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Processing of atmospheric organic matter by California radiation fogs

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Abstract

Considerable effort has been put into characterizing the ionic composition of fogs and clouds over the past twenty-five years. Recently it has become evident that clouds and fogs often contain large concentrations of organic material as well. Here we report findings from a series of studies examining the organic composition of radiation fogs in central California. Organic compounds in these fogs comprise a major fraction of total solute mass, with total organic carbon sometimes reaching levels of several tens of mg/L. This organic matter is comprised of a wide variety of compounds, ranging from low molecular weight organic acids to high molecular weight compounds with molecular masses approaching several hundred to a thousand g/mole. The most abundant individual compounds are typically formic acid, acetic acid, and formaldehyde. High concentrations are also observed of some dicarboxylic acids (e.g., oxalate) and dicarbonyls (e.g., glyoxal and methylglyoxal) and of levoglucosan, an anhydrosugar characteristically emitted by biomass combustion. Many other compounds have been identified in fog water by GC/MS, including long chain n-alkanoic acids, n-alkanes, PAH, and others, although these compounds typically comprise a total of only a few percent of fog TOC. Measurements of fog scavenging of organic and elemental carbon reveal preferential scavenging of organic carbon. Tracking of individual organic compounds utilized as source type markers suggests the fogs differentially scavenge carbonaceous particles from different source types, with more active processing of wood smoke than vehicle exhaust. Observations of high deposition velocities of fog-borne organic carbon, in excess of 1 cm/s, indicate that fogs in the region represent an important mechanism for cleansing the atmosphere of pollution.

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1. Introduction

Clouds and fogs play an important role as processors of aerosol particles and trace gases. They 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). While experimental and numerical studies of cloud and fog chemistry have become increasingly sophisticated, 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. Collett et al. (1999) showed that in California fog samples, the sum

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of concentrations of formaldehyde, formate, acetate, propionate, pyruvate, and oxalate comprised up to approximately one-third of the total organic carbon (TOC) content measured in the samples. Significant concentrations of these compounds in California fogs were already noted a decade earlier by Munger et al. (1989).

Recently the cloud chemistry community has begun to address in more detail the organic chemical composition of fogs and clouds (e.g., Anastasio et al. (1994), Fuzzi and Zappoli (1996), Laj et al. (1997), Facchini et al. (1999), Luttke et al. (1999), Decesari et al. (2000), Krivacsy et al. (2000), Limbeck and Puxbaum (2000), Gelencser et al. (2000), Voisin et al. (2000), Zhang and Anastasio (2001), Fuzzi et al. (2002), Herckes et al. (2002a,b), Loflund et al. (2002), Ervens et al. (2003)) and laboratory studies demonstrated that organic species can act efficiently as cloud condensation nuclei (e.g., Cruz and Pandis (1997), Corrigan and Novakov (1999), Yu (2000), Prenni et al. (2001, 2003)). A few field studies have addressed scavenging of carbonaceous particles or individual organic species by clouds or fogs (e.g. Facchini et al. (1992, 1999), Limbeck and Puxbaum (2000), Hitzenberger et al. (2001).

Formation of fogs is a common occurrence in California's Central Valley in the winter months (Holets and Swanson, 1981), with several days of dense fog typically occurring in the months of November and December. It is not uncommon for individual fog episodes to last 6–12 h or more at the surface and to recur on consecutive days. This paper highlights findings from recent field investigations of the interactions of organic species with these central California winter fogs. In particular we describe recent progress toward improving our understanding of processing of organic compounds by fogs by describing the chemical composition of the organic matter in sampled fog drops, by examining scavenging of carbonaceous aerosol particles emitted by different pollution source types, and by observation of removal rates of fog-borne solutes.

2. Experimental

Fog samples were collected with one-stage and two-stage active strand cloudwater collectors patterned after the Caltech Active Strand Cloudwater Collector (CASCC) (Demoz et al., 1996). Most samples were collected with stainless steel versions of the CASCC (Herckes et al., 2002a,b). Fig. 1 depicts the single-stage version of the stainless steel (ss-) CASCC. The bulk collectors operate by pulling droplet laden air across a bank of stainless steel strands where cloud/fog drops are collected by inertial impaction. The collected drops flow



Fig. 1. The stainless steel Caltech Active Strand Cloud Collector (ss-CASCC).

down into a stainless steel collection trough, through a stainless steel tube, and into a pre-baked glass bottle. Two-stage versions of the collector employ two banks of collection cylinders, stainless steel rods in the front and stainless steel strands in the back, to collect two drop size classes with a division in the 15–20 μm diameter range, depending on instrument operating conditions. The stainless steel collectors were cleaned in the laboratory prior to deployment to the field with isopropanol followed by copious quantities of high purity deionized water (> 18 Megohm-cm). Plastic collectors were cleaned with a dilute aqueous solution of Triton X-100 followed by deionized water. All cloud water collectors were cleaned in the field before each fog event using high purity deionized water and blanks collected to ensure cleanliness. Fog LWC was measured using a Particulate Volume Monitor (Gerber, 1991).

Samples were collected during two field campaigns in the Central Valley of California, one in winter 2000/01 in the southern part of the Valley (near the small town of Angiola) and one in winter 2003/04 in Fresno. Although Fresno is an urban area, samples were collected on the agricultural campus of California State University at Fresno in order to reduce urban heat island effects which sometimes prevent fog formation in the city. Fog sample aliquots were prepared for measurement of pH, TOC, carbonyl compounds, organic acids, and organic nitrogen; additional sample was refrigerated in pre-baked amber glass bottles with Teflon-lined caps.

In addition to fog sample collection, aerosol samples were also collected before, during, and after fog events using high volume collectors. Aerosol samples were collected on pre-fired quartz fiber filters. In the Angiola study, samples were collected by a 2 channel medium volume ($120 \cdot 1 \text{ min}^{-1}$) aerosol collector (Brown et al., 2002). In the absence of fog, ambient aerosol samples were collected on the ambient channel, downstream of

a $PM_{2.5}$ cyclone. When fog appeared, sampling was switched to a second channel with an inlet located inside the cloudwater collector downstream of the fog drop collection strands. This approach is designed to collect “interstitial” aerosol particles: those particles not scavenged by fog droplets. In the Fresno study aerosol samples were collected by a high volume sampler ($1.13 \text{ m}^3 \text{ min}^{-1}$, ThermoAndersen, Smyrna, GA) with a $PM_{2.5}$ impactor inlet (Tisch Environmental TE231). In the absence of fog, ambient aerosol was collected; in the presence of fog the aerosol sampler sampled interstitial aerosol particles downstream of the collection strands of the ss-CASCC. Collected filter samples were stored frozen until analysis.

Samples were analyzed back in our laboratory in Colorado by a variety of methods. Analytical methods are briefly described here. TOC was measured using a Shimadzu TOC-5000 total organic carbon analyzer. Dissolved organic carbon (DOC) was analyzed by the same method after vacuum filtering the fog sample through a quartz fiber filter (Pall Gelman Pallflex Tissuquartz). Material passing through this filter was operationally defined as “dissolved.” Molecular weight fractions of the fog organic compounds were determined through a combination of ultrafiltration using membranes with nominal cut sizes of 500 and 1000 D and TOC measurement. Carbonyls in the fog were determined using derivatization with dinitrophenylhydrazine followed by HPLC analysis (HP Model 1050 with diode array absorbance detection). Carboxylic and dicarboxylic acid concentrations were determined using ion chromatography (Dionex model DX-500). Measurements of levoglucosan were made in several of the samples using ion chromatography coupled with pulsed amperometric detection (Engling et al., 2006). Additional measurements of trace fog organic species were made by gas chromatography coupled to mass spectrometry (GC/MS; HP Model 6890/5973). Organic nitrogen was determined as the difference between inorganic nitrogen species concentrations before and after exposing the sample to UV light. Typical fog sample volumes utilized for these analyses were 15 ml (TOC, DOC), 1.4 ml (organic acids), 1 ml (HCHO), 20 ml (carbonyls), 10 ml (DON), and 100–200 ml (GC/MS).

Total, Organic and Elemental Carbon (TC, OC and EC) were measured on collected aerosol samples by the thermal optical transmission method (Birch and Cary, 1996). Molecular marker concentrations on filter samples were determined by GC/MS following extraction with dichloromethane. Detailed procedures are described elsewhere (Brown et al., 2002).

3. Results and discussion

Ten fog events were sampled in the 2000/01 study in Angiola. Four fog events were sampled in the 2003/04 study in Fresno. Samples in both cases had high pH (typically 6–7) and contained high concentrations of ammonium and nitrate with lower concentrations of sulfate and nitrite. Organic matter was observed to contribute a significant fraction of total measured fog solutes. Fig. 2 illustrates the average Fresno fog solute mass composition. Organic matter comprised approximately one-third of total measured fog solutes.

TOC concentrations in the Fresno fog samples were somewhat higher than measured in Angiola fog. The average TOC in Angiola samples was 10.1 ppmC; the average in Fresno fog was measured to be nearly twice as high at 19.7 ppmC. The TOC range, however, was similar at both locations (2–41 ppmC at Angiola, 6–36 ppmC at Fresno). In both studies we observed that only a fraction of the TOC was dissolved and measured as DOC. Fig. 3 compares DOC and TOC concentrations for the Fresno samples. On average 76% of the TOC is dissolved in these samples, similar to the finding for Angiola reported by Herckes et al. (2002a).

TOC concentrations also varied with drop size at both locations, with smaller drops significantly enriched in TOC. Fig. 4 depicts results for Fresno (the division

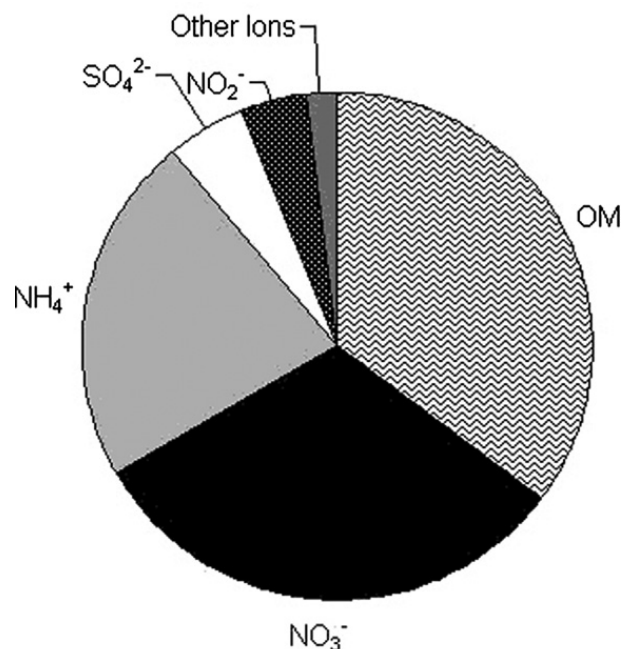


Fig. 2. Average mass composition of Fresno bulk fogwater samples. OM represents Organic Matter, assumed equal to 1.8 times the TOC concentration to represent mass contributions from hydrogen, oxygen, nitrogen and other atoms in organic molecules. Other ions include Na^+ , Cl^- , Mg^{2+} , Ca^{2+} , and K^+ .

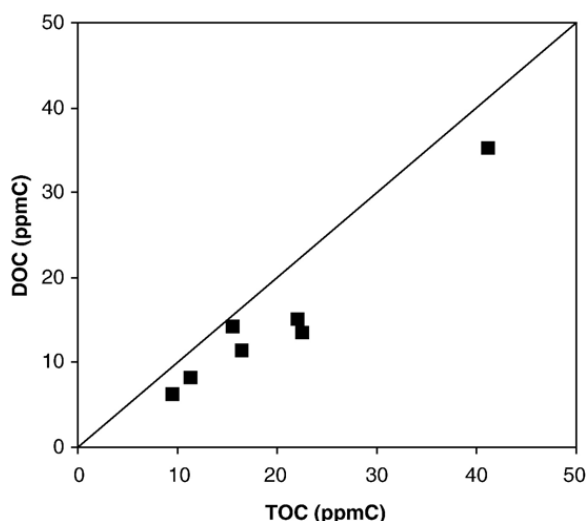


Fig. 3. Comparison of dissolved and total organic carbon in Fresno bulk fog samples.

between small and large fog drops corresponds to a drop diameter of approximately 15 μm); Herckes et al. (2002a) have shown results for Angiola. The enrichment of TOC in small drops is also reflected by drop size distributions measured for most individual organic compounds. Many inorganic species were also found to be enriched in small fog drops. One exception to solute enrichment in small fog drops is nitrite, which was typically enriched in larger drops. Distributions of individual solute species across the drop size distribution strongly influence their deposition velocities (Collett et al., 2001).

3.1. Organic speciation of fog samples

One goal of the Fresno fog study was to characterize the composition of the dissolved organic matter in the fog drops. Of the speciated organic acids, acetate accounted for the largest percentage of the DOC (21–31%), followed by formate (6–7%), oxalate (3–4%) and propionate (2–3%). Formaldehyde was the most prevalent carbonyl compound (3–4%), followed by methyl glyoxal (2–4%) and glyoxal (2–3%). The remaining speciated organic acids (pyruvic, glutaric, succinic, malonic, lactic, butyric, and pinic acids) together accounted for about 5% of the total DOC, and the remaining speciated carbonyls (acetaldehyde, acetone/acrolein, isovaleraldehyde, tolualdehyde, and hexaldehyde) accounted for about 3% of the total DOC. Levoglucosan accounted for about 1% of the DOC, but was only measured on the night of Jan. 11–12. Fig. 5 depicts a typical Fresno fog DOC composition. Roughly 43% of the DOC remains unspciated. GC/MS analysis

of organic compound families that have been found to be important constituents of organic aerosol particles (e.g., n-alkanes, long chain alkanolic acids, and polycyclic aromatic hydrocarbons) typically reveal that these compounds contribute at most 2–3% of California fog DOC. By contrast, significant concentrations of high molecular weight (>500 Da) dissolved organic material were measured in both Angiola and Fresno fog samples by ultrafiltration techniques. The presence of compounds with molecular weights in excess of 500 Da has also been observed upon California fog sample infusion into an electrospray mass spectrometer.

Measurements of dissolved organic nitrogen (DON) in the Fresno fog samples indicate that organic nitrogen compounds are significant contributors to the organic composition of these fogs, with measured concentrations varying from 1.7 to 4.5 mg N per liter. Fig. 6 illustrates the dissolved nitrogen speciation observed in three Fresno fog episodes. While the highest contributions come from inorganic nitrate and ammonium, organic nitrogen contributions are in the 10–17% range. In order to estimate the contributions of dissolved organic nitrogen species to measured dissolved organic carbon concentrations, we need to know the ratio of carbon to nitrogen molecules in the organic nitrogen. Zhang and Anastasio (2001, 2003) characterized a fraction of the DON compounds found in Davis, California fog waters. They measured both free amino compounds (FACs; i.e., amino acids and alkyl amines) and combined amino compounds (CACs; i.e., proteins and peptides). 22 dissolved organic nitrogen species were

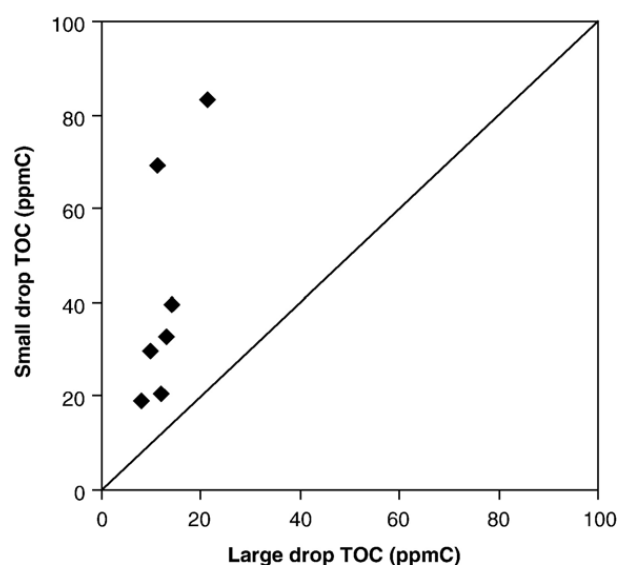


Fig. 4. Comparison of TOC in small and large Fresno fog drops. The division between small and large drops is at approximately 15 μm diameter.

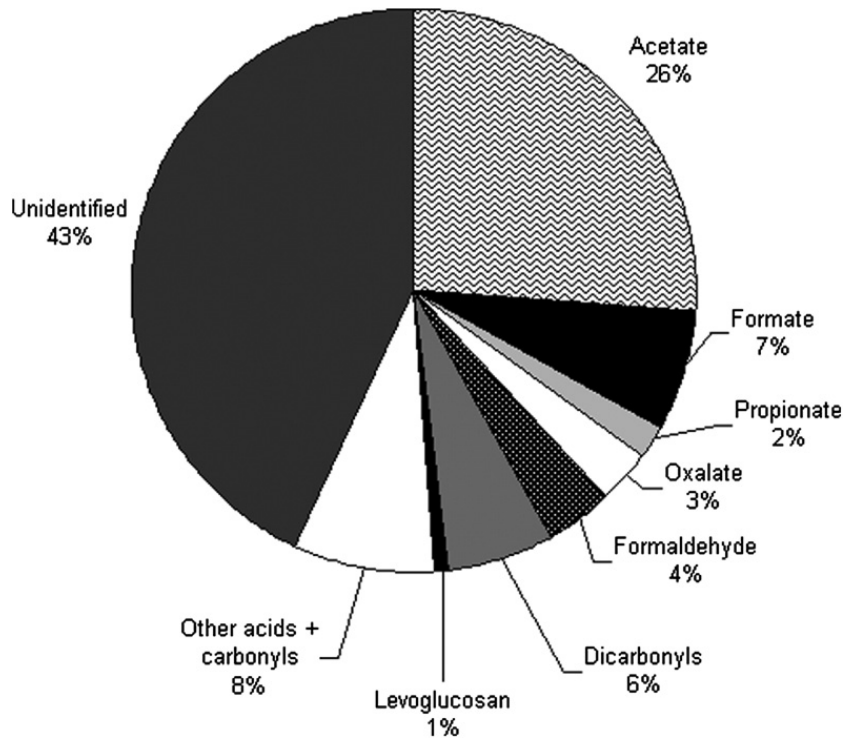


Fig. 5. Speciation of DOC in two Fresno fog events. 43% of the DOC was not identified as one of the measured organic acids, carbohydrates, or carbonyls.

measured in all. They determined that FAC accounted on average for 4% of the DON in the samples, and CACs accounted on average for 16% of the DON. Roughly 80% of the DON in the Davis fog samples remained unspicated. The average C:N ratio of the compounds speciated by Zhang and Anastasio was about 4. Such a large C:N ratio for our Fresno fog DON is unlikely, since we would overpredict the unspicated fraction of the DOC. Even assuming a low C:N ratio of 2 for measured DON nearly closes the DOC mass balance, with DON species estimated to contribute 32% of the measured DOC (43% of the DOC was unspicated in the analysis discussed above). Although there is

considerable uncertainty in the appropriate C:N ratio, it is clear that organic nitrogen compounds are important contributors to DOC in these fogs and that additional efforts to speciate fog DON should be a priority in future studies.

3.2. Scavenging and deposition of organic matter

Previous measurements of central California fog composition (Herckes et al., 2002b) have revealed the presence of organic molecules that serve as markers for various carbonaceous aerosol source types, including wood smoke, vehicle exhaust, and meat cooking. The

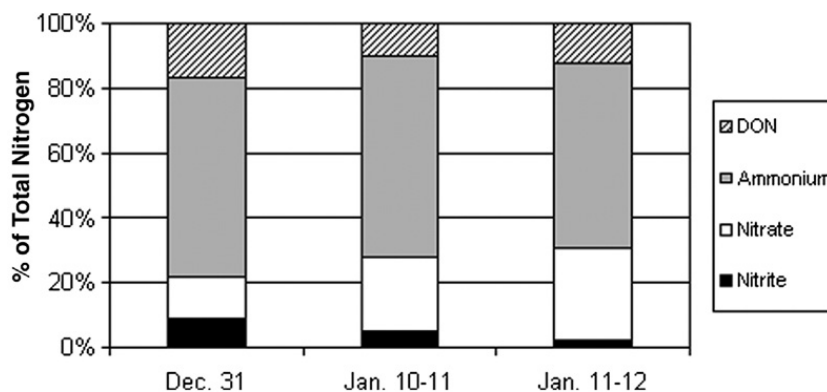


Fig. 6. Speciation of dissolved nitrogen in three Fresno fog episodes.

high TOC content of these fogs also indicate significant fog processing of atmospheric organic species. Measurements of fog solute deposition fluxes and velocities also indicate that these radiation fog events represent an important mechanism for cleansing the atmosphere. Deposition velocities were determined in Angiola and Fresno fog episodes as the ratio between the flux measured to a Teflon plate on the ground and the product of the fog liquid water content and the fog solute concentration, following an approach outlined previously (Collett et al., 2001). Observations at Angiola revealed fog TOC deposition velocities averaged almost 1.5 cm/s. In two Fresno fog episodes, fog TOC deposition fluxes averaged 2.6 $\mu\text{gC}/\text{min m}^2$ with a corresponding average fog TOC deposition velocity of 2.9 cm/s. These deposition velocities are much higher than typically observed for submicron aerosol particles, indicating the strong enhancement in pollutant deposition that occurs when fogs form. Interestingly, the fog TOC deposition velocities are somewhat lower than the observed deposition velocities for fog water itself, consistent with enrichment of TOC in smaller fog drops which experience lower settling velocities.

In order to better understand interactions of these fogs with carbonaceous aerosol particles, we utilized aerosol measurements made before and during fog episodes at both Angiola and Fresno to examine fog scavenging of several key components, including organic carbon, elemental carbon, and several individual organic molecular markers.

As a first step we consider the scavenging of total carbon (TC). It is noteworthy that while observations in Angiola and Fresno reveal a general pattern indicative of fog scavenging of TC, a few periods showed TC concentrations that did not decrease as expected. These may reflect changes in atmospheric composition during the sampling periods and/or effects of entrainment from above the boundary layer during fog growth. Also of note, post-fog carbonaceous fine particle concentrations were often somewhat higher than pre-fog concentrations, suggesting that aqueous reactions in the fog drops might transform soluble volatile organic compounds into lower volatility secondary organic aerosol (SOA) species, analogous to aqueous phase transformation of gaseous sulfur dioxide to particulate sulfate. Although transformations of this type have been predicted in the literature (e.g., Blando and Turpin, 2000), the organic chemistry of the atmospheric aqueous phase is largely unknown. Significant aqueous SOA production has not been clearly documented in any field experiment, in part because of the difficulty of adequately characterizing such a complex, multiphase system. Measurements at

Angiola and Fresno are also inadequate to do more than suggest the presence of the fogs might have contributed to SOA formation. It is also possible that increases in post-fog particulate TC concentrations resulted from other mechanisms such as fresh emissions, advection or entrainment.

It is difficult to schedule short-term aerosol measurements to correspond exactly to the desired periods before, during, and after fog especially given the rather unpredictable nature of fog onset and dissipation. Interpreting differences between pre- and post-fog samples as fog scavenging and deposition of aerosol carbon is also challenging as the depth of the boundary layer typically grows with onset of the fog, entraining material of unknown concentration and composition from above. Overall, however, our data suggest that elemental carbon (EC) is less efficiently scavenged than OC resulting in decreased OC/EC ratios in the interstitial aerosol samples.

For periods with a rapid onset of fog, well represented by ambient and interstitial aerosol filter samples, we were able to calculate scavenging efficiencies according to:

$$\eta = 1 - \frac{X_{\text{interstitial}}}{X_{\text{pre-fog}}} \quad (1)$$

where η is the scavenging efficiency of species X . Results are given in Table 1 for the events where fog scavenging appeared to dominate concentration changes (i.e., TC was observed to decrease upon fog formation). Results are presented for both the Angiola and Fresno fog campaigns. Scavenging efficiencies for OC were calculated to vary between 33 and 90%. Scavenging efficiencies for EC were much lower, ranging from 0 to 12%, again suggesting a higher efficiency for OC scavenging than for EC scavenging. The preferential scavenging of OC is consistent with the more hygroscopic character of organic carbon-containing particles compared to particles rich in EC increasing their likelihood of becoming activated. Some difference in

Table 1
Fog scavenging efficiencies (η) for organic, elemental, and total carbon

	η_{OC}	η_{EC}	η_{TC}
Angiola 12/19/00	0.90	0.12	0.84
Angiola 1/15/01	0.59	0.05	0.54
Angiola 1/17/01	0.33	0.06	0.29
Fresno 1/11/04	0.41	0.0 ^a	0.36

^a No significant difference between pre-fog and interstitial EC concentrations.

nucleation scavenging efficiency may also result from different size distributions for EC and OC. The observed differences in scavenging efficiencies have important consequences for particle lifetime, since these radiation fogs have been shown to be effective cleansers of the atmosphere. The higher fog scavenging efficiencies observed for OC suggest that its atmospheric lifetime will be limited more strongly by the occurrence of fogs than will the lifetime of EC. In a somewhat analogous situation, Lim and coworkers observed a shorter lifetime of organic carbon over the ocean and hypothesized that a contributing factor might be preferential scavenging of OC by clouds (Lim et al., 2003).

Our observed scavenging efficiencies are similar to previous observations. Hallberg and coworkers measured a scavenging efficiency of 6% for black carbon (BC) in polluted radiation fogs in the Po Valley (Hallberg et al., 1992). Hitzenberger, by contrast, observed much higher scavenging efficiencies for BC in clouds formed in more pristine areas (Hitzenberger et al., 2000; Hitzenberger et al., 2001) where particle scavenging is likely enhanced by generation of greater peak supersaturations. Hitzenberger's observed TC scavenging efficiencies, however, were similar in magnitude to those observed in the current study. Surprisingly, Sellegri and coworkers found higher EC than OC scavenging efficiencies. They hypothesized that EC was largely associated with particles rich in other hydrophilic species while OC-containing particles featured hydrophobic coatings that could suppress activation (Sellegri et al., 2003). A similar explanation was presented by Hitzenberger to account for very high BC scavenging.

Fig. 7 depicts the variation in TC scavenging efficiency determined in the current study as a function

of fog LWC. Efficiencies tend to increase with LWC (a linear regression fit to these data yields a correlation coefficient of 0.68). A similar relationship is observed between OC scavenging efficiencies and LWC. The increase in scavenging might reflect correlation of both scavenging efficiency and of fog LWC with peak fog supersaturation (which cannot be measured directly). A linkage of this type is certainly plausible although, given the limited number of observations available here, we should be hesitant in interpreting this relationship too strongly. Other authors have previously suggested a relationship between LWC and scavenging efficiencies (Hitzenberger et al., 2000; Hitzenberger et al., 2001); such a relationship was not observed, however, by Sellegri and coworkers (Sellegri et al., 2003).

We have previously reported that many organic molecular marker compounds are observed in fog samples (Herckes et al., 2002b), indicating some efficiency of the fogs for scavenging particles from the corresponding source types (e.g., wood smoke, meat cooking, and vehicle exhaust). Examination of the relative scavenging efficiencies of markers from different carbonaceous particle source types can help us determine whether fogs in the region process carbonaceous particles from some source types more actively than others. Such an observation could have important implications for understanding relative atmospheric lifetimes of different carbonaceous particle types during the foggy periods that accompany winter stagnation episodes in California's Central Valley.

Analysis here focuses on two fog episodes during which fog scavenging appeared to dominate aerosol concentration changes. A first episode occurred in Angiola on December 18/19, 2000. This event is

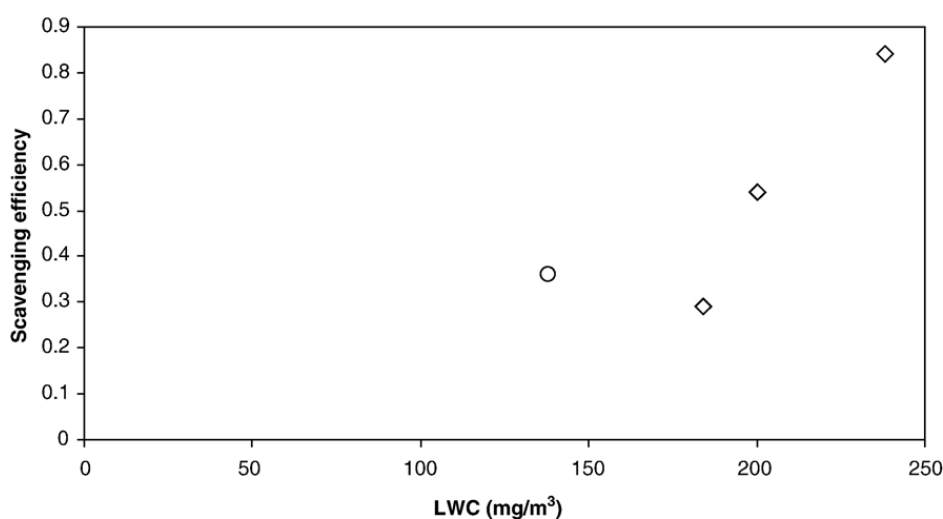


Fig. 7. Total Carbon (TC) scavenging efficiencies as a function of Liquid Water Content (LWC). Circles represent data from Fresno; diamonds represent data from Angiola.

Table 2
Fog scavenging efficiencies determined in Angiola (December 19/20, 2000) and Fresno (January 11, 2004)

Organic carbon	Angiola	Fresno	Elemental Carbon	Angiola	Fresno
n-alkanes	0.90	0.44	n-alkanoic acids	0.12	0.00
n-C21	0.57	n.d.	n-C20	0.67	n.d.
n-C22	0.56	0.69	n-C21	0.82	n.d.
n-C23	0.58	0.41	n-C22	0.76	n.d.
n-C24	0.61	0.50	n-C23	0.79	n.d.
n-C25	0.64	0.58	n-C24	0.69	n.d.
n-C26	0.61	0.69	n-C25	0.72	n.d.
n-C27	0.63	0.66	n-C26	0.79	n.d.
n-C28	0.62	0.74	n-C27	0.85	n.d.
n-C29	0.74	0.71	n-C28	0.87	n.d.
n-C30	0.55	0.77	n-C29	>0.80	n.d.
n-C31	0.73	0.50	n-C30	>0.80	n.d.
n-C32	0.34	0.71	n-C31	>0.80	n.d.
n-C33	0.66	0.40	n-C32	>0.80	n.d.
Average	0.60	0.61			
PAH			Dicarboxylic acids		
Fluoranthene	0.59	n.d.	Adipic acid (C6)	>0.97	n.d.
Pyrene	0.55	n.d.	Pimelic acid (C7)	>0.97	n.d.
Benzo(ghi)fluoranthene	0.78	n.d.	Suberic acid (C8)	>0.97	n.d.
PAH 252	0.86	n.d.	Azelaic acid (C9)	>0.86	n.d.
			Sebacic acid (C10)	>0.86	n.d.
Oxy-PAH					
9,10-Anthracenedione	>0.85	n.d.			
Benzoanthrone	>0.94	n.d.			
Other					
Syringaldehyde	n.d.	0.88	Cholesterol	n.d.	0.67
Vanillin	n.d.	0.96	Diazinon	n.d.	0.56
Retene	n.d.	0.63	17a21b hopane	0.33	0.68
Levogluconan	>0.95	0.95			

n.d. not determined.

>X, not detected in the interstitial particles, scavenging efficiencies calculated based on detection limit.

extensively discussed in a separate modeling study (Fahey et al., 2005). The second case study occurred in Fresno on January 11, 2004. Table 2 presents scavenging efficiencies of select individual organic compounds determined for both events. There are significant differences in scavenging efficiency between species; however, individual compound scavenging efficiencies

appear similar in both events. Due to short sampling integration times and relatively low aerosol sampler flows in the Angiola study, some molecular marker species were close to or below detection limit and scavenging efficiencies could not be determined.

The lowest scavenging efficiencies are observed for non-polar species, including n-alkanes and hopanes; polar species like dicarboxylic acids and levoglucosan exhibit high scavenging efficiencies. For n-alkanes, present at low concentrations, scavenging efficiencies averaged 60%. N-alkanoic acids, with their single hydrophilic carboxylic acid group, show a significantly higher scavenging efficiency than the n-alkanes. Polycyclic aromatic hydrocarbons (PAH) exhibit low scavenging efficiencies, while oxy-PAH are scavenged much more efficiently. These results are consistent with observations by Limbeck and Puxbaum (2000) that suggest a relationship between scavenging and compound solubility. As shown in previous work, a significant part of the scavenged organic material can be contained in an insoluble phase inside the cloud or fog droplets (Herckes et al., 2002a,b).

Levogluconan, a popular molecular marker for biomass burning (e.g. Simoneit et al., 1999), exhibited very high scavenging efficiencies and was essentially absent from the interstitial particulate matter. This is consistent with high levoglucosan concentrations observed in simultaneously collected fog water, where it is a major organic component. High scavenging efficiencies were also observed for other wood smoke markers, including vanillin and syringaldehyde, while retene appeared to be scavenged less efficiently. Overall, wood smoke marker molecules and, hence, smoke particles emitted from biomass combustion appear to be more efficiently scavenged than organic carbon in general. By contrast, 17 α 21 β hopane, a species frequently used as molecular tracer for vehicle emissions (e.g. Schauer et al., 1996) shows a low scavenging efficiency. These observations show that fogs interact more strongly with, and cleanse the atmosphere of, particles from select source types (e.g. wood smoke) faster than others (e.g., vehicle emissions).

4. Conclusions

Studies of radiation fogs in central California reveal that they are important processors of airborne organic material, interacting with both soluble organic gases and carbonaceous particles. Deposition velocities of fog TOC are in excess of 1 cm/s, making fogs effective cleansers of organic material from the atmosphere. Measurements of fog composition indicate that high molecular weight compounds comprise a significant

fraction of fog DOC. Speciation of lower molecular weight compounds indicates important contributors to fog DOC in this region include formaldehyde, acetaldehyde, glyoxal, methylglyoxal, formate, acetate, oxalate, levoglucosan, and organic nitrogen.

Total (TC), organic (OC) and elemental (EC) carbon scavenging efficiencies were determined based on pre-fog and interstitial aerosol concentrations. Observations indicate that the fogs efficiently process carbonaceous material, with up to 84% of the total fine particle carbon scavenged. OC was more efficiently scavenged than EC. Significant differences were observed between scavenging efficiencies for various individual organic compounds. Results indicate more active fog processing of wood smoke particles than of vehicle exhaust particles, suggesting that atmospheric lifetimes of wood smoke particles may be more strongly limited than vehicle exhaust particle lifetimes during winter stagnation episodes accompanied by fog formation.

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