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## Formaldehyde, glyoxal, and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia

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**Abstract.** As part of the Shenandoah Cloud and Photochemistry Experiment (SCAPE), we measured formaldehyde (HCHO), glyoxal (CHOCHO), and methylglyoxal (CH<sub>3</sub>C(O)CHO) concentrations in air and cloudwater at Pinnacles (elevation 1037 m) in Shenandoah National Park during September 1990. Mean gas-phase concentrations of HCHO and CHOCHO were 980 and 44 pptv, respectively. The concentration of CH<sub>3</sub>C(O)CHO rarely exceeded the detection limit of 50 pptv. Mean cloudwater concentrations of HCHO and CHOCHO were 9 and 2 μM, respectively; the mean CH<sub>3</sub>C(O)CHO concentration was below its detection limit of 0.3 μM. The maximum carbonyl concentrations were observed during stagnation events with high O<sub>3</sub>, peroxides, and CO. Outside of these events the carbonyls did not correlate significantly with O<sub>3</sub>, CO, or NO<sub>y</sub>. Carbonyl concentrations and concentration ratios were consistent with a major source for the carbonyls from isoprene oxidation. Oxidation of CH<sub>4</sub> supplies a significant background of HCHO. The carbonyl concentrations were indistinguishable in two size fractions of cloudwater having a cut at d=18 μm. Gas- and aqueous-phase concentrations of HCHO from samples collected during a nighttime cloud event agree with thermodynamic equilibria within a factor of 2. Samples collected during a daytime cloud event show HCHO supersaturation by up to a factor of 4. Positive artifacts in the cloudwater samples due to hydrolysis of hydroxymethylhydroperoxide (HOCH<sub>2</sub>OOH) could perhaps account for this discrepancy.

### 1. Introduction

Formaldehyde (HCHO), glyoxal (CHOCHO), and methylglyoxal (CH<sub>3</sub>C(O)CHO) are generated in the atmosphere from the oxidation of hydrocarbons. Formaldehyde and methylglyoxal are important atmospheric precursors of OH and peroxyacetyl nitrate (PAN), respectively. Glyoxal and methylglyoxal are tracers for the oxidation of a number of hydrocarbons, including in particular isoprene. Although HCHO has been extensively studied in urban, rural and remote atmospheres [cf. *Carlier et al.*, 1986], measurements of CHOCHO and CH<sub>3</sub>C(O)CHO have been reported only for urban air in Brazil [*Grosjean et al.*, 1990] and for cloudwater in the Los Angeles area [*Munger et al.*, 1990].

Because they have large hydration constants, HCHO, CHOCHO, and CH<sub>3</sub>C(O)CHO are moderately to highly soluble [*Betterton*, 1992]. Oxidation of HCHO by OH in fog and cloud droplets has been postulated as a source of HCOOH [*Chameides*, 1984], and S(IV) adducts with HCHO make sig-

nificant contributions to the total dissolved S(IV) [*Munger et al.*, 1986]. *Facchini et al.* [1992] report simultaneous measurements of HCHO in gas and liquid phases in the Po valley, Italy; they observed a large excess of aqueous HCHO that could not be accounted for by S(IV) adducts alone.

In this paper we report measurements of gas-phase and cloudwater HCHO, CHOCHO, and CH<sub>3</sub>C(O)CHO made at a mountain ridge site in Shenandoah National Park, Virginia, during the Shenandoah Cloud and Photochemistry Experiment (SCAPE) in September 1990. We examine diel variation of the carbonyls and their correlations with other trace gases and we compare observations with photochemical model results to evaluate our current understanding of atmospheric sources and sinks for these species. Finally, we examine the thermodynamics of partitioning between the gas phase and the cloudwater. Additional measurements during SCAPE included O<sub>3</sub>, NO<sub>y</sub>, NO, H<sub>2</sub>O<sub>2</sub>, ROOH, UV radiation, carboxylic acids, and cloudwater composition [*Jacob et al.*, this issue; *Keene et al.*, this issue; *Talbot et al.*, this issue].

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### 2. Methods

Carbonyl and cloudwater samples were collected from a 15-m tower on a ridge at Pinnacles in Shenandoah National

Park (elevation 1037 m). The tower extended 3 m above the surrounding canopy. Additional details of the sampling site are reported by Keene *et al.* [this issue].

## 2.1. Sample Collection

Gas-phase carbonyls were collected using a mist chamber filled with an acidified solution of 2,4-dinitrophenylhydrazine (DNPH) [Cofer and Edahl, 1986]. Talbot *et al.* [1988] have demonstrated that this technique efficiently samples soluble gases. Ozone causes a negative interference in HCHO sampled with 2,4-DNPH-coated silica gel cartridges, but no interference was observed when sampling with impingers [Arnts and Tejada, 1989]. An O<sub>3</sub> interference is not expected with mist chambers because, as with impingers, the 2,4-DNPH and hydrazones are distributed throughout a bulk solution rather than concentrated in a frontal zone.

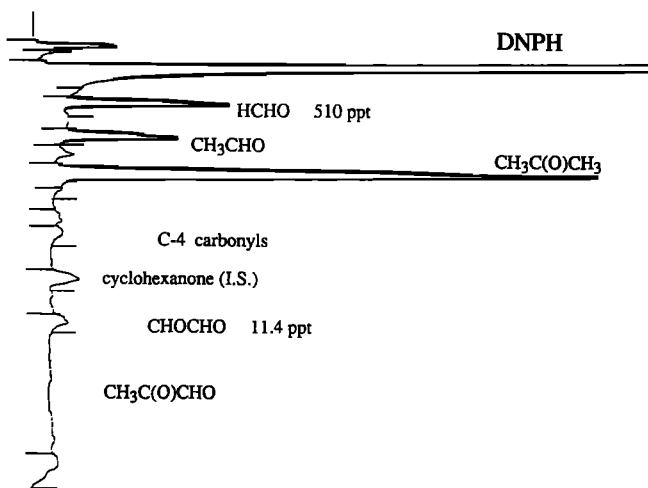
A droplet separator (section 2.3) upstream of the mist chamber excluded large drops and particles ( $d > 1 \mu\text{m}$ ) from the sample stream. Samples were collected for 1-2 hours at a nominal flow rate of  $10 \text{ L min}^{-1}$  measured with a mass-flow meter (MKS Instruments Incorporated, Andover, Massachusetts). Evaporation of the scrubbing solution limited the collection time during periods of low humidity; samples with too little volume at the end were discarded. After removing the scrubbing solution the mist chamber was rinsed with a mixture of hexane (C<sub>6</sub>H<sub>14</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>); the rinse was combined with the scrubbing solution. The hydrazone derivatives were separated by three extractions with C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> and then washed with a few milliliter of water to remove unreacted DNPH and excess acid. The hydrazones were then evaporated to dryness in a glass vial under a stream of N<sub>2</sub> and stored in a freezer until analyzed. Reagent and sampling blanks were generated by extracting unexposed aliquots from each batch of scrubbing solution and by analyzing dynamic field blanks from mist chambers that were exposed for a few seconds.

Size-segregated cloudwater samples were collected with an active-strand collector [Keene *et al.*, this issue]. Coarse droplets ( $d > 18 \mu\text{m}$ ) impacted on 9.5-mm Teflon rods and fine droplets ( $5.5 \mu\text{m} < d < 18 \mu\text{m}$ ) impacted on Teflon strands behind the rods. Each fraction drained separately to a collection bottle. This collector used more rows of smaller diameter rods than described by Munger *et al.* [1989] to achieve a sharper size cut. Liquid water content (LWC) was estimated for each size fraction of droplets from the corresponding volume of water sampled by the collector, the volume of air processed, and the theoretical collection efficiencies of the rods and strands. These data were compared with LWC measured in parallel using a device described by Valente *et al.* [1989]. Results for sampling intervals with clouds continuously present typically agreed within  $\pm 5\%$  or  $\pm 0.03 \text{ g m}^{-3}$ . At the end of the sampling interval (typically 1 - 1.5 hours) a 5-mL aliquot from each size fraction was treated with acidified 2,4-DNPH [Grosjean and Wright, 1983]. After incubation the hydrazones were extracted by the same procedure used for the mist-chamber samples.

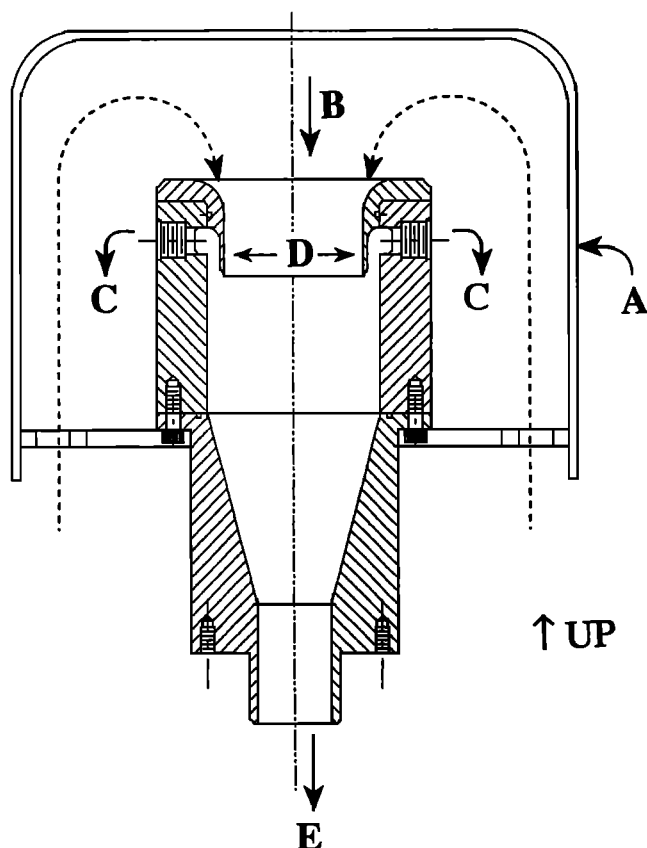
## 2.2. Carbonyl Analysis

The dried and frozen hydrazones were redissolved in C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> and analyzed by HPLC using a Dionex 4500i chromatograph with a Rheodyne 7010 injection valve. The

samples were eluted at  $1.2 \text{ mL min}^{-1}$  using a solvent program that varied from 50 to 90% CH<sub>3</sub>CN in H<sub>2</sub>O through a 4.6 x 150 mm Alltech Adsorbosphere C18 5- $\mu\text{m}$  column. Peaks were detected at 365 and 410 nm using two photometric detectors in series. The second detector at 410 nm allowed better sensitivity for the dicarbonyls, whose hydrazones have an absorbance peak shifted to higher wavelengths than the hydrazones of aldehydes [Munger *et al.*, 1990]. The ratio of peak area at the two wavelengths served as a qualitative check on peak identity. A typical chromatogram, Figure 1, shows baseline separation for the compounds of interest. The peaks were quantified using the ratio of their area to that of 2,4-dinitrophenylcyclohexanone added as an internal standard to the mist-chamber and cloudwater aliquots. Carbonyl adducts that are stable at low pH are not detected; in particular, hydroxymethanesulfonate, the S(IV) adduct, is not recovered as a hydrazone [Munger *et al.*, 1990]. Standards were made from hydrazone derivatives that were synthesized in the laboratory and from aqueous solutions of selected carbonyls that were treated as the cloudwater aliquots. Sets of standards were prepared in the field as well to check stability of the hydrazones. Data for samples were corrected based on the field blanks. Minimum detection limits were 0.5, 0.75, and 1.5 nmol/sample for HCHO, CHOCHO, and CH<sub>3</sub>C(O)CHO, respectively, based on variances of repeated standard runs. For 1-hour sampling intervals these correspond to 15, 20, and 50 pptv, respectively, in gas-phase samples. For 5-mL aliquots of cloudwater the detection limits would be 0.1, 0.15, and 0.3  $\mu\text{M}$ , respectively. Relative standard errors of the



**Figure 1.** Example chromatogram for dinitrophenylhydrazine (DNPH) carbonyl derivatives from a mist-chamber sample collected at Pinnacles in Shenandoah National Park, September 21, 1990. Peaks are absorbance at 365 nm. Retention time for the unreacted DNPH is about 3 min. Formaldehyde (HCHO) and glyoxal (CHOCHO) elute at 4.9 and 16.2 min, respectively. The methylglyoxal (CH<sub>3</sub>C(O)CHO) peak with retention time about 18 min was not recognized in this sample at 365 nm but was evident from absorbance at 410 nm. In addition, peaks were observed for an unresolved group of C-4 carbonyls, CH<sub>3</sub>CHO, and CH<sub>3</sub>C(O)CH<sub>3</sub>, but the latter compounds could not be quantified due to high blank values relative to the sample concentration.



**Figure 2.** Diagram of droplet separator. The separator is covered by a polyethylene rain shield (A). Air, as indicated by dashed curves, enters through the 10-cm diameter inlet at (B) where it is accelerated by constriction to 5 cm (D). Sample is withdrawn through a 6.3-mm slit leading to four ports (C). Because of their inertia, droplets pass along with the excess air through the exhaust port (E) to a blower and are vented at ground level 10 m downwind of the tower base. The body of the separator was made of high-density polyethylene.

HCHO, CHOCHO, and  $\text{CH}_3\text{C}(\text{O})\text{CHO}$  calibration factors were 1, 3, and 6%, respectively. The reported concentrations, which are the differences between sample and blank concentrations will have a larger overall uncertainty.

### 2.3. Droplet Separation

Reliable determination of soluble gases in the interstitial air during cloud requires that the cloud droplets be separated from the sample stream without disturbing the phase partitioning. Separation on a prefilter or by a cyclone is questionable because the droplets remain in contact with the airstream and may evaporate or scavenge vapor. We developed an inertial droplet separator for use in this experiment (see Figure 2) that eliminates contact between the interstitial air sample and the separated droplets. For normal operating conditions (Table 1) the 50% size cut based on droplet inertia and computed laminar flow streamlines for spherical particles is  $1\ \mu\text{m}$ , which is sufficient to exclude cloud droplets. Because there is negligible pressure drop before the sampling ports and the droplets are carried away in the main flow, there is little opportunity for the phase partitioning to be disturbed before the interstitial air sample is isolated from the droplets.

The droplet separator was mounted on a horizontal boom  $\sim 2$  m from the tower and used for sampling in both cloudy and clear conditions. The mist chambers used in carbonyl and carboxylic acid sampling were connected to the droplet separator via  $\sim 3$  m of 4-mm ID Teflon tubing.

## 3. Results and Discussion

### 3.1. Carbonyl Concentrations

Formaldehyde was the dominant carbonyl measured at Pinnacles, with a mean of 980 pptv, compared to 44 pptv CHOCHO and  $< 50$  pptv  $\text{CH}_3\text{C}(\text{O})\text{CHO}$ . Most previous measurements of HCHO at rural sites in North America were made during the summer months and indicate higher concentrations than reported here (Table 2). However, measurements made in March [Harris *et al.*, 1989] indicate lower concentrations. Concentrations of HCHO at Pinnacles were higher than those observed in marine air or the free troposphere, where mean values are generally 100 - 400 pptv [Lowe and Schmidt, 1983; Carlier *et al.*, 1986; Harris *et al.*, 1992; Heikes, 1992]. Maximum carbonyl concentrations were observed during pollution episodes ( $\text{O}_3 \approx 70$  ppbv;  $\text{CO} > 200$  ppbv) on September 5-8 and September 12-13 (Figure 3). These episodes were associated with warm temperatures and stagnant air masses [Jacob *et al.*, this issue]. Carbonyl concentrations were not so high during a subsequent episode a week later that had lower maximum  $\text{O}_3$  ( $\text{O}_3 \approx 50$  ppbv).

Carbonyl concentrations measured in cloudwater are listed in Table 3. Two long-duration cloud events were sampled during SCAPE commencing at 2000 eastern daylight time (EDT) on September 8 and at 0700 EDT on September 13. In both cases the clouds were associated with frontal systems and were part of widespread cloud cover. Meteorological conditions during the cloud events are summarized by Keene *et al.* [this issue]. Additional short-duration events were sampled on September 20 and 22 that are included in the statistics of Table 3 but will not be discussed in detail because they were too short to evaluate temporal trends and cloud was discontinuous. The mean HCHO ( $8\ \mu\text{M}$ ) exceeded glyoxal in the cloudwater by a factor of 4-5 (Table 3) com-

**Table 1.** Performance Characteristics of Inertial Droplet Separator

Characteristic	Value
Inlet flow	$1200\ \text{L}\ \text{min}^{-1}$
Sample flow	$50\ \text{L}\ \text{min}^{-1}$
Velocity at jet (D in Figure 2)	$10\ \text{m}\ \text{s}^{-1}$
Velocity ratio jet/sample	10.5
Reynolds Number at jet	34000
Separation size cut	$1\ \mu\text{m}$
Pressure drop	32 Pa
Outside diameter	10 cm
Inside diameter at jet	5 cm

Table 2. Gas-phase Carbonyl Concentrations at Non-urban Sites

Site	Statistic	pptv			Reference
		HCHO	CHOCHO	CH <sub>3</sub> C(O)CHO	
Pinnacles, Virginia (Sept.)	range	15 - 2600	<20 - 350	≤50	A
Pinnacles, Virginia (Sept.)	Median	755	22	≤50	A
Pinnacles, Virginia (Sept.)	quartile	500-1000	<20 - 50	≤50	A
Pinnacles, Virginia (Sept.)	Mean ± s.d.	976±805	44±66	≤50	A
Pinnacles, Virginia (Sept.)	N	93	93	93	A
Egbert Ontario (July-Aug.)	mean ±s.d.	1800±1000	--	--	B
Dorset, Ontario (July - Aug.)	mean ±s.d.	1600±1000	--	--	B
Dorset, Ontario (April)	range	500 - 2700	--	--	C
Sarnia, Ontario (June-July)	median	1500	--	--	D
Lewes, Delaware (March)	mean	500	--	--	D
Cold Creek, Ontario (July)	range	1200-3000	--	--	D
Scotia, Pennsylvania (July-Aug.)	range	1250-4250	--	--	E
North Carolina (June-July)	range	1000-9000	--	--	F

HCHO, formaldehyde; CHOCHO, glyoxal; CH<sub>3</sub>C(O)CHO, methylglyoxal. A, this study. B, Shepson *et al.* [1991]. C, Hastie *et al.* [1993]. D, Harris *et al.* 1989]. E, Martin *et al.* 1991]. F, Kleindienst *et al.* [1988].

pared to a HCHO:CHOCHO ratio of 20 in the gas phase. Methylglyoxal exceeded its detection limit in ~60% of the cloudwater samples. The ratios of carbonyl concentrations in the fine and coarse fractions were not significantly different from 1, which is expected for the free carbonyl concentrations that were measured because they are unaffected by variations in pH or concentrations of other ions. The cloudwater carbonyl concentrations at Pinnacles were lower than those previously reported for intercepted coastal stratus and inland fog at southern California sites (see Table 3).

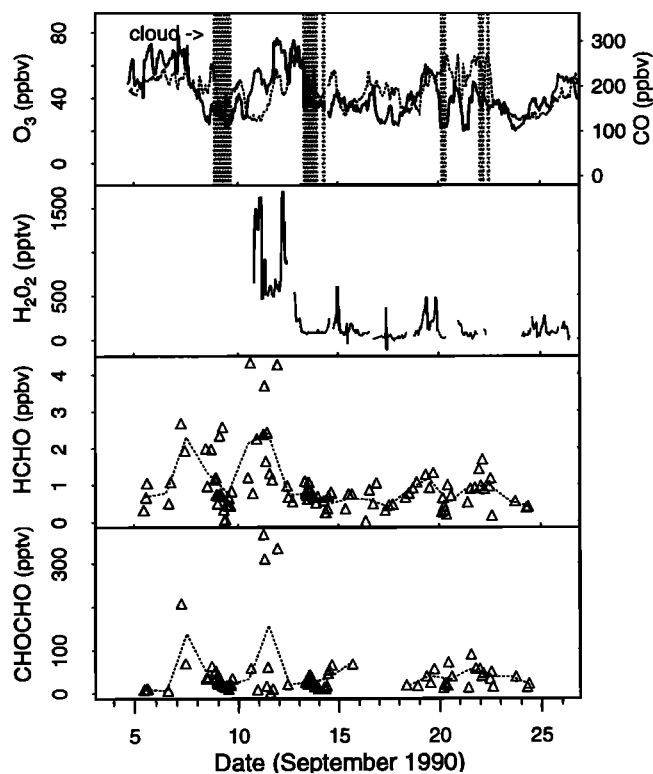
### 3.2. Diel Trends

Diel patterns in the carbonyl concentrations were small relative to synoptic-scale variations (Figure 4). Observations at flatland sites indicate minimum HCHO concentrations at

night due to deposition from a shallow mixed layer [Martin *et al.*, 1991; Hastie *et al.*, 1993]. This effect was not observed at our site because the downslope circulation at night maintained a strong ventilation. Similarly, O<sub>3</sub> and the carboxylic acids [Talbot *et al.*, this issue], which are also depleted during the night at surface sites, had weak diel cycles in our observations. Nighttime ventilation is a general characteristic of observations at mountain sites [Aneja *et al.*, 1991; Poulida *et al.*, 1991].

### 3.3. Sources of Carbonyls

HCHO was correlated with CHOCHO ( $r^2 = 0.43$ ) and with total organic peroxides ( $r^2 = 0.63$ ). The maximum concentrations of HCHO and CHOCHO were observed on September 7 and September 10-11, coincident with episodes of



**Figure 3.** Concentrations of  $O_3$  (solid curves)  $CO$  (dashed curve),  $H_2O_2$ ,  $HCHO$ , and  $CHOCHO$  are shown for the month of September 1990 at Pinnacles, Shenandoah National Park. Concentrations of  $HCHO$  and  $CHOCHO$  in individual samples are indicated by triangles; the dashed curves are 24-hour averages. Cloud interception at the site is indicated by hatching in the upper panel

elevated  $H_2O_2$  (1.5 ppbv) and  $O_3$  (70 ppbv). However, the carbonyls did not correlate with  $O_3$  or  $H_2O_2$  outside these episodes. The highest concentrations of  $NO_y$  and  $CO$  observed during SCAPE were not associated with high carbonyl concentrations. More generally, there was no correlation between carbonyls and these pollutants, implying that anthropogenic sources are not important carbonyl precursors. We also found no correlation between the carbonyls and carboxylic acids ( $HCOOH$  and  $CH_3COOH$ ).

The association between carbonyls and photochemical products, particularly  $ROOH$ , would be consistent with a dominant source for carbonyls from oxidation of biogenic hydrocarbons, e.g., isoprene. We examine this issue further with a one-dimensional photochemical model for the continental boundary layer during SCAPE [Jacob *et al.*, this issue]. Carbonyl compounds are produced in the model by oxidation of isoprene [Paulson and Seinfeld, 1992] and other hydrocarbons [Atkinson, 1990] and are removed by photolysis and reaction with  $OH$  [Atkinson *et al.*, 1993]. We used revised values for the  $CH_3C(O)CHO$  quantum yields [Raber and Moortgat, 1995] that are about twice the values recommended by Atkinson *et al.* [1993].

We present calculations with 24-hour average isoprene emissions of 0, 0.5, and  $1 \times 10^{11}$  molecules  $cm^{-2} s^{-1}$ , including a standard diel cycle [Jacob *et al.*, 1989, 1993]. Constant emissions of  $NO_x$  in the range  $1-2 \times 10^{11}$  molecules  $cm^{-2} s^{-1}$ ,

**Table 3.** Carbonyl Concentrations in Cloudwater

Location	$\mu M$		
	HCHO	CHOCHO	$CH_3C(O)CHO$
<b>Pinnacles, Virginia</b>			
Fine fraction ( $d < 18 \mu m$ )			
minimum	<0.1	<0.15	<0.3
25%ile	3.3	0.7	<0.3
median	7.1	1.9	0.4
mean $\pm$ s.d.	$8.9 \pm 8.4$	$2.2 \pm 2.8$	<0.8 <sup>a</sup>
75%ile	13.4	2.6	0.7
maximum	21.9	12.4	9.4
N	37	37	37
Coarse fraction ( $d > 18 \mu m$ )			
minimum	0.8	<3	<0.3
25%ile	4.6	0.6	<0.3
median	7.8	1.2	<0.3
mean $\pm$ s.d.	$7.9 \pm 5.9$	$1.4 \pm 1.5$	<0.3 <sup>a</sup>
75%ile	13.1	2.3	0.4
maximum	20.4	6.2	1.7
N	33	33	33
Henninger Flats, California <sup>b</sup>	11-142	--	--
San Pedro Hill, California <sup>b</sup>	5-50	--	--
Ventura, California <sup>c</sup>	3-33	5-27	3-7
Riverside, California <sup>d</sup>	4-228	35-276	25-128

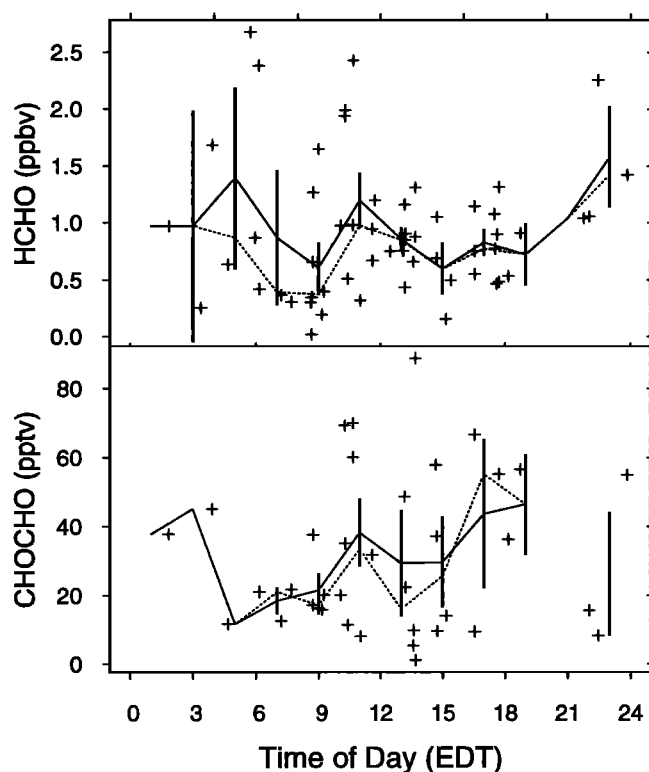
<sup>a</sup> Statistics are computed using apparent concentrations and reported as an upper limit if the result is below the detection limit.

<sup>b</sup> Range, Munger *et al.* [1989].

<sup>c</sup> Range, Munger [1989].

<sup>d</sup> Range, Munger *et al.* [1990].

depending on the isoprene flux, are assumed in order to match the mean noontime  $NO$  concentration of 0.4 ppbv measured in SCAPE. Average ethene and propene emission rates for the eastern United States are used [McKeen *et al.*, 1991], representing presumably upper limits for this site, which is relatively clean compared to most sites in the eastern United States. Fixed boundary layer concentrations of  $CO$  (200 ppbv),  $CH_4$  (1.7 ppmv),  $C_2H_6$  (2.2 ppbv),  $C_3H_8$  (1.3



**Figure 4.** Mean diel cycles of HCHO and CHOCHO gas-phase concentrations (excluding cloudy air) are shown as a function of local (eastern daylight) time. Solid lines show 2-hourly means and the associated standard errors; medians are given by dashed lines. The pluses show the concentrations in individual samples. Peak values observed on September 12 that appear as outliers in Figure 3 have been excluded from the means as being unrepresentative of the diel trends.

ppbv),  $C_6H_6$  (50 ppt), toluene (50 pptv), acetone (1 ppbv), and  $C_4$ - $C_5$  alkanes (100 pptv) are assumed [Jacob *et al.*, this issue; Trainer *et al.*, 1991; D. Pierotti, unpublished data, 1990]. The UV radiation intensities are computed for the equinox (September 21) assuming clear-sky conditions and an  $O_3$  column of 290 Dobson units. The chemical evolution of the model boundary layer is integrated for four diel cycles, starting from low initial concentrations of  $NO_x$ ,  $O_3$ , non-methane hydrocarbons and hydrocarbon oxidation products. The carbonyl concentrations are near steady state by the second day of simulation. Ozone concentrations grow from an initial concentration of 25 ppbv to a value of 40-60 ppbv, depending on isoprene flux, after 4 days.

The 24-hour average concentrations of HCHO, CHOCHO, and  $CH_3C(O)CHO$  at 1 km altitude on day 4 of the simulation are shown in Table 4. Formaldehyde production in the model is dominated by the oxidation of isoprene and methane. The dominant sources of glyoxal and methylglyoxal are the oxidation of glycolaldehyde ( $HOCH_2CHO$ ) and hydroxyacetone ( $HOCH_2C(O)CH_3$ ), respectively, which are both products of isoprene oxidation. Production of glyoxal and methylglyoxal from other hydrocarbons is negligible. Losses from photolysis and oxidation by OH lead to carbonyl lifetimes at noon of 2 hours for HCHO, 1.7 hours for CHOCHO, and 25 min for  $CH_3C(O)CHO$ .

The mean  $CH_3C(O)CHO$  concentrations predicted in the simulation are below our detection limits for  $CH_3C(O)CHO$ . The observed mean HCHO and CHOCHO concentrations (Table 2) are in reasonable agreement with the simulation using an isoprene flux of  $5 \times 10^{10}$  molecules  $cm^{-2} s^{-1}$ , which is somewhat lower than the typical midsummer value estimated for the region. Above average carbonyl concentrations, which are consistent with the high isoprene simulation, were observed only in the first half of September but not later in the month as the vegetation came closer to senescence, resulting in a shutoff of isoprene emission [Goldstein, 1994; Monson *et al.*, 1994]. Decreased solar radiation and water vapor between September 1 and October 1 [Jacob *et al.*, this issue] had a negligible effect on carbonyl concentrations, because both the formation and the destruction of carbonyls are photochemical processes. The difference noted in section 3.1 between HCHO concentrations at Pinnacles and other rural sites during the summer is consistent with a seasonal cycle of HCHO that parallels isoprene emissions. The importance of isoprene as a HCHO precursor is in agreement with Shepson *et al.* [1991] who argued that isoprene is a major source of HCHO based on observed HCHO: $CH_3CHO$  ratios at a rural site in Ontario.

### 3.4. Aqueous Phase Partitioning

Finally, we examine the phase partitioning of carbonyls during cloud events. Because carbonyl solubility is pH independent and our method does not include any adducts that may be present, carbonyl concentrations should be independent of droplet size if they are entirely controlled by equilibrium with the surrounding gas. In general, the fraction,  $f$ , of soluble gas in cloud droplets at equilibrium is given by

$$f = LRTH^*/(1+LRTH^*), \quad (1)$$

where  $L$  is the liquid water content of the cloud,  $R$  is the gas constant,  $H^*$  is an effective Henry's law constant

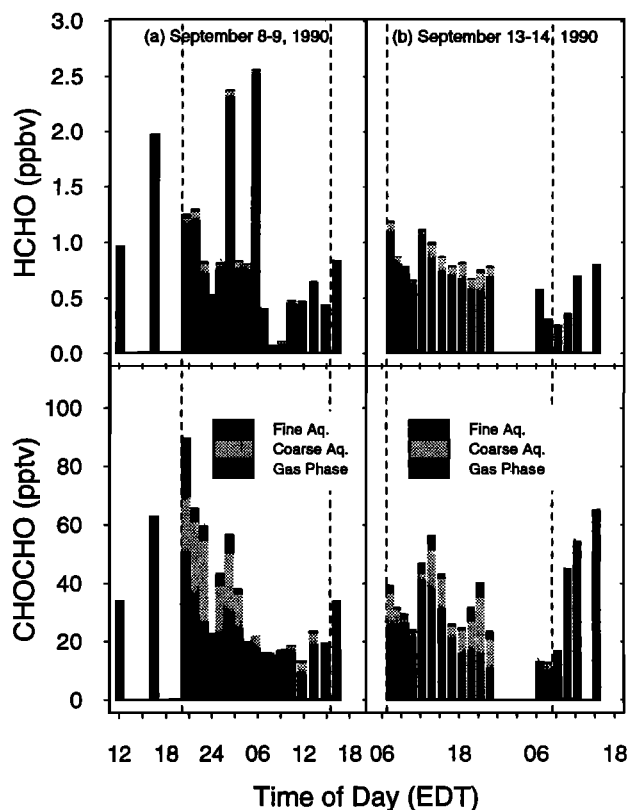
$$H^* = [C]_{total}/P \quad (2)$$

**Table 4.** Simulated Carbonyl Concentrations, pptv

	isoprene flux (molecule $cm^{-2} s^{-1}$ )		
	0	$0.5 \times 10^{11}$	$1.1 \times 10^{11}$
HCHO	700	1260	1800
CHOCHO	3.4	27	51
$CH_3C(O)CHO$	1.3	22	46
Fractional contributions to HCHO production			
isoprene	---	0.44	0.60
methane	0.73	0.41	0.28
other	0.27	0.15	0.12

Twenty-four-hour mean concentrations at 1 km altitude obtained in a one-dimensional boundary layer model for the conditions observed in Shenandoah Cloud and Photochemistry Experiment.





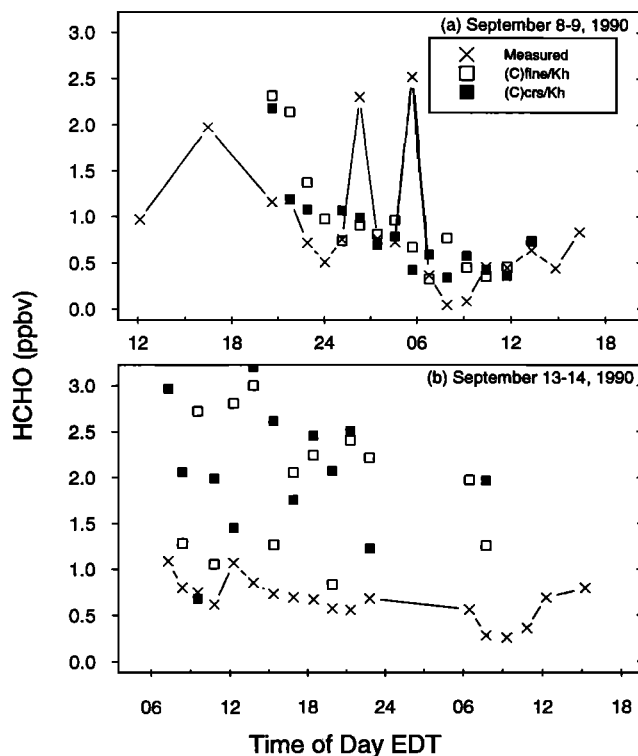
**Figure 5.** Relative contributions of gas phase, coarse cloud droplets ( $d > 18 \mu\text{m}$ ), and fine cloud droplets ( $5.5 < d < 18 \mu\text{m}$ ) to the total atmospheric concentrations of HCHO and CHOCHO are shown versus local (eastern daylight) time during cloud events sampled on (a) September 8-9, and (b) September 13, 1990, at Pinnacles, Shenandoah National Park. The fraction of carbonyl in the droplets is determined from the measured concentration and liquid water content for each fraction. Starting and ending time of the cloud event are indicated by vertical dashed lines.

that relates partial pressure,  $P$ , to total aqueous concentration,  $[C]_{\text{total}}$ , including thermodynamic equilibria (e.g., hydration, dissociation, or complexation), and  $T$  is the temperature. For the carbonyls only the hydration equilibria are included in  $H^*$ . At typical LWC of the order of  $0.1 \text{ g m}^{-3}$ ,  $H^*$  must exceed  $\sim 10^5 \text{ M atm}^{-1}$  to reach 50% partitioning in the droplets.

Gas- and aqueous-phase concentrations of HCHO and CHOCHO during the cloud events are shown in Figures 5a and 5b. Concentrations of  $\text{CH}_3\text{C(O)CHO}$  were too low for meaningful comparisons. The concentrations in fine and coarse fractions were indistinguishable (Table 3). Aqueous-phase concentrations measured in the cloudwater samples were scaled by the cloud liquid water contents [Keene *et al.*, this issue], to convert to atmospheric mixing ratios. The coarse droplets ( $d > 18 \mu\text{m}$ ) generally had a larger fraction of the LWC, which accounts for their higher contributions to total carbonyl loadings. Formaldehyde, with an effective Henry's law constant of  $2970 \text{ M atm}^{-1}$  at  $25^\circ\text{C}$  ( $\Delta H = -60 \text{ kJ mole}^{-1}$ ) [Betterson, 1992] is predominantly in the gas phase during both cloud events. Up to 50% of glyoxal, with an effective Henry's law constant of  $\geq 3 \times 10^5 \text{ M atm}^{-1}$  [Betterson and Hoffmann, 1988], is in the aqueous phase at times.

Despite differences in trajectories leading to lower pH and higher levels of inorganic acids in samples from September 13 compared to September 8 [Keene *et al.*, this issue], total carbonyl concentrations were similar for the two cloud events. During both cloud events the carbonyl concentrations tend to decrease over the duration of the cloud. Increased upslope flow associated with cloud dissipation could account for the rise in carbonyls, as well as concomitant increases in cloudwater  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  and carboxylic acids [Keene *et al.*, this issue].

Measured CHOCHO concentrations in the gas phase and CHOCHO partial pressures calculated to be in thermodynamic equilibrium with measured aqueous-phase concentrations were at or below the detection limit of 10 pptv. Although consistent with thermodynamics, limited analytical resolution precluded more detailed analysis of CHOCHO phase partitioning. Figure 6 compares the measured gas-phase HCHO with the predicted equilibrium partial pressure determined from the measured aqueous concentrations. Measured and predicted HCHO were similar, but individual points from the September 8 event varied by up to a factor of 2. Two samples with gas-phase concentrations  $> 2 \text{ ppbv}$  are suspect, but we have no independent reasons to exclude



**Figure 6.** Measured and equilibrium partial pressure of HCHO is plotted against local (eastern standard) time during the cloud events sampled at Pinnacles, Shenandoah National Park. Measured gas-phase concentrations are indicated by crosses and connected by lines. The partial pressures in equilibrium with fine ( $5.5 < d < 18 \mu\text{m}$ ) and coarse ( $d > 18 \mu\text{m}$ ) droplets are indicated by open and solid squares, respectively. The equilibrium constants and temperature coefficients used in the calculation are given in the text.

them. Keene *et al.* [this issue] also observed good agreement between measured and predicted carboxylic acid concentrations during the September 8 cloud.

The droplets were considerably oversaturated with respect to gas-phase HCHO and cloudwater concentrations were less uniform during the September 13 cloud event. Keene *et al.* [this issue] also observed the greatest deviations from equilibrium by HCOOH during the September 13 cloud event. The influence of canopy water, which they suggest would damp temporal fluctuations in the gas phase, cannot explain the consistent HCHO oversaturation. One possible explanation for the apparent excess HCHO is hydrolysis of HOCH<sub>2</sub>OOH (hydroxymethylhydroperoxide (HMHP)) after collection. Significant concentrations of HMHP have been observed in air above a forest [Lee *et al.*, 1993] and in precipitation [Hellpointner and Gäb, 1989]. Heterogeneous pathways involving H<sub>2</sub>O addition to the Criegee intermediates from ozonolysis of biogenic hydrocarbons have been suggested as possible mechanisms to form HMHP in the atmosphere [Gäb *et al.*, 1985]. HMHP has a Henry's law constant of  $5 \times 10^5 \text{ M atm}^{-1}$  at 22°C. HMHP hydrolysis to H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>C(OH)<sub>2</sub>, the hydrated form of HCHO is base catalyzed  $\tau_{1/2}$  increases from 3 min at pH 7 to > 1 hour at pH < 5.7 [Zhou and Lee, 1992]. Empirical evidence, however, indicates that HMHP partially hydrolyzes to yield artifact H<sub>2</sub>O<sub>2</sub> even at pH 3 [Lee *et al.*, 1993]. For carbonyl analysis, aliquots are brought to pH ≈ 1 and are allowed to incubate with 2,4-DNPH for several hours. Some hydrolysis may occur in this interval, or HMHP may react directly with 2,4-DNPH to form a hydrazone.

#### 4. Summary

The mean gas-phase concentrations of HCHO and CHOCHO observed during September 1990 at Pinnacles in Shenandoah National Park were 980 and 40 pptv, respectively; CH<sub>3</sub>C(O)CHO was generally < 50 pptv. The carbonyl data are consistent with oxidation of isoprene being a major source of HCHO and CHOCHO. The maximum concentrations (HCHO > 2 ppbv, CHOCHO > 100 pptv) were observed during stagnation episodes with warm temperatures and elevated levels of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. Although high levels of primary pollutants, NO<sub>y</sub> and CO, were also observed during these periods, there was no correlation between them and the carbonyls. The short lifetime against photolysis (25 min at noon) explains the generally low concentrations of CH<sub>3</sub>C(O)CHO. No strong diel cycles were observed for either HCHO or CHOCHO. As much as 50% of CHOCHO is partitioned to the aqueous phase during cloudy periods, while HCHO remains > 90% in the gas phase. The carbonyl concentrations measured in the fine and coarse droplet fractions showed no significant differences, which is consistent with rapid equilibrium between the gas and the aqueous phases. Formaldehyde concentrations in the cloudwater were significantly higher than expected from equilibrium with the gas phase during a daytime cloud event. HMHP, which can be formed from ozone-alkene reactions, is highly soluble and its hydrolysis to HCHO and H<sub>2</sub>O<sub>2</sub> during the carbonyl analysis could perhaps account for the excess HCHO.

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