Organic Matter in Central California Radiation Fogs

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Organic matter was studied in radiation fogs in the San Joaquin Valley of California during the California Regional Particulate Air Quality Study (CRAQS). Total organic carbon (TOC) concentrations ranged from 2 to 40 ppm of C. While most organic carbon was found in solution as dissolved organic carbon (DOC), 23% on average was not dissolved inside the fog drops. We observe a clear variation of organic matter concentration with droplet size. TOC concentrations in small fog drops (<17 μm) were a factor of 3, on average, higher than TOC concentrations in larger drops. As much as half of the dissolved organic matter was determined to have a molecular weight higher than 500 Da. Deposition fluxes of organic matter in fog drops were high (0.5–4.3 μg of C m⁻² min⁻¹), indicating the importance of fog processing as a vector for removal of organic matter from the atmosphere. Deposition velocities of organic matter, however, were usually found to be lower than deposition velocities for fogwater, consistent with the enrichment of the organic matter in smaller fog drops with lower terminal settling velocities.

Introduction

Over the last 20 years, many investigators have examined the chemical compositions of clouds and fogs and studied cloud/fog processing of atmospheric particles (1–4). Some studies have shown the ability of fogs to create new particulate material through gas scavenging, in-cloud reactions to form low volatility products, and subsequent drop evaporation. Fogs have also been shown to remove particles through particle scavenging followed by drop deposition. Most studies, however, have focused on processing of inorganic compounds. Little is known about the organic composition of cloud and fog drops or the processing of organic compounds by fogs and clouds.

Understanding interactions between fogs or clouds and carbonaceous aerosol particles is important for several reasons. First, it is known that organic matter comprises a large fraction of total particulate matter in many environments (5). Second, it is also known that interactions with precipitating clouds are a principal determinant of accumulation mode particle lifetimes. Third, activation of carbonaceous aerosol particles to form cloud drops may significantly alter optical properties of clouds and fog with associated effects on cloud optical depth and climate. Fourth, it is possible that aqueous reactions occurring in cloud or fog drops are important sources of secondary organic aerosol formation (6). At present, our lack of knowledge regarding interactions between carbonaceous aerosol particles and clouds (or fogs) greatly limits our ability to understand or model atmospheric processing and effects of this important class of particles.

Capel and co-workers (7) showed that fogwater collected in Duebendorf, Switzerland, contained up to 290 ppm of carbon. Subsequent studies confirmed the importance of organic matter in fog and cloud drops (1, 8). Some of these studies differentiated between total and dissolved organic carbon and found that a very large fraction of the total organic carbon was soluble. Nevertheless, the composition and the physical and chemical properties of this organic matter remain largely unknown. Although several studies have examined fog or cloud drop concentrations of specific organic compound families [e.g., pesticides (9), phenols (10), methoxynaphthalens (11), polycyclic aromatic hydrocarbons, alkanes (12)], these compounds represent only a small fraction of the total organic matter present. Herckes and co-workers (13) have shown that low molecular weight organic compounds (especially formaldehyde, formate, and acetate) are present at high concentrations in radiation fogs in California’s Central Valley, yet they comprise only 10–15% of the total organic matter present.

In more recent studies, investigators have attempted to further characterize the organic composition of fogwater. Kiss and co-workers characterized polar compounds by liquid chromatography with UV and mass spectrometric detection (14). There have also been efforts to characterize more of the higher molecular weight compounds in fogwater, including humic substances (8, 15). Zhang and Anastasio (16) have also demonstrated the presence of high concentrations of organic nitrogen in California’s Central Valley fog samples.

Another topic receiving increased attention in recent years is the variation of solute concentrations across the fog/ cloud drop size spectrum. Drop size-dependent composition is now well-established for inorganic solutes (17–20); however, little attention has been paid to drop size dependence of TOC concentrations or individual organic solute concentrations, with the exception of formaldehyde (21). Variations in solute concentrations across the fog drop size spectrum exert an important influence on solute deposition fluxes (22) since fog drop deposition velocities increase strongly with drop size, mainly due to the higher terminal settling velocities of larger drops.

In this paper, we present the first observations of the variation of organic matter content with drop size as well as new findings concerning the characteristics of organic matter in fog drops. The fogs sampled in this study were radiation fogs, which form by radiative cooling of the surface during clear sky conditions at night. These differ from advection fogs, which form in conjunction with transport of warm, moist air masses over a colder surface. Samples were collected during winter 2000/2001 as part of the California Regional Particulate Air Quality Study (CRAQS). We focus on the variations in organic carbon concentrations with drop size, the partitioning of organic carbon between soluble and insoluble phases inside fog drops, and the molecular weight distribution of the dissolved organic carbon. Fog-borne deposition fluxes of organic matter are determined and compared to fluxes of inorganic species.
Experimental Section

Fog samples were collected in December 2000 and January 2001 in the Central Valley of California as part of CRPAQS. The core sampling site for the fog study was located close to the small town of Angiola [35°35' N, 119°32' W, 60 m above sea level (asl)]. Satellite collection sites were established in Bakersfield (35°21' N, 119°3 W, 119 m asl) and close to the town of Helm (36°5' N, 120°10' W, 55 m asl). The Angiola and Helm sites were located in agricultural areas, whereas the Bakersfield site was located in the city next to a small shopping mall.

Fog samples were collected with various collectors, including the Caltech Active Strand Cloudwater Collector (CASC2), the two-stage version of that collector known as the size-fractionating CASCC (sf-CASCC), and the compact version of the CASCC known as CASCC2. These samplers collect fog/cloud drops by inertial impaction on banks of Teflon strands (CASCC, CASCC2, or second stage of sf-CASCC) or rods (first stage of sf-CASCC). The CASCC2 was used for fog collection at the Helm and Bakersfield sites. Detailed descriptions of the CASCC, CASCC2, and sf-CASCC are given by Demoz et al. (23). In addition, newly developed stainless steel (ss) versions of the CASCC and sf-CASCC, known as the ss-CASCC and ss-sf-CASCC, were utilized in order to provide samples more suitable for analysis of organic compounds. The size cut of the sf-CASCC is estimated as approximately 6 and 17 μm.

Fog liquid water content (LWC) was measured using a Gerber Scientific particulate volume monitor (model PVM-100) that was calibrated using a manufacturer-supplied disk. Fog deposition was sampled using two square Teflon deposition plates (0.30 m²) placed on top of a large plastic sheet on the ground. This technique proved to be efficient in the California radiation fogs where sedimentation is the major deposition pathway (22). Collected fogwater was sampled from the interior of the plates; a trough is milled near the perimeter of the plate to provide a defined collection area.

Immediately after sample collection, the pH of the samples was measured. Right after collection, aliquots were taken for measurement of total organic carbon (TOC). The samples were then filtered through prefired quartz filters (Pallflex Tissuquartz), and an aliquot of the filtrate was created for a discrete organic carbon (DOC) measurement. The TOC and DOC aliquots were stored, refrigerated and in the dark, in prebaked glass vials until analysis. Contamination of the collectors, of the deionized water (prepared on-site using a Barnstead EasyPure system) used for cleaning, and by the filtration procedure was checked regularly by means of field blanks.

Organic carbon concentrations (TOC and DOC) were determined using a commercial TOC analyzer (Shimadzu TOC 5000A), which oxidizes organic carbon in an injected sample on a catalyst bed at 680°C, followed by measurement of the evolved carbon dioxide. The TOC analyzer was calibrated using a series of aqueous potassium hydrogen phthalate standards; measurement precision was evaluated through replicate sample analyses.

In some samples, the organic matter was further characterized by ultrafiltration of the DOC fraction. Physical separation of DOC into molecular size ranges was completed in a pressurized and stirred ultrafiltration cell (Amicon model 8050), using the following Millipore ultrafiltration membranes: YM1 (nominal size cut of 1000 Da) and YC05 (nominal size cut of 500 Da). The filtrates were analyzed for TOC as described above. The separation efficiency of the two membranes was tested with tannic acid (MW = 581) for the 1000 MW and 500 MW cut-sizes, respectively. The YM1 membrane showed a separation efficiency of 48% relative to tannic acid, whereas the YM05 showed a 71% efficiency relative to naringin hydrate. These results show that the nominal membrane size-cuts provide only an approximate indication of the size of the organic matter retained. The effective separation depends on the structure of the solute molecule in addition to its molecular weight. DOC fractionation using the membranes will be used to provide an approximate indication of the molecular weight distribution of the organic solutes in the fogwater, although a systematic tendency to underestimate the higher molecular weight fractions appears to exist.

Results and Discussion

Comparison between Plastic and Metal Fog Collector Samples. Previous studies focusing on the inorganic composition of fog mainly used plastic collectors to sample fogwater. Teflon is often considered a material of choice for collection surfaces. TOC concentrations have sometimes been reported in samples collected with plastic collectors (1, 16, 24). To test whether the use of Teflon versus stainless steel sampling surfaces yields a difference in measured sample TOC, concentrations were compared in fog samples obtained simultaneously with two CASC2 collectors: one plastic (CASC2) and the other stainless steel (ss-CASC2). The results are illustrated in Figure 1.

Higher TOC concentrations were typically observed in samples collected with the stainless steel collector. This is probably the result of a modest adsorption loss on the plastic collector surfaces rather than contamination by the metal collector surfaces. Field blanks from both types of collector are in the same range and very low (< MDL) to 0.5 ppm C for the stainless steel collector and 0.1–0.4 ppm C for the plastic collector). Adsorption of black material was observed visually on the Teflon collection surfaces and could only be removed by cleaning with a surfactant. This blackening of plastic collection surfaces is commonly observed when sampling fogwater in polluted environments. The apparent adsorption of carbonaceous material on plastic collector surfaces suggests that use of these collector types for fog/ cloud TOC

FIGURE 1. TOC concentrations in Angiola fog samples collected using stainless (ss-CASC2) and Teflon (CASC2) fog collectors. Error bars represent the TOC measurement precision (one relative standard deviation) of 5%.

TOC - stainless steel collector (ppmC)

TOC - plastic collector (ppmC)
than observed by Capel and co-workers in Duebendorf, organic carbon soluble fraction measured here (77%) is lower present as insoluble material inside the drops. The average was typically in solution, a significant fraction was often collected by the ss-sf-CASCC. The average DOC/TOC ratio cloudwater (ss-CASCC) as well small and large fog droplets determine the fraction of TOC dissolved inside fog drops.

mechanism other than nucleation. nonactivated particle scavenged by a fog drop through a into a fog drop or a larger fraction of a hydrophobic, example, represent a small portion of an otherwise hygro- mixture of organic compounds that is entirely, or only organic compounds found in carbonaceous aerosol particles are strongly hydrophobic and insoluble. Carbonaceous aerosol particles scavenged by fog drops may contain a mixture of organic compounds that is entirely, or only partially, soluble. Insoluble organic compounds may, for example, represent a small portion of an otherwise hydroscopic cloud condensation nucleus that is activated to grow into a fog drop or a larger fraction of a hydrophobic, nonactivated particle scavenged by a fog drop through a mechanism other than nucleation.

Fog samples collected at the Angiola site were filtered to determine the fraction of TOC dissolved inside fog drops. Figure 3 compares TOC and DOC concentrations in bulk cloudwater (ss-CASCC) as well small and large fog droplets collected by the ss-sf-CASCC. The average DOC/TOC ratio was 0.77, indicating that while most of the organic material was typically in solution, a significant fraction was often present as insoluble material inside the drops. The average organic carbon soluble fraction measured here (77%) is lower than observed by Capel and co-workers in Duebendorf, Switzerland (93–97%) (7). The difference in soluble fraction probably reflects a difference in the composition of organic matter in fogs collected at the two sites but could also be influenced by any difference in filtration efficiency between the studies. TOC concentrations observed in the Duebendorf fogs were much higher (78–281 mg/L) than those found in this study (2–40 mg/L). The presence of a significant insoluble organic fraction highlights the need to consider both soluble and insoluble phases in fog droplets when evaluating carbonaceous aerosol scavenging efficiencies.

Comparison of TOC Concentrations. Table 1 compares organic carbon concentrations measured in fog samples collected during this study with fog and cloud TOC and DOC concentrations previously reported in the literature. Note that a significant fraction of fog/cloud organic carbon concentrations reported in the literature come from various sites in California.

TOC concentrations in fog samples collected at the rural Angiola site in this study range from 2 to 41 ppm C. Fog samples collected at the second rural site (Helm) also fall within this range. Only one fog sample was collected at the more urban Bakersfield site; its TOC concentration was 27 ppm C, relatively high but within the range measured at Angiola. The concentrations found in this study are similar to the concentration ranges observed in previous investigations of radiation fogs in California’s Central Valley (see Table 1 for San Joaquin Valley, Bakersfield, and Davis). Studies of stratusform clouds in southern California (see Henninger Flats and San Pedro in Table 1) have also reported roughly similar concentrations (24). The TOC concentrations observed in this study are somewhat lower than reported in northern Italy’s Po Valley (7, 30), where concentrations as high as 108 ppm C have been observed. Even higher organic carbon concentrations have been measured in Duebendorf, Switzerland (outside Zurich), and in Alaska, while much lower concentrations were reported by Hadi and co-workers (31) for cloudwater collected in rural Scotland. Concentrations reported for intercepted cloud samples collected at mountain sites in the eastern (Whiteface Mt., Mt. Mitchell, and Shenandoah) and western (Stampede Pass) United States all fall in the lower half of the range observed at Angiola.

Some concentration differences may result from differences in liquid water content, a parameter that is often not measured or reported. As liquid water content increases in a fog or cloud, solute concentrations typically decrease (33, 34) because of dilution. This trend is apparent for TOC concentrations in the fog samples collected at Angiola. Figure 4 shows that the highest TOC concentrations are observed for the lowest liquid water contents and vice-versa. The anti-
These results are somewhat surprising, as higher MW organic is significant, varying from 27% to 57% in these samples. The molecular weight (MW) distributions of the organic matter in bulk fog samples collected by the CASCC during six Angiola fog events. These distributions were measured on sample fractions treated by ultrafiltration as described above. The fraction of compounds with MW > 500 is significant, varying from 27% to 57% in these samples. These results are somewhat surprising, as higher MW organic compounds are often thought to be relatively hydrophobic, but they are consistent with observations that low MW compounds such as formaldehyde, acetate, and formate account generally for less than 20% of the organic matter in fog and cloud drops (13, 32). The importance of high MW material is also supported by previous work that revealed significant concentrations of humic material in fog drops (14).

High molecular weight organic material has also been found to be an important contributor to precipitation composition. Likens and co-workers, using ultrafiltration to characterize organic matter in precipitation (35), found that 42% of the DOC in precipitation collected at a rural site (Hubbard Brook, NH) and 54% of the DOC in precipitation collected at an urban location (Ithaca, NY) had a molecular weight higher than 1000. These percentages are slightly higher than in the Angiola fogs, perhaps reflecting the high efficiency of precipitation scavenging of coarse soil dust particles, but confirm the importance of high molecular weight organic compounds in atmospheric water droplets.

**Deposition Fluxes of Organic Carbon.** Previous studies have shown the importance of fog deposition as a removal process for inorganic aerosol species. To evaluate fog deposition fluxes of organic matter, TOC concentrations of deposited fogwater collected from deposition plates in this study were multiplied by the corresponding fogwater fluxes. Sedimentation is believed to dominate the fog deposition flux to these plates. It is possible that additional turbulent fluxes may occur to rougher natural surfaces, but this effect is expected to be minor because of low wind speeds (<1 m/s) and low surface roughness typical of the study region. Resulting TOC deposition fluxes range from 0.5 to 4.3 µg of C m⁻² min⁻¹ and averaged 1.5 µg of C m⁻² min⁻¹. To our knowledge, these represent the first reported measurements of organic carbon deposition by radiation fogs. The fluxes are comparable to fogwater deposition fluxes of major inorganic species, including ammonium (average of 1.7 µg m⁻² min⁻¹) and nitrate (2.2 µg m⁻² min⁻¹) observed in the study. Similar fluxes were also reported for radiation fogs in Davis (California) (22), with average values of 2.2 µg m⁻² min⁻¹ (ammonium) and 4.3 µg m⁻² min⁻¹ (nitrate).

The high fog deposition fluxes of organic carbon observed here support the important role fogs play as processors of carbonaceous aerosol in the boundary layer. We highlight this role further with one example. During the night of December 17–18, 2000, a fog event occurred that lasted more than 13 h. Total fogwater deposition in this event exceeded

<table>
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294 g/m² while organic carbon deposition in fog drops exceeded 1.2 mg of C/m². If we assume an average fog depth of 100 m for this event, this corresponds to an average reduction of more than 32 μg of C/m² over the fog depth, a considerable amount in an environment with typical aerosol concentrations in the range of tens of micrograms of C per cubic meter. Of course some of the organic carbon removed by the fog is associated with volatile species, like formaldehyde, that may return to the gas phase once the deposited fog evaporates.

**Deposition Velocities.** Deposition velocities were determined for fogwater and fog-borne organic carbon. The TOC deposition velocity was calculated according to the following equation:

\[ v_{TOC} = \frac{\text{Flux}_{TOC}}{LWC \times [TOC]_{aq}} \]

where \( v_{TOC} \) is the TOC deposition velocity, \( \text{Flux}_{TOC} \) is the measured flux of TOC to the deposition plates, LWC is the fog liquid water content, and [TOC] is the aqueous concentration in the simultaneously collected fog sample.

Calculated deposition velocities are presented in Figure 6. Fogwater deposition velocities ranged from 0.5 to 6 cm/s, comparable to previous observations (22) in central California radiation fogs. The TOC deposition velocity is generally similar to or smaller than the fogwater deposition velocity. The tendency for the fogwater deposition velocity to exceed the TOC deposition velocity is expected given the enrichment of TOC in small fog drops that settle from the atmosphere more slowly. Measurements of inorganic species during the present study show similar deposition velocities for sulfate (1.5 cm/s on average). Larger differences between solute and fogwater deposition velocities were reported in earlier radiation fog studies at Davis, CA (22), consistent with stronger enrichments of inorganic solutes in small fog drops (concentrations up to 20 times as high as observed in large drops) in those fogs.

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**Literature Cited**


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