Speciation of Organic Matter in Fog Droplets: How Far are We from Mass Closure?

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Background

Fog and cloud chemistry have been studied for decades with research accelerating in the last 20 years. Aqueous sulfur oxidation has received particular attention due to the important contributions of clouds and fogs to the atmospheric sulfur cycle. In recent years organic compounds in fog and cloud drops begun to receive significant attention. Most studies have focused on a few, especially toxic compounds, leaving the majority of organic matter unidentified and uncharacterized. Consequently, little is known about processing of carbonaceous material by fogs and clouds or the creation of secondary organic aerosol by in-cloud reactions of gas phase organic species. Here we assemble all the information on organic compounds acquired during a recent field study conducted in Fresno in California's Central Valley, to assess what fraction of the total organic matter in fog droplets is characterized.

Fog sampling

Fogwater samples were collected in Fresno in the San Joaquin Valley of California in winter 2003/2004. The study focused on characterization of organic matter in fog droplets. Samples were collected with stainless steel versions of the Caltech Active Strand Cloudwater Collector (ss-CASCC) and the size-fractionating version of this collector known as the ss-sf-CASCC. During fog events droplet laden air is drawn through a duct in which the droplets are collected by inertial impaction on stainless steel strands. Collected fog samples are then preserved, derivatized if necessary, and analyzed in the laboratory.

Organic matter characterization

Total (TOC) and Dissolved Organic Carbon (DOC) were determined with a commercial TOC analyzer.

Small chain organic acids (formic, acetic, propionic, oxalic, …) were determined by ion chromatography with conductivity detection.

Organic molecular marker compounds (PAH, resin acids, n-alkanoic acids, oxy-PAH,…) were identified and quantified by Gas Chromatography coupled to Mass Spectrometry (GC-MS) after Liquid/Liquid extraction with Dichloromethane or after Solid-Phase Micro-Extraction (SPME).

Total formaldehyde was determined by derivatization and fluorescence spectroscopy.

Carbonyls and di-carbonyls (acetaldehyde, glyoxal, methylglyoxal,…) were quantified by liquid chromatography with UV detection after derivatization with DNPH (in the field).

Levoglucosan was determined by liquid chromatography with pulsed amperometric detection

Acknowledgements

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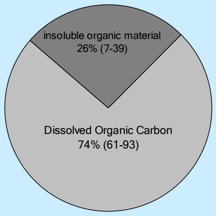
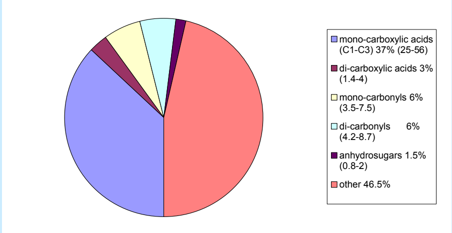
Total and Dissolved Organic Carbon



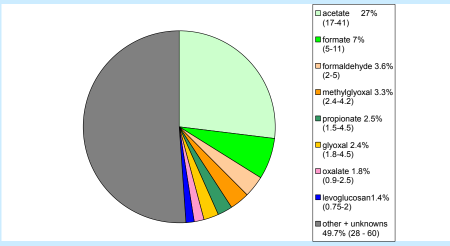
- The largest part of the organic matter in fog droplets is in solution
- Additional evidence suggests:
  - ➡ insoluble matter rich in microorganisms (bacteria?)
  - ➡ only a small contribution of soot to insoluble material

Major compound families



- Low molecular weight carboxylic acids are major individual contributors to DOC
- Carbonyls and dicarbonyls contribute significantly to DOC
- Dicarboxylic acids are only slightly more important as anhydrosugars in these samples
- A large set of molecular markers was detected in the samples, including PAHs, resin acids, n-alkanes, n-alkanoic acids,… but usually accounts for less than 1% of DOC. A previous study in a similar environment showed that of these compound families only resin acids might contribute significantly to DOC (Herckes et al., 2002a)

Major organic species



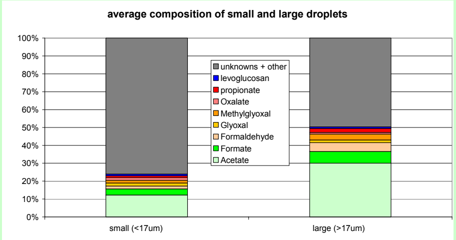
- On average 50% of the DOC is speciated
- In some cases up to 72% of the DOC is comprised of the small molecular weight, speciated species
- Acetic acid dominates the organic chemistry in Fresno fog samples
- Formic and propionic acid are also abundant
- Aldehydes are important (formaldehyde, glyoxal, methylglyoxal)
- Oxalic acid, the simplest dicarboxylic acid, contributes ~2%. Larger dicarboxylic acids, often taken as model compounds for DOC, contribute much less
- Levoglucosan, a major particle species in wood smoke is also important in the fog samples
- up to 72% of the organic matter remains unspeciated in some samples and may include a complex mixture of high molecular weight species as suggested by other studies (Herckes et al., 2002b; Gelencser et al, 2000; Krivacsy et al., 2000)

Variations with droplet size

- Organic matter is enriched in the smaller droplet fraction (D<17 µm) with the DOC concentration a factor of ~4 (3-6) higher
- Organic species concentrations vary also with size but the enrichment factor (small/large drop concentration ratio) is compound specific:

formaldehyde	1.4 (1.1-1.5)
acetate	1.8 (1.3-3.2)
formate	2.3 (1.7-4.2)
methylglyoxal	2.5 (1.6-5.4)
propionate	2.6 (1.1-4)
glyoxal	5.5 (3.7-13)
oxalate	6.7 (4.4-8)

➡ differences in relative composition



A significantly larger part of the DOC is speciated in the larger droplet fraction ➡ 43% (41-63) vs 26% (23-29)

➡ low molecular weight compounds might be less important in
➡ the small droplet fraction (greater aerosol influence?)

Oxalate and glyoxal contribute more to the small droplet DOC than to the large droplet DOC; all other species contribute less.

In these Fresno fogs, the droplet size distribution is strongly shifted to towards large droplets which explains the similarities of bulk and large droplet fractions

Summary and further work

- about 50% of the organic matter in bulk cloud droplets is speciated
- carboxylic acids, especially acetic acid, are dominant species
- dicarboxylic acids contribute less than 2% of the organic matter
  ➡ need new set of model compounds
- Smaller drops have higher organic carbon concentrations which is less well speciated ➡ resemblance to particles?
- typical aerosol molecular markers don't contribute significantly to fog organic matter mass
- ongoing work includes additional species quantification (phenols…), molecular size characterization by ultrafiltration and electrospray MS and comprehensive organic characterization by fractionation followed by IR spectroscopy and ^{13}C NMR
- In the future we hope to include biological characterization of the undissolved fraction

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