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Organic compounds in radiation fogs in Davis (California)

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Abstract

New stainless steel active fogwater collectors were designed and used in Davis (CA, USA) to collect fogwater for the speciation of organic matter. Organic compounds in fog samples were extracted by liquid–liquid extraction and analyzed by gas chromatography coupled to mass spectrometry. Numerous organic compounds, including various alkanes, polycyclic aromatic hydrocarbons (PAH) and alkanolic acids, have been identified in the fogwater samples. Higher molecular weight (MW) compounds are preferentially associated with an insoluble phase inside the fog drops, whereas lower molecular weight and more polar compounds are found predominantly in the dissolved phase. Concentrations in the dissolved phase were sometimes much higher than estimated by the compounds' aqueous solubilities.

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1. Introduction

Over the last 20 years, it has become increasingly evident that 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

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studies of cloud and fog chemistry have become increasingly sophisticated [e.g., by examining composition variations across the drop size spectrum (Bator and Collett, 1997)], 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 of concentrations of formaldehyde, formate, acetate, propionate, pyruvate and oxalate comprised from 9% to 32% of the total organic carbon (TOC) content.

In the last few years, the cloud and fog chemistry community has begun to address in more detail the organic chemical composition of fogs and clouds (e.g., Luttke and Levens (1997); Facchini et al. (1999); Luttke et al. (1999); Decesari et al. (2000); Krivacsy et al. (2000); Limbeck and Puxbaum (2000)). The long-term goals of this research are many and include examining aqueous production of secondary organic material, understanding fluxes of organic species to ecosystems, considering potential health hazards of human exposure to fogs containing hazardous organic pollutants and understanding the efficiency with which carbonaceous aerosol particles are scavenged by cloud or fog drops.

Although many organic compounds are quite hydrophobic, the partitioning of organic compounds between solution and insoluble matter inside the fog droplets has only received limited attention (Capel et al., 1990, 1991). It is common for investigators to filter fog samples prior to analysis. Since organic matter present in undissolved form may not be measured when filtered fogwater is analyzed (depending on the particle size and filtration procedures), it is important to also examine the insoluble matter when attempting to determine the total organic burden of the fog drops.

This paper describes preliminary steps toward a better understanding of processing of organic compounds by fogwater by describing the chemical composition of the organic matter in fog droplets and its partitioning between insoluble and dissolved phases as observed in radiation fogs in Davis, CA in winter 1998–1999.

2. Experimental

Fog samples were collected in December 1998 and January 1999 in Davis in the Central Valley of California. The samples were collected with newly developed cloud-water collectors, constructed of stainless steel, making them suitable for cleaning with organic solvents or by high-temperature baking to limit contamination issues. The collectors are patterned after the plastic Caltech Active Strand Cloudwater Collector (CASCC) and the compact version of that sampler known as the CASCC2. A detailed description of the CASCC and CASCC2 is given by Demoz et al. (1996). The new collectors are known as the stainless steel CASCC (ss-CASCC) and the ss-CASCC2. The collectors operate by pulling foggy air across a bank of stainless steel strands where drops are collected by inertial impaction. The collected drops flow down into a stainless steel collection trough, through a stainless steel tube and into a pre-baked glass bottle. The main

difference between the two new collectors is that the ss-CASCC is much larger than the ss-CASCC2 and features a much higher flow rate (24.5 m³/min vs. 5.8 m³/min), permitting more fog/cloud water to be collected.

Immediately after sampling, aliquots were prepared for measurement of pH and TOC. Remaining sample was later filtered through baked quartz filters (Pall Gellman Pallflex Tissuquartz) to make a distinction between the dissolved phase and the insoluble phase of the fogwater. Hereafter, “dissolved” refers to the filtrate and “insoluble” to the filter sample.

The filter and filtrate were spiked with deuterated compounds used as internal standards for quantification. The filter samples were extracted three times with 25 ml of dichloromethane (DCM). Samples of 100–200 ml of filtrate, depending on available sample, were extracted three times with 25 ml of DCM after adjusting the sample pH to 1 and sample salinity to 50 g/l by adding NaCl. The DCM from the liquid/liquid extraction was dried over Na₂SO₄. DCM extracts were concentrated to 0.25 ml using a vacuum centrifuge and/or nitrogen blowdown prior to analysis. A first fraction of the concentrated extract was injected directly into an HP 6890/5973 GC/MS for analysis. A second fraction was derivatized with diazomethane to transform organic acids to their methylester analogs prior to analysis. TOC concentrations were determined with a Shimadzu model 5000A TOC analyzer.

3. Results and discussion

Total organic carbon (TOC) concentrations collected in seven Davis fog events ranged from approximately 4–45 ppm C. TOC field blanks taken from the ss-CASCCs were always below 0.7 ppm C and usually below 0.5 ppm C.

Table 1 gives an overview of organic molecules identified and quantified in the collected samples. The list is not exhaustive but just an indicator for the large number of compounds present. Much of our species identification effort focused on molecules previously used as aerosol source tracers by other authors (e.g., Schauer and Cass, 2000). All quantified compounds in Table 1 have been previously observed in aerosol particles. The observations for alkanes, *n*-alkanoic acids and polycyclic aromatic hydrocarbons (PAH) are discussed in detail below.

3.1. *n*-Alkanes

Many long chain *n*-alkanes, ranging from 14 to 36 carbon atoms, have been quantified in the dissolved and insoluble fractions of Davis fogwater. Fig. 1 shows a typical observation where more than 90% of the *n*-alkanes are associated with the insoluble material while less than 10% are found in solution. The insoluble phase shows a clear odd carbon number preference with a carbon preference index (CPI) of 2.4 on average. This odd carbon number preference is generally attributed to natural sources of *n*-alkanes (e.g., plant wax) (Simoneit et al., 1991). The CPI of the dissolved fractions is much more variable (1 to 3.4), suggesting that sometimes there is a strong anthropogenic influence (CPI close to 1) and sometimes a strong biogenic influence (higher CPI). This may reflect different scavenging efficiencies for particles of anthropogenic vs. biogenic origin, but further investigation is required as the *n*-alkane concentrations here were very low and the

Table 1
Concentrations of selected organic compounds (ng/ml)

	Dissolved (ng/ml)	Insoluble (ng/ml)	Solubility ^a (ng/ml)
<i>n-Alkanes</i>			
<i>n</i> -Tetradecane	< d.l.	< d.l.–0.024	2.2
<i>n</i> -Pentadecane	< d.l.	< d.l.–0.075	2.87
<i>n</i> -Hexadecane	< d.l.–0.020	< d.l.	
<i>n</i> -Heptadecane	< d.l.–0.007	< d.l.–0.060	0.294
<i>n</i> -Octadecane	< d.l.–0.020	< d.l.	
<i>n</i> -Nonadecane	< d.l.–0.048	< d.l.	2.97×10^{-2}
<i>n</i> -Eicosane	0.003–0.163	< d.l.–0.044	
<i>n</i> -Heneicosane	0.012–0.250	0.32–1.32	2.9×10^{-5}
<i>n</i> -Docosane	0.010–0.343	0.59–1.94	3.87
<i>n</i> -Tricosane	< d.l.–0.352	1.3–3.6	
<i>n</i> -Tetracosane	0.010–0.95	1.4–3.4	
<i>n</i> -Pentacosane	< d.l.–1.4	1.4–3.7	2.9×10^{-5}
<i>n</i> -Hexacosane	< d.l.–2.2	1.0–2.4	1.7
<i>n</i> -Heptacosane	< d.l.–2.5	1.3–3.5	
<i>n</i> -Octacosane	< d.l.–2.7	0.7–1.8	8.84×10^{-7}
<i>n</i> -Nonacosane	< d.l.–2.4	3.4–7.9	2.76×10^{-7}
<i>n</i> -Triacontane	0.096–2	0.57–1.55	
<i>n</i> -Hentriacontane	< d.l.–5.1	4.55–10.9	2.67×10^{-8}
<i>n</i> -Dotriacontane	< d.l.–4.3	0.7–2.3	
<i>n</i> -Tritriacontane	< d.l.–2.3	1.57–4.37	2.57×10^{-9}
<i>n</i> -Tetracontane	< d.l.–1.1	0.35–2.1	
<i>n</i> -Pentatriacontane	< d.l.–0.58	0.31–1.9	
<i>n</i> -Hexatriacontane	< d.l.–0.35	0.16–0.7	1.7
Alkane CPI	1–3.4	2.3–2.6	
<i>Polycyclic aromatic hydrocarbons</i>			
Naphthalene	< d.l.–0.1	< d.l.	31000
Phenanthrene	0.028–0.169	< d.l.	1150
Anthracene	< d.l.–0.040	< d.l.	43.4
Fluoranthene	0.002–0.095	0.005–0.105	260
Acephenanthrylene	< d.l.–0.004	< d.l.	
Pyrene	0.013–0.289	0.023–0.284	1.35×10^{-4}
Benzo[ghi]fluoranthene	< d.l.–0.019	0.015–0.087	
Benzo[a]anthracene	< d.l.–0.022	0.003–0.026	9.4
Chrysene + triphenylene	0.004–0.036	0.014–0.207	2–41.1
Benzo[b]+[j]fluoranth.	< d.l.–0.18	0.255–1.309	
Benzo[e]pyrene	< d.l.–0.252	0.090–0.484	6.3
Benzo[a]pyrene	< d.l.–0.218	0.045–0.159	1.62
Perylene	< d.l.	< d.l.–0.030	0.4
Indeno[1,2,3-cd]fluoranth.	< d.l.–0.007	0.024–0.146	
Indeno[1,2,3-cd]pyrene	< d.l.–0.028	0.062–0.332	0.022
Benzo[ghi]perylene	< d.l.–0.033	0.078–0.488	0.26
Coronene	< d.l.	< d.l.–0.209	0.14
<i>Oxy-PAH</i>			
9H-fluoren-9-one	0.019–0.200	< d.l.	25300
Benzanthrone	< d.l.–0.096	< d.l.–0.108	240

Table 1 (continued)

	Dissolved (ng/ml)	Insoluble (ng/ml)	Solubility ^a (ng/ml)
<i>Oxy-PAH</i>			
Cholesterol	< d.l.–0.186	< d.l.–0.106	95
Retene	< d.l.–0.158	0.031–0.381	
Cholestanes	< d.l.	< d.l.–0.099	
Hopanes	< d.l.	0.062–0.330	
<i>n-Alkanoic acids</i>			
<i>n</i> -Nonanoic acid	0.849–3.03	< d.l.–0.145	212 000
<i>n</i> -Decanoic acid	0.186–0.932	< d.l.–0.132	61 800
<i>n</i> -Undecanoic acid	< d.l.–0.259	< d.l.	52 200
<i>n</i> -Dodecanoic acid	0.611–1.21	0.124–0.443	4810
<i>n</i> -Tridecanoic acid	< d.l.–0.178	< d.l.–0.025	33 000
<i>n</i> -Tetradecanoic acid	1.17–3.97	0.433–2.22	22 000
<i>n</i> -Pentadecanoic acid	0.443–1.54	0.21–0.75	12 000
<i>n</i> -Hexadecanoic acid	3.1–13.2	2.37–12.54	821
<i>n</i> -Heptadecanoic acid	0.068–0.579	0.0121–0.393	4200
<i>n</i> -Octadecanoic acid	1.21–6.68	1.1–7.4	340 000
<i>n</i> -Nonadecanoic acid	< d.l.–0.074	0.045–0.125	
<i>n</i> -Eicosanoic acid	0.050–0.368	0.604–1.97	0.3
<i>n</i> -Heneicosanoic acid	< d.l.–0.396	1.77–4.49	
<i>n</i> -Docosanoic acid	0.148–2.15	8.94–21.9	0.06
<i>n</i> -Tricosanoic acid	< d.l.–0.917	3.5–8.34	
<i>n</i> -Tetracosanoic acid	0.434–3.39	10.0–27.5	
<i>n</i> -Pentacosanoic acid	< d.l.–0.643	1.54–3.40	
<i>n</i> -Hexacosanoic acid	0.060–1.48	4.87–15.3	
<i>n</i> -Heptacosanoic acid	< d.l.–0.082	0.415–0.94	
<i>n</i> -Octacosanoic acid	< d.l.–0.261	1.01–2.39	
Total <i>n</i> -alkanoic acids	11–44	38–111	
Acid CPI	4.37–7.3	3.63–5.02	
<i>Resin acids</i>			
Pimaric acid	< d.l.–126	< d.l.	
Sandaracopimaric acid	< d.l.–75.5	< d.l.	
Isopimaric acid	< d.l.–91.6	< d.l.	
Dehydroabietic acid	42–3429	113–555	
<i>n-Alkenoic acids</i>			
8-Hexadecenoic acid	< d.l.–0.836	< d.l.–0.292	
9-Octadecenoic acid	< d.l.	0.326–2.09	11.5

< d.l.—lower than detection limit, detection limits vary from sample to sample depending on the amount of available sample for liquid–liquid extraction.

^a Howard and Meylan, 1997.

resulting CPIs uncertain. The dissolved phase concentrations, although very low, are often much higher than predicted by aqueous solubility. Enhanced solubility has previously been reported by others (Capel et al., 1991) and may result from the fact that fogwater is not a pure aqueous phase but contains a significant amount of organic matter (TOC 4–45 ppm C) as well as high metal and ion concentrations (Collett et al., 1999).

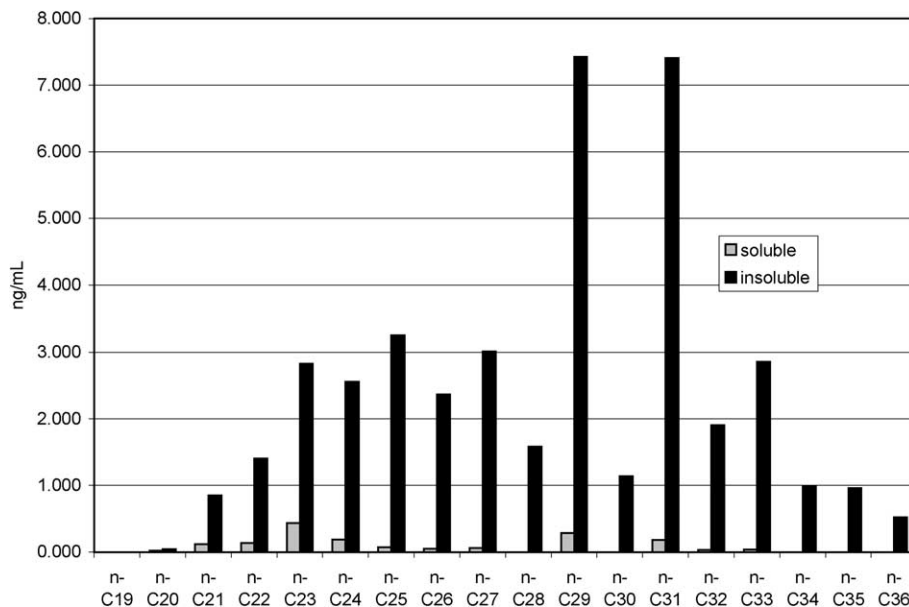


Fig. 1. *n*-Alkane concentrations in a Davis fogwater sample from January 9, 1999.

3.2. Polycyclic aromatic hydrocarbons (PAH)

Different PAH and oxygenated PAH have been quantified in the fogwater, ranging from structures with two rings (naphthalene) to seven rings (coronene). Structures with more than eight rings are unlikely to be observed using our analytical approach. Identified PAH include pyrene, benzo[*a*]pyrene, fluorene, fluorenone, and 9,10-anthracenedione. Fig. 2 shows a typical partitioning of PAH observed between the dissolved and insoluble phases inside the fogwater. Lower molecular weight (MW) PAH are found in both dissolved and insoluble fractions, while higher MW PAH are found predominantly or exclusively in the insoluble phase (e.g., coronene).

3.3. *n*-Alkanoic and other acids

Long chain (>9 carbon atoms) *n*-alkanoic acids have been identified in the dissolved and insoluble phases of the fogwater. Smaller chain acids are also present but are not discussed here as they are not determined by GC/MS. Typically, lower MW *n*-alkanoic acids are predominantly associated with the dissolved phase (Fig. 3), whereas higher MW acids are enriched in the insoluble phase. The dissolved and insoluble phases show a clear even carbon number preference (CPI around 4), evidence for a biogenic contribution to concentrations of these acids. The distribution with two maxima at C16 and C24 has been reported for aerosols. High concentrations of C9 acid are believed to result from the breakdown of C18 *n*-alkanoic acids. In addition to *n*-alkanoic acids, diacids (C4–C9),

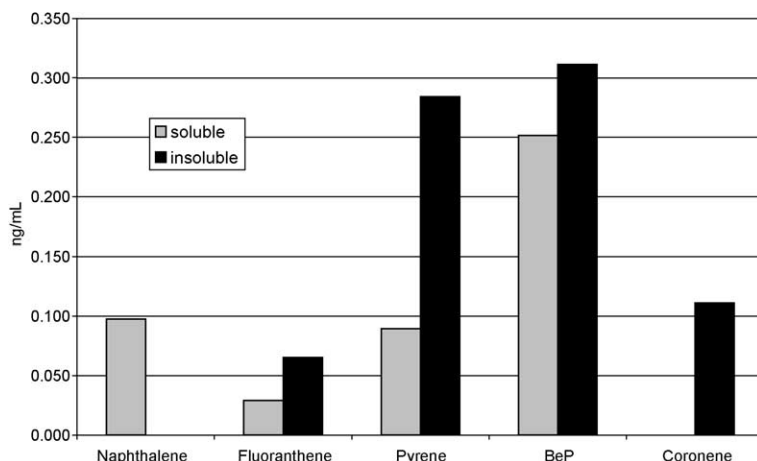


Fig. 2. Concentrations of selected PAH in a Davis fogwater sample from January 9, 1999.

resin acids (e.g., dehydroabiatic acid) and aromatic acids (e.g., benzoic and phthalic acid) have been identified in the fog samples.

3.4. Other compounds

In addition to the previous compound families, an effort has been made to identify the presence of organic molecules previously used as tracers for specific primary particle emission sources, including wood burning, vehicles and cooking activities. The goal is in the

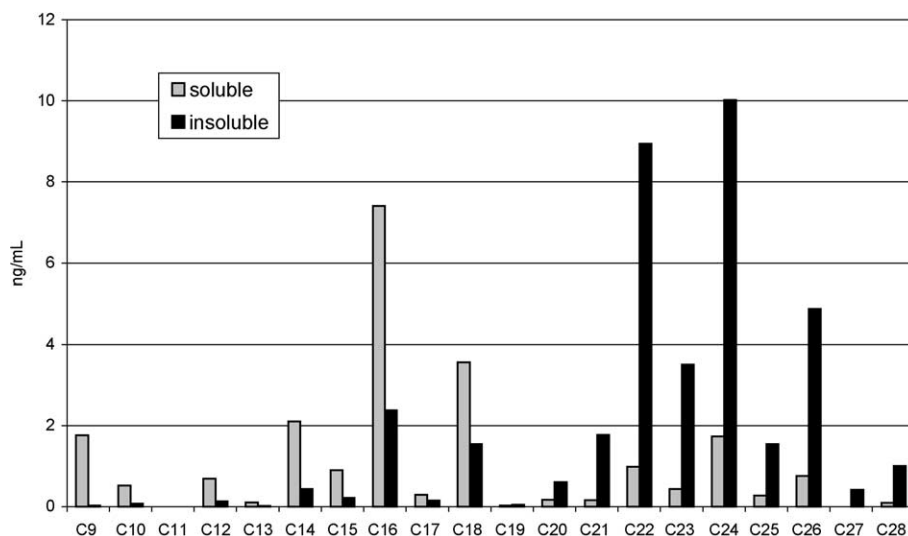


Fig. 3. Concentrations of *n*-alkanoic acids in a Davis fogwater sample.

Table 2
Contribution of different species to the total organic carbon

Species	% of total OC average (minimum–maximum)
Acetate	8 (7–9.5)
Formate	2.6 (1–4.8)
Formaldehyde	4.4 (2.4–6.3)
<i>n</i> -Alkanes	0.1 (0.002–0.3)
PAH	< 0.02
<i>n</i> -Alkanoic acids (C9–C28)	0.24 (0.1–0.35)
Quantified species	15.2 (12.8–18)
Unspeciated org. matter	84.8 (82–87.2)
All Acids (+ resin acids)	5.36 (0.58–13.2)

future to use measurements of these tracer compounds in pre-fog and interstitial aerosol, together with their fogwater concentrations, to quantify the scavenging efficiencies of various combustion aerosol types. Several organic tracers were identified in the fog samples, including vehicle emission markers (hopanes, steranes), wood smoke markers (e.g., retene, vanillin, guaiacol and resin acids) and a meat cooking tracer (cholesterol). Davis fog samples also showed high concentrations of the pesticide Diazinon, consistent with Diazinon application to fields near the sampling site shortly before the sampling campaign.

3.5. Contributions to TOC

After identifying and quantifying these organic compounds, we calculated the percentages of the organic matter that were identified. In addition to the previously detailed organic speciation measurements, we included measured concentrations of formaldehyde, formate and acetate. Table 2 shows that of all identified species, acetate, formaldehyde and formate are the dominant ones. The higher MW alkanolic acids, PAH and alkanes contribute less than 1% on average to the organic matter. Typically, only about 15% of the organic matter is speciated, leaving 85% of the total organic matter in these fogwaters unspeciated and stressing the need to further investigate the organic matter composition.

4. Conclusion

New stainless steel fog collectors were successfully used to collect Davis, CA fogwater for organic speciation. Fog samples were filtered and resulting filtrate and filter samples were extracted using DCM for analysis by GC/MS. Numerous organic compounds were identified in the dissolved and/or insoluble phases of fog droplets. Species partitioning between dissolved and insoluble phases was according to expectation, with higher MW, less polar compounds associated strongly with the insoluble phase and lower MW, more polar compounds found primarily in solution. Some species concentrations in the aqueous phase were much higher than expected based on their published aqueous solubilities.

Numerous compounds were present in both the dissolved and insoluble phases, stressing the need to include both phases in studies of scavenging behaviour. Analyses

of only the dissolved phase of fog samples may strongly bias estimations of the amounts of hydrophobic organic compounds scavenged by cloud and fog droplets.

A large fraction of the organic matter in fog droplets remains unspiciated. Typically, less than 20% of the fogwater TOC was identified via GC/MS analysis and separate analyses of formaldehyde, formate and acetate. Combined with previous observations in Central Valley fogs that indicate less than 30% of the TOC is typically comprised of formaldehyde and low MW organic acids, this suggests the majority of fog TOC in this region is yet to be identified. In the future, other techniques will be used to better characterize other fractions (including higher MW compounds) of the organic matter in fog droplets.

Successful identification of source tracer molecules for vehicle exhaust, wood smoke and cooking emissions suggests that comparisons of the aerosol/droplet distributions of these species in future studies will provide insight into the efficiency with which fogs and clouds scavenge and process primary carbonaceous aerosol emissions from different source types. The relative efficiency of particle scavenging and removal in radiation fogs occurring in urban areas, for example, could provide insight into the relative lifetimes of primary particle emissions from different combustion sources.

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