CARBONACEOUS AEROSOL PROCESSING BY CLOUDS AND FOGS

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1. INTRODUCTION

In many environments, organic compounds account for a significant fraction of fine particle mass. Because the lifetimes of accumulation mode aerosol particles are governed largely by interactions with clouds, it is important to understand how organic aerosol particles are processed by clouds and fogs. Clouds and fogs promote new particle mass formation (e.g., via rapid aqueous oxidation of sulfur dioxide to sulfate) and promote particle removal (e.g., via nucleation scavenging followed by direct drop deposition or drop incorporation into precipitation). Historically, most efforts have been directed toward understanding processing of inorganic species. Thus far we know little about cloud/fog processing of organic aerosol particles and trace gases. While a handful of compounds have received moderate attention (e.g., low molecular weight carboxylic acids), they form only a fraction of the multitude of organic compounds known to be present in the atmosphere.

Recently we have examined the organic composition of fogs and clouds in several environments, including locations in California, along the U.S. Gulf Coast, in Colorado, and in Hawaii. Observations of fog/cloud composition and processing of atmospheric organic matter are highlighted here.

2. EXPERIMENTAL

Clouds and fogs were sampled with active cloudwater collectors at a variety of locations. Most samples were collected with stainless steel versions of the Caltech Active Strand Cloud Collector (ss-CASCC); some were collected with a traditional plastic CASCC (1). Radiation fogs were sampled in the Central Valley of California, in Pittsburgh, and along the U.S. Gulf Coast in Houston and Baton Rouge. Orographic clouds were sampled at most other locations, including Mt. Schmueke (Germany), Costa Rica, Hawaii, and Storm Peak Lab near Steamboat Springs, Colorado. Stratocumulus clouds were sampled by aircraft, using a CSU/NCAR airborne cloudwater collector, over the Eastern Pacific Ocean off the coast of southern California (2).

3. RESULTS AND DISCUSSION

Observations indicate that organic matter is a significant component of the cloud/fog droplets. A summary of the average concentration of total organic carbon (TOC) in clouds and fogs collected at several locations is included in Figure 1. TOC concentrations in individual cloud and fog samples ranged from approximately 1 to 40 ppmC. The highest concentrations were observed in urban areas. The lowest concentrations were observed in remote locations, including the eastern Pacific stratocumulus and orographic clouds sampled on the island of Hawaii. Studies of phase partitioning inside the drops in California radiation fogs reveal that approximately one-fourth of the organic matter in these fog drops is associated with an undissolved phase of suspended particles. Phase partitioning is also

observed between dissolved and undissolved phases for individual organic compounds. As compounds become more hydrophobic, they are observed to be increasingly associated with suspended particulate matter (3).

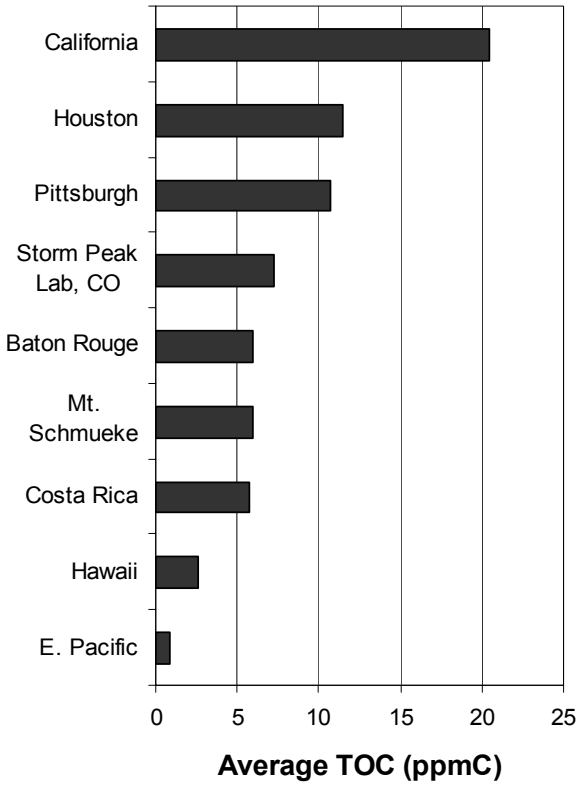

Figure 1. Average total organic carbon concentrations in cloud and fog water collected at several locations.

Studies of organic matter processing by California radiation fogs reveal that the fogs play an important role in removing organic matter from the atmosphere. Eight fog episodes in central California during winter 2000/2001, ranging in duration from 2 to 9 hours, were observed to deposit to the ground between 66 and 952 μg C/m^2. Assuming a typical fog depth of 100 m, this translates into a typical atmospheric "cleansing" rate in the boundary layer of approximately 0.7 μg/m^3. Deposition velocities in these fog systems have typically been observed between 1 and 2 cm/s for fog-borne organic carbon, much higher than dry deposition velocities for accumulation mode aerosol particles.

A variety of efforts have been made to characterize the composition of the fog organic matter, including analyses by GC/MS, HPLC, IC, NMR, IR, and LC/MS. The most abundant species are typically low molecular weight carboxylic acids and small carbonyls and dicarbonyls. These species have been observed collectively to account for roughly 20-30% of the fog dissolved organic carbon (DOC). In California radiation fogs we have also observed significant contributions from hydroxy-carboxylic acids, carbohydrates, biological material, nitrogen and sulfur-containing organics, and a range of high molecular weight components (4). Analyses also reveal the presence of organic molecular markers associated with particles produced by various combustion processes. Comparisons of pre-fog and interstitial aerosol samples reveal differences in the relative particle scavenging efficiencies of the fog drops between organic and elemental carbon and between different types of organic carbon. In one Fresno fog episode, for example, the fog scavenging efficiency for levoglucosan (a residential wood combustion tracer) was in excess of 90%, while the scavenging efficiency for 17α,21β hopane (a vehicle exhaust marker) was only about 33%. These differences likely reflect differences in hygroscopicity between wood smoke particles and vehicle exhaust particles, but may also be influenced by differences in sizes of these particles.

Recent investigations using liquid chromatography coupled with time of flight mass spectrometry (LC/MS) are shedding new light on a variety of interesting compound types present in fog water. These analyses indicate the presence of significant quantities of high molecular weight (greater than 300 Da) organic matter, consistent with earlier

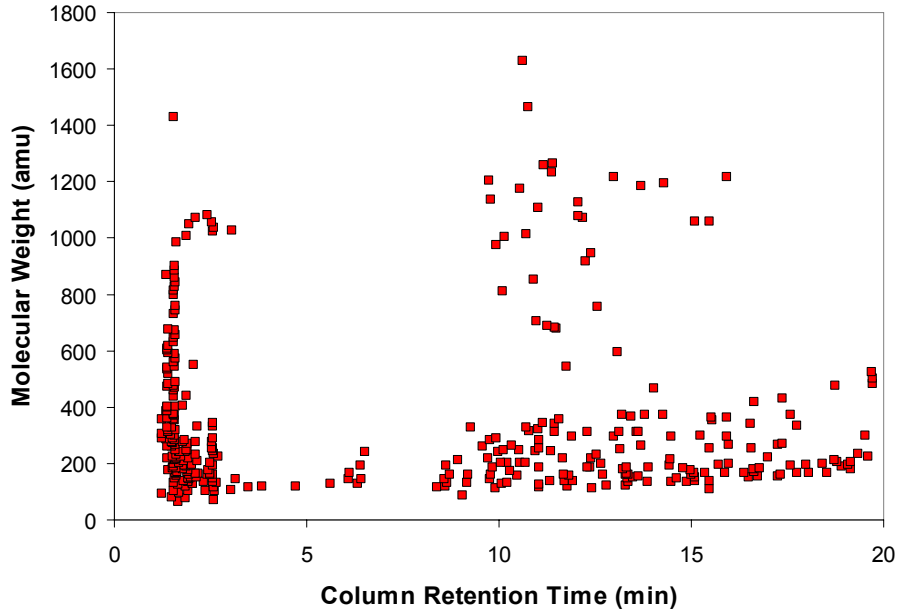

Figure 2. Masses of compounds identified in LC/MS analysis of Fresno fogwater.

measurements we have made using ultrafiltration coupled with TOC analysis (5). Figure 2 provides an overview of some of the mass features seen in LC/MS runs of Fresno fog samples. Data are presented versus chromatographic elution time (Alltech Prevail Organic Acid Column using a water/acetonitrile gradient elution).

Using the accurate mass capabilities of our Agilent TOF-LC/MS system, we are able to begin making some guesses about the molecular formulae and possible structures of fog organics. Some first guesses at molecular structures include nitrophenol (m/z = 139.026), dinitrophenol (184.011), benzoic acid, and malonic acid. Many of the compounds identified appear to be rich in nitrogen. Interestingly, there also appear to be a number of organic compounds containing both nitrogen and sulfur. Possible structures of several key molecular features identified in the fogwater are shown in Figure 3. By alternating the TOF fragmentor voltage between high and low settings we have been able to break off sulfite and sulfate groups (at high voltage), providing further evidence for the inclusion of sulfur within organic structures. Also of interest is the observation that the abundance of some of these sulfur-containing organic compounds appears to increase with time in the fog episode, possibly suggesting formation of these compounds by aqueous phase chemistry.

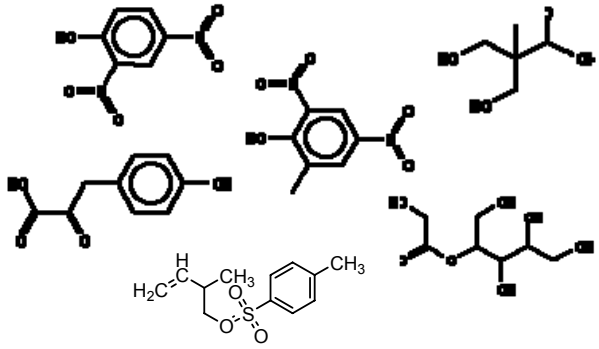

Figure 3. Possible molecular structures of several key components identified by LC/MS in Fresno fogwater.

4. BIBLIOGRAPHY

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