Formation of Secondary Organic Aerosol Mass Through Cloud Processing of Anthropogenic VOCs

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Introduction Cloud processing of gas phase species and their transformation into non-volatile species is a potential mechanism for the formation of secondary organic aerosol (SOA) material. Recent research efforts focused largely on heterogeneous chemistry as well as aqueous phase chemistry of species from predominately biogenic precursors. Few studies have focused on volatile, anthropogenic species including benzene, toluene, ethylbenzene, and xylenes (BTEX) and their processing by clouds.

Method Cloud samples and ambient VOCs (BTEX) were collected on the summit of Mt. Elden near Flagstaff, Arizona during the North American monsoon seasons of 2007 and 2008. Cloud samples were collected using the Caltech Active Strand Cloudwater Collector and ambient gas phase VOCs were collected using Radiello Passive Samplers. Cloudwater samples are analyzed using purge and trap (P&T) GCMS and ambient samples are analyzed using solvent extraction GCMS (Hutchings et al. (in press) Water, Air, and Soil Pollution).

Laboratory studies were completed using a solar simulator with a sealed, jacketed reaction vessel. The investigated solutions were Milli-Q water (>18MΩ) and water soluble extracts of aerosol filters spiked with BTEX and hydrogen peroxide. Reactant degradation was monitored over time using SPME-GC-MS.

Field Investigations Cloudwater concentrations of TEX species and ambient TEX concentrations are given below from measurements at Mt. Elden.

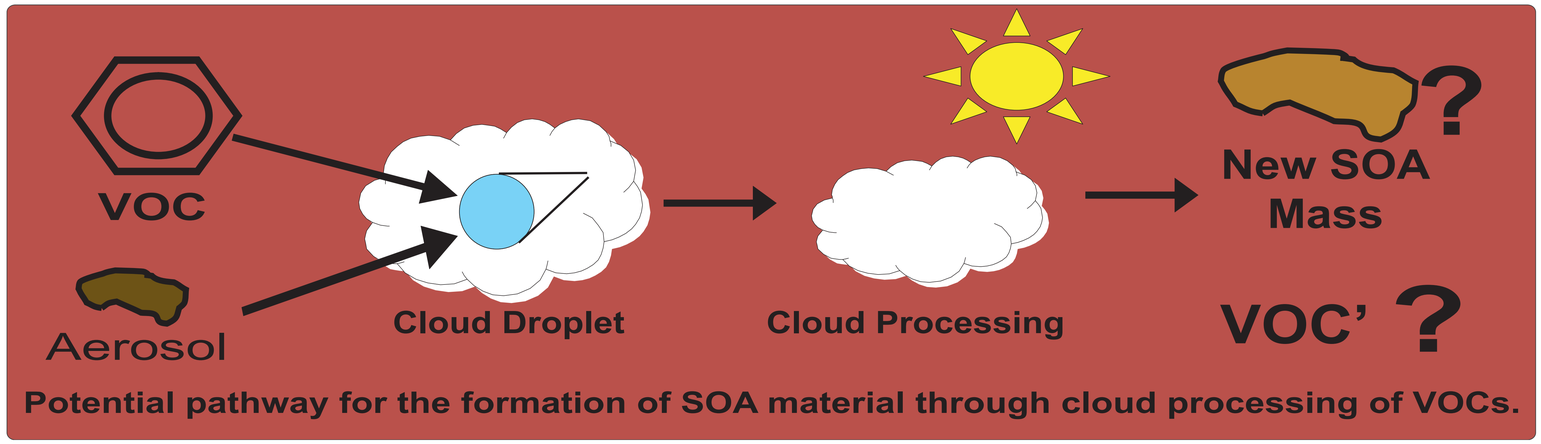
Median cloudwater concentration of VOCs (μgL^{-1})			
toluene	ethylbenzene	m&p-xylene	o-xylene
0.22	0.30	0.30	0.14

Ambient VOC concentration (μgm^{-3})			
toluene	ethylbenzene	m&p-xylene	o-xylene
0.095	0.037	0.040	0.021

Estimated cloudwater concentration of VOCs based on equilibrium, Henry's Law, and ambient concentrations of VOCs are shown below. Actual cloudwater concentrations are ~1000 times greater than estimated.

Calculated cloudwater concentration (ngL^{-1})			
toluene	ethylbenzene	m&p-xylene	o-xylene
1.8	0.45	1.0	0.35

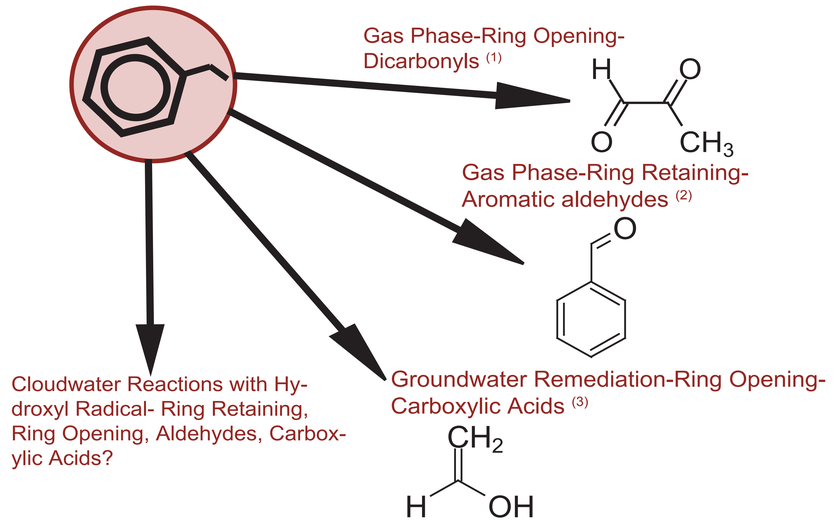
Actual cloudwater concentrations of TEX are low compared to the TOC (<1%) yet it is detectable in this rather pristine region. These substantial concentrations may be due to surface processes, interfacial adsorption, or colloidal organic material. Since these species can lead to SOA at a low concentration, this can be a measurable and potentially significant source for new SOA material.



Potential pathway for the formation of SOA material through cloud processing of VOCs.

Laboratory Investigations BTEX species show degradation in laboratory experiments. Below is an example plot of ethylbenzene degradation in Milli-Q water spiked with varying concentrations of hydrogen peroxide (HOOH) and the addition of HOOH without irradation (No Light). C/Co represents the concentration (C) at the reaction time compared to the original concentration (Co).

Reaction products are shown below from previous studies in the gas phase and in groundwater. The matrix of cloudwater is much different than these systems which could lead to vastly different products or very similar products. Many of the products are less volatile than the original reactant which cloud lead to the formation of SOA. Reaction product identification and quantification is on-going.



Key Results

* TEX species observed in cloud samples in AZ are highly concentrated in cloud droplets compared to Henry's Law predictions based on measured gas phase concentrations and supposing equilibrium. Still VOCs account for less than 1% of cloudwater TOC. Measurements of VOC in cloudwater were made by P&T-GCMS and ambient VOC were measured by solvent extracted Radiello cartridges and GCMS.

* BTEX compounds in aqueous solutions readily degrade in reactions with HOOH and simulated solar radiation, further testing will be in simulated cloud solutions and fog/cloudwater matrix to account for matrix effects.

*Detailed product identification and quantification studies are on-going. Given the differences in matrices and ambient conditions, results from atmospheric gas phase and heterogenous studies or from surface and groudwater chemistry are not directly transposable and product nature and ratios are different.

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