and terpenes. Unlike anthropogenic VOCs, biogenic VOCs in HK and the PRD show small differences in their ambient concentrations, as shown in Table 2.1. In general, ambient isoprene levels are similar between HK and GZ, while the limited number of ambient measurements indicate that concentrations of monoterpenes (α-pinene + β-pinene) are slightly higher in GZ than those in HK.

The high abundances of anthropogenic and biogenic VOCs provide considerable potential for SOA formation. Two recent studies report SOA tracer measurements in this region, one in HK [Hu et al., 2008] and another in Wan Qing Sha, a site in a suburban district but downwind densely populated urban districts of GZ. HK and Wan Qing Sha are less than 80 km apart, but relative contributions of anthropogenic and biogenic VOCs to SOA were found to differ significantly. In Wan Qing Sha, aromatics-derived SOA accounts for 80 – 86% of the sum of SOA derived from aromatics, isoprene and monoterpenes (SOA\text{sum} = SOA\text{aromatics} + SOA\text{isoprene} + SOA\text{monoterpenes}), much higher than the portion of isoprene (8 – 20%) and monoterpenes (1 – 5%)\textsuperscript{34}. The results in Hong Kong are very different: monoterpenes contribute 38 – 62% of the sum of aromatics-, isoprene- and monoterpenes-derived SOA, while aromatics and isoprene account for minor fractions (SOA\text{Aromatics}: 17 – 29%; SOA\text{Isoprene}: 21 – 33%)\textsuperscript{35}. Can such a discrepancy be explained by the different characteristics in emissions between the two locations? In this work, we have developed an emission-based 0-D box model that incorporates emissions generated for this region using Sparse Matrix Operator Kernel Emissions (SMOKE) and Model of Emissions of Gases and Aerosols from Nature (MEGAN).
to simulate the gas-phase chemistry and SOA formation. The simulation results will be evaluated against the two aforementioned tracer-based SOA measurements. The objectives are to understand the relative importance of toluene, xylenes, isoprene and monoterpenes to the SOA formation in HK and GZ in the PRD region and to identify data deficiencies in VOC emissions or SOA estimation. Note that in this work we focus on the SOA formation from aromatics, isoprene and monoterpenes, which does not necessarily suggests that these precursors can explain the total SOA in this region. In fact Hu et al \(^{35}\) indicated that toluene, isoprene and monoterpenes only account for 4 – 25% of total particulate organic matter (POM) mass. Given that SOA typically contributes to 17 – 56% of total POM mass in Hong Kong \(^{35}\), there is still significant fraction of unidentified secondary organic aerosol in this area. In recent years semi-volatile and intermediate VOCs (S/I VOCs) from primary emissions are found to form significant SOA mass upon fast oxidation \(^{10}\). Although facing challenges in predicting atomic O/C ratio \(^{85}\), this mechanism is expected to play an important role in the SOA formation in the ambient environment and greatly enhances the currently underestimated SOA mass. Primary emission of organic matters is huge in this region and therefore we suspect SOA formation through the oxidation and aging of S/I VOCs may account for a potential fraction of currently unidentified SOA.

The PRD region features high relative humidity, high ambient NO\(_x\) and VOC loadings. GZ is the largest city in the PRD and influenced by both vehicular and industrial emissions. GZ represents a typical urban condition in the PRD, where the ambient concentrations of NO\(_x\) and VOCs (especially aromatics) exceed many other places around the world. This emission-based box modeling work, together with ambient SOA measurements, provides a first-order assessment of the emission data of the important VOC precursors. This could in turn facilitate evaluations of emission input data and chemical mechanism for more comprehensive simulation of SOA formation using 3-D air quality models. Insights gained in this study help us to understand aerosols in the PRD, which is a significant aerosol source region in East Asia.

2.2. Model Description

2.2.1 Model components

The diurnal variations of temperature, relative humidity (RH) and mixing layer height in the 0-D box model are set to approximate typical summer conditions in Hong Kong, with the temperature varying from 291K at night to 295K at noon, RH from 50% to 70%. Temperature and RH have opposite diurnal patterns. Mixing layer height is assumed to have a
minimum at 500 m in the nighttime and begins to rise at 6:00 AM local time and peaks at noon with the maximum set at 1200 m. The diurnal patterns of the above parameters are simulated to vary as sinusoid functions of local time. Photolysis is assumed to take place under clear-sky condition, in which solar zenith angle (SZA) is calculated using the method described by 114. Initial concentrations for major species are based on observations in HK. Base case emissions of anthropogenic pollutants are generated by SMOKE and emission fluxes of biogenic species are by MEGAN, the details of which are discussed in the next section. Dry depositions are adopted from those described by Huang et al 115. The model is pre-run for 24 hr for the establishment of intermediate species.

A condensed mechanism CB05 is used to simulate reactions of the gas-phase species, in which photolysis rates are derived from either JPL database or IUPAC. SOA formation mechanism is based on the method used in CAMx v5.30 116, in which five VOC precursors, i.e., toluene, xylenes, isoprene, terpenes and sesquiterpenes, are considered. In this work, due to a lack of relevant data in this region, sesquiterpenes are not included in either gas-phase chemistry or SOA formation mechanism. Hence, within this paper, the term “sum SOA” refers to the sum of SOA from toluene+xylenes, isoprene, and monoterpenes, i.e., $SOA_{Toluene+xylenes}+SOA_{Isoprene}+SOA_{Monoterpenes}$. Aqueous-phase process is not included.

The entrainment and subsequent dilution due to the rising of mixing layer height is not included in the model. Although this could be an important factor in the resulting SOA concentration, the change in the mixing layer height in this work is moderate, therefore such simplification would not introduce much uncertainty. The SOA concentration simulated in this work might reflect the upper-limit with respect to additional possible processes such as the dilution due to the rising of the mixing layer.

The ordinary differential equations (ODEs) are solved numerically using the double-precision version of LSODE solver 117, which facilitates the sparse matrix manipulation and significantly enhances computational efficiency for stiff problems. Strict and dynamic tolerance control strategy is used to maintain sufficient accuracy. The model framework has been evaluated by simulating a subset of reactions extracted from MCMv3.2 (http://mcm.leeds.ac.uk/MCM) that consist of thousands of species and reactions. The same sets of reactions are simulated using FACSIMILE, a widely used commercial solver for ODE system 118,119. The model results from the two solvers have been compared and the discrepancy is found to be fairly small, indicating the reliable performance of the LSODE solver and the model framework.
For the investigation of the non-linear nature of certain processes (e.g. ozone or SOA formation), isopleths for species of interests as a function of emission factors of NO\textsubscript{x} and NMHCs are constructed by running the model with different model settings of NO\textsubscript{x} and NMHC emission factors. Values for the isopleths are taken at 15:00 (local time) on the third day for further analysis. The time 15:00 is chosen to capture the approximate maximums of HO\textsubscript{x} radicals and ozone. OH and HO\textsubscript{2} radicals would typically reach their daily maximum at around 12:00-13:00, while ozone tends to peak in late afternoons (e.g., 16:00-17:00).

2.2.2 Emissions

2.2.2.1 Emission scenarios for Hong Kong

Since this 0-D box model is emission-based, the emission inputs for major species are given special attentions and details are described below. Hourly resolved 3 km × 3 km gridded anthropogenic emissions are generated using SMOKE while biogenic emissions are generated using MEGAN. The latest available emission inventories in HK and the PRD are used\textsuperscript{105,113,120-122}. Yuen Long, an urban area in the northern part of HK, is selected to represent HK in the box model. Emissions are based on nine-grid-averaged emission outputs centered at Yuen Long, covering an area of 81 km\textsuperscript{2} surrounding Yuen Long. The raw emission outputs from SMOKE and MEGAN are used as Base Case I in this study.

Previous studies indicate that the major PM components in HK could be significantly elevated by regional transport from the PRD region, especially on days when meteorological conditions favor land-sea breeze circulation\textsuperscript{123-126}. Unlike 3-D chemical transport models, box models are incapable of simulating transport processes. To compensate for this deficiency inherent to the box model, we have increased the raw emissions by certain factors to represent local emissions plus transport input on days of significant regional influence (called regional days thereafter for ease of discussion following the convention set by Hu et al.\textsuperscript{35}). The multiplying factors were set according to the typical ambient levels measured on the regional days. More specifically, the NO\textsubscript{x} emission is multiplied by a factor of 4.5, CO by 3, methane and other anthropogenic VOCs by 5, formaldehyde by 3 and other oxygenated VOCs remains unchanged. Biogenic emissions for isoprene remain unchanged, while emissions for monoterpenes are multiplied by 3 to match the ambient measurements of monoterpenes. The modified emissions are used as Base Case II.

In summary, Base Case I is for days that are dominated by emissions local to HK while Base Case II represent days with significant regional transport (i.e., the high pollution days). The average daytime emission fluxes of NO\textsubscript{x} and major VOC species are given in Table 2.2.
The emission fluxes for both NO$_x$ and VOCs in HK calculated in this work are generally lower than but still comparable to those reported by Huang et al$^{115}$, which estimated emission fluxes using SMOKE but with previous release of emission inventories and source profiles for this region (Table 2.2).

Table 2.2. Averaged daytime emission fluxes for NO$_x$ and major VOC species obtained with SMOKE or MEGAN. Unit: molecule cm$^{-2}$ s$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>NO$_x$</th>
<th>Ethane</th>
<th>Ethene</th>
<th>Isoprene</th>
<th>Monoterpenes</th>
<th>Toluene</th>
<th>Xylenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK Base Case I</td>
<td>2.29×10$^{11}$</td>
<td>7.64×10$^9$</td>
<td>3.60×10$^{10}$</td>
<td>2.40×10$^{11}$</td>
<td>7.53×10$^9$</td>
<td>0.52×10$^{11}$</td>
<td>1.16×10$^{10}$</td>
</tr>
<tr>
<td>HK Base Case II</td>
<td>1.03×10$^{12}$</td>
<td>3.82×10$^{10}$</td>
<td>1.80×10$^{11}$</td>
<td>2.40×10$^{11}$</td>
<td>2.26×10$^{10}$</td>
<td>2.56×10$^{11}$</td>
<td>5.82×10$^{10}$</td>
</tr>
<tr>
<td>GZ Base Case</td>
<td>2.04×10$^{12}$</td>
<td>7.71×10$^{10}$</td>
<td>2.38×10$^{11}$</td>
<td>2.62×10$^{11}$</td>
<td>3.44×10$^{10}$</td>
<td>5.05×10$^{11}$</td>
<td>1.43×10$^{11}$</td>
</tr>
<tr>
<td><em>Huang et al</em></td>
<td>1.99×10$^{12}$</td>
<td>1.20×10$^{10}$</td>
<td>1.80×10$^{11}$</td>
<td>3.35×10$^{11}$</td>
<td>2.00×10$^{11}$</td>
<td>1.80×10$^{11}$</td>
<td>3.00×10$^{10}$</td>
</tr>
</tbody>
</table>

*Daytime averaged emission fluxes for typical urban Hong Kong (HK) and Guangzhou (GZ) in this work, generated by SMOKE/MEGAN with latest emission inventories$^{113,122}$ and source profiles$^{105,121}$;

Daytime averaged emission fluxes of anthropogenic species were estimated using SMOKE but with previous release of emission inventories and source profiles, and isoprene emission flux is calculated using SMOKE but monoterpenes was roughly assumed to be ~60% of isoprene.$^{115}$

2.2.2.2 Emission for Guangzhou

Emissions of NO$_x$, VOCs and other major pollutants for Guangzhou are also generated using SMOKE and MEGAN and evaluated against observational datasets. Emissions from two downtown districts in GZ (Li Wan and Tian He) are averaged to represent the emissions of urban GZ. Emissions in each district are based on nine-grid-averaged emission outputs, covering an area of 81 km$^2$ (similar to the treatment for Yuen Long, HK). As a fast growing economic region with intensive manufacturing industries, PRD has large industrial emissions (e.g., coating & solvent use, furniture manufacturing) in addition to vehicular emissions, resulting in rather high levels of aromatics in its major cities as well as in the surrounding rural areas.$^{29,111}$ In recent years control measures have been implemented to reduce emissions from high-polluting diesel-powered vehicles and motorcycles in GZ, making gasoline and Liquefied Petroleum Gas (LPG) vehicles the major mobile sources in GZ (Guangzhou Environmental Protection Bureau, http://www.gzepb.gov.cn/hjgl/). Compared with HK, GZ has larger emission fluxes for both NO$_x$ and VOCs, especially aromatics (Table 2.2). The emission flux in GZ when compared to HK is approximately 2 and 2.5 times larger for toluene and xylenes, respectively, under Base case II scenario. We note that the emission rates for isoprene and monoterpenes in GZ are only slightly higher than in HK (1.1 times for isoprene and 1.5 times for monoterpenes).
2.2.2.3 Emission Data Evaluation

Ratios of selected VOCs in the emission inputs are compared with those for the known major sources in the region as one way to evaluate the reasonability of the emission flux data. We examine below ethene/toluene and ethane/ethene ratios.

Ethene emissions are dominated by vehicular exhaust while toluene could be from both gasoline vehicles and solvent uses. Tunnel experiments and source profile studies indicate that vehicular emissions typically have higher ethene/toluene ratio (i.e., HK tunnel: 2.31; PRD tunnel: 5.49; gasoline vehicle: 3.50), but the ratio in painting & solvent use sources is nearly zero. Data from the Hong Kong Environmental Protection Department (HKEPD) indicate local emissions of VOCs in HK are dominated by road transport (mainly gasoline vehicles) in the PRD, painting & solvent accounts for a large fraction of ambient VOCs. Hence, the ratio of ethene/toluene is expected to be lower in the PRD than that in HK and such characteristic is captured in the SMOKE-generated emission data. The ethene/toluene ratio in emissions in HK (0.69-0.70) is higher than that in GZ (0.47), consistent with the known difference in VOC source characteristics among the two cities. The ethene/toluene ratio in GZ is very close to that reported in the PRD emission inventory (0.49).

The ratio of ethane/ethene in the emissions in this work (HK: 0.21; GZ: 0.32) is lower than the ambient measurements (HK: 0.34-1.15; GZ: 0.45-0.15), consistent with the expected faster degradation of ethene than ethane in the atmosphere.

The key factors influencing estimate of biogenic VOC emissions are land-type/vegetation-type, solar radiation, and temperature. Considerable spatial and temporal variance and large uncertainties are expected in the biogenic VOC emissions estimates. Table 2.2 summarizes the biogenic emission fluxes in HK and GZ used in this study. The emission ratio of isoprene/monoterpenes is ~11 in HK and 7.9 in GZ. Only limited ambient measurements of monoterpenes are available in this region, as shown in the previous section and Table 2.1. The available measurements reveal that the ambient ratio of isoprene/monoterpenes is 4.8 – 19.7 in HK and 4.6 – 10.1 in the PRD region. Ambient measurements could provide some indications for data quality of the emission estimates. However, we note that the ambient measurements of monoterpenes have considerable uncertainties for several reasons. First, monoterpenes (e.g. α-pinene, β-pinene, limonene) usually have very low ambient concentrations (at least one or two order of magnitude lower than isoprene), and the calibration concentration range adopted for other VOCs might not be appropriate for monoterpenes. Second, ozone oxidation is a considerable removal pathway for
monoterpenes, while this plays a minor role for other VOCs. A commonly accepted analytical method for VOC species is canister-sampling followed by GC-MS analysis. However, not all canister-sampling set-ups are equipped with ozone-scrubbers to remove ozone from the sampled air. Those sets-ups without ozone-scrubbers would underestimate the ambient monoterpenes. With the consideration of the analytical uncertainties for monoterpenes, the biogenic emission fluxes calculated using MEGAN are generally consistent with the ambient measurements.

With the emissions from SMOKE and MEGAN, the model-predicted concentrations of methane, ethane, toluene, xylenes, isoprene and monoterpenes in HK and GZ fall within the ranges of ambient measurements while the model slightly over-predicts CO and formaldehyde in HK (Figures 2.1). The good agreement in order of magnitude demonstrates that the emissions and photochemistry used in this model are reasonable in representing the typical conditions in HK and GZ.

![Figure 2.1. Comparison between measured ambient concentrations of CO and selected VOCs and their simulated daytime concentration ranges and in Hong Kong under Base Case II scenario. Simulation results are shown in the form of daytime range (8:00-18:00, local time).](image)

2.3. Results and Discussion

2.3.1 Basic Photochemistry

The model simulates daily maximum concentrations of OH and HO$_2$ radicals at 2.1×10$^6$ molecule/cm$^3$ and 3.5×10$^7$ molecule/cm$^3$, respectively, in good accordance with field observations in the PRD 104. Ozone is modeled to peak in late afternoon and reach 40-65 ppbv, which is also typical in urban HK. Figure 2.2 shows the noontime value of ozone, ozone+NO$_2$ as a function of emission factors of NO$_x$ and NMHCs (after pre-run for 24 hr) in HK, providing information about ozone/NO$_x$/VOC chemistry in various scenarios of precursor emissions. The ozone formation sensitivity regimes (NO titration, VOC-limited and NO$_x$-limited) are clearly
shown in this figure. Seen from Figure 2.2, ozone formation in HK is generally VOC-limited and so is the case in GZ (not shown), both consistent with previous studies in the region.97,104

The characterization of HK and GZ being in the VOC-limited photochemical region can also be demonstrated in OH radical variation in response to perturbation in isoprene emissions. In HK, a reduction of 20% in isoprene emission leads to a 33% reduction in OH level, while in GZ the corresponding reduction in OH level is 26%.

Figure 2.2. (Left) Noon value of ozone, ozone+NO₂ as a function of emission factors of NO_x and NMHCs (after pre-run for 24 hr). An emission factor of 1 for both NO_x and NMHCs denotes the Base Case II (HK) emissions. The numbers on the isopleths are concentration values in ppbv. (Right) SOA formation potential as a function of emission factors of NO_x and NMHCs in Hong Kong. The emission rates (dimensionless) are relative to the Base Case II emission rates shown in Table 2.2. Color-coding shows the noon value of OH radical concentration. Solid grayish lines are the SOA mass concentration isopleths and the numbers on the line are SOA concentrations in µg/m³.

2.3.2 SOA Formation, Yields and Impacts of Temperature and Organic Loading

Chamber-derived SOA yields under simulated atmospheric conditions are commonly used to estimate the SOA formation in models. Chamber studies could hardly bracket the complexity of SOA formation processes encountered in the ambient environment. Such a highly simplified approach is recognized to have multiple drawbacks, including: (1) failure in properly representing the higher generation oxidation; (2) inability in accounting for heterogeneous reactions / multiphase reactions; (3) likely missing certain SOA formation pathways. Despite the drawbacks, it provides a way to evaluate SOA formation from known SOA precursors and the influence of major gas-phase chemistry and some other processes. Figure 2.3 shows the simulated SOA yields from toluene and xylenes as a function of temperature and organic loading (M₀). Temperature affects the effective saturation concentration and hence alters the gas-/aerosol-phase fraction of semi-volatile organic compounds (SVOCs). Pre-existing organics would influence the extent of partitioning of
SVOCs into the aerosol-phase. From this figure it is seen that an increase of temperature leads to a decrease in SOA yields, and the elevated M₀ level would increase the SOA yields. These general trends are consistent with our current understanding of SOA formation (as shown in Figure 2.3).

In the model simulation for HK, M₀ is assumed to be 5 µg/m³ in Base Case I, and 20 µg/m³ in Base Case II, in reference to ambient measurements. In Base Case I, the SOA concentration from the three classes VOCs considered in the model is simulated to reach 1.1 µg/m³ at the end of a 48-h simulation period. In Base Case II scenario, the total SOA formation reaches 4.3 µg/m³ at the end of the simulation. If the pre-existing organics were reduced to 10 µg/m³, the SOA formation would decrease to 3.3 µg/m³ at the end of the simulation. The higher SOA predicted in Base Case II is also partially due to the emissions of NOₓ and VOCs 3-5 times higher than those in Base Case I. More detailed analysis of emission-dependence of SOA formation is given in the following section.

Figure 2.3. (Left) simulated SOA yields of toluene and xylenes versus temperature and organic loading (M₀), under Base Case II of HK. (Right) Simulated and chamber-measured SOA (µg/m³) versus parent VOCs reacted (ppbv). Chamber measured final growth SOA mass and VOC reacted data are derived under various conditions. Embedded shows simulated SOA production rate (ug/m³/hr) versus parent VOC removal rate (ppb/hr), and color-coded by time of day (hr).

2.3.3 Emission-Dependence of SOA Formation

Figure 2.2 also shows the modeled SOA formation as a function of emission rates of NOₓ and total NMHCs. As shown in this figure, increase in NMHC emissions leads to more SOA formation. The relationship of NOₓ emission rates with SOA formation, however, is more complicated. In NOₓ sensitive regime, a reduction in NOₓ emission would lead to a decrease in OH levels. This results in slight decrease in SOA formation, as OH level largely controls the initial oxidation of VOCs. But in NOₓ saturated regime (i.e., VOC-limited regime), a reduction in NOₓ emission would cause an increase in OH level, thereby an increase in the SOA
formation follows. A few scenarios of changes in SOA formation in response to NO\textsubscript{x} emissions for HK are examined and summarized in Table 3. Since HK is generally in NO\textsubscript{x}-saturated regime, a reduction of 20% in NO\textsubscript{x} emission would lead to a 16% increase in total SOA mass, in which SOA\textsubscript{aromatics} increases by \(-38\%\), SOA\textsubscript{isoprene} by 7\%, and SOA\textsubscript{monoterpenes} by 1.4\%. Similar results are found for GZ.

Table 2.3. Response of SOA and ozone formation to reduction in anthropogenic VOC (AVOC) emissions. In each scenario, only AVOC emissions are changed, while the emissions for biogenic VOCs remain unchanged.

<table>
<thead>
<tr>
<th>Emission</th>
<th>Aromatics-SOA (%) (^a)</th>
<th>Isoprene-SOA (%) (^a)</th>
<th>Monoterpenes-SOA (%) (^a)</th>
<th>Total SOA (%) (^a)</th>
<th>(\text{O}_3) (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AVOC \times 0.8</td>
<td>-27.9</td>
<td>-2.4</td>
<td>-1.4</td>
<td>-9.8</td>
<td>-35.1</td>
</tr>
<tr>
<td>AVOC \times 0.5</td>
<td>-55.5</td>
<td>-4.7</td>
<td>-4.2</td>
<td>-21.0</td>
<td>-57.5</td>
</tr>
<tr>
<td>NO\textsubscript{x} \times 0.8</td>
<td>+38.2</td>
<td>+7.7</td>
<td>+1.4</td>
<td>+16.3</td>
<td>+63.0</td>
</tr>
<tr>
<td>NO\textsubscript{x} \times 0.5</td>
<td>+43.8</td>
<td>+8.5</td>
<td>+1.5</td>
<td>+18.6</td>
<td>+71.1</td>
</tr>
<tr>
<td>GZ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AVOC \times 0.8</td>
<td>-27.8</td>
<td>-1.3</td>
<td>-0.4</td>
<td>-14.4</td>
<td>-29.5</td>
</tr>
<tr>
<td>AVOC \times 0.5</td>
<td>-59.3</td>
<td>-4.4</td>
<td>-10.4</td>
<td>-33.8</td>
<td>-56.0</td>
</tr>
<tr>
<td>NO\textsubscript{x} \times 0.8</td>
<td>+45.3</td>
<td>+5.6</td>
<td>+0.6</td>
<td>+27.8</td>
<td>+73.6</td>
</tr>
<tr>
<td>NO\textsubscript{x} \times 0.5</td>
<td>+41.5</td>
<td>+4.9</td>
<td>-0.5</td>
<td>+25.5</td>
<td>+192.5</td>
</tr>
</tbody>
</table>

\(^a\) Reduction in mass concentration;  
\(^b\) Reduction in mixing ratio.

For the variation of NMHC emission factor in Figure 2.2, both anthropogenic and biogenic VOCs are assumed to vary at the same proportion. While the emissions of anthropogenic VOCs (AVOCs) can be controlled, biogenic VOCs cannot. As such, Figure 2.2 is not suited to probe sensitivity of SOA formation to VOC emission control. We therefore run separate simulations, assuming the same base case biogenic VOCs but different anthropogenic VOCs. The results are discussed below.
VOC source apportionment studies in the PRD region indicate that the predominant VOCs sources are vehicular emissions (31-51%) and coating & solvent usage (16-44%) \(^\text{106}\). In HK, these two sources contribute substantial fractions of ambient VOCs as well (vehicular emissions: 31-54%; solvent usage: 11-18%) \(^\text{108}\). In comparison with vehicle emissions control, evaporation of fuel or solvent might be easier to control (e.g., limit the VOC content in paints, promote water-based solvent, etc). The impact of anthropogenic emissions of VOCs on SOA formation is evaluated by examining reduction in SOA in response to 20-50% reduction in AVOC (roughly corresponding to the combined contribution by evaporation-related sources). As seen in Table 2.3, in response to 50% reduction in AVOCs in HK, SOA\textsubscript{aromatics} is predicted to reduce by ~56%, biogenic-SOA by ~9% and the total SOA by 21%. In GZ, in response to 50% AVOC reduction, SOA\textsubscript{aromatics} is reduced by 59%, biogenic-SOA by ~15% and total SOA by 34%. This simple calculation demonstrates SOA reduction is not linearly proportional to reduction in AVOCs due to nonlinear nature of the VOC oxidation and SOA formation chemistry. These results are generally in line with those reported by Carlton et al. \(^\text{129}\) in their study of the interaction of anthropogenic versus biogenic processes over the continental U.S. Their modeling results showed that with 50% reduction in the total controllable emissions of AVOCs, the total reduction in anthropogenic SOA, biogenic SOA and total SOA would be ~50%, ~5% and ~10%, respectively.

2.3.4. SOA Contributions and Comparison with Tracer-Based Measurements

2.3.4.1 Hong Kong

Figure 2.4 compares the simulated SOA contributions from individual VOC precursors (aromatics, isoprene and monoterpenes) with the measured SOA in HK and PRD \(^\text{35,98}\). In the SOA tracer measurements, 2,3-dihydroxy-4-oxopentanoic acid was the tracer to estimate toluene SOA. Chamber studies suggest that this toluene tracer may also be formed from the oxidation of xylenes \(^\text{24}\). Hence, the SOA derived from this tracer is generally regarded to include the SOA formation from both toluene and xylenes. The tracer-based measurements in HK were made at four locations. The SOA concentrations and contributions were found to show little differences among the four sites \(^\text{35}\). This lack of spatial variation has been observed for other secondary PM components (e.g. sulfate) in HK \(^\text{126}\). We therefore only show the average values of the four sites in Figure 2.4. The measured SOA observed on days dominated by local emissions in HK are reasonably simulated by the model under Base Case I conditions (i.e., lower emissions and lower organic loading at M\(_0\) = 5 \(\mu g/m^3\)). Simulations under Base Case II (i.e., higher pollutant emissions and higher organic loading at M\(_0\) = 20 \(\mu g/m^3\)) show
good agreement with the measured SOA observed on regional days in both total SOA and the contributions of individual precursors.

Two simulation results in HK are worth noting: (1) In Base Case I scenario, isoprene is the most significant contributor among the three precursors. When the isoprene emission is cut by half (ISOP × 0.5 scenario in Figure 2.4), the simulation agrees better with the measurements and the contributions of isoprene and aromatics become comparable. (2) In Base Case II, a dramatic increase in monoterpenes contribution (1.78 vs. 0.19 µg/m³ in Base Case I) is modeled, primarily as a result of monoterpenes emissions increase to be 3 times that in Base Case I. If monoterpenes emissions are doubled while keeping other conditions the same as Base Case II (i.e., TERP×2 scenario in Figure 2.5), the modeled SOA_{monoterpenes} is very close to the tracer-based measurement. In TERP×2 scenario, the modeled monoterpane concentration is 0.029 – 0.085 ppbv, still quite reasonable compared with ambient concentration of monoterpenes.

The modeling results suggest that monoterpenes contribute more to SOA than toluene and isoprene in HK, despite the lower abundances of monoterpenes. This could be explained by tracking the SOA formation processes in the current SOA formation model. Figure 2.5 shows the time series of simulated removal rate of each SOA precursors (top panel), the production rates of CGs and SOA components (mid and bottom panel) in Base Case II scenario. The removal rate for isoprene is the fastest, followed by toluene and xylene, a result of the fact that the OH reaction rate of isoprene is nearly 20 times faster than that of toluene and 10 times faster than other aromatics. The removal rate of monoterpenes is rather small, due to its low ambient concentration. However, unlike isoprene and aromatics, monoterpenes have a fast ozone oxidation pathway. The ozone oxidation pathway accounts for nearly half the total removal of monoterpenes, especially in the late afternoon when OH begins to decrease while ozone is at a rather high level. For the other VOCs, the ozone oxidation pathway only makes minor contributions to SOA.

The production rate for each CG is determined by both VOC removal rate and the formation yields. The mid panel of Figure 2.5 shows the production rates for individual CGs from their precursors. Although the removal rate of monoterpenes is significantly smaller than those of isoprene and aromatics, the production rate of monoterpenes-derived CGs is noticeably more significant. This can be attributed to the fact that both OH- and ozone- oxidations of monoterpenes have much higher yields for CG5 and CG6 (see the reaction equations in Figure 2.5). The two CGs from monoterpenes (i.e., CG5 and CG6) have much lower effective saturation concentrations (see the table within Figure 2.5), that is, less volatile. When
partitioning of CGs into aerosol is considered, the significance of monoterpenes to SOA formation becomes apparent. As shown in Figure 2.5, the production rates for monoterpenes-derived SOA are comparable with isoprene and aromatics in the morning and early afternoon and exceed those from isoprene and aromatics in the late afternoon. In the end, the overall SOA production rate from monoterpenes is comparable with isoprene, toluene and xylenes, despite that the monoterpenes emission in Base Case II is only ~10% of isoprene emissions and ~7% of combined emissions of toluene and xylenes.

Monoterpenes also undergo reactions with NO₃ radical. This pathway is assumed in CB05 to form CGs at the same yields as the OH- and ozone-oxidation pathways. This channel is not shown in Figure 2.5, as it is much smaller than the other channels in both daytime and nighttime (when NO₃ is higher).

Monoterpenes also undergo reactions with NO₃ radical. This pathway is assumed in CB05 to form CGs at the same yields as the OH- and ozone-oxidation pathways. This channel is not shown in Figure 2.5, as it is much smaller than the other channels in both daytime and nighttime (when NO₃ is higher).

Figure 2.5. (a) Simulated time series of removal rate for SOA precursors. (b) Simulated production rate for condensable gases, and (c) simulated production rate for individual lumped SOA components under Base Case II scenario.

2.3.4.2 Guangzhou

The simulated SOA formation for the GZ Base Case (M₀ = 20.0 µg/m³) is compared with the tracer-based SOA measurements at Wan Qin Sha in Figure 2.4. Wan Qing Sha is ~50 km downwind GZ downtown to the south and ~25 km from the closest sub-urban district of GZ (Panyu). The time-scale of transport from urban GZ to Wan Qing Sha is estimated to be a few hours or less, consistent with the time-scale of fresh SOA formation. Hence, the model-predicted SOA formation could be compared with SOA observed at Wan Qing Sha. On days influenced by transport from GZ, the measured total SOA at Wan Qing Sha from toluene/xylenes, isoprene, and monoterpenes is 8.38±3.19 µg/m³, with the individual
contributions to be 6.08±2.57 µg/m³ from aromatics, 2.21±2.00 µg/m³ from isoprene, and 0.10±0.07 µg/m³ from monoterpenes. The simulated total SOA in the GZ Base Case scenario is 7.64 µg/m³, and the relative contributions of the above precursors are 3.88, 1.59 and 2.17 µg/m³, respectively. The GZ Base Case predicts SOA_{isoprene} in reasonable agreement with the measured amount, but under-predicts SOA_{aromatics} and over-predicts SOA_{monoterpenes}. If the toluene emissions increased by a factor of 1.5 and the other conditions remain the same as the GZ Base Case (i.e., TOL×1.5 scenario in Figure 2.4), the simulated total SOA becomes 9.30 µg/m³, and aromatics-, isoprene- and monoterpenes-derived SOA are 5.52, 1.61 and 2.17 µg/m³, respectively. The simulated air concentrations of aromatics are 14.1 – 26.5 ppbv (toluene) and 3.2 – 5.4 ppbv (xylenes) in the TOL×1.5 scenario, still within the range of observed ambient concentrations.

The simulated SOA formation from aromatics and isoprene generally agrees with the tracer-based measurements, but the model-predicted SOA_{monoterpenes} (2.17 µg/m³) is significantly higher than the measurements (~0.1 µg/m³). The measured SOA_{monoterpenes} at Wan Qing Sha was considerably lower than that measured in HK (0.25 µg/m³ on local days, 3.51 µg/m³ on regional days). We note that the ambient levels of monoterpenes in GZ measured in months from September to November in the past studies were more than twice that measured in an urban location in HK in the months from June to November (Table 1) 29,110. The air concentrations of monoterpenes simulated by the model are 0.015-0.05 ppbv for HK and 0.03-0.14 ppbv for GZ, respectively, falling in the range of the observed ambient concentrations (Figure 2.1). Therefore, we believe such discrepancy between the modeled and tracer-based measured SOA_{monoterpenes} in GZ and the large difference in SOA_{monoterpenes} between HK and GZ is less likely due to emissions being grossly over-predicted in GZ. A more likely cause is the difference in analytical techniques for the monoterpene SOA tracers, especially the selections of tracers and calibration surrogates in the two SOA trace studies. Tracers of monoterpenes used in Wan Qing Sha measurements include cis-pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricaric acid, 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid, and they were analyzed using GC coupled with quadruple MS detector (Agilent). Due to a lack of calibration standards for these tracers, pinic acid was used as the surrogate for quantifying the monoterpenes tracers 34. In the study by Hu et al, tracers for monoterpenes include 3-methyl-1,2,3-butanetricaric acid, 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, 3-isopropylpentanedioic acid, 3-acetyl pentanedioic acid and 3-acetyl hexanedioic acid; samples were analyzed using GC coupled with ion-trap MS detector (Varian) and two surrogates,
citramalic acid and pimelic acid, were used for the quantification of these tracers. The discrepancy in the measured monoterpenes-derived SOA highlights the importance of conducting inter-comparisons of analytical methods for the SOA tracers.

Figure 2.6. Ternary distributions of percentage contributions of aromatics, isoprene and monoterpenes to the total SOA simulated under different emission conditions in (a) Hong Kong and (b) Guangzhou. Simulation settings cover the following ranges of different factors: pre-existing organics (5, 10, 20µg/m³); NOx emission factor: (0.7-1.3) × Base Case; NMHC emission factor: (0.7-1.3) × Base Case; aromatics (toluene+xylenes) emission factor: (0.5-1.7) × Base Case; isoprene emission factor: (0.5-2.5) × Base Case; and monoterpenes emission factor: (0.5-2.5) × Base Case. The tracer-based SOA measurements in Hong Kong are from Hu et al., 35 and those in Guangzhou are from Ding et al., 34. The measurement data are color-coded by total SOA concentration.

2.3.5. Sensitivity Tests of SOA Formation

The earlier discussion shows that SOA formation in this region is highly dependent on the emissions of their VOC precursors. VOC emissions have considerable temporal and spatial differences and their emission inventories have large uncertainties, especially for biogenic VOCs (Table 2). In addition, NOx, total NMHC, and organic aerosol loading can significantly influence the amount of SOA formed.

To assess the multiple factors that influence SOA formation, we have carried out a comprehensive series of sensitivity tests, in which SOA is simulated as a function of 6 factors. The factors include (1) emission factor of NOx, varying from 0.7× to 1.3× Base Case; (2) emission factor of NMHCs (other than isoprene and monoterpenes), from 0.7× to 1.3× Base Case, isoprene and monoterpenes from 0.7× to 2.0× Base Case; (3) emission factor of isoprene, from 0.5× to 2.6× Base Case; (4) emission factor of monoterpenes, from 0.5× to 2.6× Base Case; (5) emission factor of aromatics (toluene+xylenes), from 0.5× to 1.7× Base Case; and (6) level of organic loadings, at 5.0, 10.0 and 20.0 µg/m³. The sensitivity tests of varying the above...
six factors are carried out under conditions of both HK Base Case I and Base Case II and for the GZ Base Case. The statistics compiled by HKEPD show that the maximum differences in pollutant emissions from 1990 to 2006 are 58% in total NOx emissions and 40% in total VOC emissions\(^\text{120}\). Therefore, it is reasonable to consider the variation ranges of these factors likely cover the majority of atmospheric conditions encountered in the region.

Ternary distribution plots of SOA contributions from toluene+xylenes, isoprene and monoterpenes are constructed to show their relative importance in HK and in GZ (Figure 2.6). Simulation results are enclosed in the shaded areas. In HK, among the three VOC precursor types, aromatics contribution is in the range of 15-43%, isoprene contribution 14-48%, and monoterpenes contribution 21-70%. Most tracer-based measurements, on both local days and regional days, fall within the model-simulated ranges. In GZ, the emissions-based box model indicate that the aromatics are a more important SOA contributor, accounting for 33-76%, while isoprene and monoterpenes contribute 13-44% and 10-45%, respectively, to the sum SOA. We note that most of the tracer-based measurements in Wan Qing Sha fall outside the model-predicted area in the ternary distribution plot, due to the extremely low SOA\(_{\text{monoterpenes}}\) derived from the tracer-based measurements in Wan Qing Sha. Despite the discrepancy between the modeled and the tracer-derived SOA\(_{\text{monoterpenes}}\), it is clear that toluene and xylenes play an important role in SOA formation in GZ area, which is different from the situation in HK.

In principle, such ternary distributions are able to cover the impacts on SOA formation from: (1) emissions of SOA precursors; (2) gas-phase chemistry and SOA formation processes. For other locations that have different emission profiles of the three VOC precursor types, the ternary distribution patterns are expected to be different from those shown in Figure 2.6.

### 2.3.6 Limitations and implications of this work

In the present work an emission-based 0-D box model is used to simulate the SOA formation from isoprene, monoterpane, and toluene/xylenes for emission scenarios typical in HK and GZ. Limitations and implications of this work mainly include:

1. Emission inputs. Similar to the model used in this work, many 3-D chemical transport models are emission-based. The quality of emission inputs is essential to the overall model performance and heavily rely on other databases, such as emission inventories, source profiles, land use type, etc. Large uncertainties may exist in these emission-related data, which may propagate into the final model results. For example, Leung et al\(^\text{121}\) estimated the BVOC emissions in Hong Kong using the latest land cover and emission factor databases, reporting
the isoprene/monoterpenes emission ratio of ~17 (annual). This ratio is more than ten times higher than the result reported one year ago \(^{130}\). In addition, Lo et al.\(^ {125}\) demonstrated the substantial importance of land-use information in accurately modeling the spatial pattern of emissions as well as the meteorological fields in the PRD region. The most updated land use information for the PRD regions is the 2003 version. As a rapid developing region, the land use types in the PRD region is expected to have altered during the past years. Emission inputs should be further evaluated against relevant datasets, such as ambient measurements, remote sensing data, to gauge their accuracy. In this work the emission fluxes have been carefully examined against available ambient observations. As discussed above, the current VOC measurement techniques are not optimized for low-concentration and reactive species such as monoterpenes. Hence, emission inputs are expected to be a major source of uncertainties for \(\text{SOA}_{\text{monoterpenes}}\) in this modeling work.

(2) Gas-phase mechanism. Our current understanding about gas-phase chemistry still has large gaps. For example, the overestimate RO\(_2\) and / or HO\(_2\) during nighttime by models reflects such knowledge deficiencies \(^ {131,132}\). Condensed mechanisms are used in this work and in 3-D models. It is known that the condensed mechanisms have their inherent limitations, e.g. the oversimplification of oxidation mechanisms beyond the first generation reactions and the chemistry of oxygenated VOCs (such as formaldehyde, glyoxal). For example, the fast formation of carbonyls from oxidation of aromatics is not included in the condensed mechanisms \(^ {31,133}\).

(3) SOA formation mechanism and other SOA precursors. SOA formation in many chemical transport models adopts semi-empirical approaches. While the thermodynamic partitioning of low-/semi-VOCs produced from the oxidation of main VOC precursors (e.g., aromatics, isoprene, monoterpenes and sesquiterpenes) are incorporated in the model, many other processes that may potentially lead to SOA formation are not included, such as the aging of organic aerosols, multi-phase chemistry. As discussed above, in this study we focus on the evaluation of the relative importance of toluene+xylenes (anthropogenic) versus isoprene and monoterpenes (BVOCs) in this region, as SOA formation from these precursors is relatively well documented. Chamber studies have demonstrated that the VOC precursors considered in this work lead to glyoxal and methylglyoxal \(^ {134-136}\). The potential importance of SOA formation from these water-soluble dicarbonyls via aqueous-particle processes has been recognized \(^ {51,52}\). Unfortunately, in CB05, chemistry of glyoxal and methylglyoxal is not treated explicitly. Hence, SOA from the VOCs considered here could be underestimated, as the aqueous-phase
processes of these water-soluble compounds may form SOA in addition to the partitioning of SVOCs.

Another shortcoming of the SOA mechanism in this work is the contribution of oxidation of S/I VOCs from primary emissions is not considered, as suggested by many recent studies. This source of SOA has not been considered in the current study as we herein primarily focus on the relative contributions of the already identified SOA precursors (i.e. isoprene, monoterpenes and aromatics). These precursors account for significant SOA formation in this region but it does not necessarily suggest they can explain all SOA formation.

Note that the emission inventories in this work are based on the year of 2006, correspondingly more recent VOC measurements (e.g. 2008-2009, Louie et al.) are not included in this work for comparison. Due to the recent emission regulations carried out in the PRD region, ambient concentrations of anthropogenic VOCs in the industrial / urban areas in the PRD region decreased significantly (e.g. toluene decreased by more than 43% on average), except for propane and butanes which increased slightly due to the promotion of alternative fuel vehicles in this region especially LPG-powered (LPG mainly consists of propane and butanes). On the other hand, ambient isoprene concentration in PRD region decreased by 8~23% on average, likely a result of continued urbanization in this region. Further updates on emission inventories in the context of recent changes in this region is required in future studies.

2.4. Conclusions

We have developed an emission-based 0-D box model that incorporates CB05 chemical mechanism and gas-particle partition of condensable VOC oxidation products to simulate SOA formation from isoprene, monoterpenes, and toluene/xylenes in Hong Kong and in Guangzhou in the PRD region, China. The emission inputs for major inorganic air pollutants and common VOCs are generated using SMOKE (anthropogenic species) and MEGAN (biogenic species) for this region. In Base Case scenarios, aromatics emission fluxes in Guangzhou are approximately double those in Hong Kong while emission fluxes of isoprene and monoterpenes are similar. The model-simulated VOCs fall within the range of ambient observations, demonstrating reasonable representation of emissions and oxidation of VOCs. In Hong Kong, monoterpenes are modeled to have more significant SOA formation than toluene/xylenes do. On the other hand, in Guangzhou, the model indicates that aromatics are a more important SOA contributor than isoprene and monoterpenes. This considerable difference in their relative contributions to SOA formation between Hong Kong and Guangzhou was observed in two recent SOA tracer-based measurement studies and correctly captured by the model. As such, it
can be inferred that the higher emission fluxes of toluene and xylenes could largely explain the dominant contributions of anthropogenic VOCs to SOA over the biogenic VOCs in Guangzhou. The model predicts that reduction in anthropogenic VOCs could lead to reduction in both SOA_{aromatics} and SOA from biogenic VOCs, as SOA formation is generally in the VOC-limited regime under the high NO_{x} conditions encountered in this region.

The model-predicted SOA formation from toluene/xylenes and isoprene agrees well with estimates derived from ambient SOA tracer measurements in Hong Kong and at Wan Qing Sha, a site downwind Guangzhou. But, the agreement was poor for the monoterpenes-derived SOA, with the measured SOA_{monoterpenes} substantially lower than the model prediction. Our analysis identifies that uncertainty in analytical techniques for the SOA tracers is suspected to be a major factor responsible for the discrepancy. This modeling study suggests that more and better measurements of monoterpenes and their SOA tracers are needed to better assess the contributions of biogenic VOCs to SOA in this region.
CHAPTER 3. SOA Formation on Wet Aerosols in Ambient Hong Kong

3.1. Overview of Aqueous-Phase Chemistry in the Atmosphere

Recent atmospheric chemical transport models still face challenges in accurately predicting secondary organic aerosol (SOA) formation, both SOA mass and atomic O/C ratio \(9, 85\). Aqueous-phase processes also form SOA. These pathways are not likely covered by or overlap with either traditional SOA pathways, or the oxidation and partition of the semi-/intermediate-volatile organic compounds \(68\).

In many ways airborne liquid water serves as a platform for various aqueous-phase processes. Water-soluble materials dissolved in water undergo a series of reactions and subsequently lead to the formation of a wide range of products, including sulfate, carboxylic acid \(45, 61, 119, 138-142\), as well as other less-well-understood components such as sulfur-containing organics \(15, 63, 143-149\), high molecular weight compounds and oligomers \(61, 64, 147, 150-153\). In addition, aqueous-phase oxidation forms highly oxidized products (with high atomic O/C ratio) as well \(61, 151, 154\), which may improve the currently underestimated O/C ratio in some state-of-the-art SOA models \(10\).

Liquid water in the atmosphere may exist in different forms, e.g. cloud/fog droplets, and aqueous aerosol or aerosol surficial water. Due to smaller diameter and larger number concentration, aqueous particles provide a much larger surface / volume ratio and hence may favor surface-related processes. On the other hand, *Ervens and Volkamer* \(51\) and *Ervens et al* \(52\) indicate that the water-soluble species (e.g. glyoxal) may exist in much higher concentration in wet aerosol water content (LWC) compared with cloud/fog droplets, as a result the chemical scheme under such condition is complete different from that in dilute system (e.g. cloud/fog droplets).

In the aqueous-phase, the OH-attack on a dissolved organic compound (e.g. glyoxal) forms an alkyl radical, which under dilute condition would be effectively depleted by dissolved \(O_2\) (~0.3 mM). Such pathways are well documented in many previous aqueous-phase chemistry mechanisms (e.g. CAPRAM \(155\)). However, under wet-aerosol conditions, the concentrations of dissolved organic compounds may be a few order of magnitude higher compared with cloud droplets, therefore radical-radical reaction may compete with \(O_2\)-channel, and subsequently forms products that cannot be explained by dilute aqueous chemistry. In the case of
organosulfate, epoxide-derived organosulfate is expected to form through acid-catalyzed nucleophilic substitution reaction with sulfate ion $^{14,156}$, while the formation of glyoxal-derived organosulfate is more likely a results of radical-initiated reaction involving sulfate radical $^{60,63,147}$. Recently, outdoor chamber experiments under atmospherically relevant conditions reported enhanced SOA formation on wet seed-aerosol, further confirming the significance of aerosol liquid water $^{42,157}$. Nevertheless, in real ambient atmosphere aqueous-particle processing and cloud-processing may substantially integrate with each other. The time scale of vertical mixing within the boundary layer is typically tens of minutes to hours, comparable with the typical lifetime of a cloud droplet. Ambient particles are usually hygroscopic, when a wet air parcel is raised to a certain altitude the particles therein may serve as cloud condensation nuclei (CCN). Upon evaporation, the low volatility products exist in the aerosol-phase $^{46,139}$. Meanwhile, evaporation may trigger oligomerization and form high molecular weight compound as well $^{150}$.

Recently a series of studies that are based on bulk aqueous experiments $^{61-64,152,153}$ reported formation of high molecular weight compounds. Major products include large di-carboxylic acids, organosulfates and oligomers. These products are consistent with reactions pathways involving radical-initiated oxidation of glyoxal and methylglyoxal in concentrated systems. These studies provide and explicit description of the complex nature of ambient particulate organic matters. SOA yields as a result of glyoxal and methylglyoxal under ambient conditions predicted by such detailed chemical scheme need to be evaluated against other parameterized schemes for predicting SOA, e.g. reactive uptake coefficients or SOA yields obtained from laboratory studies $^{95,144,147}$ as well as field observations $^{11,70}$.

In the present work, SOA formation resulting from glyoxal and a series of identified precursors (long alkanes, benzene, toluene, xylenes, isoprene, and monoterpenes) is simulated based on recent findings, focusing on the potential impacts of the aqueous-particle processing. Newly developed condensed-phase chemical schemes will be evaluated, including high molecular weight compounds, di-carboxylic acids and organosulfates. Modeling work was conducted based on a variety of field measurements obtained in summer Hong Kong, in order to explore the SOA forming potential under ambient conditions in this region. Hong Kong is situated in the southern mouth of the Pearl River Estuary, China, and is one of the most densely populated cities around the globe. Located in the sub-tropical Asia, this region features in high volatile organic compounds (VOCs) from both anthropogenic and biogenic sources and high
NO₃. In-depth studies aiming at SOA formation in such a human-influenced, high-RH and sulfate-rich environment have unique implications on the air quality as well as human health.

Table 3.1. Comparison of glyoxal molar yield from its major precursors between the modeled results in this work (using a modified RACM2) and the experimental results in the literatures.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>This work</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>0.605 – 0.624</td>
<td>Volkamer et al 2005</td>
</tr>
<tr>
<td></td>
<td>0.635</td>
<td>Volkamer et al 2005</td>
</tr>
<tr>
<td>Isoprene</td>
<td>0.024 – 0.087</td>
<td>Volkamer et al 2005</td>
</tr>
<tr>
<td></td>
<td>~0.03 (Primary)</td>
<td>Galloway et al 2011</td>
</tr>
<tr>
<td></td>
<td>0.07 – 0.08 (Further)</td>
<td>Taraborrelli et al 2009</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.254 – 0.711</td>
<td>Volkamer et al 2005</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.184 – 0.468</td>
<td>Volkamer et al 2005</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>0.028 – 0.049</td>
<td>Volkamer et al 2005</td>
</tr>
<tr>
<td></td>
<td>0.045 – 0.055</td>
<td>Volkamer et al 2005</td>
</tr>
</tbody>
</table>

Figure 3.1. Schematic diagram of glyoxal chemistry in aerosol liquid water.
3.2. An Observation-Based Model

3.2.1. Gas-Phase Mechanism

A newly updated RACM2 (Regional Atmospheric Chemistry Mechanism II) is used as the gas-phase mechanism. In addition, isoprene chemistry is updated based on recent findings, and toluene chemistry is modified according to recent works, mainly focusing on the gas-phase chemistry of glyoxal. Glyoxal yields from its major precursors derived in the modified mechanism are summarized in Table 3.1 and compared with previous studies.

3.2.2. Aqueous-Phase Mechanism

A near-explicit aqueous-phase chemistry proposed in a series of recent studies is included in this work to describe the behavior of glyoxal (as well as glycolaldehyde, methylglyoxal, etc) on wet aerosols. This aqueous-phase scheme leads to the formation of an array of products, such as di-carboxylic acids, oligomers, organosulfates as well as imidazole and its derivatives, see Figure 3.1. In addition, a updated traditional SOA module, mainly based on, is adopted in this work to describe the SOA formation from the partitioning of semi-VOCs into the pre-existing organics. Note that the aging processes and highly parameterized glyoxal-processes in the Carlton et al are not included in this work. SOA precursors include long alkanes, isoprene, monoterpenes, benzene, toluene and xylene. Since most of these SOA precursors can also contribute to glyoxal, the combination of parameterized traditional SOA module and the nearly-explicit aqueous-phase chemistry of glyoxal leads to an issue of double-counting SOA formation from glyoxal. However, it is unlikely due to the following reasons: (1) the traditional SOA module is constructed mainly based on chamber studies, and most of them were conducted under drier conditions and high organic loading, under which condition the reactive uptake of glyoxal could be limited; (2) O/C ratio obtained in chamber studies of major SOA precursors such as isoprene and monoterpenes are typically 0.3~0.4, much lower than the glyoxal-experiments; (3) A recent outdoor chamber study reported enhanced SOA formation from toluene in the presence of high loading of aerosol LWC, in which glyoxal plays an important role. Such characteristics could not be well explained by the traditional SOA formation theory.

3.2.3. Aerosol Thermodynamics

ISORROPIA II is incorporated to calculate the thermodynamic parameters such as aerosol liquid water content (LWC), aerosol acidity (pH), activity coefficients.
3.2.4. Model Constrains

3.2.4.1. Measurement inputs

This modeling work uses real-time measurements collected at the Hong Kong University of Science and Technology (HKUST) Supersite in May-August 2011. HKUST campus is located in a sparsely populated region in the coastal Hong Kong, with limited transportation and commercial activities nearby. Due to the land-sea interaction in this region, the supersite is frequently dominated by clean ocean air in summer \(^{123,125}\). The following measurements at this site are used as model inputs: NO, NO\(_2\), CO, O\(_3\) and SO\(_2\) are measured using gas analyzer systems; non-methane hydrocarbons (NMHCs) are determined using an online GC-PID/FID system (GC955-811/611); gas-/aerosol-phase water-soluble inorganic components (e.g. HONO, HNO\(_3\), sulfate, nitrate, ammonium) are measured using Monitoring AeRosols and Gases (MARGA), in which particulate inorganics (with a PM2.5 inlet) are used as ISORROPIA II inputs; PMF-resolved particulate organic components based on High-resolution Aerosol Mass Spectrometer (HR-TOF-MS, size-cut ~PM1) measurements are used (i.e. HOA: model inputs; OOA: for comparison); and temperature, relative humidity (RH) and solar irradiance are from automatic weather station. More detailed description about the instrumentation at this site can be found on the HKUST supersite website (http://www.envr.ust.hk/supersite/). The model is constrained by median diurnal patterns of all aforementioned measurements throughout May-August 2011, with 10-minute resolution. We herein focus on summer mainly because relative humidity is typically much higher in summer, e.g. 70~90\% in the modeled period. The model is spun-up for 72 hours. Dry deposition is mainly adopted from \(^{115}\). Diurnal variation of mixing lay height is assumed to be sinusoid-shaped with a daytime maximum of 1200 m (at noon) and a nocturnal minimum of 500 m.

3.2.4.2. HR-ToF-AMS Analysis

The HR-ToF-AMS was operated under V (unit mass resolution, UMR) + pToF (for sizing) and W (high resolution, HR) modes alternately for 5 min each. The principle of the instrument has been described in detail elsewhere \(^{165}\). Ionization efficiency (IE) calibrations were performed weekly using size-selected (350 nm in mobility diameter) ammonium nitrate particles. Flow rate (~80 mL/min) and size calibrations were performed before and after the campaign with negligible changes observed. A diffusion dryer (BMI, San Francisco, CA) was placed before the inlet to remove particulate water. Data were processed by data analysis toolkits SQUIRREL and PIKA (Sueper, D.: ToF-AMS data analysis software: http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html, access:
1st, June, 2011). Elemental ratios (O/C, H/C etc.) were obtained from the W-mode data for the overall O/C ratio used in this study. O/C ratios for the specific factors, including HOA, LV-OOA, and SV-OOA, were obtained from the HR spectra of those factors resolved by Positive Matrix Factorization. Detailed HR-ToF-AMS analysis at HKUST supersite can be found in Lee et al.

3.2.4.3. Phase Transfer

Phase-transfer for water-soluble compounds is crucial for the multi-phase simulation. In the present work, the effective Henry’s law constant (H_eff) of glyoxal is adopted from, measured in 0.4 mM sulfate solution. Due to the equilibrium-shifting as a result of higher concentration of sulfate, as proposed, the modeled H_eff in aerosol liquid water will be further enhanced. The mass accommodation coefficients for HO_2, NO_3, HNO_3, N_2O_5 and H_2O_2 onto dust aerosols are adopted in this work to describe the uptake of these species onto wet aerosols, which are much larger compared with the uptake coefficients estimated for cloud droplets. Mass accommodation coefficient for OH is assumed to be unity.

3.2.4.4. Chemical Composition in Different Size Modes

Three fine particle modes are considered in this work: Aitken mode, condensation mode and droplet mode, each is assumed to be monodisperse and with a uniform diameter of 0.03, 0.2 and 0.8 µm, respectively. Coarse mode is not considered, as neither of MARGA and HR-ToF-MS are capable to capture coarse particles. MOUDI data averaged over the course of summer (May–Aug 2011) is used to map the MARGA data into the three modes. We assume the distributions of aerosol inorganics among the Aitken, condensation and droplet modes do not change.

3.2.4.5. Photolysis Reactions

Photolysis of species such as O_3, NO_2, HCHO and HONO are important in the model simulation. Since no direct photolysis rate measurements are available, the photolysis rates are estimated in the following approach (take j_O1D for example), for the sake of simplicity:

\[ j_{O1D}(t) = j_{O1D\text{-clear sky}}(t) \cdot \frac{I(t)}{I(\text{max})} \]

Eq.3.1

Where \( I(t) \) is from direct measurement, and the \( I(\text{max}) \) is the maximum value recorded from May to Aug 2011 at HKUST, on a cloud-free day, which is 1109.2 W/m². The clear-sky photolysis rates (e.g. \( j_{O1D\text{-clear sky}} \)) are calculated using the approximation described in Master
Chemical Mechanism (MCM) version 3.2, in which the clear-sky photolysis rate is re-organized as the function of solar zenith angle (SZA). SZA for Hong Kong is then calculated using method described in Finlayson-Pitts and Pitts\textsuperscript{114}. The j-values estimated in this manner accord reasonably well with the field measurements in Back Garden, a rural site in the PRD region\textsuperscript{118, 169}.

### 3.2.4.6. Definitions of $H_{\text{eff}}$, $\gamma$, and $k_{\text{eff}}$

For the $H_{\text{eff}}$, we use the direct definition:

$$H_{\text{eff}} = \frac{[\text{GLY}]_{\text{aq,total}}}{[\text{GLY}]_{\text{gas}}}$$

Eq. 3.2

Where $[\text{GLY}]_{\text{gas}}$ is the gas-phase partial pressure of glyoxal (atm), and $[\text{GLY}]_{\text{aq,total}}$ is the total glyoxal concentration in the aqueous-phase (mol/kg·H$_2$O, or mol/L·H$_2$O), including hydrated/non-hydrated, monomer, dimer, trimer, oligomers (formed through dark reactions as described above). Following this definition, $H_{\text{eff}}$ can only describe the impact of reversible reactions in the condensed-phase on the solubility of glyoxal, and any irreversible processes could not be covered by the definition of $H_{\text{eff}}$.

For reactive uptake coefficient ($\gamma$) and effective SOA formation rate ($k_{\text{eff}}$, s$^{-1}$), we use the following definitions:

$$\frac{d[SOA_{\text{GLY}}]}{dt} = k_{\text{eff}}[\text{GLY}]_{\text{gas}}$$

Eq. 3.3

$$\frac{d[SOA_{\text{GLY}}]}{dt} = \frac{1}{4} \gamma \bar{u} [\text{GLY}]_{\text{gas}}$$

Eq. 3.4

Where $[SOA_{\text{GLY}}]$ is the aqueous-particle SOA formed from glyoxal (μg/m$^3$). $A$ is the total surface area (m$^2$/m$^3$·air, in this work we calculate the particle surface area using aerosol liquid water volume and assume all particles are sphere-shaped), and $\bar{u}$ is the mean molecule velocity of glyoxal (m/s). Note that in these two equations, $[\text{GLY}]_{\text{gas}}$ should be converted into mass concentration (μg/m$^3$). Differs from $H_{\text{eff}}$, these two parameters can describe the impacts of irreversible processes.

A 0-dimension box model is developed for the simulation, in which the stiff ordinary differential equations (ODE) are solved using LSODE\textsuperscript{117}. This FORTRAN-based model framework has been evaluated against FACSIMILE (a widely used commercial ODE solver)
and produces almost identical results as FACSIMILE but with much more computational efficiency and flexibility.

![Diagram](image)

**Figure 3.2.** (A) Model simulated traditional SOA and aqueous-particle SOA, along with HR-ToF-HR-ToF-MS measured OOA. (B) Distribution of aqueous-particle SOA among three size bins. (C) Chemical composition of aqueous-particle SOA and the aerosol LWC. C3-C4 di-carboxylic acids include tartaric/malonic/succinic acid.

### 3.3. General Aspects of Photochemistry

General aspects of the photochemical characteristics at HKUST supersite in May-August 2011 are briefly summarized here:

1. **NMHCs.** Since HKUST is a sub-urban, anthropogenic NMHCs observed at HKUST are in quite low level compared with other urban locations of Hong Kong, and do not show very clear diurnal pattern. For example, summertime-average level of ethene: 0.86±0.64 ppbv; benzene: 0.26±0.45 ppbv; toluene: 0.81±1.31 ppbv. Isoprene, on the other hand, shows a clear diurnal trend which peaks at 0.36±0.43 ppbv in the noon time. Note that due to the lack of real-time measurements of monoterpenes in Hong Kong, monoterpenes are assumed to be 1/8 of isoprene, according to previous canister-based VOC measurements in Hong Kong.

2. **NOx and O3.** Similar to other primary pollutants, NOx observed at HKUST is also in low level: NO: 0.98±5.86 ppbv, shows a typical diurnal pattern that has a maximum value in the early daytime due to the photolysis of NO2, and starts to decrease in the late afternoon as a result of increase of O3; NO2: 5.47±7.31 ppbv, usually builds up since the late afternoon.
and peaks at early evening, mainly because of the conversion of NO+O₃, or the meteorological condition. O₃ usually peaks at late afternoon (14:00-15:00, local time) at 39.21±25.36 ppbv as a result of photochemical processes with the present of solar radiation.

(3) HOₓ radicals. OH modeled in this work has a noontime maximum of 1.2×10⁷ molecule/cm³, accords reasonable well with that calculated pseudo-steady-state method at HKUST using same datasets (1.0×10⁷ molecule/cm³). HO₂ shows a daytime maximum of 7.3×10⁸ molecule/cm³, around 61 times higher than OH radicals, similar to that calculated using pseudo-steady-state method (5.4×10⁸ molecule/cm³).

(4) Temperature, RH, sulfate, nitrate, aerosol liquid water content and aerosol acidity. Temperature recorded at HKUST during the campaign shows a typical diurnal pattern, which peaks at ~304 K at around noon (13:00-14:00) and gradually decreases and reaches minimum at ~300 K at dawn (5:00-6:00). RH shows an anti-trend as temperature, reaching nearly 90% during nighttime and decreases to minimum at 70% at noon. Three major aerosol inorganics measured by MARGA, ammonium, sulfate and nitrate are 0.8~1.0 μg/m³, 3.8~5.5 μg/m³ and 0.8~1.2 μg/m³, respectively. Aerosol liquid water content (LWC, calculated using ISORROPIA) scales with RH: typically 0.5-1.1×10⁻¹¹ (vol·water/vol·air). pH of wet aerosol, \(-\log_{10}[H^+ \text{ (activity)}]\), is in the range of 0.5~1.3. Acidity estimated in this work is generally in line with previous studies of fine particle acidity in Hong Kong.¹⁷⁰,¹⁷¹

As described above, three different size bins are considered. Among them, droplet mode (with a uniform diameter of 0.8 μm) account for the majority of aerosol inorganics. For example, over 90% ammonium and sulfate, and 84% nitrate are found in the droplet mode. The size distribution of aerosol inorganics greatly influences the distribution of aqueous-particle SOA components as well.

(5) Gas-phase chemistry of glyoxal. Ambient glyoxal is simulated to be 0.56~0.62 ppbv, with a slight increase at around noon. Glyoxal is almost exclusively formed from the photooxidation of VOCs. In the summertime at HKUST, isoprene accounts for 56% glyoxal formation, and aromatics (benzene + toluene + xylenes) contribute 38%. The rest formation of glyoxal is from monoterpenes, acetylene and alkenes. This result at HKUST is dramatically different from that in Back Garden (PRD region), where aromatics contribute over 90% of glyoxal formation (Li, X. PhD Thesis, Peking University, 2010). This is not surprising, however, as ambient aromatics in the PRD region (e.g. toluene: 8.46±9.94 ppbv, ²⁹) is much higher than that observed at HKUST (e.g. toluene: 0.81±1.31 ppbv, this work), while isoprene is
comparable between the two locations (0.17±0.15 ppbv vs 0.36±0.43 ppbv). Glyoxal is very water soluble and hence reactive uptake of aerosol liquid water plays an important role in the glyoxal budget. In this work, around 9.4% glyoxal is uptake by wet aerosol and undergo subsequent aqueous-particle processes.

3.4. Traditional vs Wet Aerosol SOA

Figure 3.2 shows the modeled SOA, including traditional SOA as well as aqueous-particle SOA. As seen, total SOA shows a clear diurnal trend that peaks at ~2.0 μg/m³ at around noon, in reasonable agreement with HR-ToF-MS measured OOA. Note that the HR-ToF-MS has a size-cut of approximately 1 μm, which covers the majority of Aitken mode and condensation mode, but likely only a fraction of droplet mode. The droplet mode is mainly derived through in-cloud processes, which differs from the aqueous-particle process in many ways. In this work we primarily focus on the aqueous-particle process.

Isoprene and monoterpenes are the major SOA contributors, while anthropogenic VOCs play a minor role. The relative importance of biogenic and anthropogenic VOCs on SOA shown in this figure agrees reasonably well with a tracer-based SOA study in Hong Kong. The modeled aqueous-particle SOA, generally in the range of 0.38~0.42 μg/m³, account for 22~26% of total modeled SOA.

3.5. Chemical Composition and Size Distribution of Wet Aerosol SOA

In general, aqueous-particle SOA decrease slightly during daytime mainly due to the decrease in LWC, but increases slightly at around noon, although the whole diurnal variation of aqueous-particle SOA is not as distinct as traditional SOA.

As shown in Figure 3.2, aqueous-particle SOA consists of a variety of products, formed through different pathways:

(1) Dark reactions: oligomers, oganosulfate (IEPOX-sulfate), imidazole and derivatives. Literally, this pathway does not necessarily require radiation, and products through this channel scales with (LWC). The oligomers formation in dark reactions in this study is parameterized from De Haan et al, with yields of 33% and 19% for glyoxal and methylglyoxal, respectively. IEPOX formed from isoprene may undergo acid-catalyzed nucleophilic reaction with sulfate ion and forming IEPOX-sulfate. This pathway is included in this work and IEPOX-sulfate is simulated to be 34.7~49.1 ng/m³ (see detailed discussions in the following section). Noziere et al and Yu et al reported oligomers and imidazole
formation from glyoxal+NH$_4^+$ reaction, in which the reaction rate depends greatly on pH. However, under the modeling conditions of this work, the levels of these products are too low (i.e. less than 1 ng/m$^3$) due to the high particle acidity in this region (i.e. MARGA-measured NH$_4^+$: 0.89±0.05 μg/m$^3$; pH: 0.5-1.3, calculated using E-AIM). This reaction (glyoxal+NH$_4^+$) may be of importance in more neutralized particles 68.

(2) Photochemistry (radical-O$_2$ channel): glycolic/glyoxylic/oxalic acid. This pathway is generally relevant to cloud conditions. In aerosol liquid water, this pathway still plays an important role, leading to the formation of oxalic acid. Products from this pathway increase slightly with solar radiation, and under wet aerosol condition, oxalic acid is the single important and final product of this channel.

(3) Photochemistry (radical-radical channel): C3-C4 dimers & di-carboxylic acids 61, 152 and organosulfate (glycolic acid sulfate) 63. This pathway is derived from bulk aqueous-phase experiments under more concentrated conditions, forming an array of larger compounds, such as tartaric/malonic/succinic acids, even oligomers (see Lim et al., 2010). This channel becomes increasingly important in aerosol liquid water. As shown in Figure 3.2, products formed through this channel account for over half of the total aqueous-particle SOA, and increase at around noon due to the stronger solar radiation, even though the (LWC) reaches the lowest level at this time of day.

Figure 3.2 (B) shows the size distribution of aqueous-particle SOA components. It is seen that ~80% of aqueous-particle SOA is in the droplet mode. As discussed above, the droplet mode account for the majority of aerosol inorganics, therefore higher aerosol liquid water serves as an effective reactor for the aqueous-particle processes, compared with Aitken and condensation modes.

### 3.6. Model Evaluation

We evaluate the complicated multi-phase behavior of glyoxal by comparing the effective Henry’s law constant ($H_{eff}$, M/atm or mol/kg·H$_2$O/atm), reactive uptake coefficient ($\gamma$, dimensionless) and effective SOA formation rate ($k_{eff}$, s$^{-1}$) with the literatures.

Figure 3.3 summarize the above three parameters simulated in this work, as well as those derived from field 58, 70 and chamber studies 95, 147, 173, 174. Two field studies are of particular interests, one is the $H_{eff}$ measured at HKUST in July and August 2009, using denuder/filter sampling followed by PFPHA-GC-MS analysis (Ip, H. S. S, Ph.D. Thesis, The
Hong Kong University of Science and Technology, 2010), and another one is the uptake coefficient of glyoxal estimated in a rural PRD site (Back Garden, ~180 km away from Hong Kong) in July 2006, using MAX-DOAS measured daytime glyoxal followed by numerical retrieve of glyoxal uptake by aerosol surface (Li, X. Ph.D. Thesis, Peking University, 2010).

Figure 3.3. Comparison of reactive uptake coefficient, effective Henry’s law constant and effective SOA formation rate of glyoxal between this work (modeled) and the previous laboratory and field studies. Embedded figure shows the time series of reactive uptake coefficient between this work (modeled) and estimated in a rural PRD site (Li et al PhD thesis).

As shown in these figures, the three parameters derived in this work are in good agreement with previous studies, but tend to fall in the lower end of the literature reported results in field observations. For instance, the daytime uptake coefficient in Figure 3.3 shows a consistent trend with the results obtained in a rural PRD site, but lowered by a factor of ~1.5 or so. Nevertheless, as summarized in this figure that these parameters themselves may vary a few order of magnitudes among different studies. The general agreements between this work and previous studies indicate that SOA formation from glyoxal simulated in this work could represent the multi-phase behavior of glyoxal and its impact on SOA formation.

3.7. Discussions and Implications

3.7.1. Impact of aerosol LWC

Recently an indoor chamber study showed limited glyoxal uptake on ammonium sulfate seeds coated with freshly generated aromatic-derived SOA (more hygrophobic) even under humid conditions 41, while another outdoor chamber study 42, 157 reported enhanced SOA
formation under humid condition in the present of ambient background aerosols and aromatics-SOA. These experiments together imply that it is LWC, rather than RH, that has major impact on the reactive uptake of glyoxal. Under drier conditions, the reactive uptake might be further affected by slower bulk diffusion. Nevertheless, the diurnal averaged RH of summer Hong Kong is ~70-90%, close to the Deliquescence RH of ammonium sulfate (~79%) at ambient temperature, therefore ambient aerosols under such condition is likely in metastable liquid.

As discussed, SOA formation on wet aerosols is strongly influenced by aerosol (LWC). Sensitivity test with doubled particulate inorganics results in both (LWC) and aqueous-particle SOA (0.7-0.8 μg/m³) being a factor of ~2 higher. Considering these inorganic ions in fine particles are frequently observed in rather high level in Asia, SOA formation on wet aerosols may play a significant role in tropics, especially anthropogenic influenced regions.

3.7.2. Oxidants in aqueous-particle processes

OH radical also plays a central role in the photochemistry in the aqueous-particle processes. Major sources of OH radical in aerosol liquid water include (1) transport from gas-phase, (2) photolysis of aqueous-phase H₂O₂, as well as (3) other complicated processes (e.g. photosensitizer or transition-metal involved processes). (3) is so far poorly understood and not considered in this work but is possible to amplify the radical-induced processes in the particle-phase. In this work OH radical in the aerosol liquid water is simulated to be 1×10⁻¹⁴ - 3×10⁻¹³ mol/L, in which more than 60% is transferred from gas-phase, and the rest is mainly from photolysis of H₂O₂ in the aqueous-phase. As mentioned in the previous section, the mass accommodation coefficient of OH radical is assumed to be unity.

3.7.3. C3-C4 dimers and di-carboxylic acids

Oxalic acid is one major product of aqueous-particle processes of glyoxal/glycolaldehyde/glycolic acid. Oxalate measured in ambient aerosols is typically in hundreds or even thousands of ng/m³, and usually correlates with sulfate and accumulates predominately in the droplet mode, implying the formation is associated with cloud processing, which is supported by model simulation as well. Globally ~95% oxalate is formed in-cloud, and oxalate could make up to 20-50% of total modeled SOA in East Asia, although these estimates are subject to potential uncertainties due to the difficulties in predicting cloud physics/chemistry and SOA in global models. In this work the modeled oxalate in this work is 64-81 ng/m³, in the lower end of the oxalate measured in the ambient PM2.5 in this area when dominated by local photochemistry (min-max: 41-215 ng/m³; average:
Note that in this work we primarily focus on the wet-aerosol process and hence cloud process is not included. As discussed earlier, oxalic acid formation is the major channel in cloud droplets while on wet aerosols is less favored. Recently Lee and co-workers conducted aqueous-phase oxidation experiments with cloud water samples collected in a mountain area. They proposed that additional SOA material was produced by functionalizing dissolved organics via OH oxidation, where these dissolved organics are sufficiently volatile that they are not usually part of the aerosol. Furthermore, at later stage of the cloud-water oxidation fragmentation leads to organic mass reduction \(^\text{47}\). More detailed studies are needed for a systematic understanding of cloud chemistry, which is well beyond the scope of this work.

As for C3 and larger di-carboxylic acids, previous studies indicated they may be contributed by primary sources, such as motor exhausts \(^\text{182, 183}\) and wood burning \(^\text{184}\), or formed from the oxidation of unsaturated compounds \(^\text{159, 185}\), or through in-cloud processes \(^\text{139, 186}\). Note that the aforementioned secondary formation pathways are typically associated with the degradation of larger compounds. In this work, our model shows that aqueous-particle processes open a potential pathway that allows the formation of larger di-carboxylic acids from small precursors, such as glyoxal, through radical-radical channel.

**Figure 3.4.** Comparison of di-carboxylic acids between model simulation in this work (top row) and ambient measurements in various locations: HKUST is the same location where this work is performed, TW (Tuen Wan), TC (Tung Chung) and YL (Yuen Long) are three urban locations in Hong Kong. Ambient measurements in Hong Kong in summer 2006 (blackish dots) are from \(^\text{35}\), while results in YL in summer 2004 (shaded bars) are from \(^\text{187}\). PV (Spring 2008) \(^\text{188}\) and other abbreviations (summer 2002-2004) \(^\text{189}\) denote various locations in the Europe. See the literatures for more details. All dots and error bars in this figure represent average±standard deviation, while the shaded bars show the measured range. Note that at SIL and PDD, a PM\(_{10}\) inlet was used, while for all other locations in this figure PM\(_{2.5}\) inlet was used.
Figure 3.4 shows the comparison of succinic and malonic acid between the model simulation in this work and the ambient measurements in a number of locations. As seen in this figure that these two di-carboxylic acids simulated in this work agrees reasonably well with ambient measurements in both Hong Kong and other locations cited here.

These two acids only account for a small fraction of aqueous-particle SOA. According to 61, such C3-C4 dimers are formed from the bonding of a few primary or secondary radical products from glyoxal-OH reaction. A noteworthy aspect is, the Lim et al mechanism predicts rather high level of tartaric acid (GLY+OH=GLY*, GLY*+GLY*=Tartaric acid), i.e. over 90 ng/m$^3$ in this work. However, tartaric acid measured in ambient aerosol samples rarely exceeds 10 ng/m$^3$, mostly around detection limit even in polluted environment 35, 188-191. In general, since the α-hydrogen atom on the α-hydroxy carboxylic acid molecule would be rather reactive, we suspect even if tartaric acid were generated at high yield, it may eventually transform into other aqueous-phase products. Therefore, tartaric acid in this work could be regarded as a model compound that represents the product from radical-radical reactions, and the tartaric-acid-like C4 compound in this work is classified as C4 dimer.

Nevertheless, Figure 3.4 does not necessarily suggest these acids in aerosols were actually from aqueous-particle processes. We at this stage cannot simply rule out the other sources of these di-carboxylic acids. On the other hand, nowadays chemical speciation in the aerosol-phase still faces challenges, and the commonly used analytical methods for di-carboxylic acids in the particle-phase usually require sufficiently long sampling periods and hence may not be able to provide adequate time-resolution for further process analysis. Di-carboxylic acids account for a remarkable fraction of organic aerosol mass, and play an active role in the aerosol chemical and physical properties, such as oxidation state or hygroscopisity. Further developments in both di-carboxylic acid chemistry as well as analytical technique are in crucial need.

3.7.4. Organosulfates

Organosulfates have in recent years received increasing attention. Two formation mechanisms have been proposed: acid-catalyzed nucleophilic reaction of epoxide (formed from isoprene and terpene species) and sulfate ion 14, 25, and the radical-radical channel involving sulfate radical 60, 63.

(1) Glycolic acid sulfate: Perri et al 63 reported the formation of α-hydroxy-organosulfate from glyoxal/glycolaldehyde/glycolic acid with the presence of UV radiation,
and based on experimental results a radical-radical mechanism of organosulfates was proposed, in which sulfate radical formed from the OH attack of H$_2$SO$_4$ or HSO$_4^-$ plays a central role. This mechanism is supported by dark experiments with K$_2$S$_2$O$_8$ (generates sulfate radical upon heating) $^{60}$. However, $^{192}$ pointed that the α-hydroxy structured organosulfate might not be stable in aqueous solution. They further indicate that the glyoxal-derived (or glyaldehyde/glycolic acid-derived) organosulfate should be glycolic acid sulfate.

In this work, glycolic acid sulfate formation from glycolaldehyde/glycolic acid and sulfate radical is adopted, using kinetics proposed by $^{63}$. Glycolic acid sulfate is simulated to be 9–12 ng/m$^3$, generally in line with ambient aerosol measurements $^{192}$. Glycolic acid sulfate has been observed in chamber studies $^{143, 147}$, field measurements $^{143, 186, 187, 192}$ as well as rainwater samples $^{193}$. In this work we show that wet aerosol serves as a possible reactor for the formation of this widely observed compound. Nevertheless, Galloway et al $^{147}$ also reported glycolic acid sulfate formation from glyoxal. It is currently unclear how to connect glyoxal with glycolic acid sulfate. Considering the much higher abundance of glyoxal than glycolaldehyde/glycolic acid, glyoxal-derived organosulfates in the ambient might be even higher.

(2) Epoxide-sulfate formation is also examined in this work, but only limited to IEPOX formed from isoprene. Paulot et al $^{13}$ reported IEPOX formation from isoprene oxidation under low NO$_x$ condition. The simulated gas-phase IEPOX in this work reaches 36 pptv in late afternoon, and is sensitive to NO$_x$ level. IEPOX is highly water soluble, and its Henry’s low constant is estimated to be 1.9×$10^7$ ~ 9.6×$10^8$ M/atm at 298K $^{15}$.

Kinetics of IEPOX and sulfate ion is based on the apparent ring-opening rate in the sulfate solution depends on H$^+$, HSO$_4^-$ (as a general acid) and SO$_4^{2-}$ (nucleophile) $^{156}$:

$$k_{obs} = k_{H^+}a_{H^+} + k_{nuc}[nuc]a_{H^+} + k_{ga}[ga]$$  \hspace{1cm} \text{Eq. 3.5}

Where $k_{obs}$ is the observed ring-opening rate of IEPOX, $k_{H^+}$ is the hydrolysis rate, $k_{nuc}$ is the rate due to the nucleophile (in this case SO$_4^{2-}$), $k_{ga}$ is the rate due to general acid (in this case HSO$_4^-$). $a_{H^+}$ is the activity of H$^+$, and [nuc] and [ga] are the concentrations of nucleophile and general acid. The hydrolysis rate ($k_{H^+}$, slow step) of epoxybutane-diol is 0.0013~0.0022 M$^{-1}$ s$^{-1}$, and the yield of sulfate ester yield from cis-2,3-epoxybutane-1,4-diol ranges vastly from 4% to 40% in H$_2$SO$_4$/Na$_2$SO$_4$ solution, as shown in figure 6. In this work, we assume the ring-opening rate to be 0.0013 M$^{-1}$ s$^{-1}$, and the molar yield of IEPOX-sulfate is assumed to be 4%.
Figure 3.5. IEPOX-sulfate yield as a function of activities of $SO_4^{2-}$ and $H^+$. Color-coded by molar yield. Shaded area shows the model simulated activities of $SO_4^{2-}$ and $H^+$ in aerosol liquid water in this work. Triangle markers denote the IEPOX-sulfate yields estimated using data reported by $^{15}$ from two U.S. sites, Atlanta and Yorkville from AMIGAS campaign, while activity results are calculated using data published in $^{194}$. Activities (298K) in this figure are all calculated using E-AIM $^{195}$.

The reason we choose 4%, the lower end of yield observed in laboratory study are three folds: (i) together with the lower ends of Henry’s law constant and ring-opening rate of IEPOX, the kinetics here represent a lower limit of IEPOX-sulfate formation under the modeled condition; (ii) $^{156}$ further indicated that NO$_3^-$ may as well undergo similar nucleophilic reaction, which is supported by recent works in this region $^{27}$. Therefore the yield of IEPOX-sulfate may be even lower due to the presence of considerable amount of nitrate. Formation of nitrate ester is not included in this work. (iii) as shown in Figure 3.5, the modeled results in this work appear to have lower $SO_4^{2-}$ activity but much higher $H^+$ activity, compared with the $^{156}$ experiments. Therefore the IEPOX-sulfate yield under the modeling condition might be effectively lower than 0.09–0.18, as labeled on this figure.

Two kinetic studies about epoxide-sulfate both imply that the sulfate ester yield correlates with total sulfate concentration$^{156,196}$, e.g. up to 40% in 0.1M H$_2$SO$_4$/2.0M Na$_2$SO$_4$ solution. If such high yield (40%) were used in this model, the simulated IEPOX-SOA alone could be a few μg/m$^3$. Given the total SOA level in the modeled condition is only this much, it is unlikely the epoxide-sulfate yield could be as high as 40% under ambient condition. Further, we suspect the activity of $SO_4^{2-}$ plays a more important role than total sulfate concentration; also it seems plausible that acidity may influence the yield as well. Although increased acidity favors the hydrolysis of IEPOX (and hence $H_{eff}$ of IEPOX), in the meantime more $SO_4^{2-}$ would be converted into HSO$_4^-$. The latter acts as a general acid rather than the nucleophile $^{156}$, as a result, the yield may decrease under high acidity. $^{15}$ reported 2-methyltetrols, C5-
alkenetriols and IEPOX-sulfate in aerosol samples collected in two U.S. sites in the AMIGAS campaign. In the condensed-phase chemistry of IEPOX, 2-methyltetrols and C5-alkenetriols are both formed from the nucleophilic reaction with H2O after the hydrolysis of IEPOX, while IEPOX-sulfate is a competing product of IEPOX+SO4^2- reaction. Using their relative abundance in the aerosol samples collected in the two locations in the AMIGAS campaign, the IEPOX-sulfate molar yield could be roughly estimated:

\[
Y_{\text{IEPOX-Sulfate}} = \frac{C(\text{IEPOX-Sulfate})}{C(\text{IEPOX-Sulfate}) + C(2-\text{Methyltetrols}) + C(\text{C5-alkenetriols})}
\]

Eq.3.6

Where \(C(\text{IEPOX-sulfate}), C(2\text{-methyltetrols})\) and \(C(\text{C5-alkenetriols})\) are their aerosol-phase molar concentration (μmol/m^3). Using this method, the IEPOX-sulfate yields in the two AMIGAS sites are estimated to be 11~25% (average: 16%) and 9~24% (average: 14%), respectively. Note that these yields are likely the upper bound since possible IEPOX-nitrate is not considered. Besides, using water-soluble inorganics reported by 194, the aerosol aerosol pH in the AMIGAS campaign is 2.5~2.7 (calculated using E-AIM), higher than calculated in this work (0.5~1.3), as seen in Figure 3.5. The lower acidity together with the lower sulfate level in AMIGAS sites lead to a lower hydrolysis rate, since the un-reacted IEPOX in the aerosol-phase (1~24 ng/m^3, quantified using synthesized standard 15) is somewhat higher than the IEPOX modeled in this work (3.8~14.0 ng/m^3, assuming the lower bound of H_eff, 1.9×10^7 M/atm). If the above conjectures of the impacts of acidity and activity of SO4^2- were valid, the IEPOX-sulfate yield in this work may be lower than that in the AMIGAS campaign and the Eddingsaar experiments.

With the combination of the gas- and aqueous-phase processes, the simulated IEPOX-sulfate is in the range of 34.7~49.1 ng/m^3, in good agreement with that quantified in two sites in the AMIGAS campaign, 6.7~64 ng/m^3, and 5.1~46 ng/m^3, respectively, and as discussed this level is likely a lower limit under this condition. Detailed sensitivity tests about IEPOX-sulfate formation can be found in McNeill et al 65 who examined IEPOX-pathway under low-NOx condition (when IEPOX pathways contribute 66-100% aqueous aerosol SOA) and high NOx condition (when no IEPOX is expected to be formed).

To sum up, our modeling results show that aqueous-particle processes may explain the formation of IEPOX-derived organosulfate and glycolic acid sulfate in the ambient. In addition, IEPOX-organosulfate tends to be of higher abundance than glycolic acid sulfate. Such relative abundance is supported by another field study conducted in various sites in Asia 187. Organosulfate simulated in this work may have potential uncertainties from (and not limited
to): Henry’s law constant and sulfate ester yield of IEPOX, and the mechanism of glyoxal-
sulfate formation.

3.7.5. Atomic O/C ratio

For traditional SOA, O/C ratios of different SOA components are estimated using
OM/OC obtained from $^{37}$. The modeled O/C ratio of traditional SOA is 0.43±0.01, quite close
to the reported isoprene- and monoterpenes-SOA $^{163}$, since these two are the predominate SOA
precursor in this area.

For the aqueous-particle SOA, O/C ratio can be calculated for each individual product.
The aqueous-particle SOA consists of highly oxidized compounds with rather high atomic O/C
ratio, e.g. oxalic acid: 2; other C2-C4 di-carboxylic acids: 1.0~1.6; glyoxal-oligomers: ~1.2 $^{61}$;
glycolic acid sulfate (C$_2$H$_3$O$_6$S$^-$): 3; IEPOX-sulfate (C$_5$H$_{11}$O$_7$S$^-$): 1.4. All these SOA
components have much higher O/C ratio than PMF-resolved HOA (0.15), SV-OOA (0.16) and
even LV-OOA (0.8). Lee and co-workers $^{151,154}$ pointed out that aqueous-phase chemistry leads
to a better representation of aging of observed ambient SOA, in which m/z 44 (CO$_2^+$) increases
throughout the whole oxidation processes. Other studies also indicated that highly oxidized
compounds are the major products in the aqueous-phase chemistry $^{51,61,139}$. Based on the
modeling results we show that the formation of highly oxidized products in the aqueous-
particle processes may help bridge the gap between the modeled and measured O/C ratio.

Based on the composition of aqueous-particle SOA, the modeled O/C ratio of aqueous-
particle SOA exhibits O/C ratio as high as 1.41~1.53, in good agreement with glyoxal-
laboratory experiments (1.0~1.8) $^{61,154}$. The combination of traditional SOA and aqueous-
particle SOA generates an overall O/C ratio in the range of 0.56~0.58, in reasonable agreement
with HR-ToF-MS-measured O/C ratio for OOA, which is 0.51±0.12 throughout the
measurement period. Apparently aqueous-particle processes enhance the overall O/C ratio for
the fine particulate organics, although their contribution in mass concentration may not be very
high, in this case 1/4-1/5 of total SOA.

3.8. Conclusions

SOA formation at a sub-urban site (HKUST) with limited anthropogenic influences in
Hong Kong is simulated, based on recently proposed gas-phase and aqueous-phase
mechanisms mainly focus on the impact of aqueous-particle processes. The simulation reveals
that aqueous-particle processes may contribute 1/4-1/5 of traditional SOA in this region. Major
products include di-carboxylic acids, high molecular weight compounds, and organosulfates, formed through both dark and photochemical reactions. Under aqueous-particle condition, radical-radical mechanism plays an increasingly important role. We further show that aqueous-particle processes could be a plausible source for di-carboxylic acids as well as organosulfates. This work sheds light on the potential importance of aqueous-particle processes, especially in tropical and subtropical areas with high relative humidity.

*Knote et al* 69 incorporated parameterized glyoxal-derived SOA on wet aerosols into 3D model and found that in California U.S. (~32°N-44°N) glyoxal accounts for 1-15% of total SOA (cloud process is not considered), where the condition differs from Hong Kong (e.g. somewhat lower LWC and higher pH). This is, to our knowledge, the only study that incorporates wet aerosol processes on wet aerosols. More work is desired in the future to evaluate the importance of such processes.
CHAPTER 4. Reactive Uptake of Glyoxal on Ammonium Sulfate Particles under Humid Conditions: A Controlled Chamber Studies

4.1. Overview

Glyoxal, the smallest di-carbonyl compound, has been widely detected in earth’s atmosphere. It is highly water-soluble, with an effective Henry’s law constant ranging from $10^5$ to $10^9$ M atm$^{-1}$ (e.g. in deliquesced sulfate particles). Glyoxal aqueous processes are an important sink of gas-phase glyoxal, and another potential pathway for the formation of secondary organic aerosols (SOA) in the atmosphere. Major glyoxal pathways in the aqueous-phase include: (i) Hydration forming glyoxal mono-/di-hydrates; (ii) Photochemical reactions with OH radicals forming an array of compounds such as carboxylic acids, organosulfates, oligomers; (iii) Dark reactions producing oligomers and imidazoles; (iv) photosensitization initializing oxidation and particle growth; and (v) surface-related processes inferred from ambient and laboratory studies.

The glyoxal-induced SOA formation is highly complex; a wide range of physical and chemical properties of multi-phase systems together determine the fate of glyoxal. Speciated glyoxal aqueous-phase mechanisms have been established mostly based on bulk aqueous experiments. Recent efforts have been made to mimic the aqueous-aerosol relevant conditions (e.g. under more concentrated aqueous mixtures). However, there are essential kinetic considerations unique to aerosols which are challenging to evaluate under bulk experiment conditions, leaving these detailed understandings largely untested in aerosol systems.

In 2013, a series of indoor chamber experiments were conducted at the Paul Scherrer Institute (PSI), Switzerland, to examine the reactive glyoxal uptake on inorganic seeds under humid conditions. In this work we use a multi-phase kinetic model to examine the reactive uptake of glyoxal on ammonium sulfate seeds, and the modeled SOA is evaluated with HR-ToF-AMS measured organics.

4.2. Experiments

The PSI smog chamber is a 27 m$^3$ indoor Teflon bag with temperature and relative humidity (RH) controls. A total number of 17 experiments were conducted in May-July.
2013, under different conditions but mostly humid (RH 50-90%) and room temperature. Experimental settings were similar to that described in Kampf et al. Briefly, gas-phase glyoxal was produced from the reaction between acetylene (C$_2$H$_2$) and hydroxyl (OH) radicals, with a molar yield of ~65%. OH radicals were produced from the UV photolysis of HONO (monitored by a Long Path Absorption Photometer instrument, LOPAP, QUMA, Wuppertal Germany). Gas-phase glyoxal was monitored by a Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) system. Submicron aerosol chemical composition was measured by an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). Particle size distribution was measured by a TSI Scanning Mobility Particle Sizer (SMPS). Records of pressure, temperature and RH sensors, gas analyzers (e.g. O$_3$, NO$_x$) were acquired and samples of particular matter were collected for laboratory analyses.

### Table 4.1. Experimental descriptions

<table>
<thead>
<tr>
<th>Exp.</th>
<th>RH (%)</th>
<th>GLY (ppbv)*</th>
<th>Inorg. (μg m$^{-3}$)†</th>
<th>Org. (μg m$^{-3}$)‡</th>
<th>LWC (10$^{-11}$)§</th>
<th>pH¶</th>
<th>Modeled (%) #</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4^{2-}$</td>
<td>NH$_4^+$</td>
<td>NO$_3^-$</td>
<td>SO$_4^{2-}$</td>
<td>NH$_4^+$</td>
</tr>
<tr>
<td>1 (NH$_3$)</td>
<td>~80</td>
<td>53</td>
<td>10</td>
<td>7.0</td>
<td>11</td>
<td>18</td>
<td>6.3</td>
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<tr>
<td>2 (NH$_3$)</td>
<td>~80</td>
<td>32</td>
<td>19</td>
<td>6.9</td>
<td>1.0</td>
<td>10</td>
<td>7.7</td>
</tr>
<tr>
<td>11 (NH$_3$)</td>
<td>~62</td>
<td>36</td>
<td>19</td>
<td>7.7</td>
<td>0.25</td>
<td>1.6</td>
<td>3.9</td>
</tr>
<tr>
<td>5</td>
<td>~76</td>
<td>21</td>
<td>15</td>
<td>5.5</td>
<td>0.52</td>
<td>1.8</td>
<td>5.2</td>
</tr>
<tr>
<td>17</td>
<td>~82</td>
<td>28</td>
<td>37</td>
<td>14</td>
<td>5.4</td>
<td>6.8</td>
<td>14</td>
</tr>
</tbody>
</table>

Note:
* Maximum glyoxal level throughout the experiment. In Exp17 value shows $^{13}$C glyoxal and average $^{12}$C glyoxal level in Exp17 was 0.3 ppbv.
† HR-ToF-AMS inorganic components at 1st glyoxal production (1st UV light on after HONO/C$_2$H$_2$ injections).
‡ Maximum HR-ToF-AMS organics recorded throughout the experiment.
§ Average LWC throughout the experiment, in volume ratio. LWC calculated using E-AIM.
¶ Average particle pH, $-\lg(aH^+)$, calculated using E-AIM. Numbers in brackets in Exp1, Exp2 and Exp11 are the pH values under which the sensitivity tests were conducted.
# Modeled mass contribution of major organic components: Surf. (surface product), Olig. (oligomers formed from NH$_4^+$ catalyzed reactions), IM (imidazoles) and Dihyd. (glyoxal monomer dihydrate). For Exp1 and Exp2, also shown in brackets sensitivity runs when pH=10.

The effective Henry’s law constant of glyoxal increases dramatically with increasing inorganic ions such as sulfate, which is driven by the salt-in effect. In this work we focus on ammonium sulfate (AS) seed experiments only, primarily because there are salt-
in constants of glyoxal available and hence the partitioning of glyoxal could be reasonably constrained. Table 1 lists experiments considered in this study (Exp1, Exp2, Exp5, Exp11 and Exp17) along with summaries of the corresponding experimental conditions. In Exp1, Exp2 and Exp11 around 80 ppbv NH$_3$ gas was injected to neutralize the particle acidity in order to examine the pH-effect on glyoxal reactive uptake.

The general procedure of an experiment included: (i) seeding with (NH$_4$)$_2$SO$_4$ aerosol generated from solution (0.08 g / 50 ml pure water) using an atomizer; (ii) HONO injection (~10 ppbv); (iii) NO injection (~100 ppbv, to suppress O$_3$); (iv) UV light on (to check whether there is background organics formed in the absence of glyoxal); (v) C$_2$H$_2$ injection (~10 ppm); (vi) NH$_3$ injection (~80 ppbv), only in certain experiments; (vii) UV light on (glyoxal production). In the later stages of experiments, steps (iii), (vi) and (vii) were repeated multiple times. Each time UV light was on for ~3 minutes.

**Table 4.2. Reactions & parameterizations**

<table>
<thead>
<tr>
<th>Reactions &amp; Key Parameters</th>
<th>Rate Coefficient &amp; Values</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CHOCHO = CHOCH(OH)$_2$</td>
<td>7 s$^{-1}$</td>
<td>51</td>
</tr>
<tr>
<td>2 CHOCH(OH)$_2$ = CH(OH)$_2$CH(OH)$_2$</td>
<td>4 s$^{-1}$</td>
<td>51</td>
</tr>
<tr>
<td>3 CHOCH(OH)$_2$ = CHOCHO</td>
<td>0.02 s$^{-1}$</td>
<td>51</td>
</tr>
<tr>
<td>4 CH(OH)$_2$CH(OH)$_2$ = CHOCH(OH)$_2$</td>
<td>0.02 s$^{-1}$</td>
<td>51</td>
</tr>
<tr>
<td>5 2 CH(OH)$_2$CH(OH)$_2$ = C$_4$H$_8$O$_6$</td>
<td>0.0035<del>1.2 M$^{-1}$ s$^{-1}$ (pH=3</del>7)</td>
<td>51</td>
</tr>
<tr>
<td>6 C$_4$H$_8$O$_6$ = 2 CH(OH)$_2$CH(OH)$_2$</td>
<td>0.006<del>2 s$^{-1}$ (pH=3</del>7)</td>
<td>51</td>
</tr>
<tr>
<td>7 CHOCH(OH)$_2$ + NH$_4^+$ = Olig + x IM</td>
<td>2x10$^{-10}$ exp(1.5aNH$_4^+$)exp(2.5pH) M$^{-1}$ s$^{-1}$</td>
<td>59</td>
</tr>
</tbody>
</table>

| Mass accommodation coefficient $\alpha$ | 0.023 | 51 |
| $H_{eff}$ | Pure water: 4.2x10$^5$ M atm$^{-1}$ | 56 |
| Salt-in constant | Ammonium sulfate: -0.24 ± 0.02 m$^{-1}$ | 197 |

Note: Olig denotes the oligomers formed from the ammonium catalyzed reaction, and IM is the imidazole and derivatives. IM yield (x, assume upper limit from experiments, 20%) and a correction (+15%) of the overall rate coefficient of reaction 7 are obtained from Noziere et al manuscript in preparation. Also assume this reaction could occur to all glyoxal monomer hydration forms.

### 4.3. Model description

Since the chamber organic background is fairly low, we assume the HR-ToF-AMS measured organics is the total SOA from glyoxal, therefore the reactive uptake coefficient of glyoxal ($\gamma_{eff}$) could be estimated as follows:

$$\frac{d\text{Org}}{dt} = \frac{1}{4} \gamma_{eff} cAC_{gas} - k_{wall}\text{Org}$$  \hspace{1cm} \text{Eq.1}
Where Org (μg m⁻³) is the HR-ToF-AMS measured total organics, \( \gamma_{\text{eff}} \) is the overall uptake coefficient of glyoxal, including both surface and bulk processes, \( \bar{c} \) (cm s⁻¹) is the mean molecular speed, and \( A \) (cm² cm⁻³) is the aerosol surface area per unit volume, calculated using SMPS data (assume particles are all spherical). \( C_{\text{gas}} \) is the gas-phase glyoxal concentration measured by CE-DOAS (assume in equilibrium with chamber walls; converted into μg m⁻³). \( k_{\text{wall}} \) (s⁻¹) is the 1st order wall-loss rate of aerosols and is estimated using HR-ToF-AMS sulfate and SMPS particle counts.

In general, kinetic descriptions of phase-transfer and aqueous-phase chemistry in this work conceptually follow Schwartz 1986 and Seinfeld and Pandis 2007. The surface and bulk products in this work are separately described. The evolution of unhydrated glyoxal in the bulk aqueous-phase is governed by:

\[
\frac{dC_{\text{bulk}}}{dt} = k_i (C_{\text{gas}} \cdot LWC - \frac{C_{\text{bulk}}}{HRT}) - k_{\text{wall}} C_{\text{bulk}} + \sum R_{i,\text{bulk}} \quad \text{Eq. 2}
\]

\[
k_i = \left( \frac{r^2}{3D_g} + \frac{4r}{3c\alpha} \right)^{-1} \quad \text{Eq. 3}
\]

\[
R_{i,\text{bulk}} = Q_i k_i^{1st} C_{i,\text{bulk}}, \quad Q_i = 3\left( \cosh(q_i) - \frac{1}{q_i^2} \right), \quad q_i = r \sqrt{\frac{k_i^{1st}}{D_{\text{bulk}}}} \quad \text{Eq. 4}
\]

Where \( C_{\text{bulk}} \) is the bulk aqueous-phase concentration of the unhydrated glyoxal (hydrations are described separately as reactions). Therefore the first two terms in Eq.2 represent the phase-transfer and the wall loss, and the last term is the sum of the rates of all reactions in the bulk involving the unhydrated glyoxal. \( k_i \) (s⁻¹) is the mass transfer coefficient. LWC (vol vol⁻¹) is the liquid water content. \( H \) (M atm⁻¹) is the Henry’s law constant of unhydrated glyoxal. \( D_g \) and \( D_{\text{bulk}} \) (cm² s⁻¹) are the diffusion coefficients in gas- and bulk aqueous-phase, respectively. \( D_{\text{bulk}} \) value is typically \( 10^{-5} \) (for liquid), \( 10^{-7} \text{~} 10^{-9} \) (for semi-solid) and \( <10^{-10} \) (for solid). \( r \) (cm) is the radius of particles. In this work we model the particle-phase evolution in 9 log-spaced size bins ranging from 15 to 511 nm (i.e. SMPS range). \( \alpha \) is the mass accommodation coefficient for glyoxal (0.023) which sets the upper limit of the reactive uptake coefficient. Reactions do not involve unhydrated glyoxal are described in similar ways as Eq.2, except that the phase-transfer (of glyoxal mono-/di-hydrates, oligomers, IM) is ignored.
1\textsuperscript{st} order bulk reaction rates are corrected for the bulk diffusion by Eq.4, where $Q_i$ is the dimensionless correction factor ranges from 0 to 1, $k_i$ (s\(^{-1}\)) is the rate coefficient and $C_{i,\text{bulk}}$ is the reactant concentration. Note that all 2\textsuperscript{nd} order reactions are treated as pseudo-1\textsuperscript{st} order when calculating the $Q$ values, i.e. assume the concentration of the more abundant reactant does not change over the course of integration. Finally the sum of all bulk products are defined as the SOA formed in the bulk aerosols, i.e. SOA\textsubscript{bulk} = Nonhydrate + Monohydrate + Dihydrate + Oligomers + IM. IM is assumed to be fully retained in the aerosol-phase.

The surface process is not explicitly described in this work, but is constrained by a fraction of the “overall” uptake coefficient:

$$\frac{d[\text{SOA}_{\text{surface}}]}{dt} = f_{\text{surface}} \cdot \frac{1}{4} \gamma_{\text{eff}} cAC_{\text{gas}} - k_{\text{wall}}[\text{SOA}_{\text{surface}}]$$

Eq.5

Where the dimensionless factor $f_{\text{surface}}$ (0~1) describes the surface contribution to the overall uptake. This factor is to avoid overlap between bulk processes and the overall uptake coefficient. In the model $f_{\text{surface}}$ is tuned so that the modeled total SOA (SOA\textsubscript{total} = SOA\textsubscript{surface} + SOA\textsubscript{bulk}) would match with HR-ToF-AMS measured total organics (within uncertainties).

LWC, pH, activities of particle-phase inorganic ions (e.g. H\(^{+}\), NH\(_4\)\(^{+}\)) are calculated using E-AIM, with temperature, RH and HR-ToF-AMS sulfate, nitrate and ammonium as inputs\(^{195}\). Due to the lack of measurements of HNO\(_3\) and NH\(_3\) gases, HR-ToF-AMS measured particulate nitrate and ammonium are assumed to be in equilibrium with their corresponding gases. pH calculation in this way may be subject to potential uncertainties and sensitivity runs have been conducted to evaluate the effects of pH on the modeling results. Also as the chamber is seeded using solution/atomizer, we assume the aerosols are in liquid or metastable liquid, formation of any solid is forbidden in the E-AIM calculation.

4.4. Mass Transfer Considerations

In principle, the reactions of soluble gases in the aqueous-phase involves the following processes: (i) diffusion in the gas-phase, characteristic time $\tau_{\text{gas}} = \frac{r^2}{3D_g}$; (ii) interfacial transport, characteristic time $\tau_{\text{interfacial}} = \frac{4r}{3c\alpha}$; (iii) diffusion in the aqueous-phase, characteristic time $\tau_{\text{bulk}} = \frac{r^2}{\pi^2D_{\text{bulk}}}$; and (iv) aqueous-phase reaction, characteristic time $\tau_{\text{aq-chem}} = \frac{1}{k}$. The slowest step limits how fast the entire process proceeds. Gas-phase diffusion (i) is usually fast and hence mostly not the limiting step, except for compounds with very high mass
accommodation coefficient (such as OH radicals). For extremely water-soluble species the interfacial transport (ii) may be limiting, such as glyoxal; and for rapid aqueous-phase reactions, the bulk diffusion (iii) may be limiting, such as the protonation of NH₃ in water, especially in highly viscous liquid or semi-solid (i.e. low bulk diffusion coefficient D_{bulk}).

![Figure 4.1. Mass transport considerations for glyoxal aqueous-phase processing. Y-axis is the (effective) Henry’s law constant for glyoxal (unhydrated, monohydrate or dihydrate), and X-axis is the 1st order rate coefficient of aqueous-phase reactions. Four sets of red lines represent scenarios with aerosol radius ranges from 0.1~1 μm, and with typical bulk diffusion coefficient D_{bulk} for liquid (10⁻⁵ cm² s⁻¹) to semi-solid (10⁻⁹ cm² s⁻¹). Thick black lines represent different reactions, see main text for details.]

To examine whether mass transport limits the overall rate of an aqueous-phase, one could plot the effective Henry’s law constant of a soluble gas versus its 1st order aqueous-phase reaction rate coefficient, such as in Figure 4.1. A set of mass transport limitation conditions (dark red lines) are shown for aerosols under different conditions (radius 0.1~1 μm, D_{bulk} 10⁻⁵~10⁻⁹ cm² s⁻¹), i.e. aqueous aerosol or semi-solid. Below or to the left of the boundary defined by the mass transport lines represent the regime with no mass transport limitations (i.e. chemistry is slower), while above or to the right of the boundary show regime in which the overall process could be limited by interfacial and/or bulk diffusion. Here “not limiting” means “mass transport limitation does not exceed 10%” and is elaborated in literatures ²⁰², ²⁰³. A set of thick black lines represent major aqueous-phase reactions of glyoxal. For example, the glyoxal mono-hydration (R1 in Table 4.2; the Henry’s law constant of unhydrated glyoxal in pure water is 5.8 M atm⁻¹, and the mono-hydration rate constant is 7 s⁻¹) in pure water can be
described by a single point (7 s⁻¹, 5.8 M atm⁻¹). With the presence of inorganic ions, the solubility of glyoxal could be enhanced by up to 4 orders of magnitude, therefore this point can be extended vertically by 4 orders of magnitude of $H_{eff}$. Similarly we show glyoxal di-hydration, NH₄⁺ catalyzed oligomerization with different pH (occur primarily to glyoxal monohydrate which is the most reactive hydration form), and the OH oxidation (assume occur to all glyoxal hydration forms).

Usually bulk diffusion is fast in aqueous aerosols, but it may be a limiting step in semi-solids, especially for fast reactions. Figure 1 indicates that glyoxal mono-/di-hydration are mostly not limited by mass transport for aqueous aerosols ($D_{bulk} \sim 10^{-5}$ cm² s⁻¹), but for semi-solids ($D_{bulk} \sim 10^{-9}$ cm² s⁻¹) the bulk diffusion could be slow, and also interfacial transport may be limiting if the solubility is enhanced by the salting-in effect, which is inferred from previous studies. NH₄⁺ catalyzed oligomerization depends on pH. Under acidic conditions this reaction is slow and hence unlikely limited by mass transport, while under neutral conditions mass transport may limit the overall rate, especially for semi-solid. For the OH oxidation in the aqueous-phase, interfacial transport may limit when the effective Henry’s law constant is high.

4.5. Surface vs bulk

Wall loss is a key process in chamber experiments. In this work wall loss rate was estimated using the time series of HR-ToF-AMS sulfate ($dC_{sulfate}/dt$) and SMPS total number count ($dN_{total}/dt$). These two approaches gave similar estimates in all five experiments (relative difference 8~43%) and usually SMPS-derived number loss rate was slightly higher due to possible coagulation. HR-ToF-AMS sulfate decay is on a mass basis and is insensitive to coagulation but may be subject to issues such as bouncing effect. Average wall loss rate estimated in these two ways were 7.0 (Exp1), 3.5 (Exp2), 3.6 (Exp5), 4.2 (Exp11) and 3.1 (Exp17) × 10⁻⁵ s⁻¹, corresponding to a lifetime of 4~9 hours. Wall loss rate estimated here set the lower bound for the removal process of organic components which may undergo evaporation.

Figure 4.2 shows the results of all five experiments, in which measured and modeled organics all normalized with HR-ToF-AMS measured sulfate. In Exp5 RH was maintained between 79~73%. Estimated $\gamma_{eff}$ in Exp5 was 3.7±3.0×10⁻⁶. As seen, bulk reactions could only explain 40% of observed SOA mass in Exp5 (average since 1st UV light on). Bulk products were mainly glyoxal dihydrate and other products were minor. Given the minor contribution
of bulk pathways, varying bulk diffusion coefficient does not have significant effect on the total SOA. E-AIM calculated particle pH was ~2.5.

**Figure 4.2.** Modeling results in Exp1, Exp2, Exp5, Exp11 and Exp17. Gray scatters are the HR-ToF-AMS measured total organics (background subtracted) normalized by sulfate. All modeling results are also normalized with sulfate. High $D_{\text{bulk}}$ refers to typical liquid conditions while low $D_{\text{bulk}}$ refers to semi-solid conditions. Highlighted vertical bands show moments when $\text{C}_2\text{H}_2$ or $\text{NH}_3$ was injected or UV was on. Error bars show estimated ~10% relative uncertainty of HR-ToF-AMS Org / Sulfate mass ratio.
Figure 4.3. (Left) time series of changes of normalized Org68 signals with respect to experimental background since the 1\textsuperscript{st} glyoxal production in each experiment. Shaded areas show total uncertainties estimated as 30\% of measurements (HR-ToF-AMS relative uncertainty of organics) + instrument background times 3 (e.g. quantitative detection limit). Instrument background of Org68 is assumed to be 0.025 μg m\textsuperscript{-3}. See main text for details. (Right) $\gamma_{\text{eff}}$ vs HR-ToF-AMS measured Org68 signal (normalized, see main text). Org68 level before glyoxal production (experimental background) was subtracted. Error bars represent the variations since 1\textsuperscript{st} glyoxal production. Exp1, Exp2 and Exp11 were with NH\textsubscript{3} injection.

Exp11 was quite different: RH was around 62\% (lowest of all experiments and below the deliquesced RH of ammonium sulfate, ~79\%\textsuperscript{204}), and HR-ToF-AMS recorded lowest organics, only a few μg m\textsuperscript{-3}. Estimated $\gamma_{\text{eff}}$ was 1.4±2.0×10\textsuperscript{-6}. In this experiment, if $D_{\text{bulk}}$ value were set to typical liquid condition (10\textsuperscript{-5} cm\textsuperscript{2} s\textsuperscript{-1}), bulk products would far exceed the measured total SOA, and increasing $k_{\text{wall}}$ too much did not help improving the total SOA profile shape. Reducing $D_{\text{bulk}}$ to ~10\textsuperscript{-9} cm\textsuperscript{2} s\textsuperscript{-1}, however, would bring the modeled total SOA close to the measurements (assume 10\% uncertainty to the HR-ToF-AMS Org / Sulfate mass ratio). Therefore it is likely that under Exp11 condition the bulk reactions are limited by bulk diffusion, due to relatively lower RH and high inorganic loadings. It is challenging to directly estimate $D_{\text{bulk}}$, yet the kinetic modeling in Exp11 implied a rather low $D_{\text{bulk}}$, while in all other experiments (Exp1, Exp2, Exp5, and Exp17) $D_{\text{bulk}}$ still remains unclear. Given that inorganic concentration per unit LWC in Exp11 was the highest in all these experiments (e.g. sulfate in mol L\textsuperscript{-1} water: Exp1: 1.7; Exp2: 2.6; Exp5: 3.0; Exp11: 5.1; Exp17: 2.8), we suspect $D_{\text{bulk}}$ in Exp11 may be the lowest. Also, in Exp11 ~80 ppbv NH\textsubscript{3} gas was injected, as a result the E-AIM calculated particle pH was ~10, therefore the NH\textsubscript{4}\textsuperscript{+} catalyzed oligomerization was much faster, and the modeled bulk products consists of mostly oligomers and imidazoles. The total bulk products together contribute to 89\% total SOA.
Exp1, Exp2 and Exp17 were also under high RH and the major results are summarized in Table 4.1. Since RH in these experiments were all high (~80%), it is likely that aerosols existed as liquid. Similar to Exp5, bulk products contribute to minor total SOA and hence the modeled total SOA is less affected by the $D_{\text{bulk}}$ and it is difficult to estimate $D_{\text{bulk}}$ for these experiments in this work.

As seen, the bulk chemistry can only explain up to 49% of total measured SOA on acidic particles (bulk products mainly glyoxal monomer dihydrate), while on neutralized particles the measured-modeled discrepancies could be greatly reduced by the $\text{NH}_4^+$ catalyzed oligomerization, although the overall oligomerization rate may be limited by mass transport. This is generally consistent with Waxman et al.\textsuperscript{68} who reported that in Mexico City under acidic conditions >89% glyoxal-induced SOA formation could not be explained by bulk chemistry. Note in this work HR-ToF-AMS measured glyoxal-SOA might be biased low, since the vacuum environment required by the AMS techniques may cause the evaporation loss of fast glyoxal reservoirs in the particles\textsuperscript{197}.

Finally, aqueous-phase OH oxidation is one major pathway of glyoxal processing by atmospheric waters\textsuperscript{51, 61, 65}. OH radicals in the aqueous-phase could be transferred from gas-phase, or formed through aqueous-phase processes. Given the condition of the chamber experiments in this work (e.g. ~10 ppmv C$_2$H$_2$, tens of ppbv glyoxal, and tens of ppbv NO$_x$), OH radicals in the gas-phase should be mostly scavenged, and transferring to the particles is likely minor. Aerosol-phase radical sources, although is plausible but mostly requires radiation and hence should be minor as well since the experiments were mostly under dark conditions. The minor significance of aqueous-phase OH oxidation in this work is supported by the filter sampling followed by Nano-DESI/ESI-MS analysis and no glyoxal-derived carboxylic acids or organosulfates were found (Waxman et al manuscript in preparation). In principle glyoxal-derived carboxylid acids and organosulfates both require OH radicals\textsuperscript{60, 61, 147}.

### 4.6. HR-ToF-AMS Org68 & Imidazoles

Figure 4.3 shows the evolution of HR-ToF-AMS unit mass resolution m/z 68 (Org68) signal (experimental background subtracted). Org68 is a fragment of imidazole and its derivatives under AMS condition. Before 1\textsuperscript{st} glyoxal production Org68 showed little variation and hence was subtracted as experimental background (i.e. $\Delta$Org68 = Org68 – Org68\textsubscript{background}). The background subtracted signal was then normalized to 10 ppbv glyoxal, $10^{-10}$ LWC (vol vol$^{-1}$) and 0.1 a$\text{NH}_4^+$ (i.e. $\Delta$Org68\textsubscript{norm} = $\Delta$Org68 × (10/GLY$_{\text{avg}}$) × ($10^{-10}$/LWC$_{\text{avg}}$) ×
(0.1/aNH$_4^+$$_{avg}$). GLY$_{avg}$, LWC$_{avg}$ and aNH$_4^+$$_{avg}$ are averaged since 1$^{st}$ glyoxal production). Note that Org68 here was not normalized with sulfate, as sulfate levels may vary among experiments and hence the inter-experiment differences in Org68 may be diminished. In these ammonium sulfate experiments, Exp1, Exp2 and Exp11 were injected with ~80 ppbv NH$_3$ gas, and correspondingly the Org68 signals were unambiguously detected (30% HR-ToF-AMS relative uncertainty of organics and 3 times of instrument background of Org68 were both considered. The instrument background was estimated as ~0.025 μg m$^{-3}$, e.g. in Exp5 no NH$_3$ was injected and Org68 was 0.025±0.025 μg m$^{-3}$ throughout the experiment; and in Exp17 with $^{13}$C glyoxal the Org68, from “normal” $^{12}$C glyoxal was 0.026±0.003 μg m$^{-3}$). Also shown is $\gamma_{eff}$ versus normalized Org68 signal. Also in these three experiments $\gamma_{eff}$ is positively correlated with normalized Org68 signal, implying perhaps the surface process on neutralized particles is related to imidazole. Given that imidazoles are byproducts of NH$_4^+$ catalyzed oligomerization$^{162, 172, 199}$, it is possible that the surface product on neutralized particles is mainly oligomers, whose production is favored under neutral conditions. Modeling results suggest under neutralized conditions oligomers account for over 90% of bulk products too.

As for the experiments under acidic conditions, e.g. Exp5, Org68 signal is close to the instrument background implying there were no significant productions of imidazoles. Surface process under acidic conditions may associate with other mechanisms, as the NH$_4^+$ catalyzed oligomerization rate could be 10 orders of magnitude slower under acidic conditions. Previous chamber experiments$^{174}$ reported reactive uptake of glyoxal on very acidic particles, in which increased uptake coefficient was associated with increasing particle acidity, implying acid catalyzed reactions.

### 4.7. Particle Acidity

Particle acidity is a key parameter in the model. In these experiments OH radicals was produced by HONO and was controlled by UV lights. LOPAP recorded persistent HONO levels throughout each experiment (e.g. Exp1: 6-8 ppbv; Exp2: 6-11 ppbv), implying continuous formation of HONO. In all experiments NO was injected to suppress O$_3$ level, leading to considerable NO$_2$ (e.g. Exp1 had >37 ppbv NO$_2$ since the 1$^{st}$ UV-on till the end, and Exp2 had >55 ppbv), therefore HNO$_3$ may form in the gas-phase (NO$_2$+OH). In the meantime NO$_2$ may undergo heterogeneous reactions on moisture particle surface or chamber walls to form HONO and HNO$_3$ (reported $\gamma_{NO2}$ on the order of 10$^{-3}$)$^{205}$. This mechanism may explain the persistent HONO level in the experiments and the acidity of particles. In this work the pH
calculated using particle composition with E-AIM were typically 2~3 for experiments without NH$_3$ injection, much lower than (NH$_4$)$_2$SO$_4$ solution.

In Exp1, Exp2 and Exp11 ~80 ppbv NH$_3$ gas was injected to tune particle pH. The calculated pH in Exp11 was ~10 (a bit high yet somewhat within expectation), but in Exp1 and Exp2 the calculated pH was rather low 1.0~2.5. In both Exp1 and Exp2, background molar ratio of NO$_3^-$/SO$_4^{2-}$ and NH$_4^+$/SO$_4^{2-}$ (before UV on) were: Exp1: NO$_3^-$/SO$_4^{2-}$: 0.14±0.00 (error bar shows variation), NH$_4^+$/SO$_4^{2-}$: 2.09±0.03; Exp2: NO$_3^-$/SO$_4^{2-}$: 0.07±0.02, NH$_4^+$/SO$_4^{2-}$: 1.90±0.02, as in the initial stage there were little nitrate and NH$_4^+$/SO$_4^{2-}$ was more or less the same as in the solution. As shown in Figure 4.4, in Exp1 and Exp2, in the first few minutes after UV on, molar ratio of NO$_3^-$/SO$_4^{2-}$ and NH$_4^+$/SO$_4^{2-}$ (background subtracted) both increased and the amount was comparable, implying the uptake of NH$_4$NO$_3$. But later on the increase in NO$_3^-$/SO$_4^{2-}$ exceeded that of NH$_4^+$/SO$_4^{2-}$, implying particulate nitrate content in addition to NH$_4$NO$_3$ uptake. ~80 ppbv NH$_3$ was injected every time before UV light on, therefore there should be sufficient NH$_3$ to neutralize HNO$_3$ formed in the gas-phase, but perhaps the NH$_3$ gas was incapable of fully neutralizing HNO$_3$ formed in the particle-phase. The effective Henry’s law constant of NH$_3$ depends on pH. For typical chamber condition (NH$_4^+$: 10 μg m$^{-3}$, LWC: 10$^{10}$), the gas-phase NH$_3$ in equilibrium would depend on pH as well, e.g. 5.3 ppbv (pH=2), 53 ppbv (pH=3). Although ~80 ppbv NH$_3$ was injected each time, it might deposit on chamber walls (may be reversible or irreversible) and would partly react with HNO$_3$ gas, therefore the actual NH$_3$ concentration is difficult to estimate but definitely lower than 80 ppbv. Also, ammonium content may well be concentrated in the particle surficial water layer and hence result in much higher equilibrium NH$_3$ gas concentration. Therefore we suspect it might be possible that even if significant amount of NH$_3$ were injected, it might not be able to fully neutralize the acidity.

Excess of particulate NO$_3^-$ content (in addition to NH$_4$NO$_3$) was not observed in Exp11: both molar ratios of NO$_3^-$/SO$_4^{2-}$ and NH$_4^+$/SO$_4^{2-}$ remained fairly stable throughout the entire experiment (NO$_3^-$/SO$_4^{2-}$: 0.05±0.03 and NH$_4^+$/SO$_4^{2-}$: 2.13±0.04, error bars show variations), and only very minor increase of NO$_3^-$ was observed in the later stage of experiment (3$^{rd}$ UV-on, $\Delta$(NO$_3^-$/SO$_4^{2-}$)≈0.16), which was accompanied by virtually the same amount of NH$_4^+$ increase. The low NO$_3^-$ content in this experiment was not likely a result of measurement uncertainties, as here we examine molar ratios and the uncertainty, in principle, is smaller than individual measurements and some effects (e.g. wall loss, collection efficiency) would be cancelled out.
Figure 4.4. Time series of $\Delta$(NO$_3^-$/SO$_4^{2-}$) and $\Delta$(NH$_4^+$/SO$_4^{2-}$), calculated using HR-ToF-AMS measurements, all molar ratio and background subtracted. Excess NO$_3^-$ content in addition to NH$_4$NO$_3$ uptake was found in Exp1 and Exp2, despite NH$_3$ gas was injected. Shading areas show ~10% uncertainties in molar ratios. Uncertainty in AMS molar ratios in principle is smaller than that for the absolute concentrations.

To sum up, high pH in Exp1 and Exp2 expected from NH$_3$ injection is consistent with HR-ToF-AMS Org68, in which Org68 levels were more than one order of magnitude above the background. But it is inconsistent with the E-AIM calculations and the fact that excess amount of nitrated (in addition to NH$_4$NO$_3$) in Exp1 and Exp2. Some possible explanations are:

1. Thermodynamic calculation is sensitive to the gas-phase NH$_3$ inputs$^{206, 207}$. In this study there is no direct NH$_3$ measurement available, and it is challenging to estimate actual NH$_3$ levels.

2. Uncertainties in aerosol chemical composition measurements may introduce additional uncertainties in the charge balance and hence the thermodynamic models.

3. There might be another possibility that, even if NH$_3$ gas was injected in Exp1 and Exp2, the interior of the particles might still remain acidic while surface is neutralized, while the chemical composition measurements mainly reflect the bulk. If this is the case, the positive correlation between $\gamma_{\text{eff}}$ and normalized Org$_{68}$ suggests that imidazole may primarily form on surface.

Sensitivity tests in Exp1 and Exp2 with pH=10 (i.e. similar condition as in Exp11 when NH$_3$ was also injected) show that the bulk contribution more than doubled (mainly oligomers), to 29% and 47% of the total SOA, respectively. High pH in Exp11 and in sensitivity runs for Exp1 and Exp2 in principle will increase the bulk reaction rate, however for high pH ~10 the
overall rate will be limited by interfacial transport (glyoxal + NH$_4^+$ when pH=10, if plotted in Figure 4.1 will be close to the Monohydrate + H$_2$O line, therefore is not shown). That is, although pH calculation in Exp1 and Exp2 were highly uncertain, the conclusion that bulk chemistry cannot explain the observed SOA remains unchanged – there must be other mechanisms responsible for the mass imbalance in these experiments. Besides, given that pH calculation in Exp11 is also subject to potential uncertainties, sensitivity tests on pH=7 have been conducted for Exp11. pH=7 is already sufficiently high to make the NH$_4^+$ catalyzed oligomerization the dominant pathway in Exp11. Also the difference between the pH=7 run and the pH=~10 (actually calculated) is small, as mass transport limits the overall rate. Mass contributions in each experiment and sensitivity runs are summarized in Table 4.1.

4.8. Implications

Various natural and anthropogenic sources release glyoxal into the atmosphere. It has been recognized that glyoxal has great potential to form SOA, mainly via aqueous-phase processes. Great efforts have been made to probe the bulk aqueous chemical mechanisms of glyoxal, yet relevance of this chemistry to aerosolized systems remains poorly understood. The reactive uptake of glyoxal on ammonium sulfate seeds, one of the most common inorganic components of atmospheric aerosols, under humid conditions (RH>60%) were investigated.

In this work we show that bulk glyoxal chemistry (except for OH oxidation which may not be favored under the experimental conditions) can only explain up to 44~47% of observed total SOA under high RH (e.g. 73% and above). The majority of observed glyoxal-SOA may be surface products, consistent with a recent study. Previous chamber works also reported rapid glyoxal uptake on very acidic particles and implied acid catalyzed heterogeneous mechanism. In this work we found on neutralized seeds increased reactive uptake of glyoxal was accompanied with increasing imidazole tracer (sensitive to acidity), implying the reactive uptake on neutralized particles proceeds at high efficiency as well, mainly via NH$_4^+$ catalyzed oligomerization. The modeling results also show that mass transfer might be the limiting step of the reactive uptake even for fine particles under intermediate RH level (e.g. 60%). Glyoxal reactive uptake under ambient conditions may well be subject to kinetic limitation, especially on neutralized particles. It is likely that the rapid surface accommodation leads to the accumulation of glyoxal monomers on the surface, limiting the diffusion to the interior and triggering the oligomerization in the meantime. Molecular level understanding of surface chemical composition is desired.
The reactive uptake coefficient of glyoxal ($\gamma_{\text{eff}}$) estimated in this work is mostly $10^{-6}$-$10^{-5}$, much lower than $\gamma_{\text{eff}}$ ($10^{-3}$-$10^{-3}$) reported on acidic seeds (>49% RH, ~5 ppbv glyoxal)\textsuperscript{174}, which is however primarily due to the higher glyoxal concentration used in this work (tens of ppbv). Another work with even higher glyoxal concentration (20~150 ppmv) reported even lower $\gamma_{\text{eff}}$ ($10^{-8}$)\textsuperscript{208}.

Finally, particle acidity plays an important role in the aerosol physics and chemistry. We found that acidity estimated using aerosol inorganic composition with thermodynamic model (E-AIM) is sometimes, while not always, inconsistent with pH-sensitive tracer measurements (such as Org68/imidazole). The inconsistency may result from the uncertainties in the thermodynamic models and / or the particle inorganic composition measurements, or imply the different chemical environment between the surface and the interior of the particles.
CHAPTER 5. Hopane Degradation in the Ambient Environment: Implications for Source Apportionment of Particulate Organics

5.1. Overview

Identifying types and contributions of emission sources is crucial in formulating pollution control strategies. Vehicular emissions are one major emission category that contributes substantially to particulate organic matter in the urban environment, affecting air quality and human health. Hopanes are widely used as a fingerprint of vehicular emissions (mainly gasoline vehicles and to a lesser extent, diesel exhaust) in receptor-based source apportionment techniques. However, recent field and chamber studies provide evidence that particle-phase hopanes may undergo significant degradation. Hence, source apportionment directly using hopanes as tracers, such as Chemical Mass Balance (CMB), could be potentially biased. Degradation of particulate hopanes is likely related to their semi-volatile nature. Volatility measurements of a number of other widely used motor vehicle molecular markers indicated that they all can, at least, partially exist in the gas-phase, but to our knowledge no direct volatility measurements are available for hopanes. Sihabut et al. found during a field study in summer urban Philadelphia (U.S.) 9-13% of the hopanes were present on the backup filter, and Mandalakis et al. reported a 17% gas-phase hopane fraction in summer urban Athens (Greek), which is qualitatively consistent with the volatilities measured for other marker compounds of vehicular emissions as reported in May et al., as well as hopane volatility estimated using the EPI suite in this work. Therefore, under typical chamber and ambient conditions, an appreciable fraction of hopanes exist in the gas-phase and are vulnerable to attack by hydroxyl (OH) radicals (k_{OH} = 3.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}, with 50\% uncertainty, estimated using Structure-Activity Relationship, see ). Chamber experiments further indicate that the effective uptake coefficient of OH radicals far exceeds unity implying that the particle-phase secondary chemistry and heterogeneous OH oxidation may be insufficient to explain such fast degradation.

Chamber studies reported effective degradation rate coefficients of hopane species spanning a wide range of 0.04-6.2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}, and yet the discrepancies are not fully understood. Furthermore, the applicability of chamber-derived effective hopane degradation coefficients to an ambient analysis remains largely unverified. Firstly, organic loadings in chamber experiments are typically high. As such, more semi-volatile materials
would be trapped in the particle-phase. Secondly, vehicular exhaust in the ambient environment rapidly undergoes mixing processes with background air, leading to significant decreases in both gaseous and particulate hopanes, while dilution is negligible in chambers. Finally, organic vapors in chambers could also lose to the walls and may establish equilibrium with wall-adsorbed organics \(^7\), while vapor-phase dilution loss is virtually irreversible in the ambient environment.

In this work, we estimate the effective degradation rate coefficients of particle-phase hopanes using ambient data collected in Hong Kong, a densely populated city located in southern China (see Figure 1). Degradation of hopanes is assumed to occur through both gas-phase OH oxidation and dilution with background air, while condensed-phase oxidation is of low impact and thus ignored in this study \(^8\).

![Google map of MK Roadside station and HKUST supersite. In general grayish colors are densely built areas, green is vegetation covered terrain and blue is ocean. The black-dotted rectangle in the embedded map shows the spatial range of the satellite image.](image)

5.2. Effective loss rate coefficients of particulate hopanes

We herein describe the apparent loss rate of particulate hopane (\(C_{\text{particle}}\, \mu g\ m^{-3}\)) in the form of a 2\(^{nd}\) order reaction. The derivation of the loss rate conceptually follows Lambe et al \(^8\). \(C_{\text{total}}\) (\(\mu g\ m^{-3}\)) is the total concentration of hopane in both gas- and particle-phase (\(C_{\text{total}} = C_{\text{gas}} + C_{\text{particle}}\)). The partitioning coefficient \(K_{\text{gas-particle}}\) (dimensionless) is defined as the ratio of \(C_{\text{gas}}\) and \(C_{\text{particle}}\) (\(K_{\text{gas-particle}} = C_{\text{gas}} / C_{\text{particle}}\)). Therefore the loss rate of total hopane with respect to gas-phase OH radicals can be given as:

\[
\frac{dC_{\text{total}}}{dt} = -k_{\text{gas}} C_{\text{gas}} - k_{\text{particle}} C_{\text{particle}} - k_{\text{wall}} C_{\text{total}}
\]
Where \([OH]\) is the OH concentration (molec cm\(^{-3}\)) and \(k_{\text{eff,total}}\) (cm\(^3\) molec\(^{-1}\) s\(^{-1}\)) is the effective loss rate coefficient of total hopane content. \(\tau_{\text{dilution}}\) (s) is the characteristic time of the dilution by background air. For simplicity we assume the background air is “clean” and free of vehicular signatures. \(k_{OH}\) (cm\(^3\) molec\(^{-1}\) s\(^{-1}\)) is the gas-phase OH oxidation rate coefficient of hopane, and \(k_{\text{particle-phase}}\) (s\(^{-1}\)) is the particle-phase hopane loss rate coefficient. Ignoring the last term, i.e. particle-phase hopane chemical loss, we get:

\[
k_{\text{eff,total}} = k_{OH}K_{\text{gas-particle}} + \frac{K_{\text{gas-particle}} + 1}{[OH]\tau_{\text{dilution}}}
\]

The gas-particle partitioning coefficient is given by the partitioning theory \(^{203}\):

\[
K_{\text{gas-particle}} = \frac{C_{\text{gas}}}{C_{\text{particle}}} = \frac{C^*}{C_{\text{particle}}} \approx \frac{1}{\frac{MW}{C_{\text{particle}}} + \frac{C_{\text{OM}}}{MW_{\text{OM}}}} = \frac{C^*}{C_{\text{OM}}} \frac{MW_{\text{OM}}}{MW}
\]

Where \(C_{\text{OM}}\) (\(\mu g\) m\(^{-3}\)) and \(MW_{\text{OM}}\) (g mol\(^{-1}\)) are the organic loading and mean molecular weight of total particulate organic materials, respectively. \(MW\) (g mol\(^{-1}\)) is the molecular weight of hopane. The effective saturation vapor concentration, \(C^*\) (\(\mu g\) m\(^{-3}\)), is estimated using the EPI suite \(^{213}\), which provides three methods to calculate the saturation vapor pressure, among which the Modified Grain method gives the highest values, a factor of \(~5\) higher than the lowest value. In this work we choose the Modified Grain method to represent the maximum effect of gas-phase processes leading to the degradation of particulate hopanes. Using the estimated \(C^*\) and measured OC and temperature, an average of 39% hopane exists in the gas-phase in warmer months (May, Aug; TEMP\(_{\text{avg}} = 300\) K) while 13% in cooler months (Nov, Feb, TEMP\(_{\text{avg}} = 292\) K), generally consistent with the partitioning measurements \(^{211,212}\).
Assuming an instantaneous gas-particle equilibrium, i.e. \( \frac{dC_{\text{particle}}}{dt} = \frac{1}{1 + K_{\text{gas-particle}}} \frac{dC_{\text{total}}}{dt} \), degradation of particulate hopane and the effective loss rate coefficient of particulate hopane, \( k_{\text{eff,particle}} \) (cm\(^3\) molec\(^{-1}\) s\(^{-1}\)) are given by:

\[
\frac{dC_{\text{particle}}}{dt} = -k_{\text{eff,particle}}[OH]C_{\text{particle}}
\]

Eq. 5.4

\[
k_{\text{eff,particle}} = \frac{1}{K_{\text{gas-particle}} + 1} k_{\text{eff,total}} = \frac{K_{\text{gas-particle}}}{K_{\text{gas-particle}} + 1} k_{\text{OH}} + \frac{1}{[OH] \tau_{\text{dilute}}}
\]

Eq. 5.5

Integrate Eq. 5.4 with \( t=0 \rightarrow t \), \( C_{\text{particle}}=C_{\text{particle,0}} \rightarrow C_{\text{particle,}t} \)

\[
\ln C_{\text{particle,0}} - \ln C_{\text{particle,}t} = k_{\text{eff,particle}} \int_0^t [OH]dt
\]

Eq. 5.6.

Where subscript 0 represent “source” or “initial” condition, while subscript \( t \) refers to receptor condition at time \( t \) (s).

Elemental carbon (EC), as defined by the working protocol of the Elemental and Organic Carbon (EC/OC) analyzing techniques, corresponds to the soot-like particulate carbon materials emitted during most combustion processes. Vehicular emissions are the major source of EC in urban environments. EC in the ambient air is fairly stable and the main process (other than deposition) for its concentration reduction is dilution with clean background air. Therefore the loss of EC (μg m\(^{-3}\)) is constrained by:

\[
\ln EC_0 - \ln EC_t = \frac{1}{\tau_{\text{dilution}}} t = \frac{1}{[OH] \tau_{\text{dilute}}} \int_0^t [OH]dt
\]

Eq. 5.7.

Combining Eq. 5.6 and Eq. 5.7 we get:

\[
\ln \left( \frac{C_{\text{particle}}}{EC} \right)_0 - \ln \left( \frac{C_{\text{particle}}}{EC} \right)_t = (k_{\text{eff,particle}} - \frac{1}{[OH] \tau_{\text{dilute}}}) \int_0^t [OH]dt
\]

Eq. 5.8.

As seen by normalizing hopane with EC, the effect of dilution on particulate hopane is eliminated from \( k_{\text{eff,particle}} \). Similarly, any process that has equal effects on particulate hopanes and EC (e.g. deposition) will also be cancelled out by normalizing with EC.

The toluene to benzene ratio is an ideal photochemical clock on the urban scale:
\[ \int_0^t [OH] \, dt = \frac{\ln \frac{Tol}{Benz} \, |_0 - \ln \frac{Tol}{Benz} \, |_t}{k_{Tol} - k_{Benz}} \]  

Eq. 5.9

Where \( k_{Tol} \) and \( k_{Benz} \) (both in \( \text{cm}^3 \text{molec}^{-1} \text{s}^{-1} \)) are the OH oxidation coefficients of toluene and benzene, respectively. Thus plugging Eq. 5.9 into Eq. 5.8:

\[ \ln \frac{C_{\text{particle}}}{EC} \, |_0 - \ln \frac{C_{\text{particle}}}{EC} \, |_t = \left( k_{\text{eff}, \text{particle}} - \frac{1}{[OH]_{\text{dilution}}} \right) \ln \frac{Tol}{Benz} \, |_0 - \ln \frac{Tol}{Benz} \, |_t \]

Eq. 5.10

Plot the left-hand-side \( \ln \frac{C_{\text{particle}}}{EC} \, |_0 - \ln \frac{C_{\text{particle}}}{EC} \, |_t \) versus the OH exposure expressed by VOCs

\[ \ln \frac{Tol}{Benz} \, |_0 - \ln \frac{Tol}{Benz} \, |_t \]

and the slope is therefore \( k_{\text{eff}, \text{particle}} - \frac{1}{[OH]_{\text{dilution}}} \). Define this term as \( k'_{\text{eff}, \text{particle}} \):

\[ k'_{\text{eff}, \text{particle}} = k_{\text{eff}, \text{particle}} - \frac{1}{[OH]_{\text{dilution}}} = \frac{K_{\text{gas-particle}}}{K_{\text{gas-particle}} + 1} k_{OH} \]  

Eq. 5.11

The factor \( \frac{K_{\text{gas-particle}}}{K_{\text{gas-particle}} + 1} \) is really the gas fraction of hopane (\( C_{\text{gas}} / C_{\text{total}} \)). Figure 5.2 shows \( k'_{\text{eff}, \text{particle}} \) data estimated with Eq. 5.10 and ambient VOC, EC, particulate hopane concentrations collected over nine months where the complexity and variations of ambient parameters lead to the wide and scattered distribution. Under simpler conditions, such as chambers or well-defined source-receptor regions, the scattered points should align over the course of aging.

To sum up, the overall atmospheric lifetime of particulate hopane is determined by gas-phase oxidation and dilution, and the effective OH rate coefficient can be calculated using Eq. 5.5. The dilution-corrected (i.e. oxidation only) can be calculated using Eq. 5.11. Calculating the effective degradation rate coefficients in such a “bottom up” manner requires priori knowledge of the hopane partitioning coefficient, gas-phase oxidation rate coefficient, and (for overall degradation rate only) the OH level and the dilution time scale. Alternatively, the dilution-corrected rate coefficient can be estimated using ambient data only, using Eq. 5.10, which does not need any priori knowledge of physical and chemical properties of hopanes.
Note that in this work we assume \( \tau_{\text{dilution}} \) to be the lifetime due to dilution with clean background air. When background air contains hopane vapors, the resulting \( \tau_{\text{dilution}} \) would in principle be longer, as a result the analysis in this work sets the upper limit of the dilution effect.

Figure 5.2. Hopane/EC differences between MK (source) and HKUST (receptor) versus OH exposure calculated using co-emitted VOC ratios. The resulting slope is then \( k'_{\text{eff, particle}} \). Panel (A) and (B) show abHopane and norHopane respectively. Shaded areas show chamber measured effective degradation rate coefficients under different conditions \(^{60, 80}\).

5.3. Measurements

Mong Kok Roadside (MK) station is located near the junction of Nathan Road and Lai Chi Lok Road in Kowloon, Hong Kong. The site is in a downtown urban area with heavy traffic loadings and is influenced by the street canyon effect as the sampling site is flanked by tall buildings nearby (http://www.epd-asg.gov.hk/english/backgd/Mong_Kok.html). The sampling probes are set up at around 2 meters above ground level and are directly exposed to vehicular exhaust. The Hong Kong University of Science and Technology (HKUST) Supersite is located in a sparsely populated area in Clear Water Bay, with little transportation and commercial development nearby (http://www.envr.ust.hk/supersite/), but is frequently affected by urban plumes \(^{215}\). We herein use data collected in MK as the “source” or “initial” condition, while HKUST is assumed to be a receptor area for the urban plume (not necessarily from MK though). The measurements were obtained in May, Aug, Nov 2011 and Feb 2012. See Figure 5.1 for more details about the sampling locations.

Particulate hopanes were sampled using 24-hour high-volume PM2.5 samplers on pre-baked 8×10’ quartz fiber filters at a flow rate of approximately 1.13 m\(^3\) min\(^{-1}\), followed by analysis using the Thermal Desorption-Gas Chromatography / Mass Spectrometry (TD-
GC/MS) technique. Quality assurance / quality control and technical details can be found elsewhere \(^{210, 216}\). The two most abundant hopane species, 17\(\alpha\)(H)-21\(\beta\)(H)-30-hopane and 17\(\alpha\)(H)-21\(\beta\)(H)-29-norhopane, are used in this work to estimate their effective loss rate coefficients in the ambient environment, and are denoted hereafter as abHopane and norHopane.

OC and EC were analyzed using the thermal / optical transmittance (TOT) method with an Aerosol OCEC analyzer (Sunset Laboratory, OR, USA), using the same quartz fiber filters. The analysis protocol follows the NIOSH protocol \(^{215, 217}\).

Non-methane volatile organic compounds were measured using an online Gas Chromatography-Photo Ionization Detector / Flame Ionization Detector (GC-PID/FID) system (GC955-811/611) with a time resolution of around 30 min \(^{218}\). 24-hour averages of the VOC data were calculated for filter sample days.

Uncertainties for each individual species are estimated as \(u + \text{MDL}/3\), where \(u\) is the analytical uncertainty and \(\text{MDL}\) is the method detection limit. For hopanes, the analytical uncertainty is 10% of individual measurements and MDLs of 0.33 and 0.15 ng per sample of abHopane and norHopane, respectively \(^{216}\). Uncertainties for EC and OC are ~10% based on calculations using US EPA protocol \(^{219}\). For VOCs the relative uncertainty is assumed to be 20% and the MDL is around 0.06 ppbv for the species of interest in this work.

5.4. Estimate of OH exposure

As mentioned above, we use the ratio between toluene and benzene as a photochemical clock \(^7\). However, mixing of photochemically different air masses could introduce considerable uncertainties to the OH exposure calculation. The MK roadside station is predominantly affected by vehicular emissions, while the receptor site, HKUST, may be under a wide range of influences, e.g. evaporation sources such as solvent use and building painting, biomass burning, or long range transport, that all have their own source signature VOC profile. In this work we use specific VOC ratios from source profile measurements in Hong Kong \(^{109, 220}\) and the adjacent Pearl River Delta Region, China \(^{105}\) to identify and reduce these influences.

5.4.1. Ratio of toluene / iso-pentane

Iso-pentane is a specific tracer of gasoline vehicle exhaust and evaporation \(^{105, 109}\). Solvent use, building painting and biomass burning emissions contain rather low iso-pentane but very high toluene, leading to a Toluene / iso-Pentane ratio of 7.43±1.58 and above \(^{105}\). Vehicular emissions, however, have a relatively lower ratio: 1.17±0.33 for gasoline and
1.54±0.99 for diesel. Previous studies reported ratios of 2.01±1.29, 1.76±0.69, and 1.39±0.92 in three tunnels in Hong Kong. In this work a Toluene / iso-Pentane ≤ 3.3 is used to isolate data primarily under vehicle emission influence and remove samples under significant influence of fresh solvent use, building painting and biomass burning. Also both toluene and iso-pentane above MDL (~0.06 ppbv) were used in the calculation to reduce the influence of clean and extremely aged air masses.

Figure 5.3. Distributions of measured Toluene / iso-Pentane and iso-Butane / n-Butane, as well as the source ratios in the Hong Kong and PRD region. Shaded-grey areas show the data used to calculate the OH exposure. The area under the probability density curve represent “the probability of VOC ratios in this range”.

5.4.2. Ratio of iso-Butane / n-Butane

Iso-butane and n-butane have relatively low and very similar reactivity with OH. As a result the iso-butane / n-butane ratio remains fairly stable during the atmospheric aging process, therefore the ratio is an ideal indicator of the air mass homogeneity. The two compounds are major components of liquefied petroleum gas (LPG). The ratio also varies among sources: gasoline LDV: 0.67±0.27; diesel: 0.84±0.46; LPG: approximately 0.48; building painting: 0.08±0.02; biomass burning: 2.66±0.25 and the tunnel ratio is 0.50±0.27. In this work ratios of 0.5 ≤ iso-Butane / n-Butane ≤ 0.8 (both VOCs above MDL of ~ 0.06 ppbv) are used to eliminate the influence of biomass burning and building painting, and to minimize the influence of LPG-powered vehicles.
Figure 5.3 summarizes the distribution of the toluene / iso-pentane and iso-butane / n-butane ratios in this study’s dataset and the filters applied to focus on vehicle emissions. In general, the combination of the two VOC ratio filters eliminates the influence of biomass burning and building painting, and minimizes the influence of LPG and mixing of very aged air masses. 24 of the 42 daily samples (hopane, EC and VOCs) are used for the analysis in this study, while the rest are largely contaminated by other sources or extremely aged air masses.

Figure 5.4. Time series of hopanes, EC, OC, C_gas / C_total and k’eff,particle. Dashed lines in the top panel show the detection limits of norHopane and abHopane. The black line in the bottom panel shows the k’eff,particle, with gray shading showing the uncertainty propagated from k_OH (50%, see Lambe et al), C* (assume 50% uncertainty) and OC (10%×OC + MDL).

5.5. Dilution-corrected loss rate coefficient - k’eff,particle

Figure 5.4 shows the time series of k’eff,particle estimated using ambient data from the four sampling months. Also shown in Figure 3 is the gas-fraction of hopane estimated based on partitioning theory, where the effective saturation vapor concentration, C* (in this work: 0.8–15 μg m^-3 between 284 and 304 K), is estimated using EPI suite (Modified Grain method)\(^{213}\), organic loading is estimated as 1.6 × OC (μg m^-3) where 1.6 is assumed to be the ratio of
organic matter versus organic carbon, and the mean molecular weight of particulate organic matter (MW0) is assumed to be 150 g mol⁻¹. As seen in warmer months (May and Aug), higher ambient temperature and lower organic loading together drive more hopane to the gas-phase, while in relatively colder months Nov and Feb more hopane is trapped in the particles.

The average ± standard deviation (AVG ± SD) $k'_{\text{eff,particle}}$ for abHopane and norHopane are $8.06\pm6.87 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ and $1.77\pm1.47 \times 10^{-11}$ cm³ molec⁻¹ s⁻¹, respectively, where $k'_{\text{eff,particle}}$ for norHopane is a factor of ~2 higher than for abHopane (with DoF ≈ 20 the t-test value is 2.5 with 98% confidence levels, respectively; $t_{\text{calculated}} = 2.7$) although the individual uncertainty ranges are largely overlapped. Figure 4a (and Figure 3, top panel) shows norHopane concentrations are higher than abHopane in MK (1.37±0.38 vs 1.01±0.30 ng m⁻³, significantly different with 98% confidence level), while at HKUST norHopane concentrations are slightly lower (0.030±0.029 vs 0.056±0.049 ng m⁻³, significantly different with 98% confidence level), leading to higher slopes in Eq. 5.10. Previous studies reported consistently smaller-than-unity norHopane / abHopane mass ratio in urban, suburban and rural Hong Kong (5 locations; excluding roadside and tunnel; 2000-2001, 2006; 2011) ⁷⁹,²¹⁰, while in roadside or tunnel studies sometimes greater-than-unity norHopane / abHopane mass ratio was reported (MK, 2000-2001) ⁷⁹. The significantly higher norHopane than abHopane in MK in this work (and in ⁷⁹) might imply non-vehicular hopane contributions such as coal combustion ²²¹,²²². Due to the coarse time resolution of the filter-based samples, it is challenging to isolate such effect. Controlled chamber experiments reported non-distinguishable effective OH degradation rate coefficients for these two hopanes in motor oil (0.04−1.3×10⁻¹¹ cm³ molec⁻¹ s⁻¹) ⁴⁰, implying the differences in gas-phase reactivity and volatility may be small. Another chamber study ⁸⁰ reported a much faster decay of hopane in diesel POA (3.6−6.2×10⁻¹¹ cm³ molec⁻¹ s⁻¹, up to a factor of 2 higher than the gas-phase OH oxidation rate coefficient of hopane vapor) than in this study implying a much larger fraction exists in the gas-phase, and perhaps additional removal pathways (e.g. heterogeneous oxidation). In general, the dilution-corrected effective degradation coefficient of hopane species estimated using ambient data in this study is in good agreement with available chamber measurements.

As seen, although the trend of measurement-derived $k'_{\text{eff,particle}}$ tracks closely with that calculated using Eq.5.11, it is systematically higher in cooler months (Nov, Feb), perhaps due to the influence of non-vehicular EC. Mixing with background air containing considerable amounts of non-vehicular EC will in principle amplify the “apparent” degree of aging, leading to a positive bias to the measurement-derived $k'_{\text{eff,particle}}$. Given the coarse time resolution of
hopane measurements (24 hour), it is challenging to avoid such an effect. As seen in Figure 5.5 shows only moderate correlations for hopanes vs. EC (norHopane vs EC: \( r = 0.45 \) in MK and 0.44 at HKUST; abHopane vs EC: \( r = 0.58 \) in MK and 0.58 at HKUST) compared with the strong correlation between norHopane and abHopane (MK: \( r = 0.91 \); HKUST: \( r = 0.93 \)). In fall and winter seasons Hong Kong is frequently influenced by northerly long-range transport passing through the adjacent PRD region, resulting in elevated levels of pollutants including EC in the background air. Nevertheless, uncertainties in the measurements lead to fairly wide uncertainties in both measurement-derived and calculated \( k'_{\text{eff,particle}} \), which largely overlap.

Only partial data survived the filtering process in the warmer months (May, Aug), primarily due to Hong Kong being dominated by clean air from the ocean and hence HKUST is less influenced by the urban plume. In general the measurement-derived and calculated \( k'_{\text{eff,particle}} \) show reasonable agreement within the error bars during the warmer months.

![Figure 5.5. (A) norHopane versus abHopane in MK and HKUST. MK: slope=1.27±0.09, \( r = 0.91 \); HKUST: slope=0.66±0.04, \( r = 0.93 \). (B) Hopane versus EC in MK and HKUST. norHopane vs EC in MK: slope=0.10±0.03, \( r = 0.45 \); norHopane vs EC at HKUST: slope=0.03±0.01, \( r = 0.44 \); abHopane vs EC in MK: slope=0.10±0.02; \( r = 0.58 \); abHopane vs EC at HKUST: slope=0.06±0.01, \( r = 0.58 \). All Orthogonal Distance Regression (ODR) fitting.](image)

5.6. Effective loss rate coefficient (dilution included) - \( k_{\text{eff,particle}} \)

As discussed above, the dilution effect plays an important role under ambient conditions, but is negligible in chambers. The combined effect, \( k_{\text{eff,particle}} \) as described in Eq.5.5, depends on oxidation capacity (OH level) and how fast dilution is proceeding (\( \tau_{\text{dilution}} \)).

The effects of [OH] and \( \tau_{\text{dilution}} \) are examined in Figure 5.6. As seen in Figure 5.6(A) at a constant OH level of \( 5 \times 10^6 \) molec cm\(^{-3} \), \( \tau_{\text{dilution}} = 1 \) hour makes \( k_{\text{eff,particle}} \) a factor of 2.4-140
higher than the dilution-free effective loss rate coefficient $k_{\text{eff,particle}}'$ ($\tau_{\text{dilution}} \to \infty$, solid red line), and as a result at least 58% hopane is lost by dilution. When $\tau_{\text{dilution}} = 0.5$ hour, at least 73% hopane loss is attributed to the dilution effect. In Figure 5.6(B) with a constant $\tau_{\text{dilution}} = 1$ hour, lower OH concentrations lead to a faster particulate hopane degradation rate. This is because under this condition ($\tau_{\text{dilution}} = 1$ hour, $[\text{OH}] = 2.5\sim7.5\times10^6$ molec cm$^{-3}$), dilution is generally faster than OH oxidation (lifetime due to dilution 1 hour vs lifetime due to OH oxidation 0.9~2.8 hours), therefore lower OH level leads to a higher branching ratio of dilution loss and hence a faster hopane degradation.

$\tau_{\text{dilution}}$ can be roughly estimated using a simple Gaussian dispersion model Gaussian dispersion model $^{223}$. Consider a continuous point source in a 3D space emits an inert compound at a certain rate $Q$ (kg s$^{-1}$), which is elevated above the ground at height $h$ (m, in this work $h = 0$). Further assume this compound does not deposit to and is not adsorbed by the ground. Windspeed ($u$, m s$^{-1}$) in the $x$-direction advects this compound while dispersion occurs in the $y$- and $z$-directions, which can be enhanced by atmospheric turbulence. In principle such dispersion is bounded by the boundary layer. If windspeed and emission rate remain constant, after a sufficiently long time, the following equation yields a stable concentration field $C(x,y,z)$ (kg m$^{-3}$) that does not evolve with time:

$$C(x, y, z) = \frac{Q}{2\pi \sigma_y \sigma_z u} \exp(-\frac{y^2}{2\sigma_y^2})\left[\exp(-\frac{(z-h)^2}{2\sigma_z^2}) + \exp(-\frac{(z+h)^2}{2\sigma_z^2})\right]$$

Eq.5.12
Where \( \sigma_y \) and \( \sigma_z \) (m) are the dispersion terms in the y- and z-direction, respectively. \( \sigma_y \) and \( \sigma_z \) are functions of x (in the form of \( \sigma_y = mx(1+nx)^p \), where m, n and p are parameters), and the parameterizations depend on the atmospheric stability (e.g. stable/neutral/unstable) and scenario (e.g. urban/open-country, day/night)\(^{223}\). Typically \( \sigma_y \) and \( \sigma_z \) are on the order of \( 10^0\)-\( 10^1 \) m at 100 m downwind of the source. As this example compound is chemically inert, and the concentration gradient in the 3D space is solely a result of mixing with background air (free of this compound), it can be assumed the mixing proceeds in a 1st order manner. Therefore the effective dilution time scale \( \tau_{\text{dilution}} \) is given by:

\[
\tau_{\text{dilution}} = \frac{t_{\text{transport}}}{\ln \left( \frac{C(x_0, y_0, z_0)}{C(x_t, y_t, z_t)} \right)}
\]

Eq.5.13

Where \( t_{\text{transport}} \) (s) is the transport time (\( t_{\text{transport}} = \text{distance} / \text{windspeed} \)). Figure 5.7 shows the estimated \( \tau_{\text{dilution}} \) for a 10-km sized area. As seen under various conditions (e.g. urban/open-country, stable/neutral/unstable, day/night) \( \tau_{\text{dilution}} \) is mostly <1 hour for the direct transport between “source” and downwind “receptor”. Although the concentration gradient in the downwind direction may vary vastly depending on atmospheric conditions, and estimated \( \tau_{\text{dilution}} \) spans a rather narrow range, due to the \( \ln(C_0/C_t) \) term in Eq.S13.

Figure 5.7. Estimated \( \tau_{\text{dilution}} \) as a function of equivalent windspeed in a 10-km sized area (i.e. roughly the distance between HKUST and urban Hong Kong). Equivalent windspeed is the distance divided by transport time. Shading indicates the ranges of typical ambient conditions (urban / open-country; stable / neutral / unstable conditions; day / night). See Visscher et al.\(^{223}\) and references therein for details about the parameterizations. Embedded is the diagram of an example calculation: a Gaussian plume disperses in a 1km\( \times \)1km\( \times \)1km sized 3D space with constant wind is in the x-direction), and the x-y plate is color-coded with ground level concentration of this dispersed species. For simplicity the source is assumed to be a ground-level point source and the plume rising is neglected.

As seen, the dilution time scale into clean background air is <1 hour between “source” and downwind “receptor” on an urban scale. Note that this is the mixing-time scale with background air containing no hopanes. In reality there should be a non-zero hopane level in the
background air, therefore the lifetime due to dilution might be longer. Eq.5.7 provides an indirect way to estimate $\tau_{dilution}$ using the concentration gradient of EC between source and receptor site, depending on the physical transport time. In this work $\ln(\text{EC}_{MK}/\text{EC}_{HKUST}) \approx 2.3$, and hence a typical $\tau_{dilution}$ on an urban scale of 0.5-1 hour can be inferred.

The dilution effect would be even more pronounced in the initial mixing stage of the roadside / street canyon air masses with background air. The physical dilution time scale in the roadside environment is typically on the order of 10 minutes or less. Previous work in Tsuen Wan, Hong Kong, a typical urban area with mixed residential and commercial activities, where sampling probes are located on a building rooftop (~17 meters above the ground) along a major road, the observed particulate hopane level and hopane/EC ratio (ng μg$^{-1}$) are already a factor of 3.5-11 and 1.1-2.9 lower than those in the roadside environment. This serves as ambient evidence of the dilution effect, as the hopane lifetime due to gas-phase oxidation (~85 min at $[\text{OH}] = 5.0 \times 10^6$ cm$^{-3}$) is much longer than the mixing time scale in this case.

Figure 5.8. Contour plots of organic loading versus ambient temperature, color-coded by $k_{eff,\text{particle}}$ and white contour lines are the ratio of $C_{\text{gas}} / C_{\text{total}}$, assume $\tau_{dilution} = 1$ hour.

5.7. Impacts of organic loading and ambient temperature

Organic loading and ambient temperature together affect the partitioning of hopane between gas- and particle-phase, which further affects the effective loss rate coefficient of hopanes. Figure 5.8 summarizes sensitivity test results with $[\text{OH}]_{avg} = 5 \times 10^6$ molec cm$^{-3}$ and $\tau_{dilution} = 1$ hour across varying temperatures and organic loadings. In general, when ambient temperature is higher and / or organic loading is lower, more hopane exists in the gas-phase, making it more vulnerable to gas-phase oxidation processes.
However, additional factors should be considered for gas-particle partitioning for hopanes. Chamber studies reported slower effective hopane degradation under higher RH, likely resulting from the surficial water layer trapping hopane in the condensed-phase, leading to a slower overall loss rate. This is qualitatively consistent with the RH-induced changes in mean molecular weight of particulate organics and the subsequent increase in partitioning to the aerosol particulate matter. In this work the estimated partitioning coefficient has a relative uncertainty of ~54% (propagated from C* and simultaneous OC measurements), and the empirical OM/OC ratio of 1.6 and an assumed mean molecular weight of OM (150 g mol⁻¹) add additional uncertainties. A further complication is that evaluating RH-induced changes on the partitioning coefficient requires knowledge of the absorbed water content. Therefore the RH effect on partitioning is not considered, and the calculations in this work represent a maximum extent of gas-phase hopane fraction and hence set an upper bound of effective loss rate coefficients of hopanes. Moreover, a few fundamental assumptions should be noted as well. In this work we assume the hopanes form an ideal liquid with pre-existing particulate organics which may not always hold in reality. Also, given that the initial mixing is proceeds on a time scale of ~10 min is comparable with the time required to establish gas-particle equilibrium, therefore the instantaneous gas-particle equilibrium assumption may not hold in the initial stage of vehicular emissions mixing with background air.

5.8. Implications

The effective loss rate coefficients of particulate hopane species are estimated in this work using ambient measurements. The process is driven by gas-particle partitioning, followed by gas-phase OH oxidation and dilution. This degradation can be rapid leading to a rather short effective lifetime of particle-phase hopanes in the ambient environment, and hence the source signature could be largely diminished in only a few hours. Recent works have reported semivolatilities of other vehicular tracers, which in principle should also be subject to potential degradation. Zheng et al conducted a source apportionment study using CMB in urban Hong Kong where gasoline-powered vehicles make up a considerable fraction of daily traffic, and yet the results suggested that the gasoline contribution to fine particulate organic matter is small.

Particulate hopanes in urban and suburban environments are typically 10⁻¹-10¹ ng m⁻³, while in remote location can exist in 10⁻²-10⁻¹ ng m⁻³ range or even below the limit of detection (e.g. marine, mountain). In this work we show that at HKUST, a suburban location only ~10 km away from downtown Hong Kong and hundreds of meters from nearby
major roads, hopane levels are already a factor of 22-68 lower than roadside levels, and the hopane/EC ratio (ng μg⁻¹) at HKUST is a factor of 1.7-3.3 lower.

Chamber experiments provide direct evidence of rapid degradation of these semi-volatile organic compounds. However in the ambient environment these compounds may be depleted by dilution as well. Under ambient conditions, hopane loss can be largely attributed to dilution. If dilution is not considered (i.e. chamber equivalent), the hopane lifetime is 3-28 hours (5-50% exists in the gas-phase), already not stable enough for CMB, while taking dilution into consideration brings the particulate hopane lifetime down to less than two hours. Degradations of semi-volatile organic markers such as hopanes must be considered in source apportionment in urban to suburban locations.

It is also worthy to note that, the effective loss rate coefficient of hopanes estimated using ambient data in this work has fairly large uncertainties. Potential sources of uncertainties include: (1) to our knowledge no direct measurement of hopane volatility or the gas-phase OH+hopane bimolecular rate constant; (2) limitations in analytical techniques require long sampling time of particulate hopanes and hence greatly reduce the time resolution of ambient measurements. Given the possible short lifetime of hopane species, higher time-solution measurements are appreciated
CHAPTER 6. Conclusions and Future Directions

6.1. Conclusions

Great progress has been made in the past decades in understanding the formation and evolution of organic aerosols in the earth’s atmosphere, and their broad impacts on the global climate and the regional air quality. This dissertation is a collection of works using models to explore the SOA formation in the atmosphere. The major conclusions are summarized as follows:

In chapter 2 SOA formation in Hong Kong and the adjacent PRD region from three major classes of precursors, isoprene, monoterpenes and aromatics, is explored and compared with tracer-based measurements. Monoterpene contribution in Hong Kong exceeds those from isoprene and aromatics, while in the PRD region aromatics are the major contributor, generally consistent with the updated emission inventories and ambient measurements of these precursors. Sensitivity tests show that Hong Kong and PRD regions are generally VOC-limited, and a reduction in NOx emission would cause an increase in OH level and hence an increase in the SOA formation. Note that due to the limitation of the tracer-based SOA estimates (i.e. SOA formation from S/IVOCs is not yet captured), this chapter used traditional scheme and hence cannot capture total SOA either. Further understandings of S/IVOCs in the emission inventories in this region are in crucial need.

Chapter 3 explores the potential of SOA formation on wet aerosols in ambient Hong Kong. Hong Kong lies in the tropical latitude and the ambient RH is high all year around. Coupled regional chemical and dynamical processes result in the fact that ambient aerosols in Hong Kong are rich in hygroscopic components such as sulfate and nitrate therefore profound aerosol liquid content is expected. Oxidation of biogenic and anthropogenic VOCs produces considerable amount of water soluble compounds such as glyoxal and epoxides and therefore aqueous aerosol processing may contribution to SOA formation. The combination of a kinetic model and a wide range of simultaneous measurements at HKUST supersite suggests that aqueous aerosol processes may contribution to 1/5~1/4 of modeled SOA, and the major products include highly oxidized di-carboxylic acids, organosulfates and oligomers. This is the first attempt to investigate the aqueous aerosol processes in this region, which is also difficult to evaluate at this stage due to the lack of some key species (e.g. gas-phase glyoxal), as well as the limitations of major products in the particle-phase (e.g. di-carboxylic acids, organosulfates).
Glyoxal is of particular interests in atmospheric aqueous chemistry due to its potential to contribute to SOA, yet the many key processes remain poorly understood. Chapter 4 shows the controlled chamber study (PSI Switzerland) of reactive glyoxal uptake on ammonium sulfate seeds under humid conditions, and the kinetic behavior is explored using a multiphase model. Meanwhile the pH dependency is examined. It has been found that the bulk particle-phase reactions are subject to kinetic limitation even under intermediate RH (\sim 60\%), and a surface process is needed to explain the observed glyoxal-SOA mass. pH greatly affects the rate of ammonium catalyzed oligomerization and imidazole formation, which occurs fast on neutralized seeds but will be limited by interfacial transport and even bulk diffusion. It is possible that the bulk diffusion leads to the accumulation of glyoxal on surface that triggers oligomerization on aerosol surface. Previous studies reported increased glyoxal uptake with increasing acidity on acidic seeds, likely acid-catalyzed oligomerization. While in this chapter it is found that even on neutralized seeds the oligomerization proceeds at high efficiency too and catalyzed by ammonium.

In Chapter 5 a method is developed to estimate the effective degradation of semi-volatile organic compounds using ambient data, and the application on estimating the degradation of particulate hopanes in ambient Hong Kong. Hopanes are widely used as motor vehicle tracers in source apportionment techniques such as CMB, but the semi-volatile nature of hopane species determines that a considerable fraction of hopanes exist in the gas-phase and hence become vulnerable to various gas-phase degradation processes, and eventually bias the CMB analysis. In this chapter the effective degradation rate is estimate and found to be in good agreement with chamber studies. It has also been found that the atmospheric lifetime of hopane species may be as low as a few hours due to the rapid dilution and hence the source signature might be largely diminished during transport.

6.2. Future Directions

Despite the recent progress, a number of key aspects of SOA formation require further investigation and some are discussed as follows, in the context of our current understandings:

(1) Traditional SOA formation schemes have been incorporated into chemical transport models (CTM) for a rather long time. These schemes focus mostly on volatile organic precursors such as isoprene, terpenes, aromatics, and to a lesser extent, other precursors such as long chain alkanes. Most of these precursors are too volatile that virtually all exist in the gas-phase under atmospheric conditions, yet their oxidation products can be low volatile and
partition into the particle-phase. These traditional schemes are based on parameterizations of laboratory experiments and have been evaluated in numerous studies. In most cases SOA is underestimated, especially in aged air masses. Meanwhile the observed organic matter is frequently more oxidized than the model predicted. Nevertheless the significance of the aforementioned volatile organic precursors have not been questioned. Various attempts have been made to implement the traditional SOA formation schemes, e.g. adding highly parameterized oligomerization processes to mimic the aging processes, however the improvements on model performance are still limited (both SOA mass and oxidation state), implying something fundamental is still missing. In recent years it has been reported that the primary emissions contain a significant fraction of semivolatile organic compounds – both in the gas-phase and the particle-phase, and the partitioning is also affected by dilution. Upon oxidation, the volatilities of products decrease and hence the partitioning is shifted to the particle-phase. These semivolatile organic compounds with emission strength comparable with the volatile precursors, have been missed in traditional schemes. New SOA formation frameworks (e.g. VBS) have been proposed, in which the previously missing semi-/intermediate-volatile organic compounds (S/IVOC) are mapped into 1D (volatility only) or 2D (volatility + oxidation state) spaces, and the aging processes (via OH, O₃ oxidation etc) are parameterized in the context of functionalization, fragmentation and oligomerization.

VBS-based models have been evaluated in chamber studies, mainly motor vehicle emissions and biomass burning, and a limited number of ambient studies and the performance is generally improved but still faces difficulties, partially due to the fact that so far only a limited number and types of sources have been studied. Essentially all major natural and anthropogenic emission sources need to be re-examined and the emissions and aging of S/IVOCs from these sources need to be considered. Challenges existing in but not limited to: source and ambient abundance of these S/IVOCs and their thermodynamic properties, and the molecular-leveled understanding of the aging processes. As of now only a limited number of CTM applications have incorporated the VBS framework.

(2) The impacts of atmospheric waters on the aerosol chemical and physical properties remain poorly understood. Cloud (or ice) droplets related processes have received much attentions due to their contributions in ozone depletion in the Polar Regions and in the stratosphere, as well as the contributions to the sulfate formation in the mid-low latitudes and in the troposphere. In recent years the formation and aging of organic aerosols under the cloud-relevant conditions have also been evaluated on global and regional scale. However to this day
cloud physics still remain highly uncertain in atmospheric models, which is partially originated from previous processes, such as nucleation and cloud condensation nuclei (CCN) formation, not to mention that the dynamics of the atmosphere (e.g. deep convection) are also highly uncertain. A better constrain of cloud physics is required for the thoughtful evaluation of cloud processing on SOA formation. On the other hand, in recent years it has been found that the aerosol liquid water content under subsaturated conditions (i.e. RH<100%) may also play a significant role, e.g. changes in viscosity and the deviations from ideal mixing solution assumptions, and the subsequent influence on the partitioning of condensable gases. Chemistry of major water soluble components in the aerosol liquid water content has been investigated, but mostly based on bulk aqueous experiments. Aerosol systems are quite unique and there are key aspects that are tricky and difficult to mimic by the bulk aqueous systems, especially the mass transfer considerations, therefore the mechanisms derived from recent bulk aqueous experiments remain largely untested in aerosol systems.

One potential step forward in the scope of this work, is to implement both cloud processing and wet aerosol processing into the existing 3D CTM frameworks. PRD region is an ideal proving ground for the aforementioned aqueous-phase processes, not only because of the ever-growing understandings of the sources, sinks and transport of atmospheric components in this region, but also that the existing (and expanding) observation network provided extended possibility of model evaluation (e.g. sulfate and oxalate as indicators of cloud processing). Glyoxal is a major player in atmospheric waters and its oligomerization and oxidation mechanisms discussed in previous sections can be incorporated in to the 3D CTM. Similarly, epoxy intermediates formed from isoprene oxidation are expected to largely influence isoprene SOA formation, which can also be included.

The exponential growth of computational power in the past decades makes explicit chemical processes not any more computationally expensive in large scale models, yet the lack of molecular-leveled understandings of atmospheric aerosols (especially organic) are still one major limitation in the evaluation of atmospheric aerosols in climate and regional air quality. Measurement techniques capable of providing molecular-leveled chemical information with high temporal resolution are desired. Numerical models provide unique perspectives in interpreted the measurements and probing the mechanisms. The combination of measurement techniques and models is expected to better shape our understandings about the physical and chemical processes in the atmosphere.
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