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## Shenandoah Cloud and Photochemistry Experiment (SCAPE): Overview

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### Introduction

The Shenandoah Cloud and Photochemistry Experiment (SCAPE) investigated the chemistry of the atmosphere at a high-elevation forested site in central Virginia with particular focus on the factors controlling concentrations of ozone, carbonyl compounds, and carboxylic acids. Carbonyl compounds and carboxylic acids are ubiquitous chemical constituents of the global troposphere, but many aspects of their biogeochemical cycling are poorly understood. Carbonyls are generated from the oxidation of hydrocarbons; formaldehyde (HCHO) produced via this pathway is an important precursor for OH. Thus the carbonyls are intermediates in and tracers of tropospheric photochemistry [e.g., *Carlier et al.*, 1988]. Carboxylic acids are major natural sources of atmospheric acidity thereby partially controlling pH-dependent chemical transformations in clouds [e.g., *Keene and Gallo-way*, 1988]. The aqueous-phase oxidation of HCHO in clouds has been hypothesized as a significant source of formic acid (HCOOH) and the aqueous-phase oxidation of HCOO<sup>-</sup> a potentially important in-cloud sink for OH [*Chameides and Davis*, 1983; *Jacob*, 1986]. Under many conditions, clouds should be a net sink for tropospheric HCOOH [*Jacob and Wofsy*, 1988]. Specific research objectives were (1) to assess the relative importance of NO<sub>x</sub> and hydrocarbons in limiting regional ozone production, (2) to investigate sources and sinks for carbonyl compounds and carboxylic acids, and (3) to examine the droplet-size dependence of solute concentrations and the thermodynamics of phase partitioning for carbonyl compounds and carboxylic acids in clouds.

### Experimental Design

SCAPE was a collaborative effort involving investigators from several institutions. Measurement and modeling activities are summarized in Table 1; readers are referred to the accompanying papers for additional details.

The field experiment was conducted between September 1 and October 1, 1990. Most of the chemical species and physical parameters were measured from a 15-m tower on a mountain ridge at Pinnacles (1037-m elevation) in the north

central section of the Shenandoah National Park, Virginia (38° 37'N, 78° 21'W). The top of the tower was 3 m above the surrounding forest canopy. O<sub>3</sub>, CO, NO, NO<sub>y</sub>, and peroxides were continuously measured through a 10-m sampling mast on a portable laboratory van in a clearing approximately 20 m from the base of the tower.

When clouds enveloped the site, coarse (>18-μm diameter) and fine (19- to 5.5-μm diameter) droplets and liquid-water content were sequentially sampled. Cloud-water pH and aqueous-phase and vapor-phase concentrations of carbonyls and carboxylic acids are measured in parallel over 1.0- to 1.5-hour intervals. Volatile carbonyls and carboxylic acids were also sampled over diel cycles during noncloud periods.

### Overview of Results

On the basis of measured O<sub>3</sub>, CO, NO, NO<sub>y</sub>, H<sub>2</sub>O<sub>2</sub>, and HCHO, *Jacob et al.* [this issue] found evidence for a seasonal transition from NO<sub>x</sub>-limited to hydrocarbon-limited O<sub>3</sub> production during September. They argue that such a seasonal transition in photochemical regime should be a general phenomenon over the eastern United States.

*Munger et al.* [this issue] report that the oxidation of isoprene was a major source for ambient HCHO and CHOCHO. They observed maximum concentrations (HCHO > 2 parts per billion by volume; CHOCHO > 100 parts per trillion by volume (pptv) during stagnation episodes in association with warm temperatures and elevated O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. Concentrations of CH<sub>3</sub>C(O)CHO were generally below the detection limit of 50 pptv.

*Talbot et al.* [this issue] infer that direct emissions from vegetation and soils were the dominant sources of carboxylic acids; model calculations and correlation analyses using various tracer compounds suggest that the decomposition of hydrocarbons and combustion of biomass or fossil fuels were relatively less important.

Both *Munger et al.* [this issue] and *Keene et al.* [this issue] found that aqueous-phase concentrations of carbonyls and carboxylic acids in clouds did not differ significantly between fine- and coarse-droplet-size fractions. Aqueous HCHO was supersaturated relative to the gas phase during a daytime cloud event; *Munger et al.* [this issue] hypothesize the hydrolysis of HOCH<sub>2</sub>OOH as a possible explanation.

The phase partitioning for CH<sub>3</sub>COOH measured by *Keene et al.* [this issue] in clouds was within the uncertainty of thermodynamic data. However, temporal variability in gaseous HCOOH was damped relative to equilibria with the aqueous phase suggesting that liquid water on the forest canopy may have buffered HCOOH in near-surface clouds. No evidence was found for significant HCOOH production in clouds; cloud-water deposition to the forest canopy appeared to be an important sink for HCOOH.

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**Table 1.** Sampling, Measurement, and Modeling Components of SCAPE

Species	Media	Institution	Investigator
Carbonyl compounds <sup>a</sup>	vapor, <sup>b</sup> cloud water, <sup>c</sup> precipitation <sup>d</sup>	Harvard University	J.W. Munger, B.C. Daube, D.J. Jacob
Carboxyl acids <sup>e</sup>	vapor <sup>b</sup>	University of New Hampshire	B.W. Mosher, R.W. Talbot
Carboxyl acids, major inorganic ions <sup>f</sup>	cloud water, <sup>c</sup> precipitation <sup>d</sup>	University of Virginia	W.C. Keene, J.R. Maben
O <sub>3</sub> , CO, NO, NO <sub>y</sub> , H <sub>2</sub> O <sub>2</sub> , organic peroxides, UV radiation <sup>g,h</sup>	vapor	University of Rhode Island	B.G. Heikes, M. Lee
Hydrocarbons <sup>i</sup>	vapor	University of California, Santa Barbara	D. Pierotti
Liquid-water content <sup>j</sup>	cloud	University of Virginia	W.C. Keene, J.R. Maben
Temperature, pressure, RH, wind speed and direction	---	University of Virginia	P. Thompson, J. Sigmon
Meteorology, trajectory analyses	---	NOAA ARL, University of Virginia	R.S. Artz, J.L. Moody
Photochemical modeling	---	Harvard University	D.J. Jacob, L.W. Horowitz

<sup>a</sup>Formaldehyde (HCHO), glyoxal (CHOCHO), and methylglyoxal (CH<sub>3</sub>C(O)CHO).

<sup>b</sup>Sampled using mist chambers; an inertial separator developed by B. C. Daube was positioned at the inlet to remove cloud droplets and coarse aerosol (> 1- $\mu$ m diameter) from the sample air.

<sup>c</sup>Sampled using size-segregating collector developed by B. C. Daube and operated by W. C. Keene and J. R. Maben.

<sup>d</sup>Manually sampled by W. C. Keene and J. R. Maben during precipitation events; sampling intervals varied as a function of sample volume.

<sup>e</sup>Formic (HCOOH), acetic (CH<sub>3</sub>COOH), and pyruvic (CH<sub>3</sub>(CO)COOH) acids.

<sup>f</sup>HCOOH<sub>t</sub> (HCOOH<sub>aq</sub> + HCOO<sup>-</sup>), CH<sub>3</sub>COOH<sub>t</sub> (CH<sub>3</sub>COOH<sub>aq</sub> + CH<sub>3</sub>COO<sup>-</sup>), H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>.

<sup>g</sup>Measured continuously.

<sup>h</sup>Instrumentation to measure O<sub>3</sub>, CO, NO, and NO<sub>y</sub> was provided by R. R. Dickerson, B. G. Doddridge, and K. Civerolo at the University of Maryland.

<sup>i</sup>Grab samples were collected between September 4 and 14, 1990.

<sup>j</sup>Measured using two independent techniques.

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