

## **Chapter 6**

### **Conclusions and Future Studies**

## 6.1 Conclusions

This thesis has focused on the composition of atmospherically relevant aerosols. Composition was shown to be a key tool in determining how aerosols are formed in both chamber experiments and airborne field studies. While many techniques were used to measure composition, special focus was given to mass spectrometry and online mass spectrometry in particular. The use of online mass spectrometry was critical for both the chamber experiments and the field experiments presented. In the chamber, while offline techniques based on extracting filters allow for detailed chemical identification of a fraction of the aerosol mass, online mass spectrometry allows for quantification of the entire aerosol mass. As shown in Chapter 2, the combination of online and offline mass spectrometric techniques is an important step to confirm that chemical products observed in using various offline techniques are not the result of the extensive extraction and preparation steps needed for those techniques. In the field, online mass spectrometry is the only method currently available with the speed and sensitivity necessary to make quantitative, size-resolved measurements of aerosol chemistry in narrow emission plumes near source regions. As discussed in Chapters 4 and 5, while the C-ToF-AMS online aerosol mass spectrometer is fast and sensitive, uncertainties in the collection efficiency make it necessary to compare the results from this instrument with as many other instruments as possible if quantitative results are desired (in this thesis comparisons were most frequently made with the PILS-IC and DMA). An area of great interest for the future is the incorporation of light scattering into the AMS to enable determination of the collection efficiency without the need for further instrumentation (Cross et al., 2008).

Chapters 2 and 3 presented chamber results for chemical compounds that had previously been largely overlooked in terms of aerosol production, isoprene and amines. While isoprene was known to have large gas-phase concentrations (emissions of  $\sim 500$  Tg year<sup>-1</sup>), it was not understood how its oxidation products could have low enough vapor pressures to form aerosol. Amines and their oxidation products were also thought to be much too volatile for aerosol production. While the aerosol yield from isoprene (see Appendix A for details) is modest (roughly 1-3 percent), its gas-phase emissions are so large that this small yield significantly impacts global secondary organic aerosol (SOA) burdens. On the other hand, because amines are strong bases and form extremely nonvolatile salts when reacted with acidic species, the aerosol yields from atmospheric reactions of amines can approach 100 percent under the right conditions. The potential for high aerosol yields and the fact that amines are the only atmospheric bases other than ammonia, mean that amines play a significant role in aerosol formation even though their emissions are relatively modest.

Chapter 2 described in detail the mechanism by which the oxidation products of isoprene can obtain low enough volatilities to enter the aerosol phase. Under high-NO<sub>x</sub> conditions a key part of the answer is the formation of low volatility oligomers of 2-methylglyceric acid through esterification reactions; these oligomers account for  $\sim 22$ – $34\%$  of the aerosol mass. Confirmation of the existence and mass spectral properties of the oligomers using online mass spectrometry was crucial to confirm that the oligomers did not form on filters during aerosol collection or extraction. Under low-NO<sub>x</sub> conditions a major fraction of the aerosol mass forms peroxides that are non-volatile enough to enter into the aerosol phase. In both low and high-NO<sub>x</sub> photooxidation

experiments of isoprene, compounds were identified that have also been identified in ambient aerosol ( $C_5$  alkene triols and 2-methyltetrols and 2-methylglyceric acid).

Identification of these compounds is a key finding because it confirms that the reactions occurring in the chamber are at least partially relevant to what occurs in the actual atmosphere.

During both the low- $NO_x$  isoprene photooxidation experiments and the amine photooxidation experiments, aerosol mass formed and then decayed back to the gas-phase. In both cases, this is thought to be the result of equilibria shift as species are further reacted in either the gas or aerosol-phase. For isoprene oxidized in low- $NO_x$  conditions, it appears that peroxides initially form aerosol and then are released back to the gas-phase. It is unclear whether the equilibrium shift of peroxides back to the gas-phase occurs because gas-phase peroxides are further reacted or because particle phase peroxides are reacted to form more volatile species. For amine photooxidations, aminium salts are formed at the beginning of photooxidation and return to the gas-phase as the experiment proceeds. In this case, the shift of the aminium salts back to the gas-phase could be caused by the further reaction of gas-phase amines, particle-phase amines, or the loss of nitric acid to the chamber walls. Independent of the exact mechanism of particulate mass loss, both the isoprene and amine experiments clearly show cases where the aerosol formed is semi-volatile and in a sensitive equilibrium with the gas-phase. For both the low- $NO_x$  isoprene and amine photooxidations, aerosol-phase species which did not repartition back to the gas-phase as the reaction proceeded were also formed. In the case of isoprene, these non-volatile products appeared to consist largely of oligomers while for the amine system they were highly oxidized, non-salt, organics.

Aminium nitrates observed in the chamber reactions of Chapter 3 were quantified in ambient aerosol during the airborne study of a major bovine source described in Chapter 4. Both diethylamine (DEA) and ethylamine (EA) aerosol were observed during the study, though the mass of DEA was significantly higher and constituted up to 6 % of the observed total organic mass. The observation that diethylammonium nitrate was the most abundant aminium nitrate in the plume from the bovine source is consistent with it having the lowest theoretical dissociation constant of all amines considered in the thermodynamic calculations presented in Chapter 3. The ambient results of Chapter 4 show that amines are important atmospheric bases even in the presence of ammonia. Particulate amine concentrations are estimated to be 14–23% of that of ammonium in the aerosol plume from the bovine source. Emissions from the source were also shown to contain significant amounts of organics, ammonium, and nitrate with organics being the dominant chemical component constituting ~ 56–64% of the aerosol mass. This organic mass was found to suppress both the sub and supersaturated water uptake behavior of aerosols in the plume from the bovine source.

In Chapter 5, organics were found to constitute a larger fraction of the total aerosol mass emitted from container ships than previously estimated. For the ship studied, the mass ratio of particulate organic carbon to sulfate at the base of the stack was  $0.23 \pm 0.03$ , increasing to  $0.30 \pm 0.01$  in the airborne exhaust plume. This organic mass was found to be hydrophobic, significantly suppressing the subsaturated hygroscopic growth of particles in the ship-exhaust plume. The mass spectra of the organic aerosol in the exhaust plume strongly resembles hydrocarbon-like organic aerosol (HOA) from other diesel sources and there is no sign of oxidation or aging of the organic aerosol

within the first hour after emission. The organic aerosol mass is also not observed to repartition to the gas phase as the exhaust plume dilutes into the marine boundary layer. Organic mass was observed to be concentrated largely in particles below 100 nm in diameter, a significant finding given that these smaller diameters are where particles begin to be active as cloud condensation nuclei. A significant number of ultrafine particles were also observed during the study which could have implications for human health in coastal cities.

## **6.2 Future Studies**

### **6.2.1 Tracing Organic Aerosol Production from Cloud Processing Reactions**

A main focus of this thesis has been the formation of organic aerosol; the thesis described organic aerosol that was emitted as a primary emission, formed secondarily as the result of photooxidation or ozonolysis, and formed secondarily as the result of organic salt formation. A route that was not discussed, but is thought to be atmospherically important, is the formation of organic aerosol through liquid phase reactions in cloud droplets or high humidity aerosol.

Data that has been collected during the airborne field campaigns conducted for this thesis may have the potential to lend insight into this route of organic aerosol production. Preliminary analysis of data from field projects in Ohio, the Gulf of Mexico and Houston, and the Central California Coast indicate that the fraction of the total particulate organic mass composed of oxalate is significantly higher when an airmass has interacted with clouds. Additionally, the  $m/z$  44 peak in the C-ToF-AMS ( $m/z$  44 =  $\text{CO}_2^+$  and is a marker peak for oxidized organics) appears to have much higher correlations

with oxalate mass when an airmass has been exposed to clouds or very high humidity. Determining the exact relationship between oxalate, total organic mass, and  $m/z$  44 will be complicated by the fact that certain primary emissions, including ship and truck exhaust, contain oxalate. Nonetheless, this avenue of research is promising and may provide a tracer for when aerosols have been processed by clouds.

### **6.2.2 Determining the Chemical Characteristics of Ice Nuclei**

In addition to focusing on the formation of organic aerosol, another focus of this thesis was the impact of organics on the hygroscopic growth and activity as cloud condensation nuclei of ambient aerosols. All of the research presented in the thesis focused on nucleation of liquid clouds. The Ice in Clouds Experiment-Layer Clouds (ICE-L) was conducted on the NCAR C-130 research aircraft from October 25<sup>th</sup> to December 16<sup>th</sup>, 2007, with the aim of quantifying the aerosol and microphysical conditions necessary for first ice formation in the troposphere. During the 3 test flights and 12 research flights conducted along the Front Range of the Rocky Mountains in Colorado and Wyoming, numerous ice-forming wave (or layer) clouds and several mixed-phase upslope cloud events were observed. The ICE-L mission was the first airborne campaign in which detailed aerosol chemistry and ice nuclei (IN) measurements were made outside of a cloud, followed by identical measurements of dried ice crystal residuals inside of the cloud. This strategy should enable assessment of the degree to which the chemical characteristics of aerosol entering a cloud determined the rate of ice formation within that cloud. In reality, this is a very complex issue because the water content, temperature and dynamical properties of each cloud must be accounted for before it is possible to determine if chemistry or dynamics played the central role in ice

formation. Nonetheless, the dataset collected during ICE-L, including data from the Caltech C-ToF-AMS, has already yielded insights into the role of aerosol chemistry in ice formation and, while analysis is ongoing, some preliminary results are given here.

Particle chemistry was measured during ICE-L primarily by two instruments: the Caltech Aerodyne Compact Time of Flight Aerosol Mass Spectrometer (C-ToF-AMS) and an Aerosol Time of Flight Mass Spectrometer (ATOFMS) from the Prather group at the University of California San Diego (UCSD). The rationale for deploying two mass spectrometers was that the C-ToF-AMS can provide quantitative mass measurements of non-refractory aerosol species and the ATOFMS, while not equally quantitative, can detect refractory species such as dust and unmodified soot that are thought to be important IN. IN themselves were measured by a Continuous Flow Diffusion Chamber (CFDC) from Colorado State University. When flying through a cloud, ice crystal residuals were fed to both mass spectrometers and the CFDC using a Counterflow Virtual Impactor (CVI) inlet operated by Cynthia Twohy of Oregon State University.

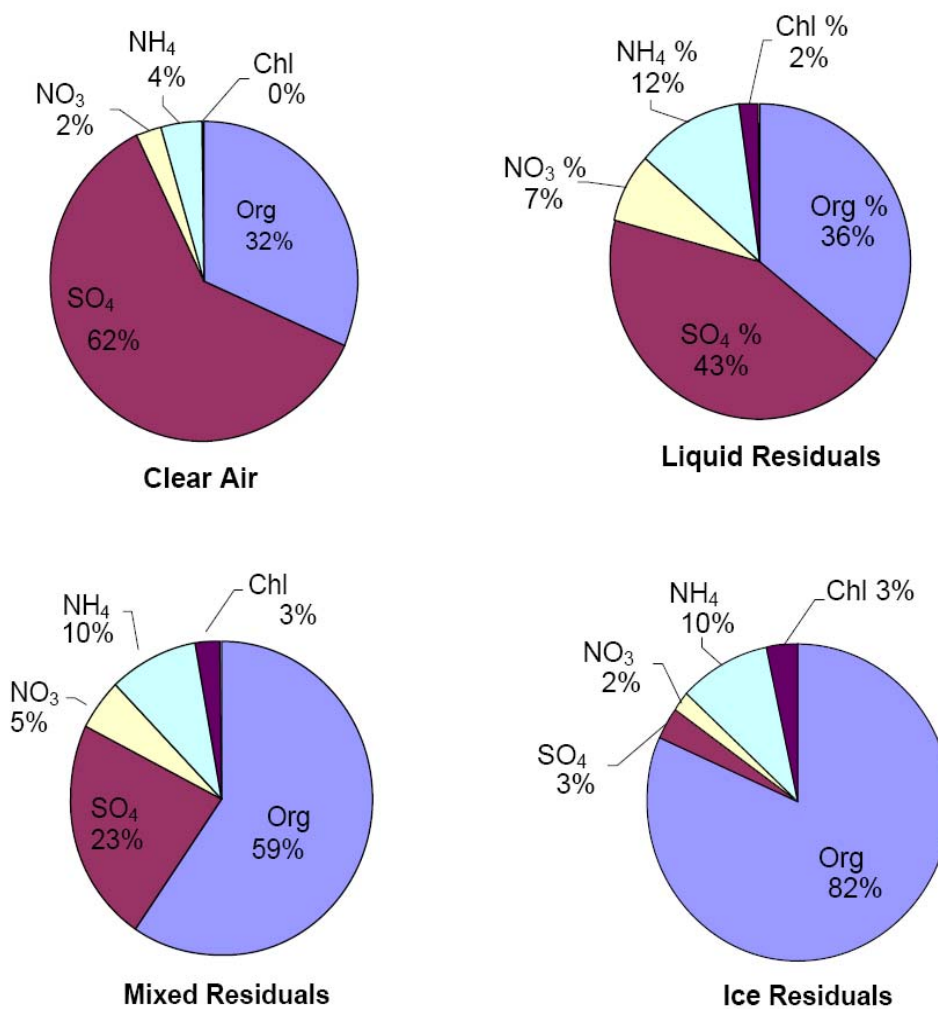
During several wave cloud flights, the chemistry of dried ice crystal residuals measured from the CVI inlet was very different from the chemistry of the out of cloud aerosol. Data from the C-ToF-AMS during Research Flight 3 is given in Figure 6.1. Higher amounts of chloride and organics are found in the ice and mixed cloud residuals than in the out of cloud aerosol. The increase in chloride mass is probably significantly more dramatic than shown because the C-ToF-AMS does not efficiently detect most chloride salts because they do not efficiently volatilize at the instrument's vaporizer temperature of  $\sim 550^{\circ}\text{C}$ . More ice crystals were formed in these clouds than would be predicted based on the number of heterogeneous IN measured by the CFDC at the



temperature of the flight level within the cloud, indicating that some of the ice measured may have been homogeneously frozen droplets falling from above. Nonetheless, the chemical results clearly show that certain chemical species, predominantly salts and organics, preferentially formed ice crystals. Currently analysis is underway to determine if this occurred because larger sized particles had higher salt and organic content or if chemistry alone was driving the process. While ice formation near homogeneous freezing temperatures was not the original focus of ICE-L, information on which particles freeze first in this temperature regime is very relevant to cirrus and other high tropospheric clouds, which are perhaps the most relevant ice clouds for climate.

### 6.3 References

- 1.) Cross, E. S., et al. (2008), Sources and Transformations of Organic Aerosol Particles Measured With a new Single Particle Technique During the MILAGRO 2006 Field Campaign in Mexico City, Eos Trans. *AGU*, 89(53), Fall Meet. Suppl., Abstract A22B-08



**Figure 6.1:** C-ToF-AMS data from Research Flight 3 of the ICE-L field campaign showing enhanced organic and chloride in mixed phase and ice clouds. Chemical measurements within cloud were made using a counterflow virtual impactor to measure the chemistry of evaporated cloud droplets and ice crystals.