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Intercomparison of six ambient [CH_2O] measurement techniques

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Abstract. From May 29 to June 3, 1995 a blind intercomparison of six ambient formaldehyde measurement techniques took place at a field site near the National Center for Atmospheric Research in Boulder, Colorado. The continuous measurement methods intercompared were tunable diode laser absorption spectroscopy, (TDLAS); coil/2,4-dinitrophenylhydrazine, (CDNPH); 1,3-cyclohexanedione-diffusion scrubber (CHDDS); and the coil enzyme method (CENZ). In addition, two different cartridge methods were compared: silica gel-2,4-dinitrophenylhydrazine (DPNH) systems and a C-18-DNPH system. The intercomparison was conducted with spiked zero air (part 1) and ambient air (part 2). The CH_2O standards for part 1 were calibrated by several independent methods and delivered to participants via a common glass manifold with potential trace gas interferants common to ambient air (O_3, SO_2, NO_2, isoprene, H_2O). The TDLAS system was used to confirm the absolute accuracy of the standards and served as a mission reference for part 1. The ambient phase lasted 44 hours with all participants sampling from a common glass tower. Differences between the ambient [CH_2O] observed by the TDLAS and the other continuous methods were significant in some cases. For matched ambient measurement times the average ratios ($\pm 1\sigma$) $[CH_2O]_{measured}/[CH_2O]_{TDLAS}$ were: 0.89 ± 0.12 (CDNPH); 1.30 ± 0.02 (CHDDS); 0.63 ± 0.03 (CENZ). The methods showed similar variations but different absolute values and the divergences appeared to result largely from calibration differences (no gas phase standards were used by groups other than NCAR). When the regressions of the participant [CH_2O] values versus the TDLAS values, (measured in part 1), were used to normalize all of the results to the common gas phase standards of the NCAR group, the average ratios ($\pm 1\sigma$), $[CH_2O]_{corrected}/[CH_2O]_{TDLAS}$ for the first measurement period were much closer to unity: 1.04 ± 0.14 (CDNPH), 1.00 ± 0.11 (CHDDS), and 0.82 ± 0.08 (CENZ). With the continuous methods used here, no unequivocal interferences were seen when SO_2, NO_2, O_3, and isoprene impurities were added to prepared mixtures or when these were present in ambient air. The measurements with the C-18 DNPH (no O_3 scrubber) and silica gel DNPH cartridges (with O_3 scrubber) showed a reasonable correlation with the TDLAS measurements, although the results from the silica cartridges were about a factor of two below the standards in the spike experiments and about 35% below in the ambient measurements. Using the NCAR gas-phase spike data to calibrate the response of the silica gel cartridges in the ambient studies, the results are the same within statistical uncertainty. When the same gas phase calibration was used with the C-18 cartridges, the results showed a positive bias of about 35%, presumably reflecting a positive ozone interference in this case (no ozone scrubber used). The silica DNPH cartridge results from the second participant were highly scattered and showed no significant correlation with the TDLAS measurements.

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1. Introduction

Formaldehyde (CH_2O) is a ubiquitous component of both the remote atmosphere and polluted urban atmospheres. It is a primary emission product from hydrocarbon combustion sources, such as the internal combustion engine, and is produced in the atmosphere by the photochemical oxidation of methane and the great variety of nonmethane hydrocarbons (NMHCs) which are present in most tropospheric air masses [National Research Council (NRC), 1981]. The predominant source of urban formaldehyde is believed to be the photooxidation of the many hydrocarbons that are present in the atmosphere [*Altshuller*, 1993]. In rural areas of dense vegetation, biogenic sources are often the dominant precursor. For example, isoprene oxidation initiated by reactions with either OH or O_3 efficiently forms formaldehyde along with several other key atmospheric species [*Paulson et al.*, 1992a, b]. Formaldehyde is the most abundant gas-phase carbonyl

compound in both urban areas and the remote troposphere. In the late 60's, formaldehyde concentrations greater than 120 ppbv (parts per billion by volume) were observed by unambiguous spectroscopic techniques (Fourier transform infrared (FTIR)) in polluted urban areas near Los Angeles [*Scott Research Laboratories*, 1969]. During the 1980-1995 period the sparse data available show that the average concentrations in many major cities ranged from about 3 to 16 ppbv with maxima as high as 68 ppbv in Downey, California [*Grosjean et al.*, 1993]. Representative of more remote locations, typical average concentrations for the Colorado Mountains are around 1 ppbv during the summer-fall months [*Harder et al.*, 1997a] and between 50-500 pptv (parts per trillion by volume) for Mauna Loa Observatory, Hawaii [*Zhou et al.*, 1996; *Mackay et al.*, 1996; *Heikes*, 1992; *Heikes et al.*, 1996].

Interest in ambient concentrations of CH_2O derives both from concerns over health effects [*NRC*, 1976, 1981] and from the primary role that formaldehyde plays in tropospheric chemistry cycles [*Calvert*, 1980]. Photodecomposition of formaldehyde occurs through two distinct modes [*Horowitz and Calvert*, 1978; *Moortgat and Warneck*, 1979; *Moortgat et al.*, 1980, 1983]:

$$CH_2O + h\nu\ (\lambda < 337\ \text{nm}) \rightarrow HCO + H \qquad (1a)$$

$$CH_2O + h\nu\ (\lambda < 360\ \text{nm}) \rightarrow H_2 + CO \qquad (1b)$$

In the lower atmosphere the primary process 1a is always followed by the generation of HO_2 radicals:

$$H + O_2 + M(N_2/O_2) \rightarrow HO_2 + M\ (N_2/O_2) \qquad (2)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (3)$$

Through reactions 1a, 2, and 3, formaldehyde is a major source of odd hydrogen ([HO_2] + [OH] + [H]) in the atmosphere, and as such, it is an important driving force in converting NO to NO_2 with subsequent O_3 generation [*Cantrell et al.*, 1990]. The process 1b represents one of the major sources of atmospheric CO and molecular hydrogen in the nonurban troposphere.

Accurate measurements of formaldehyde are critical to our understanding of the overall tropospheric chemistry associated with hydrocarbon oxidation, the processes controlling the odd hydrogen and the nitrogen cycles, the global budgets of OH and CO, and tropospheric ozone generation [*NRC*, 1991], all key issues in atmospheric science today. Because of the importance of formaldehyde, researchers have developed several independent techniques for its measurement in ambient air. Several spectroscopic techniques have been employed: Fourier transform infrared spectroscopy (FTIR) [*Scott Research Laboratories*, 1969; *Lawson et al.*, 1990], differential optical absorption spectroscopy (DOAS) [*Platt and Perner*, 1980; *Harder et al.*, 1997b], and tunable diode laser absorption spectroscopy (TDLAS) [*Harris et al.*, 1989, 1992; *Mackay et al.*, 1990, 1996; *Harder et al.*, 1997a]. Several continuous, automated solution phase methods have been developed also: the coil enzyme (CENZ) fluorometric method [*Lazrus et al.*, 1988; *Heikes*, 1992; and *Heikes et al.*, 1996], the cyclohexanedione diffusion scrubber (CHDDS) method [*Fan and Dasgupta*, 1994], and a coil 2,4-dinitrophenylhydrazine (DNPH) derivatization technique (CDNPH) [*Lee and Zhou*, 1993; *Zhou et al.*, 1996]. In addition to these continuous measurement methods, a widespread use has been made of DNPH silica gel cartridges (SGC) and DNPH octadecylsilica cartridges (C-18 SGC) [e.g., *Fung and Grosjean*, 1981; *Zhou and Mopper*, 1990]; for example, these techniques are now employed in the extensive measurement program of the Photochemical Assessment and Monitoring Stations (PAMS) in U.S. urban areas which exceed the national ambient air quality standard for ozone. Arising from such widespread use, considerable effort has been devoted to studying and comparing the results from the various DNPH cartridge methods. These studies suggest that there may be subtle but important differences for sampling with C-18 silica gel versus silica gel and that the presence of ozone in the sampled air (unscrubbed) may exacerbate these differences [e.g., *Rodier and Birks*, 1994; *Rodier et al.*, 1993; *Sirju and Shepson*, 1995; *Arnts and Tejada*, 1989].

Several intercomparisons of both the continuous and the integrated cartridge techniques of [CH_2O] measurements have been carried out in recent years: *Kleindienst et al.* [1988] compared TDLAS, CENZ, CHDDS, CDNPH, and SGC methods for [CH_2O] (1-100 ppbv) in prepared laboratory mixtures and ambient air; *Lawson et al.* [1990] employed FTIR, DOAS, TDLAS, CHDDS, CENZ, and SGC methods to determine [CH_2O] (4-25 ppbv) in urban ambient air; *Heikes et al.* [1996] and *Mackay et al.* [1996] compared [CH_2O] measurements using a TDLAS, CDNPH, CENZ, and an immobilized enzyme system [G. Kok, National Center for Atmospheric Research (NCAR), private communication, 1991-1992] in clean remote background air at Mauna Loa, Hawaii (50-500 pptv); *Mücke et al.* [1996] compared [CH_2O] in standards (no interferants added) and in ambient air (0.8-15 ppbv) using TDLAS and CENZ techniques; *Harder et al.* [1997a] intercompared TDLAS and long-path DOAS systems in measurements of [CH_2O] in ambient Colorado mountain air (0.8-1.5 ppbv). Typical of the variations seen between different techniques in previous [CH_2O] intercomparisons are those reported from the urban air study of *Lawson et al.* [1990]. In the 4-25 ppbv range of [CH_2O] the spectroscopic techniques agreed to within 15% of their common mean. Compared with the spectroscopic mean, the CENZ technique gave results that were about 25% higher, the CHDDS method gave values about 25% lower, and the DNPH SGC cartridges gave values 15-20% lower, with somewhat lower values for the longer sampling periods. Much larger differences were obtained in an intercomparison in pristine air masses [*Heikes et al.*, 1996].

The results of all previous intercomparisons point to unresolved fundamental measurement and calibration issues and suggest strongly that further work is necessary to resolve these problems. Common CH_2O standards were not employed in most of the previous studies, and the reasons for the deviations seen between methods remains largely unexplained. The present CH_2O intercomparison study was designed to address these issues; it employed the generation and verification of CH_2O reference standards, based on several independent experimental approaches. This proved to be invaluable in the subsequent interpretation of the data.

In part 1 of this study, CH_2O reference standards (0.3 to 6 ppbv) in a synthetic air matrix, including potential interferants, were input to an all-glass-sampling manifold and presented as unknowns to the operators of the six experimental techniques. The concentration range employed bridges the gap between tropospheric background levels and those encountered in rural to moderately polluted urban areas. In this part of

the study, a TDLAS developed at NCAR [*Fried et al.*, 1997] was employed as part of the mission reference. Six [CH_2O] measurement techniques, representative of a cross section of the methods currently used in field measurement programs, were intercompared in this study: the DNPH coil technique (Y.-N. Lee, Brookhaven National Laboratory (BNL) [*Lee and Zhou*, 1993]); CHDDS employing the Hantzsch reaction (Z. Genfa and P. Dasgupta, Texas Tech University (TTU) [*Fan and Dasgupta*, 1994]); the flowing, coil enzyme method (B. Heikes, University of Rhode Island (URI) [*Heikes*, 1992]); two integrated sampling techniques employing silica gel cartridges impregnated with DNPH (B. Hopkins and H. Westberg, Washington State University (WSU) and T. Kleindienst, ManTech Environmental (MTE)), and the DNPH-C-18-SGC integrated sample technique (T. Kleindienst, MTE).

In part 2 of this study, the same six methods were used to sample ambient air supplied from a common glass inlet tower. During this phase the TDLAS was an active participant. The results of the present study will help in defining the limitations of current methodologies and in the formulation of recommendations for CH_2O measurement and calibration strategies to be deployed in future large-scale field studies.

2. Experiment

Site location and protocol. The 1995 intercomparison study was held at a field site located on the grounds of the NCAR Mesa Laboratory (39°58′45″ latitude, 1880 m elevation) during the period, May 29 to June 3, 1995. The time and location of the intercomparison were chosen in order to obtain both the low background levels of formaldehyde (500 pptv) and the potential for higher levels (>10 ppbv), characteristic of urban environments. Ambient measurements for CH_2O were taken by all participants at the NCAR site from 1200 of June 1 until 1800 of June 2, 1995 (first period). However, both the TDLAS (NCAR) and the CENZ (URI) systems continued to sample from 1800 of June 2 until the 0800 of June 3 (second measurement period). Samples were taken continuously except for periods of calibration and necessary interrupts during the measurement cycles of the continuous instruments; for the cartridges, sampling times ranged between 2 and 6 hours. During the first day of the ambient measurements (June 1) the weather was sunny and clear with moderate temperatures (20°-25°C) during the day and clear with a slight wind at night. The second day (June 2) was also sunny until late afternoon when it rained with increasing intensity throughout the day, resulting in somewhat cooler temperatures.

Because of the role of the TDLAS system during part 1 of the study (the standards phase), the scientist in charge of its operation (Fried) was an integral part of the referee group for this phase. In addition to providing verification of the calibration source, the TDLAS system was also used to measure the actual CH_2O concentrations delivered to the glass manifold on a continuous basis. During part 2, the ambient measurement phase of the study, the TDLAS system was treated as another participant, and these results were submitted blind to the referees (Calvert, Apel, Gilpin).

The physical arrangements at the intercomparison site consisted of two large shipping containers (sea-tainers) set up to house the participants and their equipment during the experiment. Sea-tainer-I (Figure 1a) housed the NCAR

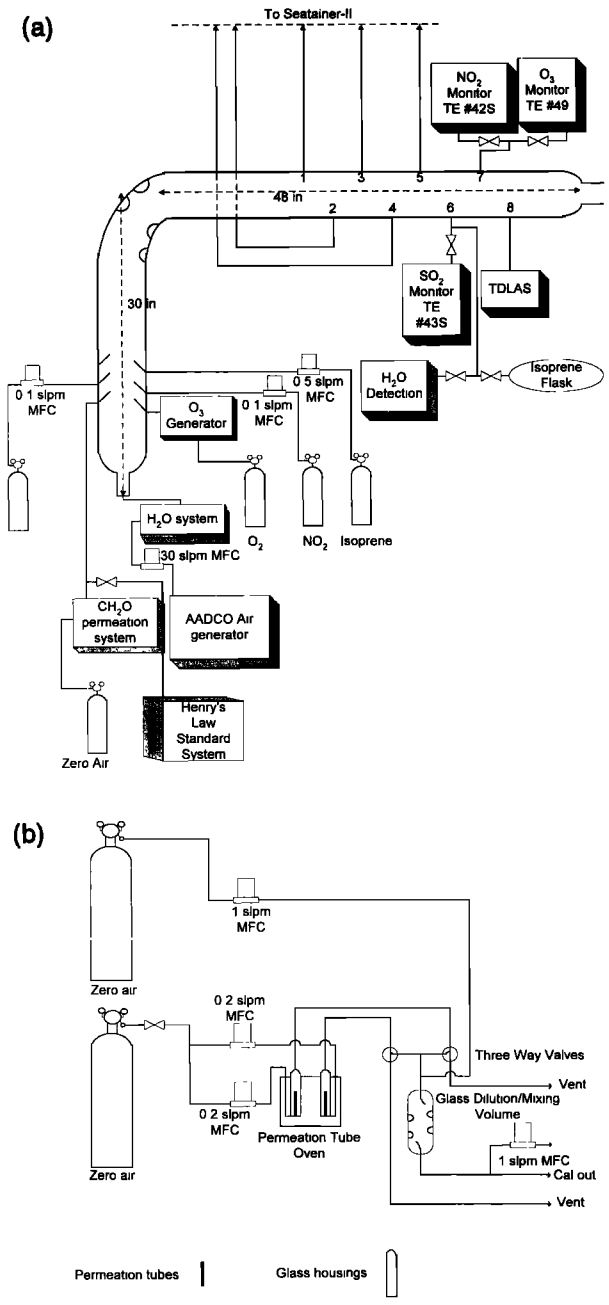

Figure 1. (a) Diagram of the glass manifold in sea-tainer-I used in the preparation and delivery of the prepared standard [CH_2O] mixtures to the participants in sea-tainer-II; see text for details of its use. (b) Diagram of the permeation/diffusion tube system employed in the intercomparison. See the discussion in the text. MFC represents a mass flow controller.

personnel along with the TDLAS, synthetic air manifold, and standards generation equipment. Sea-tainer-II housed all five other participants and their equipment.

In part 1 of this study, participants were challenged with a synthetic air mixture from a common glass manifold containing accurately calibrated standard samples of CH_2O (composition known only to NCAR personnel, sea-tainer-I) and varying concentrations of the potential interferants, NO_2, SO_2, O_3, isoprene, and water vapor, representing either interesting test case scenarios or ambient air. In part 2, ambient air was

Table 1. Comparison of Spike Sample Results From NCAR Formaldehyde Intercomparison, May 29 to June 3, 1995

	Formaldehyde Concentration, ppbv										Added Impurities, ppbv					
Expt	NCAR[a] (source)	NCAR (TDLAS)	BNL CDNPH	TTU CHDDS	URI(a)[b] CENZ	URI(b)[b] CENZ	WSU(a)[c] Silica	WSU(b)[c] Silica	MTE(a)[d] C-18	MTE(b)[d] Silica	O_3	C_5H_8	NO_2	SO_2	H_2O (%RH)	Scrub[e]
1a[f]	1.70	1.71 ± 0.14[g]	2.04 ± 0.22	2.28 ± 0.20	1.35 ± 0.06	1.36 ± 0.04	0.67	1.13	1.03 ± 0.14	1.14 ± 0.07	...	...	...	...	...	out
2a	0.00	-0.03 ± 0.12	0.02 ± 0.03	0.0	0.01 ± 0.02	0.02 ± 0.02	1.56	2.63	BDL	BDL	...	...	...	...	...	in
1b	1.51	1.53 ± 0.14	1.34 ± 0.07	2.35 ± 0.08	1.62 ± 0.04	1.61 ± 0.04	2.11	3.56	2.01 ± 0.14	0.64 ± 0.07	50	...	...	...	...	in
1b′	1.60	1.78 ± 0.42[h]	1.43 ± 0.10	2.37 ± 0.12	1.60 ± 0.06	1.62 ± 0.06	NS	NS	NS	NS	50	...	...	...	...	in
2b	1.28	1.32 ± 0.16	1.07 ± 0.04	1.90 ± 0.10	1.06 ± 0.10	1.09 ± 0.10	2.70	4.54	0.84 ± 0.14	0.89 ± 0.08	...	...	27	52	...	in
3b	0.29	0.28 ± 0.08	0.29 ± 0.04	0.47 ± 0.06	0.27 ± 0.04	0.27 ± 0.04	2.19	3.68	0.11 ± 0.14	0.18 ± 0.08	...	...	...	...	...	in
4b	1.23	1.37 ± 0.07	1.16 ± 0.12	2.03 ± 0.22	1.22 ± 0.02	1.24 ± 0.02	1.87	3.15	1.93 ± 0.10	0.41 ± 0.05	54	9	...	...	...	in
5b	0.28	0.38 ± 0.08	0.31 ± 0.04	0.53 ± 0.06	0.33 ± 0.08	0.33 ± 0.06	1.81	3.05	1.40 ± 0.14	0.17 ± 0.07	54	5	4	4	...	in
1c	5.64	5.30 ± 0.13	5.67 ± 0.96[i]	6.87 ± 0.28	4.20 ± 0.26	4.21 ± 0.16	3.27	5.51	3.73 ± .14	4.04 ± 0.07	...	...	...	...	...	in
2c	5.29	5.35 ± 0.26	4.43 ± 0.18	7.27 ± 0.34	3.89 ± 0.08	3.90 ± 0.06	3.04	5.12	NS	NS	100	10	41	41	7.5	in
3c	5.24	5.56 ± 0.04	4.22 ± 0.26	7.16 ± 0.28	NS	NS	1.15	1.94	4.90 ± 0.21	1.74 ± 0.11	95	6	40	40	7.0	out
4c	5.30	5.52 ± 0.13	4.36 ± 0.10	7.23 ± 0.22	3.99 ± 0.10	4.03 ± 0.14	2.26	3.81	5.01 ± 0.21	2.38 ± 0.12	95	10	40	40	7.0	in
5c	5.25	5.43 ± 0.14	4.33 ± 0.20	7.80 ± 0.20	4.03 ± 0.24	4.05 ± 0.20	1.97	3.31	5.08 ± 0.21	3.95 ± 0.11	90	...	40	40	78	in
6c	5.27	5.54 ± 0.04	4.21 ± 0.36	7.66 ± 1.02	3.97 ± 0.20	4.08 ± 0.16	3.91	6.58	4.50 ± 0.21	3.85 ± 0.10	50	10	...	...	78	in
6c′	4.74	4.94 ± 0.20	3.89 ± 0.14	6.85 ± 0.14	3.70 ± 0.04	3.73 ± 0.06	NS	NS	NS	NS	50	10	...	...	78	in

NCAR, National Center for Atmospheric Research; Expt, experiment; NS, not sampled; BDL, below detection limit.

[a]Values from the calibration sources (Henry's law and permeation tube sources) and do not include the small amount of CH_2O formed from isoprene-ozone reaction; see text for estimates of these amounts.

[b]URI(a) and URI(b) are results of University of Rhode Island (B. Heikes) using two different detectors but with the same coil collector and enzyme-catalyzed chemical derivatization method.

[c](a) Values were first reported; (b) corrected values reported September 15, 1995. The estimated precision (from multiple analyses of standards) is ± 0.1 ppbv; the LOD for the 90 min sampling period and flow rates used here was about 0.4 ppbv.

[d]For MTE(a) and MTE(b), C-18 (DNPH) and silica gel (DNPH) cartridges, respectively, were used by ManTech Environmental (T. Kleindienst). The uncertainties given are calculated from 3 times the variation in the blank value/mole of air sampled.

[e]KI O_3 scrubbers were used only by the participants using the DNPH-silica cartridges (not the C-18) in the experiments marked "in."

[f]Letter indicates the sequence of days, while the number gives the order of the experiments for that day.

[g]For all continuous instrument measurements the range shown gives the 2σ distribution of measured values during the measurement period.

[h]This value may be unreliable (reflected in the large uncertainty in the value) which may have resulted from insufficient manifold flow to TDLAS during this experiment.

[i]The rather large range here resulted from a drift in the BNL instrument signal during these measurements; see text for a discussion of this point.

sampled from a common glass manifold tower, 6.1 m in length, entrance 6.0 m above the ground; a 180° bend at the top of the column pointed the inlet toward the ground and prevented precipitation from entering.

The referee group disclosed to the participants the general range of the standard spikes of CH_2O (0.1 to 10 ppbv) and the times to begin and to stop sampling. Preliminary data from the continuous techniques, including the TDLAS system, were submitted to the NCAR referee group immediately after the first standards test (experiment 1a, Table 1) with the intent to identify any potential major problems at the earliest possible stage. Analyses for the two cartridge groups were performed at their home laboratories, and their results obtained in part 1 could not be reported to the referees until after the study was completed. The reported preliminary [CH_2O] results from the CENZ (URI) system were approximately a factor of 2 lower than both the TDLAS measured values and the calculated input values. The TTU scientists reported an uncertainty in the accuracy of the CHDDS system which required a home laboratory calibration, so the preliminary results were reported during the intercomparison as uncalibrated instrument signals. A preliminary value ≥ 1.5 ppbv was reported for experiment 1a from the CDNPH system by the BNL scientist (NCAR value 1.70 ppbv). The referee group at that time asked the participants to check their systems to ensure that they were operating properly. Neither the direction nor the magnitude of the discrepancy were divulged. A comprehensive discussion of these results and the associated explanations are given in section 4.

At no time were data exchanged between groups during or after the intercomparison. Preliminary results were reported to the referees (CHDDS as raw signals) at the end of each day by the operators of the continuous methods. Final results of all measurements were returned within a few weeks directly to the NCAR referee group. The reported results, together with a summary of a preliminary study of these results by the NCAR group, were sent to all participants on July 28, 1995, and a workshop to discuss the results was held at NCAR from October 11-12, 1995.

Calibration of formaldehyde gas phase standards. An important and unique aspect of the present intercomparison study is the high degree of confidence in the absolute accuracy of the CH_2O gas-phase standards employed. The output concentration of these standards was determined and/or verified by employing four independent techniques: (1) a standard generation system based on Henry's law, (2) direct absorption spectroscopy using the TDLAS system, (3) a dual-chambered permeation calibration system, and (4) two cartridge techniques. The Henry's law device (HLD), which was utilized for TDLAS calibration, provided the common standard against which the other approaches were referenced. In a fifth technique the HLD output was ratioed to a methane standard to provide assurance that this system was stable throughout the study. The HLD provided the 5 ppbv range working standards for part 1 of this study (experiments 1c-6c', Table 1). Lower concentrations in the 0.2-2 ppbv range were generated by the permeation calibration system (experiments 1a-5b, Table 1). These approaches have been discussed in detail by *Fried et al.* [1997] and will thus be described only briefly here.

The HLD was also an integral part of the TDLAS system. It was used to deliver known CH_2O concentrations in the 3-12 ppbv range to the TDLAS for frequent calibration purposes [see *Fried et al.*, 1997]. The HLD-calibrated output was determined using the temperature-dependent Henry's law coefficients of *Dong and Dasgupta* [1986], along with measurements of pressure, temperature, flow, and solution concentrations. On April 15, 1995 (approximately 1.5 months prior to the intercomparison study), a fresh aqueous solution of CH_2O (6.41 ± 0.03 mM) was prepared and standardized by using the Dimedon reagent (5,5-dimethylcyclohexane-1,3-dione) suggested by *Yoe and Reid* [1941]. Approximately 0.3 L was used to fill the HLD, and the remainder (≈ 0.7 L) was stored in the dark in a volumetric flask for later dissemination to the participants. The HLD was maintained at 18.2° C throughout this study. A series of HLD output concentrations ranging from 130 to 272 ppbv were generated using only one stage of dilution and measured by direct absorption using the TDLAS system. A total of 40 direct absorption determinations were carried out on April 24, 1995. In this procedure the laser modulation was turned off, and the incident and transmitted intensities were measured as the laser was repetitively scanned across the CH_2O absorption feature at 2831.6417 cm^{-1} (see Figure 2). This absorption line, which was employed for all TDLAS measurements throughout this study, is clear of any known spectral interferences [*Fried et al.*, 1997]. The above intensities were used together with measurements of sample pressure (≈ 30 torr), cell temperature (26.8°C), path length (100 m), and known spectroscopic parameters (absorption coefficient, Doppler, and pressure-broadening coefficients) in a nonlinear least squares fitting routine to determine both the absorption at the line center and the integrated absorption across the line. The HLD output concentration, which was determined from both parameters, typically agreed to within 3%. Figure 2 shows the observed fit, and residual spectra obtained for one of the measurement runs employing a 272 ppbv CH_2O standard. The 40 direct absorption determinations resulted in HLD output concentrations which averaged 2.4% ± 0.6% (1σ precision) lower than that calculated from the Henry's law parameters at 18.2°C. Given that the direct absorption determinations have a total 1σ uncertainty (estimated systematic plus random) of 4%, this level of agreement was considered to be excellent.

Because the HLD was an integral part of this study, a ratioing technique employing a CH_4 standard was implemented to guard against systematic error due to degradation of the HLD solution concentration [*Fried et al.*, 1997]. This procedure uses CH_4 as an internal standard for the TDLAS and allows one to check on the stability of the CH_2O standard. On seven occasions from April 27 to May 9, 1995, the well-characterized HLD output concentration was sampled by the TDLAS system simultaneously with known concentrations of CH_4 (a 1.749 ppmv (parts per million by volume) CH_4/air mixture) employing a CH_4 absorption line at 2831.9199 cm^{-1}. The response factors, R_{CH_2O} and R_{CH_4} (where R = signal counts $ppbv^{-1}$ per unit laser power) were determined, and an average ratio $R_{CH_4} / R_{CH_2O} = 0.0302 \pm 0.0005$ (1σ precision, n = 67) was calculated. The calculated Henry's law concentrations were employed for this purpose. Upon completion of the intercomparison study on June 3, 1995, we measured a $R_{CH_4} / R_{CH_2O} = 0.0311 \pm 0.003$ (1σ precision, n = 10). This indicated that the HLD solution concentration was stable to within 3% over the course of the 1.5-month time span covering the preparations and the intercomparison study.

A further test of the [CH_2O] output of the HLD was made using two cartridge techniques which were tied to known

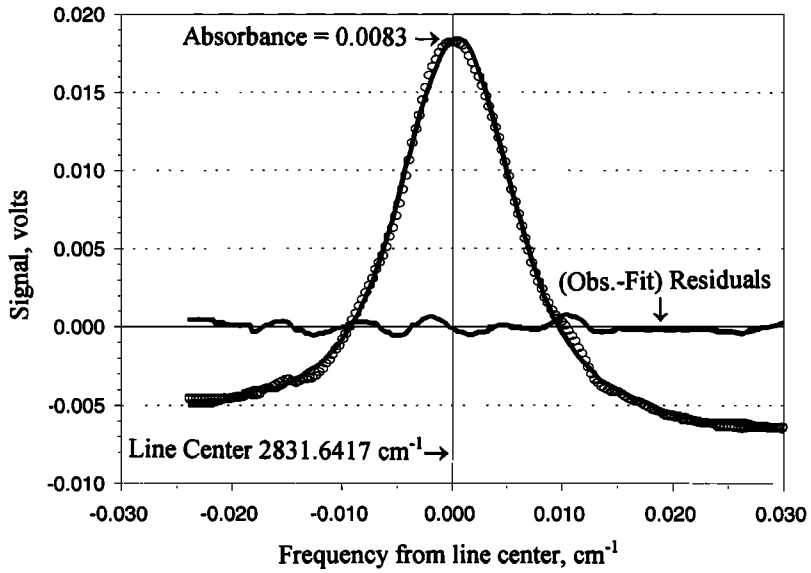

Figure 2. Direct absorption measurements of formaldehyde from the output of the Henry's law device (HLD) at temperature = 18.2°C, $[CH_2O]_{soln}$ = 6.41 mM; measurements were made approximately 1 month prior to the intercomparison. The data were acquired using the Tunable Diode Laser Absorption Spectroscopy (TDLAS) system (2831.6417 cm^{-1}; sample pressure, 29.6 torr; pathlength, 9998 cm, cell temperature, 26.8°C). Under these conditions the absorption line profile is accurately represented by a Voigt function. The curve (thick solid line) and points (open circles) are the Voigt fit (nonlinear least squares) and original data, respectively. The resulting fit yields a [CH_2O] of 266 ± 11 ppbv (total 1σ random and systematic uncertainty estimate) compared with a calculated HLD value of 272 ppbv.

gas-phase standards and cartridge specific blanks. In the absence of interferants, these techniques, calibrated by gravimetrically prepared standard solutions of the appropriate derivatives, should provide a useful additional CH_2O calibration method of limited precision. Samples taken by Rhonda Skaggs and Dave Lehmpuhl (graduate students with J. Birks at University of Colorado, Boulder) on May 2 and 3, 1995, were analyzed by two different techniques. One method employed silica gel cartridges coated with dansylhydrazine and analyzed by High Pressure Liquid Chromatography (HPLC). The other method employed C-18 cartridges coated with trichlorophenylhydrazine and analyzed by Gas Chromatography (GC). Collectively, all the cartridge determinations (n = 8) gave an average [CH_2O] which was 2.6% ± 16.5% lower than the calculated HLD concentrations.

An important aspect setting this study apart from past intercomparisons of CH_2O measurement techniques was the development of a second independent CH_2O standard generation system based on permeation tubes and employing gravimetry as the method of calibration. This development was considered crucial in order to investigate the overall accuracy of this study. Independent methods of standards generation which agree increase the confidence in the overall accuracy of the standards. This system consisted of an aluminum oven kept at 50.0 ± 0.1°C which housed two CH_2O permeation tubes containing α-polyoxymethylene; refer to Figure 1b. These tubes were contained in glass housings with hydrocarbon-free air continuously flowing over them. Three-way perfluoroalkoxy (PFA) Teflon valves, a 1 slm (standard liters (760 torr, 0°C) per minute) mass flow controller, and a glass dilution volume were used to control, mix, and dilute the permeation tube CH_2O effluent to the parts per million and parts per billion by volume range of concentrations; these were then further diluted to lower part per billion and part per trillion by volume levels within the glass manifold (Figure 1a). From previous studies it appeared possible that the permeation weight loss could have a substantial contribution from products other than formaldehyde (such as H_2O, CO, H_2, CO_2, and CH_3OH [e.g., *Spence and Wild*, 1935; *Calvert and Steacie*, 1951], formed during the generation of CH_2O vapor from the thermal depolymerization of the polymer and/or heterogeneous thermal decomposition of CH_2O itself. If this occurred, it would give rise to systematically high CH_2O calibrations. The Kin-Tek CH_2O tubes employ α-polyoxymethylene instead of paraformaldehyde. As discussed by *Walker* [1964], the α-form has essentially the same structure as the para-form except the degree of polymerization is much higher. This results in higher crystalline structure with less H_2O chemically combined or physically adsorbed than in paraformaldehyde. The two permeation tubes were characterized over a 1.5-year period using a Mettler balance capable of measuring to ± 10 μg. Rates of weight loss of 12.3 ± 0.3 (2σ) and 52.6 ± 0.3 (2σ) ng/min, respectively, were found for the two tubes held at 50.0 ± 0.1°C. The first permeation tube, when cross calibrated with the Henry's law standard using the TDLAS as the measurement device, gave [CH_2O] estimates that were 3.7 ± 7.8% lower (n = 20) than the weight loss measurements. The second permeation tube gave values 3.9 ± 1.3% higher (n = 9) than the weight loss measurements. Thus products from the permeation tubes other than CH_2O vapor are unimportant here. The four independent techniques resulted in equivalent CH_2O calibration concentrations within a ± 6% range. This agreement is good considering the reactive nature of CH_2O and problems encountered in previous standard determinations.

Experimental design of the intercomparison. Part 1 of

the intercomparison was designed to evaluate the accuracy and agreement between the various techniques measuring CH_2O. It made use of the well-characterized common source of CH_2O in a matrix of ultrapure zero air, with and without added impurities. A glass manifold (Figure 1a) was constructed and set up in sea-tainer-I with the sampling inlet ports of each participant connected by 1/4 inch PFA Teflon tubing (lengths varied from 4.3 to 10 m) to their individual instrumentation housed in sea-tainer-II. Scrubbed ambient air, with less than 1 ppmv water and ambient levels of CO_2, was supplied at rates up to 33 slm to the manifold by a zero air generator (Aadco 737-12). The manifold (shown in Figure 1a) was configured in an L shape from 2 inch diameter Pyrex glass; the gas introduction section was 30 inches long and the outlet section 48 inches long. The gas introduction ports were curved, and glass indentations located at the bend generated turbulence to facilitate mixing of gases being diluted with zero air.

The CH_2O standards were introduced into the manifold along with several potential interferants, SO_2, NO_2, and isoprene, from high-pressure cylinders that contained concentrations of 20, 9.5, and 10 ppmv, respectively. These standard mixtures were prepared by Scott Specialty Gases, Inc., cross calibrated against standards previously characterized at NCAR within the Atmospheric Chemistry Division, and introduced into the manifold through mass flow controllers at appropriate flows to give the desired part per billion by volume concentrations when diluted by the main flow (30 slm). The final concentrations of NO_2 and SO_2 were monitored using a TE 42S chemiluminescence NO-NO_2-NO_x analyzer (in the NO_2 mode) and a TE 43S pulsed fluorescence SO_2 analyzer (Thermo Environmental Instruments Inc., Watham, Masschusetts). Isoprene concentrations were monitored through grab samples taken with stainless steel flasks with analysis by a gas chromatograph equipped with a flame ionization detector system (Hewlett Packard system II 5890). Ozone was delivered into the manifold by flowing ultrahigh purity (Matheson purity) O_2 over a UV lamp (TE 565 O_3 calibrator). Ozone concentrations were sampled by a TE 49 O_3 analyzer (Thermo Environmental Instruments Inc.) which was calibrated against a system (Walega/Ridley, NCAR/ACD) traceable to an Environmental Protection Agency (EPA) equivalent method (EQA0880-047).

Water vapor was introduced into the manifold from a system designed and built by F. Eisele's group (Georgia Institute of Technology/NCAR). High-purity water (J. T. Baker HPLC grade) was drawn through a capillary tubing into a heated zone, vaporized, diluted, and flushed into the glass manifold with Aadco zero air. Water vapor concentrations as high as 78% relative humidity could be achieved in the manifold and were monitored through an outlet port with a dew point hygrometer (Kahn series 2000).

The TDLAS measurements of CH_2O were used by the referees to monitor the system performance. The TDLAS instrument sampled from port 8 (Figure 1a) for most of the measurements through a 4.3 m length of 1/4 inch PFA Teflon line. Port 7 was also employed for some of the early experiments (1a - 2b'). Prior to the intercomparison, the glass manifold was characterized. In a qualitative experiment, SO_2 standards were introduced into the manifold and diluted with zero air to generate mixtures around 50 ppbv. The SO_2 monitor, sampling at each of the eight port positions, gave equal results to within ± 10%. The TDLAS system was further used to characterize the manifold port consistency. Prior to the study the TDLAS was switched to various sampling ports to verify equivalent CH_2O/air concentrations. Low concentration CH_2O standards around 0.4 ppbv were generated in the glass manifold using the permeation system and the Aadco zero air generator. TDLAS measurements at ports 1 and 7 retrieved CH_2O concentrations that were within 26 pptv of the input values. The agreement indicates that (1) the mixing and dilution in the glass manifold is accurately predicted by the flow/dilution ratio; (2) no apparent losses of CH_2O at the sub-ppbv concentration range occurred in either the transit line connecting the permeation generator to the manifold or the manifold; and (3) there were nearly identical CH_2O concentrations at positions 1 and 7, and by inference, at all manifold ports.

An additional test was carried out during the intercomparison study to further check the glass manifold as well as the 1/4 inch PFA sampling tubes used by the participants. To begin, the TDLAS system sampled a 1.3 ppbv CH_2O standard at port 8. The TDLAS system sampled the same standard from port 1 through the serially combined sample tubes of the CHDDS (TTU) and CENZ (URI) equipment (each consisted of about 10 m of tubing). This was repeated by sampling from port 4 through the combined tubes used with the CDNPH (BNL) and cartridge equipment of MTE (each with about 8 m of tubing). In both cases the measurements were within 10% of the reference value at port 8.

The formaldehyde and interferant gas concentrations for part 1 are listed in Table 1. Spiked CH_2O mixtures were generated by NCAR scientists and were sampled by the participants in a blind fashion. At the appointed start time, all groups began collecting samples simultaneously. The duration of each experiment in part 1 was determined by the sample size requirements of the cartridge techniques which required the longest sampling time. Although necessarily abbreviated because of time constraints, the combinations described in Table 1 covered an important range of possible ambient scenarios one might encounter in field studies.

In part 2 of the study, each participant determined ambient formaldehyde concentrations using the glass tower inlet manifold. This tower contained multiple inlets spaced about 5 cm apart. Each participant sampled the center portion of a flowing airstream within the tower. Ambient air was continuously drawn through the top of the tower at approximately 1000 to 1700 slm using a high-speed blower, resulting in tower residence times of about 0.3-0.5 s. To test for surface effects, ambient air containing CH_2O at about 5 ppbv was sampled by the TDLAS system first through the tower and subsequently through black Teflon tubing of similar path length with an inlet close to that of the tower. Identical results to within 3% indicated that surface effects in the tower are unimportant.

Participant experimental methods. A brief description is given here of the experimental procedures and methods used by each of the participants in the intercomparison.

Tunable diode laser absorption spectrometer (TDLAS) of NCAR: The TDLAS system of NCAR has been described in detail recently by *Sewell et al.* [1994] and by *Fried et al.* [1997], and only a brief description need be given here. A Pb-salt diode laser beam is continuously scanned through a strong, isolated CH_2O feature at 2831.6417 cm^{-1} at 40 Hz. Sample air, from either the sampling manifold of part 1 or the ambient air sampling tower, was continuously drawn through a heated inlet box (30°-35°C) and into a 3 L volume multipass

(100 m path length) astigmatic Herriott cell (Aerodyne Incorporated) at flow rates around 10 slm. The inlet box contained Telfon solenoid valves for frequent addition of zero air and/or CH_2O standards from the HLD (approximately 6 ppbv when diluted). The point of zero air addition to the TDLAS system was about 8 cm from that of the ambient air sample. The sample gas then passed through a 1 to 2 μm Teflon filter followed by a Teflon needle valve to drop the pressure to 25 torr. The entire system was controlled by computer, which automatically switched the inlet solenoids to acquire a measurement sequence. In this process, a 20 s baseline was first acquired (using the Aadco zero air generator or Scott-Marrin ultrapure air). After a 7 s delay, which was used throughout (10 cell *e*-folding times), a 20 s calibration was acquired. This was followed by another delay and a second baseline. Ambient and baseline spectra (20 s each) were then alternately acquired with delay periods after every switch. After five ambient measurements, requiring approximately 5 min, a new calibration spectrum was acquired, beginning the start of a new sequence. The rapid acquisition and subtraction of baseline spectra not only minimizes optical noise but also inlet memory effects.

On the basis of numerous replicate standards in the 0.28 to 2 ppbv range, the limit of detection (LOD) at the 2σ level routinely ranged between 80 and 140 pptv and averaged 113 pptv for a 5-min acquisition period (actual sample integration time of 100 s) for the present field system. The TDLAS replicate precisions (2σ level) for individual part 1 standard experiments are given in Table 1. The average LOD, when combined in quadrature with an estimated systematic uncertainty of 6%, yields an overall 2σ uncertainty of 129 pptv for ambient [CH_2O] measurements around 1 ppbv.

Coil/DNPH method (CDNPH, BNL): With this technique, ambient formaldehyde is scrubbed into an aqueous solution, derivatized with DNPH and analyzed as a hydrazone using HPLC. The principle and operation of this on-line continuous technique have been described previously [*Lee and Zhou*, 1993], and the experimental setup used in this intercomparison study was nearly identical to that reported recently [*Zhou et al.*, 1996]. Briefly, sample air was pulled through a 28 turn glass coil together with a scrubbing solution containing 0.1 mM DNPH adjusted to *p*H 2.50 ± 0.2. The liquid that contained the scrubbed formaldehyde was pumped through a section of Teflon tubing (0.32 cm OD) housed in a thermostated enclosure maintained at 70.0° ± 0.5°C to obtain derivatization equilibrium; it then passed through a 0.5 mL sample loop fitted to a 6 port, electrically actuated valve injector (VICI Valco) which was part of the automated HPLC system. This system, consisting of an HPLC pump (model 6200A, Hitachi), a C-18 reverse phase column (microsorb-MV, 3 μm, Rainin Instruments), and a UV-visible detector (model UV-2000, Spectra-Physics). The injector was controlled by an HPLC software package (Rainin Dynamax) running on a Macintosh computer to perform automatic sample injection and data collection and storage. The chromatographic analysis was performed using isocratic elution (60% H_2O: 40% CH_3OH) and a monitor wavelength of 370 nm; sample injection (0.5 mL) was made every 5.0 min and represented an average over a time period of 2.5 ± 0.2 min. The experimental conditions employed were sample gas flow rate, 2.0 ± 0.1 slm; liquid flow rate, 0.29 ± 0.1 mL min^{-1}; total delay time (from coil inlet to midpoint of the HPLC sample loop), 15.1 ± 0.3 min.

Calibration of the formaldehyde signal was achieved by analyzing a DNPH solution freshly mixed with a known amount of CH_2O (yielding a final concentration of 0.5 to 2 μM) and. The blank signal was determined in a similar fashion using the DNPH scrubbing solution alone. Blanks were determined at the beginning and at the end of each batch of DNPH scrubbing solution, and the calibration was performed typically 5 times for each batch of DNPH solution, approximately midway through the batch. The DNPH scrubbing solution was prepared daily from a concentrated DNPH stock using purified water [*Lee and Zhou*, 1993].

The collection efficiency for CH_2O in the solution in a 28 turn coil was determined after the intercomparison in the laboratory using an altitude chamber under a range of conditions, namely, gas flow rate (F_g = 2 - 4 slm), liquid flow rate (F_l = 0.2 - 0.4 mL min^{-1}), and the results have been reported elsewhere [*Lee et al.*, 1996]. The collection efficiency appropriate for the current intercomparison experiment (F_g = 2.0 slm, F_l = 0.29 mL min^{-1}, and ambient pressure of 0.81 atm) was 0.63 ± 0.04.

The major uncertainties responsible for the overall precision and accuracy of this technique are chromatographic integration (± 4%, including subtraction of background signal), coil scrubbing efficiency (± 6%), gas flow rate (± 3%), liquid flow rate (± 3%), and the slope of concentration calibration (± 3%). The overall uncertainty is estimated to be ± 12% + 20 pptv with an LOD of about 30 pptv (at the 2σ level).

Cyclohexanedione-diffusion scrubber method (CHDDS, TTU): The diffusion scrubber technique for the measurement of CH_2O is incorporated in an automated, continuous, fluorometric determination system. It can measure atmospheric formaldehyde in near real time. The sample was collected by drawing the air through a Nafion membrane based diffusion scrubber at 1.50 L/min. Gaseous formaldehyde is collected at the surface of the hydrophilic membrane tube and permeates inside into a flowing stream of water. Aqueous CH_2O then reacts with 1,3-cyclohexanedione (CHD) and ammonium acetate at *p*H 5.0 (at a temperature of 95°C) to produce a strongly fluorescent compound (a dihydropyridine derivative) which is measured by a filter fluorimeter. The technique is sensitive, and it is also selective over other carbonyl compounds. The LOD in the liquid phase is 6 nmol, and given sufficient sampling time, the gas phase LOD is 10 pptv. The technique has been described in detail [*Fan and Dasgupta*, 1994]. For measurement at low levels, best results are obtained when the instrument aspirates sample air for a short period and then zero air for a longer period. This results in sample peaks rather than a continuous trace, and any baseline drift is made evident. In this study, the period for sampling air was 2 min with a 4 min period for the zero air (UP grade air, Scott-Marrin), resulting in a time resolution of 6 min. For the present study, instrument components were hard mounted on a 17 × 24 × 1 inch Plexiglas board to facilitate transport. The CHD reagent is normally refrigerated even during use, but this was not possible during this study. This may have contributed some to background drift and a somewhat higher background fluorescence than usual; the LOD under these conditions of sampling time was 70 pptv (2σ level). However, the values measured during this study were normally above the LOD except for the background experiment 2a of Table I. For this system, liquid phase calibration provides a check on the liquid phase measurement system. The

instrument was calibrated with a 10 μM liquid phase standard before, during and after the study. The relative standard deviation ranged from 0.5 to 3.5%, and within limits of this precision, the mean response was unchanged, indicating satisfactory performance and unchanged sensitivity of the liquid phase analytical system. Since the diffusion scrubber is not a quantitative collector, the TTU investigators consider gas-phase calibration during the study to be critical; however, such calibrations were not carried out during this study.

Coil enzyme method (CENZ, URI): The University of Rhode Island group analyzed for CH_2O using the method described first by *Lazrus et al.* [1988] and as more recently employed by *Heikes* [1992] and *Heikes et al.* [1996]. The method is based on the fluorescence measurement of the reduced form of nicotinamide dinucleotide (NADH), which is produced by the reduction of its oxidized form (NAD+) by CH_2O, using formaldehyde dehydrogenase enzyme (FDH) as the catalyst. In the application of the method, ambient CH_2O vapor is collected in aqueous solution using a coil collector, the collection efficiency of which must be determined. The NADH fluorescence derived from the collected CH_2O is then measured as the difference between the ambient signal and a blank. Sample blanks were determined by switching the sample coil between ultra-pure air (Scott-Marrin) and the sample airstream (test mixtures or ambient air). UP air was introduced immediately before the collection coil. The instrument duty cycle was 15 min of ambient measurement followed by 15 min of blank determination. The cycle was started on the hour and the one-half hour. Signals were recorded as 1 min averages on a computer. CH_2O calibrations were performed using aqueous standards. In a calibration the collection solution is replaced by an aqueous standard solution. Aqueous standards were prepared by serial dilution of a stock CH_2O solution prepared from either the dissolution of solid paraformaldehyde (Kodak) or a 37% solution of CH_2O (Aldrich). The stock solutions were standardized gravimetrically using Dimedon reagent [*Yoe and Reid*, 1941]. The estimated precision of the method (3σ of the blanks) is 50 pptv; the estimated accuracy is about 50 pptv at CH_2O levels of 100 pptv and 0.1 ppbv at levels of 1 ppbv. In summary, the four continuous methods report approximately equivalent uncertainties (~ 0.1 ppbv) for the measurement of [CH_2O] around 1 ppbv.

DNPH cartridge techniques: Aldehydes and ketones react with DNPH to form hydrazones, which are separated by HPLC using acetonitrile water or other solvent mixtures. Detection of the derivatives is made using UV absorption near 360 nm. For a homologous series, hydrazones corresponding to the higher molecular weight carbonyl compounds elute later during the chromatographic separation. The formaldehyde concentration is obtained from the given volume of air passed through the cartridge and the mass of the eluant.

At the start of each experiment, all groups began collecting samples simultaneously. The cartridge collections both by the MTE and WSU groups represent an integrated sample over the period of each spike experiment in part 1.

Silica DNPH cartridge measurements by the Washington State University group. The silica gel DNPH cartridges were prepared in house using a solution containing 0.125 g of recrystallized DNPH in 250 mL of acetonitrile with 0.6 mL of HCl. Each cartridge was flushed with 5 mL of acetonitrile. The cartridges were loaded with 10 mL of the coating solution (2.5 μmol of DNPH/cartridge) and dried with nitrogen gas on a custom built stand, capped with Luer plugs, labeled, sealed in glass vials with carbonyl traps (DNPH reagent on filter papers), and then placed in metal cans. The cartridges were refrigerated when not in use.

Sample air was passed through PFA Teflon tubing (0.25 in) which was connected to a KI ozone scrubber and then to the cartridge by a short piece of flexible silicon tubing. The sample flow (1.5 slm) was generated by a small air pump that was connected to a flow totalizer (Schlumberger Gallus 2000) to measure the volume of air which passed through the cartridge. Cartridges were exposed to sample air for periods of 1 to 6 hours. After collection the cartridges were labeled, capped, and refrigerated until shipped back to WSU for HPLC analysis. The KI ozone traps used in most of the measurements (except runs 1a and 3c of Table 1) were prepared in house by packing a 10 cm length of 1.27 cm OD Teflon tubing with granular KI and plugging the ends with Teflon wool.

For analysis the cartridges were extracted with 4 mL of acetonitrile. Sample aliquots were then transferred to small vials with septum caps. These vials were analyzed using a gradient elution of the derivatives effected with acetonitrile-water mixtures, beginning with a 50:50 water:acetonitrile ratio, changing to a 30:70 ratio over the period from 5 to 17 min. The HPLC unit used was a Hewlett Packard 1090 series II with a Rainin 10 cm OD-MPS reverse phase column. The individual carbonyl hydrazone derivatives were identified by matching the retention times on the sample chromatograms with those on the standard chromatograms, and peak areas were used to calculate the actual amounts of the carbonyl compounds.

Blank cartridge loadings were determined by placing an unused cartridge next to the sample train during at least one experiment each day. The cartridge, used as a blank, was removed from its glass vial and placed on the table without removing the end plugs. At the end of the experiment, the blank was returned to its glass vial and from there on treated like all the other cartridges. Analysis of the eight blank cartridges yielded a mean formaldehyde hydrazone derivative loading of 0.20 μg with a high, low, and standard deviation of 0.28, 0.09, and 0.06, respectively. Three times the standard deviation of the blanks (in this case, 0.18 μg or 0.86 nmole) is commonly assigned as the lower detection limit in this type of analysis. At a flow rate of 1.0 slm, this corresponds to an LOD for formaldehyhde of 0.32, 0.16, and 0.11 ppbv for collection periods of 1, 2, and 3 hours. Standards were prepared using the method of *Shriner et. al.* [1980]. By analyzing standards several times, the estimated precision was determined to be ± 0.1 ppbv with a collection efficiency of about 94%.

Cartridge measurements by the ManTech Environmental group. Typical cartridges from commercial suppliers were used in this work rather than the alternative of in-house-prepared cartridges that require extensive laboratory procedures to obtain ultralow background levels of the hydrazones. SEP-PAK DNPH-SGC cartridges were obtained from Waters Chromatography (part 37500, Milford, Massachusetts). These cartridges have a typical loading of 5 μmol DNPH per cartridge. The manufacturer quotes a CH_2O blank level of 5 nmol/ cartridge. For this and other work, a background level ranging between 1 and 1.5 nmol/cartridge is generally found. The blank value is generally lot dependent. The DNPH C-18 cartridges were obtained from Atmospheric Analysis and Consulting (Ventura, California). CH_2O blanks from the C-18 cartridges tended to be somewhat higher,

generally between 1.5 and 2.5 nmol/cartridge. Cartridges of both types, when not in use, were kept at freezer temperatures (about -8°C) until 0.5 hours before the beginning of the sampling period, during which time the cartridges were allowed to equilibrate to room temperature.

The ManTech sampler is a dual channel device which allows for simultaneous measurements from two cartridge devices. A sample from the common manifold is pulled to a secondary manifold to which are attached the devices. Channel 1 was used to collect CH_2O with a DNPH C-18 cartridge; channel 2 was used to collect CH_2O with a DNPH-SGC. A KI scrubber was placed in line immediately prior to the DNPH-SGC (except as noted for experiments 1a and 3c of Table 1). The scrubbing device comprised a SEP-PAK cartridge body filled with granular KI and produced a relatively low-pressure drop. The scrubbers have been found to have an ozone scrubbing capacity of more than 25,000 ppbv but nontheless were replaced on a daily basis. Prior to use, the scrubbers were flushed with zero air for about 15 min at 1.3 L/min to remove residual CH_2O that may have been incorporated within the scrubber system. Samples were drawn through the cartridges at a constant mass flow rate using a mass flow controller (series 830; Sierra Instruments, Inc., Monterey, California) and diaphragm pump. The mass flow controllers were calibrated before and following the study at the home laboratory, and both channels were set to give a flow rate of 1.3 slm (i.e., 46 mmol of air min^{-1} at 810 mbar).

For each sampling period, cartridges and scrubbers were placed in line 5 min before the beginning of the sampling period and removed immediately following the sampling period. The sampling started as the pumps were turned on. Depending on the pressure drop of each sampling system, the sampling systems required from 15 to 30 s to stabilize. The time to reach stability represented less than 0.5% of the entire sampling period and contributed negligibly to the uncertainty in the total collected volume. Voltage readings on the face of the control module were recorded 3-4 times per hour during sampling. The sampling periods ranged from 2 hours for most of the spiked CH_2O air mixtures and ambient measurements to 6 hours for the overnight ambient measurements. Daily flow checks at the common manifold were made with a rotameter to ensure that the system was free of leaks. The manifold temperature was approximately 25°C during the measurements.

Following collection, the SGC and C-18 cartridges were removed from the sampling system, double sealed in foil-lined bags, and returned to the freezer. Two to three field blanks (unopened) of each cartridge type were taken each day during the study. At the end of most measurement days, the samples were placed in a cooled container and shipped by overnight express to the home laboratory for analysis. The transit time was typically 12 hours. For analysis the cartridges were extracted with 5 mL of acetonitrile in a laboratory configuration similar to that found in EPA method TO-11 [*EPA*, 1988]. The acetonitrile was obtained from Burdick and Jackson (Muskegon, Michigan; HPLC grade) and had a typical CH_2O impurity level less than 0.050 nmol mL^{-1}. The extracts were diluted as required to 5.00 mL using volumetric flasks. Extraction efficiencies had been measured in previous work and found to be near 100% for liquid extraction volumes greater than 3 mL. Following extraction the samples from each batch were placed in an autosampler for automated analysis. In addition to the samples and field blanks, calibration standards, quality assurance standards, and laboratory blanks were run with each batch. Moreover, the level of the CH_2O impurity in the acetonitrile used to extract the cartridges was determined for each batch. Both SGC and C-18 cartridges were eluted and analyzed in the same manner.

The analysis technique involved separation of the CH_2O-hydrazone by HPLC with a three component eluant (acetonitrile, methanol, and water) gradient program. This program used in the standard analysis for this laboratory allows optimum separation of the target compounds as well as the C_3 (propionaldehyde, acetone, and acrolein hydrazones) and C_4 (*sys-* and *anti*-methyl ethyl ketone and *n*-butyraldehyde hydrazones) carbonyl compounds [*Smith et al.*, 1989]. The CH_2O hydrazone was quantified from a previously developed multipoint calibration curve. The instrument has a very high month-to-month stability which is verified in each batch run. The CH_2O values for each sample were corrected with the appropriate field blanks.

During the course of the study, 11 blanks were obtained for each cartridge type. For SGC the blank levels ranged between 0.98 and 1.31 nmol/cartridge with an average cartridge blank value of 1.13 ± 0.13 (1σ) nmol/cartridge. For C-18 cartridges the blank levels ranged between 1.33 and 2.17 nmol/cartridge with an average cartridge blank value of 1.69 ± 0.24 (1σ) nmol/cartridge. For each cartridge type, the average of the field blanks was indistinguishable from that of the laboratory blanks. The variation in the blanks represent the major factor used in determining the precision of the CH_2O measurements. The absolute precision depends on the total quantity of air passing through the cartridge, 6.1 to 20.6 mol in these experiments. Taking 3σ of the blank uncertainty as the precision criterion, the precision of the CH_2O measurements from silica gel ranged from 19 to 63 pptv. For C-18 the CH_2O precision ranged from 35 to 120 pptv.

3. Results

Spike tests. Summarized in Table 1 are the spike experiments, which allow a normalization of the results of all of the participants to common CH_2O standards; they also give an indication of possible interferences in the various CH_2O analysis methods employed. Shown are the results from known synthetic air mixtures of both pure CH_2O and CH_2O with added trace gases in air (spike mixtures). In the experiments 1a-6c' there is good agreement between the CH_2O source concentration, calculated from the output of the permeation calibration system and the appropriate dilution flows employed, and that measured by the TDLAS (NCAR) system, calibrated by the HLD; compare columns labeled "NCAR (source)" and "NCAR (TDLAS)." The good agreement is also seen in Figure 3 for [CH_2O] ranging from 0.3 to 5 ppbv (source is the solid line; solid circles are the TDLAS data). In experiments 1c-6c both the NCAR source and the TDLAS system used the same reference HLD source, so agreement here should be expected. There is a small increase in [CH_2O] above that expected from the calibration source alone for those spike experiments in which isoprene and ozone are both added as impurities. However, in experiment 5c in which isoprene was not added, a 3% increase in the [CH_2O] was also measured by the TDLAS. In most cases the magnitude of the increase (100 to 220 pptv) is consistent with that expected from the O_3-isoprene reaction during the dilution and mixing of the component gases. Most of the formaldehyde forms in the glass-

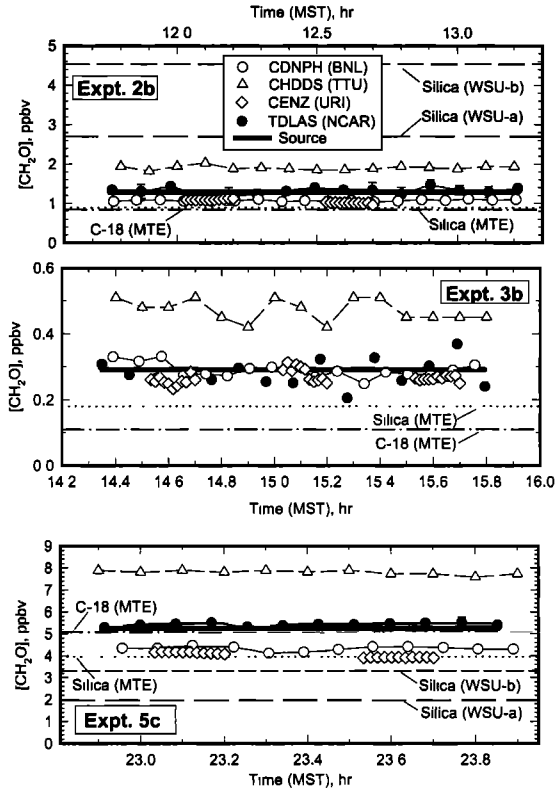

Figure 3. Summary of [CH_2O] measurements made by the six participants during representative spiking tests at CH_2O concentrations which are intermediate (experiment 2b), low (3b), and high (5c). These and similar [CH_2O] versus time records were used to derive the averages and 2σ values given in Table 1. The measurements made by the various participants are indicated by the code given in the figure. The silica dinitrophenyl hydrazine (DNPH) cartridge data of Washington State University (WSU) do not appear for experiment 3b, since an expanded scale was used to show better the spread of the other data.

sampling manifold before complete dilution of the O_3-rich and isoprene-rich gas flows occurs. When the O_3 and the isoprene are diluted to their final concentrations, one expects little CH_2O to form during the rather short transit times to the various instruments (ranging from about 1 s for the NCAR-TDLAS to about 20 s for the TTU instrument); at complete dilution, a rate of CH_2O generation of about 20 pptv/min is expected for the typical O_3 and isoprene concentrations employed here. We estimate from the amount of CH_2O formed during the dilution that one e-folding time for mixing of the impurity gas streams in our mixing chamber is <0.5 s.

Examples of the complete time history of the original measurements (experiments 2b, 3b, and 5c) from which Table 1 was constructed, are given in Figure 3. These represent the midrange, the smallest, and the largest [CH_2O] employed here. Summarized in Table 1 are the averages of all measurements reported for each standard sample and ± 2σ precision as derived from the variations in the specific measurement technique during the given measurement period.

Experiments in Table 1 with labels containing an *a*, *b*, and *c* were carried out on May 29, 30, and 31, respectively, in the order given by the numeral. In 4 of the 15 experiments, no interferants were added (1a, 1c, 2a, 3b). In all others, amounts of O_3, isoprene, NO_2, SO_2 and H_2O (%RH) were added to test for possible interferant effects. Participants using the silica cartridges for measurement employed a scrubber to remove ozone in all but two experiments (1a, 3c of Table 1). These scrubbers work most effectively in humidified air. For the dry air to which O_3 has been added, we anticipate that O_3 interference on SGC may still be present. For the data shown in columns 6 and 7, two different detectors were used with the same coil collector and chemical derivatization. There is no significant difference seen between these two results.

Columns 8 and 9, in Table 1 are derived from the same measurements of the Washington State University group using silica gel (DNPH) cartridges, but column 8 data are as first reported (June 7, 1995); column 9 data represent corrected values reported on September 15, 1995, after WSU personnel discovered an error in the flow rates used originally in the calculation. The data in columns 10 and 11, are from measurements of the ManTech Environmental group using the C-18 (DNPH) and silica gel (DNPH) cartridges, respectively.

The results of the CHDDS (TTU) method (triangles in Figure 3) are seen to be significantly higher (48-62%) relative to the calibration sample concentration, while those of the CDNPH (BNL) technique (open circles) and the CENZ (URI) technique (diamonds) are somewhat lower. At the highest [CH_2O] (experiment 5c) the discrepancy with the calibration source is -18% (CDNPH) and -23% (CENZ). At the midrange level (experiment 2b) the discrepancy with the calibration source is -16% (CDNPH) and -17% (CENZ). At the lowest level (experiment 3b) the discrepancies with the calibration source were smaller, 0% (CDNPH) and -7% (CENZ) for the two instruments. The thin, dashed horizontal lines give the results derived from the two cartridge techniques; the WSU group results are significantly higher in experiments 2b (255%) and 3b (1179%, off scale here) and lower in 5c (-37%). The MTE group results are somewhat lower than

Table 2. Ratios of Estimates of CH_2O in Experiments 1b/1b′ and 6c/6c′

Ratio[a]	NCAR (Source)	NCAR TDLAS	BNL CDNPH	TTU CHDDS	URI CENZ
1b/1b′	0.94	0.86[b]	0.97	0.99	1.01
6c/6c′	1.11	1.12	1.08	1.12	1.07

[a]In experiments 1b and 6c, [CH_2O]: 1.53 and 5.54 ppbv, respectively; Δ[CH_2O], 90 and 530 pptv, respectively.
[b]Value may be unreliable due to insufficient manifold flow for theTDLAS.

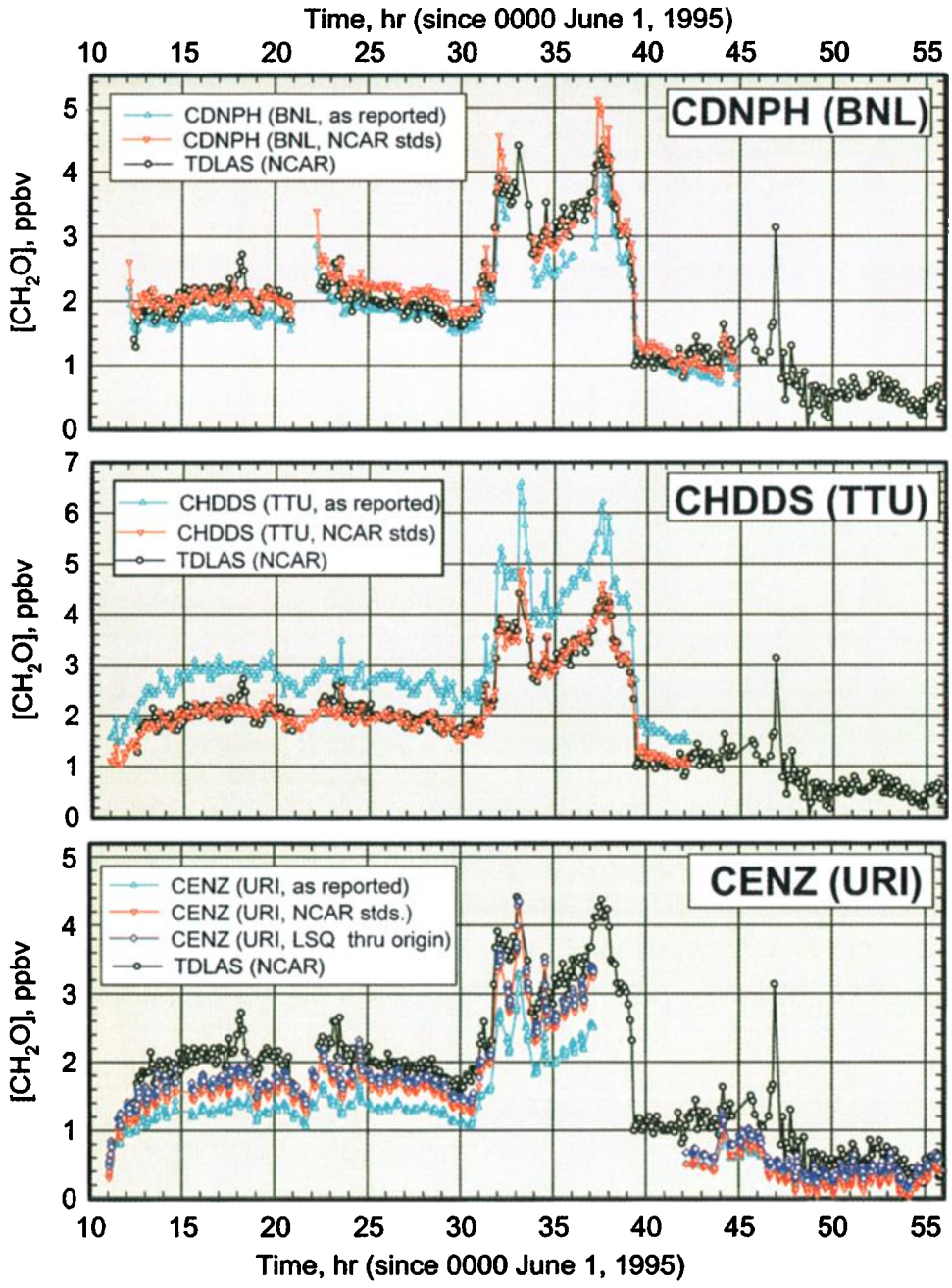

Plate 1. Comparison of the results of the ambient air analyses for [CH_2O] during the June 1-3, 1995, period at National Center for Atmospheric Research (NCAR) in Boulder, Colorado. The light blue symbols are the results observed by the coil dinitrophenylhydrazine (CDNPH) system of Brookhaven National Laboratory (BNL) (top), the cyclohexadione diffusion scrubber (CHDDS) system of Texas Tech University (TTU) (middle), and the coil enzyme (CENZ) system of University of Rhode Island (URI) (bottom). The red symbols are the data as recalculated from the measurements of each group when calibrated using the NCAR CH_2O standards given in Table 1; the data from the tunable diode laser absorption spectroscopy (TDLAS) system of NCAR are shown as the black circles and lines. The dark blue points in the CENZ plot are the recalculated data using the slope (not the complete regression equation) of CENZ versus TDLAS (Figure 5c) with the least squares weighted fit forced through the origin.

expected in experiments 2b (30-34%) and 3b (38-62%), but near equal (-3%) for the C-18 data in experiment 5c.

An interesting and important test of the sensitivity of the various continuous measurement methods is shown in Table 2. In experiments 1b and 6c, small changes (6% and 11%, respectively) in the diluting gas flows from the calibration source were made during the experiment (labeled 1b′ and 6c′, respectively). All of the continuous methods employed here can readily observe changes in [CH_2O] of 530 pptv as seen in experiment 6c/6c′. The ratios of the original [CH_2O] (5.27 ppbv) to that after the dilution flow change are NCAR calibration source, 1.11; TDLAS (NCAR), 1.12; CDNPH, 1.08; CHDDS, 1.12; CENZ, 1.07. Changes of the order of 90 pptv, 6% change in the 1.51 ppbv sample (the magnitude of

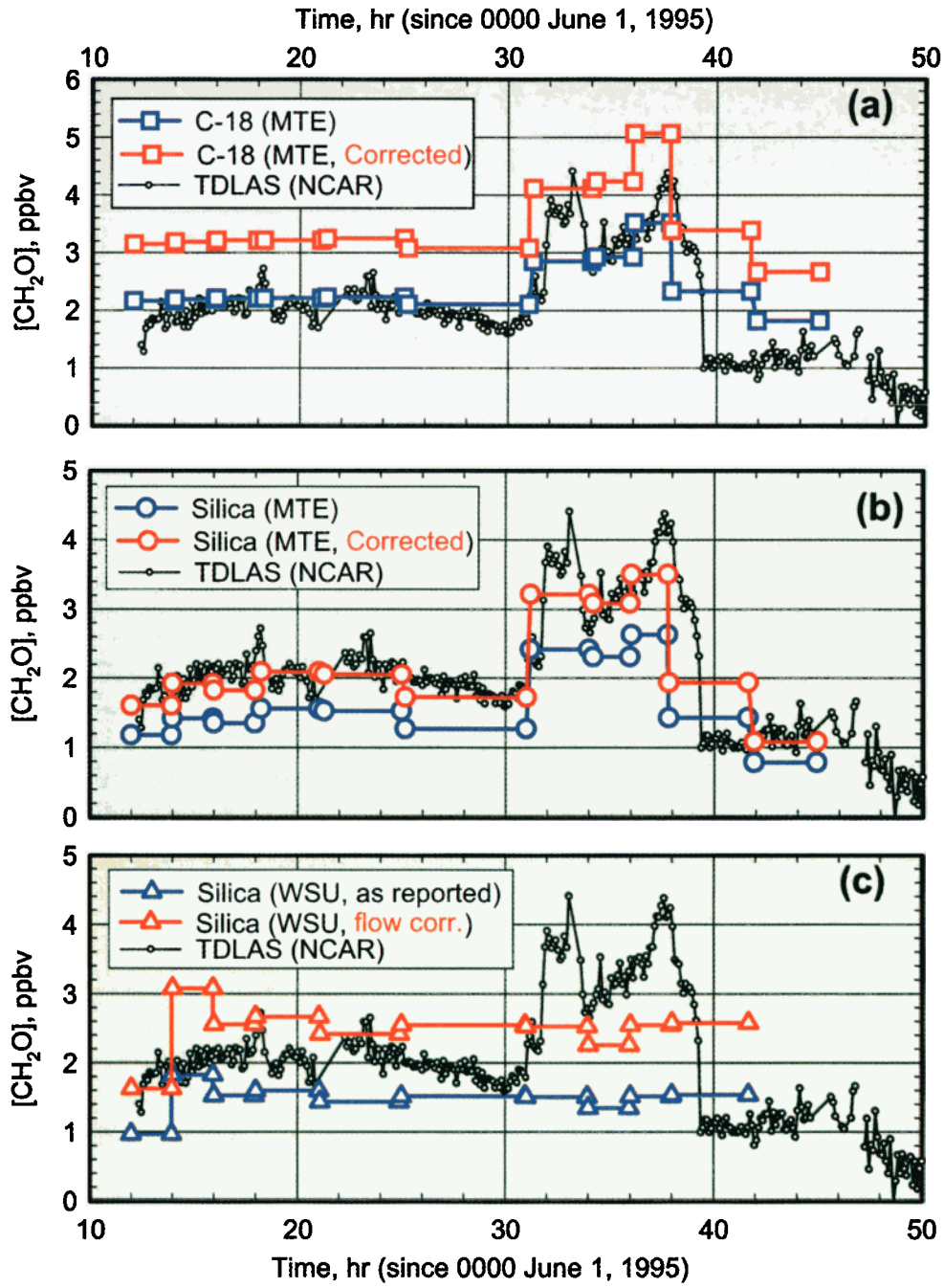

Plate 2. Comparison of the DNPH cartridge measurements of ambient air sampled at NCAR in Boulder (June 1-3, 1995) with those measured by the TDLAS system of NCAR (black circles and lines); the blue symbols and lines represent the data as originally reported by each investigator, while in Plate 2a and 2b, the red symbols and lines are the data from the cartridge data of ManTech Environmental (MTE) (labeled "corrected") as recalibrated using the NCAR pure CH_2O spike experiments. The blue and red symbols, respectively, are the silica cartridge data observed by WSU scientists (Plate 2c) as reported originally and as corrected for a flow rate determination problem. The horizontal lines drawn between the symbols show the duration of the measurement periods.

the range of precisions as estimated post experiment), are not observed in a predictable manner by all of the methods as seen in experiment 1b/1b′. Here the ratios of the original concentration to that after flow change, as expected from the NCAR calibration source, was 0.94. The TDLAS (NCAR), CDNPH, CHDDS, and CENZ reported 0.86, 0.97, 0.99, 1.01, respectively. During experiment 1b′ it was pointed out to the referees by the TDLAS operator that the value determined from the TDLAS during 1b′ may be unreliable since there may have been an insufficient manifold flow for the TDLAS (last port on manifold) in view of the total flow of air supplied and the sum of actual flows used by all of the instruments. This potential problem occurred only during the 1b′ experiment. The magnitude of the total flow was increased following this experiment.

Ambient measurements. All of the ambient data for

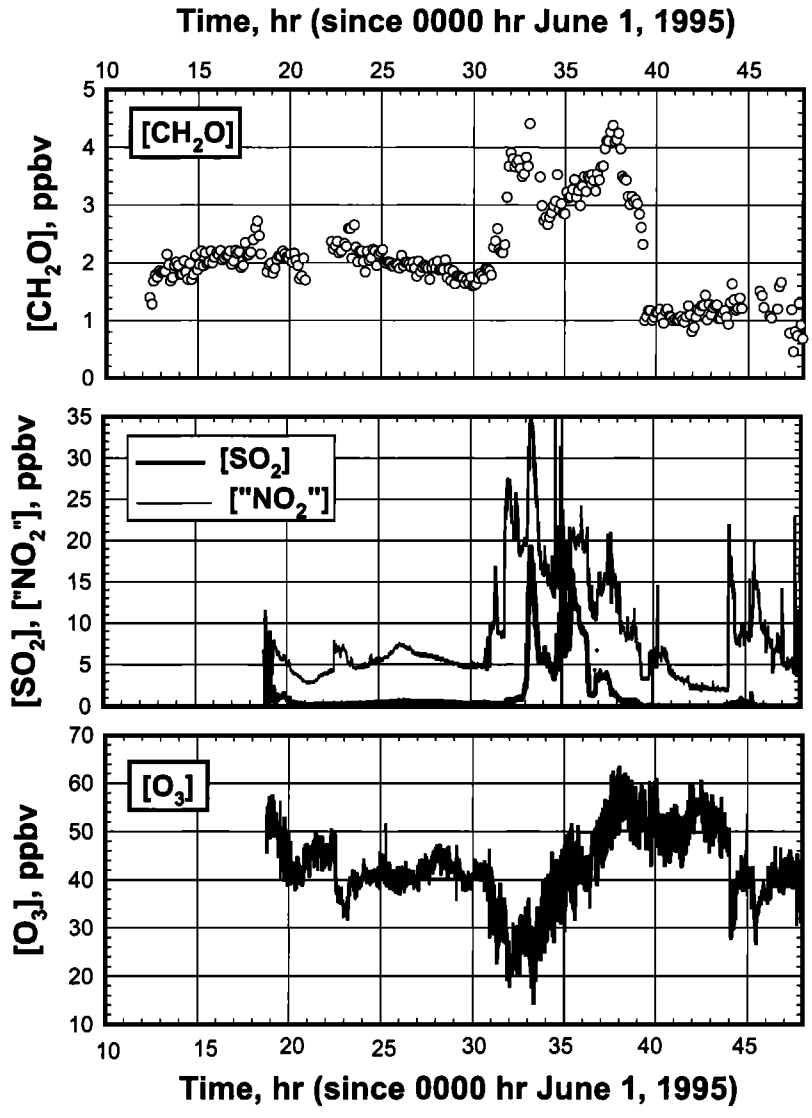

Figure 4. Measurements of the concentrations of the trace gases, CH_2O, SO_2, NO_2, and O_3, present in the ambient air sampled during the ambient air-phase of the intercomparison held at NCAR on June 1-3, 1995. The "NO_2" reported is the reading of the TE 42S chemiluminescence NO-NO_2-NO_x analyzer operated in the NO_2 mode. Note that the [O_3] and [NO_2] are anticorrelated during the period of high [NO_2].

[CH_2O] as measured by the continuous methods are summarized in Plate 1. The TDLAS (NCAR) determinations (averaged over the 5-min measurement cycle) are shown as the black symbols in all of the figures, while the data as reported to the referee from the instruments of BNL, TTU, and URI are each shown as blue symbols. The results as reported from the cartridge measurements (blue symbols and lines) are compared with those for the TDLAS (black symbols and lines) in Plate 2.

Additional trace gases, O_3, NO_2, and SO_2, were measured in the ambient air during the intercomparison of the CH_2O ambient measurements (Figure 4). The large variations in SO_2 and NO_2 which occurred during the ambient air analyses, although unexpected and uncontrolled, provided an excellent test for possible interferences in [CH_2O] ambient air measurement. Plumes rich in NO_2 and SO_2 were sampled by the intake manifold feeding the measurement equipment during the period of high CH_2O. The NO_2 spikes, which occurred before the SO_2-rich plume arrived, probably originated largely from the NO_x-rich auto exhaust emissions as the NCAR employee cars arrived at the nearby parking lot (within 200 m of the sampling site). Note that the time dependence of the O_3 structure, observed after the 30-hour time period, is anticorrelated with that seen in the NO_2; obviously ozone present before the incursion of the plume has been titrated in part by the NO in the plumes. The arrival of another plume, very rich in both NO_2 (and presumably NO) and SO_2, is apparent at about the 33 hours in Figure 4. From the direction of the local wind at this time, it is highly probable that this originated largely from the stack of the Boulder power plant (about 6.4 km NE of the site).

4. Discussion

Comparison of Continuous Methods of [CH_2O] Measurement

Spike tests. The level of agreement between the absolute values of [CH_2O] as determined by the different methods and

the reference TDLAS during part 1 of the study can be seen in Table 1 and Figure 3. The variety of independent methods used to characterize the [CH_2O] added to the sampling manifold and the consistency among these different methods gives the referees confidence in their knowledge of the [CH_2O] present in the mixtures. The disagreement between the reported values and the input concentrations, or that measured by the TDLAS (NCAR) system, is somewhat larger than the referees expected in view of the preintercomparison reports of the participants, and the measurements do not show a common direction of bias.

The analysis of a liquid phase sample of known [CH_2O], provided as an unknown to each participant immediately after the experiment 1a of Table 1, was in reasonable accord: NCAR analysis using Dimedon as described by *Yoe and Reid* [1941): 6.41 mM (determined April 11, 1995); 6.38 mM (determined on July 12, 1995); CDNPH: 6.5 mM; CHDDS: 6.3 mM; CENZ: 5.93 mM. It is clear that liquid phase calibration cannot provide a complete test of the gas-phase response to CH_2O, as it merely checks on the operation of the liquid phase analysis system, an important first step in testing for consistency in the operation of the instruments. However, all of the solution methods used here also depend upon a measured collection efficiency of gaseous CH_2O by either a collector coil or a diffusion denuder, and this must be determined and used in calibrating the net response, unless, of course, calibrations are made using known gaseous CH_2O mixtures in air at the inlet of the system.

Bivariant least squares regressions [*York*, 1966] of the [CH_2O] values as measured by each of the groups versus those measured by the TDLAS are given in Figure 5 (continuous measurements) and Figure 6 (cartridge measurements). In the least squares treatment the 2σ precision values given in Table 1 were used in weighting each measurement by $(2\sigma)^{-2}$. These precision estimates are also shown in Figures 5 and 6 as error bars. For the continuous measurement methods (Figure 5), the intercepts are near zero: CDNPH, 0.06 ± 0.04 (2σ) (all data); 0.01 ± 0.10 (only pure CH_2O experiments, as reported); CHDDS, 0.08 ± 0.07; CENZ, 0.14 ± 0.04. A near-linear response between the two variables is seen; however, the slopes are significantly different from unity: CDNPH, 0.79 ± 0.02 (2σ) (all data as reported; solid line in Figure 5); 1.24 ± 0.20 (pure CH_2O only; dotted line in Figure 5); CHDDS, 1.34 ± 0.03 (all data); CENZ, 0.73 ± 0.02 (all data). Similar regressions using the cartridge data (shown in Figure 6) give for intercepts: silica cartridge data of WSU (a), 1.67 ± 0.48; WSU(b), 2.67 ± 0.05; C-18 cartridge data of MTE, 0.36 ± 0.07 (all data) and -0.07 ± 0.11 (pure CH_2O only, black circles); silica cartridge data of MTE, -0.17 ± 0.04 (all data) and -0.04 ± 0.07 (pure CH_2O only, black circles). The slopes of the regressions are: silica cartridge data, WSU(a), 0.17 ± 0.01; silica cartridge data, WSU(b), 0.33 ± 0.01; C-18 cartridge data of MTE, 0.78 ± 0.02 (all data) and 0.71 ± 0.04 (pure CH_2O only); silica cartridge data of MTE, 0.63 ± 0.01 (all data) and 0.76 ± 0.03 (pure CH_2O only).

There is no significant evidence of interferences in the CHDDS and CENZ continuous measurements. The difference in the slopes for the CDNPH data for pure CH_2O and CH_2O in various mixtures suggests some possible interference in the BNL instrument. Evidence for the significance of these differences come largely from the slope-controlling datum point of experiment 1c using pure CH_2O in which the 2σ value (0.96 ppbv) was much larger than in the other CDNPH data. Pure CH_2O samples were introduced on each of the three days

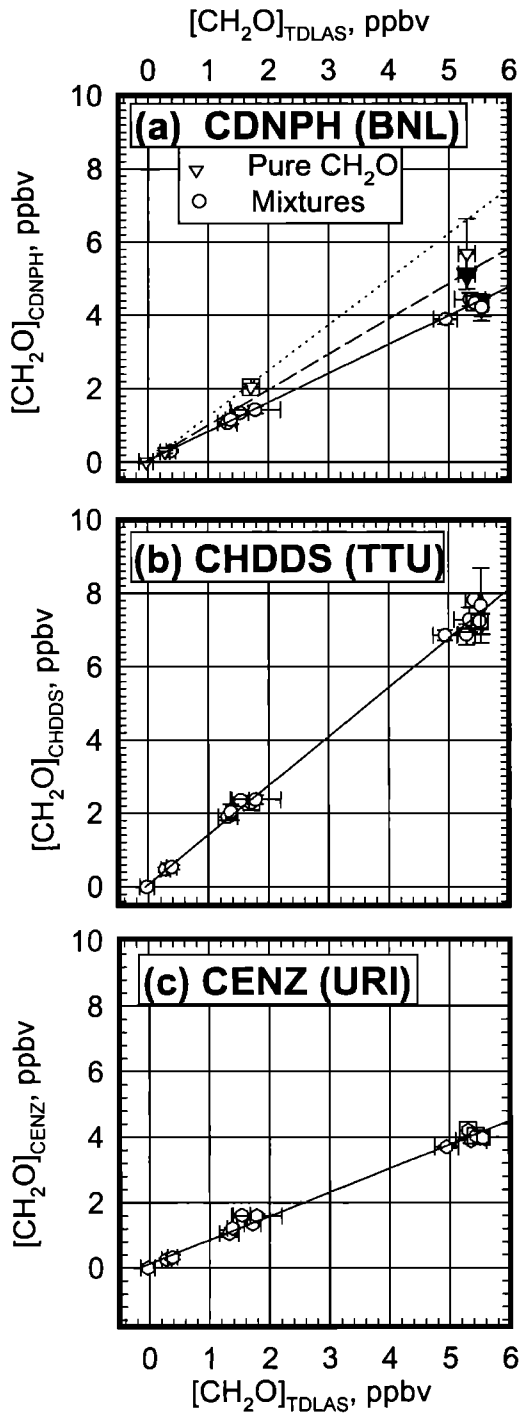

Figure 5. Regressions of the results of the [CH_2O] as measured by the continuous techniques plotted versus the TDLAS measurements of NCAR for the spike mixtures provided as unknowns: (a) CDNPH; (b) CHDDS; (c) CENZ data. The solid lines drawn through the data are the weighted, bivariant, least squares fit to all the data (both pure CH_2O and spiked mixtures). The dotted and dashed lines, respectively, in the CDNPH plot (top) are the fits using only the pure CH_2O data (inverted triangles) as reported in Table 1 and these data with the stabilized value for run 1c (solid, inverted triangle); the CH_2O mixtures with interferants added are shown as open circles in the CDNPH-TDLAS plot. The slopes of the regressions (± 2σ) are for CDNPH, 0.79 ± 0.02 (all data); 1.24 ± 0.20 (pure CH_2O data only); CHDDS, 1.34 ± 0.03; CENZ, 0.73 ± 0.02.

of the spike studies (experiments 1a, 2a, 3b, and 1c). The CDNPH instrument signal drifted during experiment 1c from a high value of 6.43 and eventually reached a stable value near 5 ppbv about halfway through the period of the experiment. The NCAR-TDLAS and the other continuous instruments show no significant change with time during this experiment. If one assumes that the BNL instrument was not stabilized for some reason during the first part of this experiment and only the last eight measurements are included in the average, a value of [CH_2O] = 5.12 ± 0.092 (2σ) is obtained (shown in Figure 5 as a solid, inverted triangle). If one uses this datum for run 1c, then the plot of CDNPH versus TDLAS (NCAR) for the pure CH_2O spikes alone gives a slope of 0.965 ± 0.035 and an intercept of 0.044 ± 0.074 (dashed line in Figure 5). Thus even if a stabilized value is used for the 1c point, there is an apparent difference between the pure [CH_2O] and the mixture results. If the "stabilized value" for 1c replaces the unstabilized average 1c of Table 1, and all the spike data are employed, the bivariant least squares fit to the data is $y_{CDNPH} = 0.027 \pm 0.046 + (0.838 \pm 0.017)x_{TDLAS}$. It seems probable to the referees that this equation is the most appropriate one to describe the fit of the CDNPH-TDLAS spike data, and this slope has been used for the calibration in calculating the corrected ambient data shown in Plate 1 (red symbols). The difference between the pure CH_2O plot and the plot including all CDNPH spike data (with and without impurities added) does suggest some possible negative interference may be affecting the BNL results. However, if this is the case, then O_3, NO_2, and SO_2 all seem to interfere to about the same extent. In the method paper describing the CDNPH (BNL) technique [*Lee and Zhou*, 1993], the potential interferants, O_3 (up to 400 ppbv) and SO_2 (up to 20 ppbv), have been examined, and no significant effects were found. Therefore it remains a possibility that the difference in slopes between the results obtained for pure CH_2O and spiked experiments (about 16%) can be ascribed to either instrumental drift or calibration change over the period.

Ambient measurements. The extensive ambient data can also be used to test the relative response of each instrument to that of the TDLAS (NCAR), much in the same manner as used with the spiking tests. Only those measurements were selected for which a time overlap of the measurement periods occurred, and these are plotted in Figure 7. The slopes of these plots for each technique versus the TDLAS (NCAR) measurements are CDNPH (267 pairs of points), 0.89 ± 0.02; CHDDS (276 pairs of points), 1.30 ± 0.02; CENZ (first measurement period only, 11-37 hours in Plate 1; 98 pairs of points), 0.63 ± 0.03. Note that the slopes obtained using these matched ambient data compare reasonably well with the spike calibration slopes of Figure 5: CDNPH, 0.84 ± 0.02; CHDDS, 1.34 ± 0.03; CENZ, 0.73 ± 0.02. They also compare well with the average ratios $[CH_2O]_x/[CH_2O]_{TDLAS}$ as reported for the ambient data at matched times: 0.89 ± 0.12 (CDNPH); 1.30 ± 0.14 (CHDDS); 0.63 ± 0.06 (CENZ, first period only). Thus it is very likely that differences from the TDLAS measurements observed in the

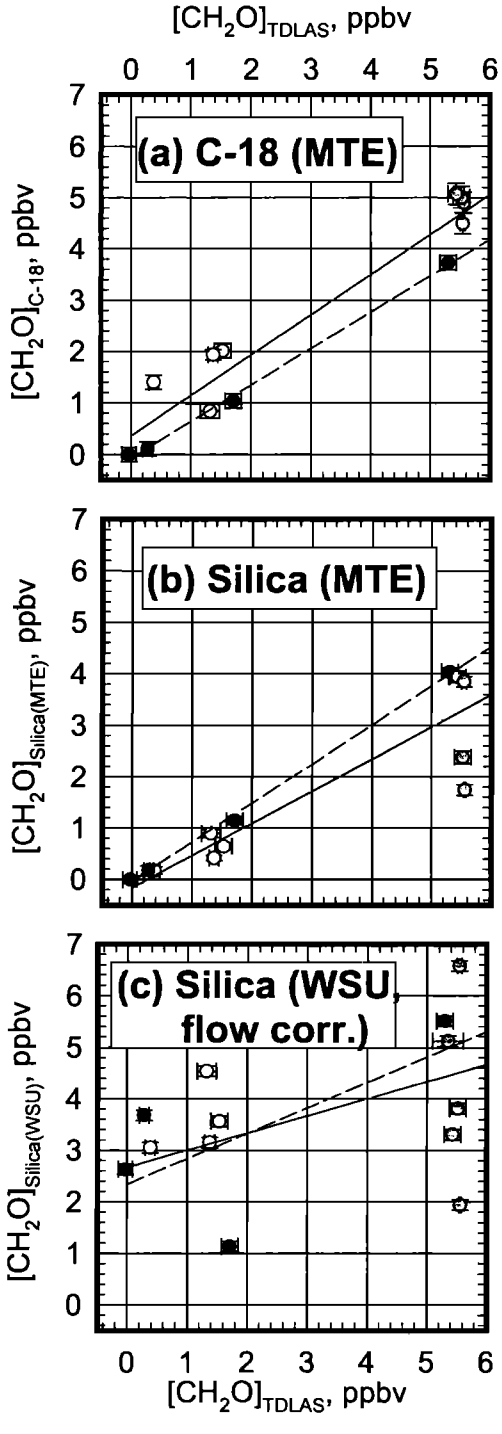

Figure 6. Regressions of the DNPH-cartridge results for [CH_2O] standard mixtures plotted versus those of the TDLAS system of NCAR: (a) the C-18 DNPH system of MTE, (b) the silica DNPH cartridges of MTE, and (c) the silica cartridges of WSU (corrected for a flow measurement problem). In each plot the solid circles are from experiments containing only pure CH_2O in an air matrix; the open circles are from CH_2O mixtures with added impurities (O_3, SO_2, NO_2, and/or isoprene) but at low relative humidity (< 0.5%); shaded circles are from experiments 2c through 6c in which significant water vapor was added (7.5-78% relative humidity) in addition to the impurities. The solid and dashed lines, respectively, are the bivariant, least squares linear fits using all the data or pure CH_2O data only. Slopes of the regressions (± 2σ) are C-18 (MTE), 0.78 ± 0.02 (all data); 0.71 ± 0.04 (pure CH_2O only); silica (MTE): 0.63 ± 0.01 (all data); 0.76 ± 0.03 (pure CH_2O only); silica (WSU): 0.33 ± 0.01 (all data); 0.49 ± 0.10 (pure CH_2O only).

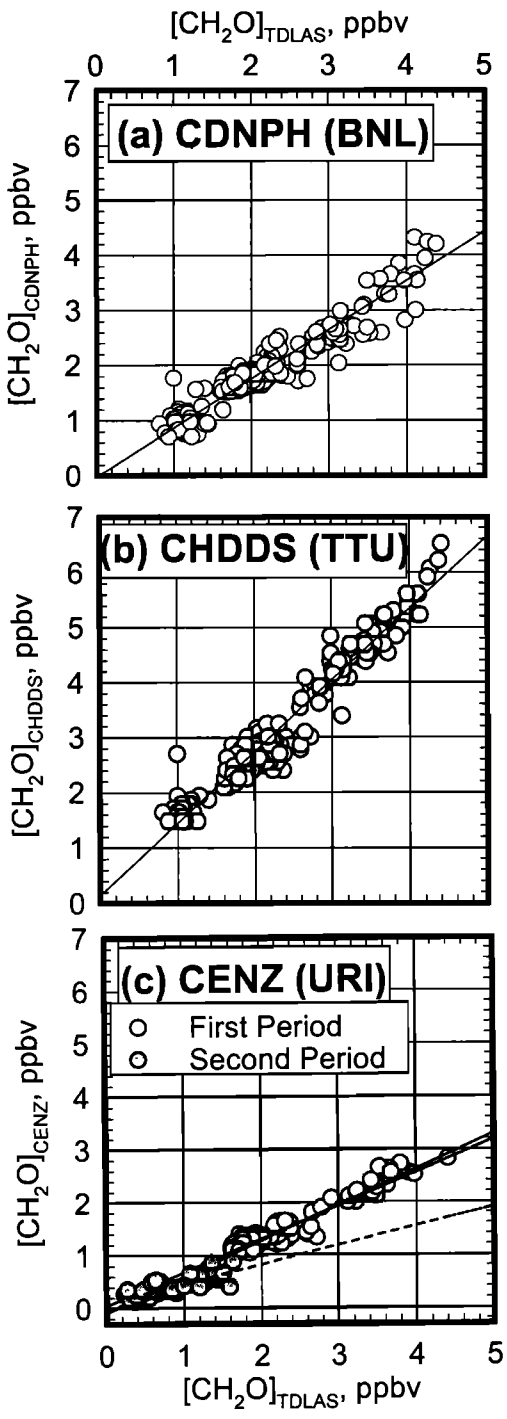

Figure 7. Regression plots of the ambient [CH_2O] measured by instruments from (a) CDNPH (267 pairs of points), (b) CHDDS (267 pairs of points), and (c) CENZ versus the TDLAS measurements of NCAR for matched times of measurements. The three lines shown in the CENZ plot show the weighted least squares bivariant fit for (1) all the data, 154 pairs of points (solid line); (2) only the data from the first measurement period (11-37 hours, Plate 1 (open circles)), 98 pairs of points (long-dashed line); and (3) shaded circles are from the second measurement period (42-56 hours, Plate 1), all matching data, 56 pairs of points (short-dashed line), respectively. The slopes of the regressions are CDNPH, 0.89 ± 0.02; CHDDS, 1.30 ± 0.02; CENZ, 0.63 ± 0.03 (first period only); 0.36 ± 0.03 (second period only).

[CH_2O] reported from the CDNPH, CHDDS, and CENZ measurements arise largely from calibration issues, namely, the magnitude of the collection efficiencies of the respective instruments at the time of the NCAR intercomparsion. If this is the case, then corrected calibrations can be generated using the calibration regressions derived from the blind spike data of Table 1. When the new calibrations are applied to the reported [CH_2O] ambient data, the curves shown in red in Plate 1 are obtained. In each case the improved agreement with the TDLAS measurements over the reported data (light blue curves) is striking; the match with the NCAR data appears in each case to be within the expected uncertainties of the measurements. The average ratios $[CH_2O]_X/[CH_2O]_{TDLAS}$ for matched times after calibration correction are 1.04 ± 0.14 (CDNPH); 1.00 ± 0.11 (CHDDS); 0.82 ± 0.08 (CENZ collected during first period only). The relatively large inconsistency, which remains between the CENZ (recalibrated) and the TDLAS data, is unexplained. The corrected numbers are influenced significantly by the relatively large intercept in the standard spike regression. For example, the match is improved somewhat (dark blue curve in Plate 1) when one uses the slope of the least squares plot of the CENZ spike data versus the TDLAS observations forced through the origin (slope = 0.754). With this data treatment, one finds an average ratio $[CH_2O]_{CENZ}/[CH_2O]_{TDLAS}$ which is somewhat closer to unity for the first period: 0.87 ± 0.08. The remaining inconsistency between the recalibrated CENZ (URI) instrument and the TDLAS [CH_2O] measurements during the first period, although larger than that observed with the other instruments, is still within the combined uncertainties of the measurement methods.

The CENZ and TDLAS instruments alone continued measurements into a second time period (42-56 hours in Plate 1). A steady rain persisted throughout most of this period, and the ambient CH_2O concentrations dropped by a factor of 4, conditions which present an interesting additional regime for testing both instruments. The regressions derived from the data of Figure 7c from the first and second measurement periods, respectively, 0.63 ± 0.032 and 0.36 ± 0.03, suggest that a change in response of one or both instruments during the second period and/or inlet effects. The average ratio of $[CH_2O]_{CENZ}/[CH_2O]_{TDLAS}$ for matched times during the second period, 0.45 ± 0.21, also shows this discrepancy. As the TDLAS instrument was recalibrated with a gas-phase standard every 5 min, it seemed unlikely the TDLAS calibration changed. During the CH_2O reference measurements (part 1) and the entire first ambient measurement period, the TDLAS calibration factors were constant to better than 6% and oftentimes better than 2% over many days. In view of the increased divergence during the second period, the referee group suggested that the TDLAS operators check on the consistency of the standard introduced during the second period as well. Indeed, spikes in the TDLAS calibration response factors, peculiar to this second measurement period, were observed at times through-out the period. Correction of the data to eliminate the spikes led to an average increase of about 13% in the ambient [CH_2O] determined by the TDLAS, a direction of change that is opposite to that required to bring the results into line with those of URI. The TDLAS operators speculate that the spiking in the standards may have arisen from trailer temperature instabilities which were reflected in the HLD output concentrations during the second period. The

reasons for the large divergence in the CENZ and TDLAS results during the second period remains unexplained.

The spectral data retrieved from the TDLAS near the 47 hour mark of the second measurement period shows a large and unambiguous spike in [CH_2O]; see Plate 1. This did not result from a calibration spike. However, it could not have been observed by the CENZ instrument, since the large maximum in the spike occurred during the CENZ-15 min nonmeasurement mode.

We conclude from these observations that in the measurement of gaseous [CH_2O] by any technique, it is imperative to use an accurate gas-phase standard in the calibration of the instrument. The extraction efficiency of liquid-based systems can be altered by minor changes in geometry (in the case of the CHDDS instrument) and operating conditions, and the use of liquid phase standards alone will not uncover this problem.

After the intercomparison, some of the problems noted in the discussion were explained by each of the participants. In the case of the CHDDS system, it is believed that the location of a membrane within the diffusion scrubber of the system apparently shifted during transport between Boulder and Lubbock, resulting in a change in collection efficiency. There were some problems with the gas-phase calibration of the TTU-diffusion scrubber system prior to this study, and as a result, all data reported to NCAR were therefore based on a gas-phase calibration conducted with a stable membrane-based source upon return to Texas after the intercomparison study. However, this procedure also created uncertainty; potential changes in the exact positioning of the membrane in the diffusion scrubber during transport could change the calibration, resulting in the scenario that the post-mission calibration would not reflect accurately the true calibration during the study. The Lubbock calibration was used in calculating the reported [CH_2O]. A smaller error may also have resulted from the difference in pressure and temperature between Lubbock, Texas, and Boulder, Colorado. Certainly, the use of a gas-phase [CH_2O] calibration standard at the measurement site could have obviated such questions.

As was stated earlier, the referee group asked the participants early in the intercomparison to check their systems to be sure they were operating as expected. In response to this request, the URI participant carried out several tests on the CENZ equipment: aqueous flow rates and air sample flow rates were recalibrated, and both were at their expected values. Sample line transfer efficiency was checked and found to be near 100% and not an issue. Aqueous standards were exchanged and found to agree within a few percent. CH_2O coil collection efficiency was checked, as both *Lazrus et al.* [1988] and *Lee and Zhou* [1993] have shown that the aqueous coil collection systems may not achieve thermodynamic equilibrium. The following experiment was performed by the URI participant on the third day of the intercomparison (experiment 3c of Table 1), when test CH_2O gas concentrations were held nearly constant (5.56 ppbv). The sample air flow rate was reduced from 2.0 to 1.0 to 0.5 L min^{-1} (760 Torr, 0°C). The CH_2O response was nonlinear to sample flow rate, indicating that the coil collection efficiency was an issue. An on-site preliminary estimate of the collection efficiency gave about 0.64. Upon return to URI the collection efficiency was determined to be 0.65 ± 0.02 (mean $\pm 1\sigma$) using a serial coil procedure. This result is significantly different from that determined in the CENZ URI earlier studies where it was determined to be greater than 0.9. The CENZ data reported to the referee and used in Table 1 and all the figures were calculated using a collection efficiency of 0.65. The results obtained by the URI participant using what he deemed to be the best calibration were still about 27% lower than the NCAR-TDLAS results. It is the referees' opinion that the difference seen between the CENZ data which were reported and the TDLAS (NCAR) results, most likely arises from inaccuracy in the knowledge of the collection efficiency of the CENZ URI coils while measurements at NCAR were being made. This again reinforces the need to employ accurate gas-phase CH_2O standards at the measurement site.

It is important to note that the TDLAS system, as implemented in this study, as well as the CHDDS and CENZ systems all require zero air to obtain backgrounds. This of course necessitates background air which contains no CH_2O. The CDNPH BNL system by contrast does not employ zero air for background acquisition and hence is not susceptible to errors caused by a residual background CH_2O in the zero air source. However, in the present intercomparison this potential error source for the continuous methods (TDLAS, CHDDS, CENZ) is unlikely. In experiment 2a no CH_2O was added to the Aadco zero airflow. The TDLAS, CHDDS, and CENZ instruments, which used their own zero air cylinder sources as well as the CDNPH instrument, all retrieved zero [CH_2O] for the pure Aadco zero air matrix within the instrument uncertainties. Significant nonzero background CH_2O in any of the cylinders would certainly show up as a statistically significant negative value for the "blank." In addition, the BNL instrument also directly sampled from one of the zero air cylinders (Scott-Marrin ultrapure grade), contained in the batch of cylinders primarily used by all the continuous methods, and detected no residual CH_2O. Important in this regard is the observation that subsequent to this study, a different batch of the zero air contained [CH_2O] ranging from 150 to 300 pptv as analyzed both by the TDLAS (NCAR) and the CDNPH (BNL) instruments. It cannot be assumed that "zero air" purchased commercially has no CH_2O in it.

The current intercomparison shows that the three continuous techniques of ambient [CH_2O] measurement tested show little, if any, interference from O_3 (up to 100 ppbv), SO_2 (up to 50 ppbv), or NO_2 (up to 40 ppbv). As noted previously, the difference in response of the CDNPH instrument observed in this study with pure CH_2O and CH_2O-impurity mixtures suggests that there may be a mild negative interference for CH_2O in O_3, NO_2, and/or SO_2 containing mixtures in air. A test for changes in response of the CDNPH instrument to that of the TDLAS during the influx of the highly NO_2 and SO_2 rich air mass observed during the ambient measurements was inconclusive. The ratio $[CH_2O]_{CDNPH}/[CH_2O]_{NCAR}$ shows a decrease (about 20%) in the ratio at the time of the high SO_2-NO_2 concentrations, but there are also periods showing a similar ratio decrease when ambient SO_2 and NO_2 remained relatively low. Further tests of the CDNPH BNL instrument will be necessary to check this point. There appears to be no artifact [CH_2O] seen by any of the continuous measurement instruments as a result of the presence of isoprene (up to 10 ppbv) with O_3 (up to 100 ppbv).

Comparison of Cartridge Techniques of CH_2O Measurement

Cartridge spiking tests: WSU. Two different types of DNPH-loaded cartridges were employed in the intercomparison: silica gel cartridges (MTE and WSU) and C-18 cartridges (MTE). Table 1 provides a summary of the

cartridge results from the three days of spiking experiments (a, b, c). Experiment 1a was used to identify major problems in the analysis of formaldehyde at the start of the intercomparison (section 2). This was helpful for methods employing on site analysis; however, since the cartridge techniques used postexperiment analysis, it was not possible to know whether analytical problems existed at this stage. Formaldehyde at 1.70 ppbv was the sole component present in experiment 1a. The MTE and WSU silica cartridges exhibited nearly identical results, 1.14 and 1.13 ppbv, while the C-18 technique measured a somewhat lower value (1.03 ppbv). Thus the three cartridges were about 35% below the source concentration and lower than all of the formaldehyde concentrations determined by the continuous methods. In experiment 2a, formaldehyde-free air was passed through the cartridges, and both MTE cartridge systems correctly observed levels below the detection limit, while the silica cartridge data of WSU gave a formaldehyde concentration of 2.63 ppbv. The major difference in the cartridges between experiments 1a and 2a was the addition of an O_3 scrubber in the latter experiment. Two explanations of the WSU cartridge results in experiment 2a appear possible: (1) the KI used in the O_3 scrubber by WSU scientists may not have been entirely purged of formaldehyde during the cleaning process, and/or (2) some trailer air, which contained relatively high concentrations of formaldehyde, was drawn inadvertently through the WSU cartridge. Blank runs on cartridges in the laboratory showed no indication of contamination from laboratory air. Whatever the cause, it is clear that a contamination problem persisted throughout the b series of experiments as well.

Experiments 1-5b were designed to test the validity of the cartridge method at low concentrations of formaldehyde together with varying amounts of ozone, isoprene, NO_2, and SO_2. As can be seen from the results in Table 1, WSU silica cartridges showed much higher concentrations than the NCAR source provided. The WSU personnel suggest that this is most likely the result of the contamination problem noted during and after experiment 2a. However, the WSU personnel state that even without a contamination problem it is doubtful that they could have made meaningful measurements in the 3b and 5b experiments (0.29 and 0.28 ppbv, respectively), since the sample collection time was 90 min during which about 93 standard liters of air passed through the WSU cartridge, and a formaldhyde-hydrazone mass accumulation of only about 0.23 μg on the cartridge is expected, essentially the same as the WSU silica cartridge blank correction (0.20 ± 0.06 μg/cartridge). However, this does not explain either the discrepancies observed in experiments 1b, 2b, and 4b which had source concentrations about 5 times higher or the order of magnitude difference observed in experiments 3b and 5b. Conclusions concerning the behavior of the silica DNPH cartridges employed by WSU based on this series of tests alone are limited.

In experiments 1c-6c the concentrations of CH_2O were increased to approximately 5 ppbv, and any possible detection limit issues of the b series should be alleviated here. For the WSU silica cartridges the 1.5 hour collection times defined the LOD at 0.4 ppbv. The agreement between silica cartridges of WSU and TDLAS (NCAR) values for experiments 1c and 2c is excellent (5.51 versus 5.64 and 5.12 versus 5.29 ppbv, respectively). Experiment 1c had no other trace gases, while all the possible interferants were present in experiment 2c. These results alone suggest that the interferants used here had little or no effect on the WSU silica cartridge results. However, when the ozone scrubber was removed (experiment 3c) with approximately the same [CH_2O] present, the [CH_2O] detected by the WSU cartridges dropped to 1.94 ppbv, well below the expected 5.24 ppbv. This may reflect a negative interference from the 95 ppbv of ozone present in the cartridge flow in this case. However, the wide divergence of the formaldehyde concentrations observed by the WSU silica cartridges from the source values for tests 4-6c is puzzling, because conditions in test 4c were nearly identical to 2c where the WSU silica cartridge showed excellent agreement with the source concentration.

The foregoing analysis of the WSU silica cartridge results from the spike tests was based upon sample-by-sample comparison between the control and the additive tests in each series of experiments. Other evaluations of the WSU silica cartridge data were attempted to rationalize the results. The data of Table 1 were used to derive ratios of the WSU cartridge measurements to those of the TDLAS system of NCAR; these are given in Table 3. The WSU silica cartridge data are highly scattered with an average ratio: silica (WSU)/TDLAS(NCAR) = 1.83 ± 2.4 as first reported, and 2.89 ± 3.9 as corrected. In Figure 6c the regression of the $[CH_2O]_{silica(WSU)}$ versus $[CH_2O]_{TDLAS}$ has a significant nonzero intercept and a small slope: $[CH_2O]_{silica(WSU)\text{-corrected}} = 2.67 \pm 0.05 + (0.33 \pm 0.01)[CH_2O]_{TDLAS}$. A negative interference with the silica gel DNPH cartridges appears to be a common finding in the presence of O_3 [e.g., *Arnts and Tejada*, 1989]. Presumably ozone reacts with DNPH and its product formaldehyde hydrazone in the silica gel cartridge to reduce the [CH_2O] retrieved. It has been suggested that the removal of O_3 with a KI scrubber prior to collection with a DNPH silica cartridge solves this problem. Since both the WSU and the MTE silica cartridge systems employed such a scrubber in this study, O_3 interference should not be a problem here. Conceivably, the dry air used in experiments 1a-1c (relative humidity < 0.5%) may lower the removal efficiency of the scrubber. However, this is not an adequate explanation for the large scatter in the silica (WSU)-TDLAS data. Note that the four data points with no added interferants (shaded circles in Figure 6c) also show a large scatter and poor correlation with the source concentration. In addition, the five data points shown as gray circles, experiments with significant water vapor added to the sampling mixture, still reveal significant scatter. With the exception of the amount of water added and the presence of isoprene in one case, the interference levels were nearly equivalent in four of these five high-[H_2O] cases.

At this point it is impossible to reconcile unequivocally the observed behavior of the silica DNPH cartridges employed by WSU, even with no added interferants. Two potential explanations were presented. Air leaks on either side of the cartridges could play some role here. Drawing in trailer air ([CH_2O] (≈ 5 ppbv) on the front side of the cartridges would result in unexpectedly high measured [CH_2O] values, i.e., a large intercept in Figure 6c. A leak downstream of the cartridges would cause the true cartridge volume flow to be lower than that measured, resulting in the $[CH_2O]_{measured} < [CH_2O]_{true}$. It is conceivable that leaks in both ends could simultaneously give rise to a high intercept and a low slope in Figure 6c. With the limited number of tests allowed by the time frame of the present intercomparison, further speculation on the origin of the problems encountered in the silica DNPH cartridges of WSU during the spiking experiments cannot be tested in more depth. In future formaldehyde intercomparisons aimed at defining cartridge behavior, it would be desirable to

Table 3. [CH_2O] Estimates of Spike Samples With Cartridge Techniques and NCAR-TDLAS Method

	(1) NCAR TDLAS	(2) WSU[a] Silica	(3) WSU[b] Silica	(4) MTE Silica	(5) MTE C-18	(2)/(1)	(3)/(1)	(4)/(1)	(5)/(1)
Experiment									
1a	1.71	0.67	1.13	1.14	1.03	0.39	0.66	0.67	0.60
2a	-0.03	1.56	2.63	bd[c]	bd[c]	----	----	----	----
1b	1.53	2.11	3.56	0.64	2.01	1.38	2.33	0.42	1 31
2b	1.32	2.70	4.54	0.89	0.84	2.05	3.44	0.67	0.64
3b	0.28	2.19	3 68	0.18	0.11	7.82	13.1	0.64	0.39
4b	1.37	1.87	3.15	0 41	1.93	1.37	2.30	0.30	1.41
5b	0.38	1 81	3.05	0.17	1.40	4.76	8.02	0.45	3 68
1c	5.30	3.27	5.51	4.04	3.73	0.62	1.04	0.76	0.70
2c	5.35	3.04	5.12	nd[d]	nd[d]	0.57	0.96	----	----
3c	5.56	1.15	1.94	1.74	4.90	0.21	0.35	0.31	0.88
4c	5.52	2.26	3 81	2.38	5.01	0.41	0.69	0.43	0.92
5c	5.43	1.97	3.31	3.94	5 08	0.36	0.61	0.73	0.94
6c	5.54	3.91	6.58	3.85	4.50	0.71	1.19	0.69	0.81
Average						1.83	2.89	0 55	1.12
±1σ						2.4	3.9	0.17	0.90

[a]As first reported, June 7, 1995.
[b]Same experimental data used in deriving data of column 2 but as corrected for flow error by WSU scientists, September 15, 1995
[c]Below detection limits.
[d]Not determined.

have several cartridge samples collected at each of the spiking and control levels and to employ different KI traps. Analyses of the cartridges made directly following exposure would also help identify problems earlier. However, this protocol would be very different than that employed in most field studies and would not duplicate possible CH_2O derivative generation or destruction during the storage period before the cartridges were returned from the field to the home laboratory for analyses.

Cartridge spiking tests: DNPH cartridges of MTE. The DNPH silica gel cartridge data from MTE are significantly different from those of WSU for all but experiment 1a (Table 1). For the MTE DNPH silica gel cartridge spiking tests, the ratio $[CH_2O]_{silica(MTE)}/[CH_2O]_{TDLAS} = 0.55 \pm 0.17$ (Table 3), while the linear regression equation for all the data (solid line in Figure 6b) is given by $[CH_2O]_{silica(MTE)} = -0.16 \pm 0.04 + (0.63 \pm 0.01)\ [CH_2O]_{TDLAS}$. The equation using only the four points without added interferants (dashed line in Figure 6b), $[CH_2O]_{silica(MTE)} = -0.04 \pm 0.07 + (0.76 \pm 0.03)\ [CH_2O]_{TDLAS}$, is similar except that the slope is 20% higher. While determined to be effective, the KI scrubber requires the presence of moisture to eliminate the systematic error when O_3 is present [Kleindienst, private communication]. Experiments 1b, 4b, 5b, 2c, and 4c were conducted at moisture levels that may be insufficient for proper scrubber operation. A relative humidity level of 7% at 25°C equates to a water concentration of 2100 ppmv. Recent measurements of [Kleindienst, private communication] have suggested that a conservative water vapor level of 5000 ppmv (>17% RH) is required to ensure quantitative removal of ozone from the airstream entering the cartridge. A comparison of samples 4c and 5c shows a 66% increase in the [CH_2O] determination for experiment 5c; the only important difference between 4c and 5c is the increased water vapor concentration in the system (2100 versus 24000 ppmv). The CH_2O difference in sample 5c, however, is still 27% lower than the value from the TDLAS (NCAR). It is possible that the DNPH-derivatized CH_2O is destroyed in part by reactions with one or more of the other impurity gases added in these experiments. However, as in the case with the results from the continuous measurements, when the four spike experiments without interferences are used for calibration, the remaining synthetic gas mixtures and ambient air MTE silica gel cartridge results compare well with the NCAR TDLAS measurements. (See the following discussion.)

The average ratio $[CH_2O]_{C\text{-}18(MTE)}/[CH_2O]_{TDLAS}$ for all of the spike samples (Table 3) = 1.12 ± 0.90; if the result from the smallest CH_2O sample 5b, and as a result least accurate by cartridge analysis, is excluded, then the average ratio = 0.86 ± 0.31. Sample 5b is expected to show the largest percent difference from the TDLAS measurement since it has the highest ozone to CH_2O ratio (~ 200); see the following discussion. The linear regression without added interferants (solid circles and dashed line in Figure 6a) is $[CH_2O]_{C\text{-}18(MTE)} = -0.07 \pm 0.11 + (0.71 \pm 0.04)[CH_2O]_{TDLAS}$, while the complete data set gives $[CH_2O]_{C\text{-}18(MTE)} = 0.36 \pm 0.07 + (0.78 \pm 0.02)\ [CH_2O]_{TDLAS}$.

Although it is now widely accepted that O_3 causes a negative interference in CH_2O determinations with silica gel DNPH cartridges (hence the common practice of employing an O_3 scrubbber), the presence of an interference and the direction of the effect with C-18 DNPH cartridges is debated. For example, *Smith et al.* [1989], [Kleindienst, private communication], *Parmer and Urgarova* [1995], and *Vairavamurthy et al.* [1993] have all observed positive interferences with C-18 cartridges in the presence of O_3. One possible explanation for the observed effect is that O_3 reacts with DNPH on C-18 cartridges to form decomposition products which coelute with the CH_2O hydrazone in the HPLC analysis. *Smith et al.* [1989] have observed several such peaks. Presumably the usual CH_2O analysis does not resolve these peaks from that of the CH_2O hydrazone, and the enhanced peak area often more than offsets any negative

interference (caused by O_3-generated reactions with the CH_2O hydrazone), resulting in a net positive interference. By contrast, *Sirju and Shepson* [1995] report a negative interference from O_3, even at 42 ppbv of O_3 ($[O_3]/[CH_2O]$ = 20), and concluded that the C-18 technique can only be used to measure carbonyl compounds accurately if the O_3 is first removed. However, *Sirju and Shepson* [1995] used a different HPLC analysis column than typically employed (C-8 rather than C-18), and this may of allowed them to separate the artifact peaks from the CH_2O-hydrazone peak. Consequently, these researchers observed the negative interference commonly experienced with silica gel DNPH cartridges. The behavior of C-18 cartridges upon O_3 exposure may also depend upon the DNPH reagent loadings as well as differences in the octadecylsilica substrate.

The C-18 data of the present study, where no O_3 scrubber was employed, are useful in providing further evidence for a possible artifact CH_2O problem. A test of the mechanism of the O_3 interference seen in the cartridge results can be made using the spike test data. Reactions (4) and (5) represent a possible mechanism:

$$CH_2O + 2,4\text{-DNPH} \rightarrow \alpha[CH_2O]_{TDLAS} \quad (4)$$

$$O_3 + 2,4\text{-DNPH} \rightarrow \beta[CH_2O]_{artifact} \quad (5)$$

Here α is the fraction of CH_2O present in the air which is actually derivatized and detected in the cartridge analysis. $[CH_2O]_{artifact}$ represents a 2,4-dinitrophenyl hydrazone derivative or an artifact compound which has a similar HPLC elution time which is formed by the O_3 oxidation of the hydrazine reagent. Since the 2,4-DNPH is in large excess in the cartridges of identical geometry, which are exposed to O_3 for the same period of time in each of the spike experiments, one expects the $[CH_2O]_{artifact}$ generation to be proportional to the $[O_3]$. If (4) and (5) are the only important sources of the CH_2O derivative formed, then one expects the total "2,4-dinitrophenyl hydrazone" detected by the HPLC analysis to be given by

$$[CH_2O]_{cart} = \alpha[CH_2O]_{TDLAS} + \beta[O_3] \quad (6)$$

and the ratio $[CH_2O]_{cart}/[CH_2O]_{TDLAS}$ to be given by

$$[CH_2O]_{cart}/[CH_2O]_{TDLAS} = \alpha + \beta[O_3]/[CH_2O]_{TDLAS} \quad (7)$$

Thus if the O_3 interference in the cartridge method results from reaction (5), one expects a linear relationship to exist between $[CH_2O]_{cart}/[CH_2O]_{TDLAS}$ and $[O_3]/[CH_2O]_{TDLAS}$. A plot of these variables is given in Figure 8. The data from the spike tests using the DNPH-C-18 cartridges without an O_3 scrubber (triangles) show a good linear relationship; correlation coefficient = 0.99. The data from the DNPH silica cartridges (open circles) show little influence of O_3, consistent with the removal of a large fraction of O_3 by the O_3 scrubber employed in this system.

Note that the two largest values of the $[O_3]/[CH_2O]$ ratio in Figure 8 are from experiments 4b and 5b of Table 1, which contained both O_3 and isoprene. This conceivably could indicate that an additional mechanism of CH_2O generation may be operative here: artifact CH_2O generation formed via a heterogeneous O_3-isoprene reaction, catalyzed in the C-18 cartridge [*Rodier and Birks*, 1994]. This possibility cannot be

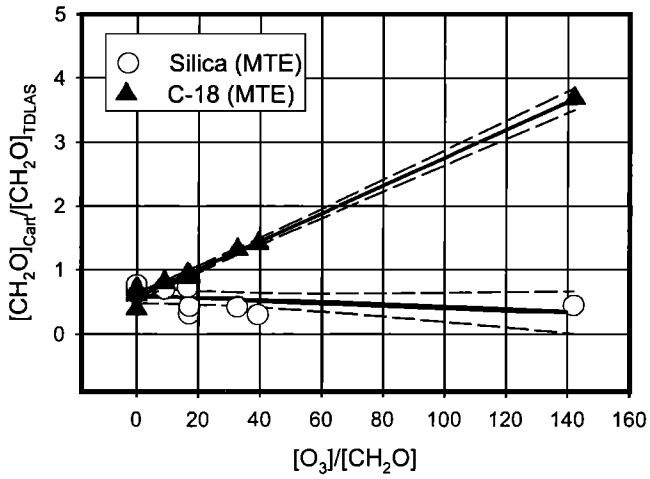

Figure 8. The ratio of $[CH_2O]$ from the silica DNPH cartridges of MTE, employing a KI O_3 scrubber (open circles) and C-18 DNPH cartridges of MTE, unscrubbed for O_3 (solid triangles) to that from the TDLAS of NCAR plotted versus the $[O_3]/[CH_2O]_{TDLAS}$ ratio; solid lines are the least squares linear fits, while the short-dashed lines give the range for the 95% confidence limits of the fits. Slopes ($\pm 2\sigma$) of the plot for the silica DNPH (unscrubbed for O_3) are 0.022 $\pm$ 0.001 (all data); 0.024 $\pm$ 0.004 (only experiments with no isoprene added).

important, at least for the present conditions, since elimination of all of the data points in Figure 8 for which O_3 and isoprene were present simultaneously in the spike experiments leads to the same slope (β) within the experimental error: for all data, 0.022 $\pm$ 0.001(2σ); for runs without O_3 and isoprene, 0.024 $\pm$ 0.004 (2σ). The near equality of the intercepts (α) of the C-18 and silica data plots in Figure 8 (C-18, 0.54 $\pm$ 0.02; silica, 0.51 $\pm$ 0.02) suggests that there is a common underestimation (by about 50%) of CH_2O by both these techniques, a somewhat larger underestimation than suggested by the slopes of the regressions in Figure 6 (pure CH_2O in air).

This positive interference of ozone seen here in the C-18 cartridge studies is consistent with that found in other recent studies [Kleindienst, private communication; *Parmer and Ugarova*, 1995; *Vairavamurthy et al.*, 1993], but it is inconsistent with the observations of *Arnts and Tejada* [1989] who reported no interference from O_3 (up to 120 ppbv) using C-18 cartridges. However, these investigators appeared to have focused on a negative CH_2O interference and may not have detected the modest positive CH_2O interference that might have been present for the relative high CH_2O levels used in their study.

An examination of results from experiments 1a, 2a, 3b, and 1c (pure CH_2O only) show a systematic reduction in CH_2O values for both the silica gel and the C-18 cartridges when compared to the source values. These data suggest that when the O_3 issue above is not present, there is an underlying discrepancy in the CH_2O hydrazone calibration for each of the silica and C-18 MTE results. It is important to recognize that the technique was not previously validated under the environmental conditions of the intercomparison site, in particular under conditions where the atmospheric pressure is substantially less than one atmosphere (0.8 atm). The mass flow controller was calibrated for molar mass flow of air at the

home laboratory (barometric pressure 1013 mbar) with corrections for temperature and pressure. At the intercomparison site, the mass flow was consistent with previous measurements, although the volume flow through the cartridges was 25% higher than that normally used. Thus samples were collected at a volume flow of 1.3 L min^{-1} versus the normal flow used by MTE of 1.0 L min^{-1}. Based on a result from previous studies, collection efficiencies were assumed to be unaffected, although they were not independently determined under the conditions at the intercomparison site.

Like the continuous methods, the cartridge measurements may be systematically low due to CH_2O losses, incomplete conversion to the DNPH derivative, and/or incomplete extraction. Recognizing the potential for such unrecognized systematic errors when using the CH_2O hydrazone calibration directly, the samples without interferences added (experiments 1a, 2a, 3b, 1c) were adopted as the basis for generating a gas-phase calibration curve for each type of cartridge. For this determination, the TDLAS (NCAR) value was taken as the gas-phase CH_2O assay value, and a new calibration curve was determined for both the silica gel and the C-18 substrates; see Figures 6a and 6b (dashed lines). For silica gel, $[CH_2O]_{silica(MTE)} = -0.04 \pm 0.07 + (0.76 \pm 0.03)\ [CH_2O]_{TDLAS}$; for C-18, $[CH_2O]_{C\text{-}18(MTE)} = -0.07 \pm 0.11 + (0.71 \pm 0.04)\ [CH_2O]_{TDLAS}$. Thus it is seen from these data alone that the response of both the MTE silica and the MTE C-18 cartridges to [CH_2O] is about 25% less than that expected. The use of these new calibration curves should remove the effect of systematic errors from the CH_2O hydrazone determination exclusive of chemical interferences. The procedures employed previously using the calibration curves derived from gas-phase regressions can be tested for interferants, in cases where ozone is not present (such as in experiment 2b) as well as in cases where the scrubber is being operated in a higher humidity regime (such as in experiments 5c and 6c). For example, in sample 2b the corrected CH_2O value for C-18 by inverting the regression equation is 1.28 ± 0.21 ppbv; similarly, the corrected CH_2O value for silica gel is 1.22 ± 0.11 ppbv. These values compare to the NCAR source value of 1.28 ppbv and the TDLAS (NCAR) value of 1.32 ppbv. This single data point would suggest that these cartridges do not show an interference for NO_2 and SO_2 at concentrations at or below normal atmospheric levels, if the gas-phase CH_2O calibration is used. When the regression equation is applied in samples 5c and 6c for the CH_2O measurement by silica gel, the CH_2O values of 5.23 ± 0.15 ppbv (sample 5c) and 5.10 ± 0.13 ppbv (sample 6c) are found. These values are reasonably consistent with the NCAR source (5.25) and TDLAS (5.43 ± 0.14) values for these samples. By contrast, when the regression for the CH_2O gas phase calibration is applied to the data from the C-18 cartridges where no O_3 scrubber was employed, CH_2O values of 7.25 ± 0.30 and 6.44 ± 0.30 ppbv are found for samples 5c and 6c, respectively. Comparison of these values to an average of the NCAR source and TDLAS values shows the corrected values to be higher (by 36 and 19%, respectively), suggesting again a positive ozone interference is present for the C-18 cartridges when using the gas-phase calibration and no O_3 scrubber. Possibly, the use of a KI scrubber with the C-18 cartridges would have rendered CH_2O values closer to the source values.

Ambient samples. The ambient data from the cartridge experiments are summarized in Tables 4 and 5 and Plate 2 and Figure 9. Ambient cartridge-TDLAS comparison must be analyzed in terms of the different types of cartridge behavior just described. To summarize, DNPH-SGCs, when used with a KI O_3 scrubber and with [H_2O] > 5000 ppmv, are expected to yield correct CH_2O concentrations when calibrated using a gas-phase source. By contrast, C-18 cartridges, which do not typically employ O_3 scrubbers, exhibit two different types of behavior depending upon the ratio of [O_3]/[CH_2O]: at low ratios indicative of high ambient [CH_2O], there does not appear to be a positive artifact CH_2O from the number of potential causes. Only the same calibration issue as the SGCs appears to be important here. At high ratios indicative of low ambient [CH_2O] and/or high [O_3], Figure 8 shows a definite positive bias in addition to the calibration issue. Thus by employing C-18 cartridges, one may arrive at the correct answer in certain circumstances from the cancellation of a combination of opposing errors. The ratios of the ambient [CH_2O] measured by silica and C-18 MTE cartridges (without using NCAR standards) to that measured by the TDLAS (columns 6 and 7 in Table 5) suggest that when the usual CH_2O hydrazone calibration is used, the best cartridge results are found with the MTE C-18 cartridge technique; the average

Table 4. Comparison of Ambient [CH_2O] As Measured by WSU Scientists Using Silica Cartridges Coated With DNPH and NCAR TDLAS Measurements Averaged Over Same Time Period

	$[CH_2O]_{WSU}/[CH_2O]_{TDLAS}$ (WSU As First Reported, June 7, 1995)	$[CH_2O]_{WSU}/[CH_2O]_{TDLAS}$ (WSU Corrected September 15, 1995)
Sample period		
12.00–13.95, June1	0.53	0.90
14.00–15.95, June 1	0.93	1.57
16.00–17.92, June 1	0.72	1.20
18.00–21.03, June 1	0.66	1.12
21.07–00.90, June 1–2	0.64	1.09
01.00–06.95, June 2	0.81	1.09
07.00–09.95, June 2	0.47	0.79
10.00–11.95, June 2	0.44	0.73
12.00–13.95, June 2	0.40	0.67
14.00–17.67, June 2	0.85	1.42
Average, ±1σ	0.65 ± 0.18	1.06 ± 0.29

Table 5. Comparison of Ambient [CH_2O] As Measured and Reported Using MTE DNPH Silica Gel (2) and DNPH-C-18 Cartridges (3) Employing the Usual CH_2O-Hydrazone Calibration, and Data From MTE DNPH-Silica Gel (4) and DNPH-C-18 Cartridges (5) Corrected Using the NCAR Gas-Phase Standards in Spike Tests

(1)	(2) [CH_2O], ppbv MTE Silica Hydrazone Calibration	(3) [CH_2O], ppbv (MTE, C-18) Hydrazone Calibration	(4) [CH_2O], ppbv (MTE, Silica) NCAR Calibration	(5) [CH_2O], ppbv (MTE, C-18) NCAR Calibration	(6) [CH_2O], ppbv NCAR TDLAS (Average)	(7) (2)/(6)	(8) (3)/(6)	(9) (4)/(6)	(10) (5)/(6)
Time period									
12.00-13.95, June 1	1.18 ± 0.06	2.16 ± 0 11	1.60 ± 0.09	3 14 ± 0.16	1.80 ± 0 22	0.66	1.20	0 89	1.74
14 00-15.95, June 1	1.42 ± 0.06	2 19 ± 0.11	1.92 ± 0.09	3 18 ± 0.16	1.96 ± 0 16	0 72	1 12	0 98	1.62
16.00-17.95, June 1	1 35 ± 0.06	2.21 ± 0.11	1.82 ± 0 09	3 21 ± 0.16	2.12 ± 0.10	0.64	1.04	0.86	1.51
18.25-21.02, June 1	1.55 ± 0.04	2.21 ± 0 08	2.09 ± 0.06	3.21 ± 0 12	2.05 ± 0.22	0.76	1 08	1.02	1.57
21.27-01.00, June 1-2	1.52 ± 0.03	2.23 ± 0.06	2.05 ± 0.04	3 24 ± 0 09	2 20 ± 0 21	0.69	1 01	0 93	1.47
01 17-07.00, June 2	1.27 ± 0.02	2.10 ± 0.04	1 72 ± 0 03	3 07 ± 0.06	1.88 ± 0.15	0.68	1.12	0.91	1.63
07.20-10.00, June 2	2 41 ± 0.04	2.85 ± 0 07	3.21 ± 0.06	4 11 ± 0.10	3.20 ± 0.66	0.75	0.89	1.00	1.28
10.20-11.95, June 2	2.31 ± 0.06	2 93 ± 0 12	3.08 ± 0.09	4 23 ± 0.17	3.10 ± 0.21	0.75	0.95	0 99	1.36
12 03-13.77, June 2	2.63 ± 0.06	3.52 ± 0.12	3.50 ± 0 09	5 06 ± 0.17	3.72 ± 0.36	0.71	0 95	0.94	1.36
13.82-17.62, June 2	1.43 ± 0.03	2.33 ± 0.05	1.93 ± 0.04	3 38 ± 0.07	1.94 ± 1.14	0.74	1.20	0.99	1.74
17.92-20.92, June 2	0.78 ± 0.04	1.82 ± 0 07	1.08 ± 0.06	2 66 ± 0.10	1.18 ± 0.17	0.66	1.54	0 92	2.25
Average						0.71	1 10	0.95	1.59
±1σ						0.04	0.18	0.05	0.27

The NCAR TDLAS measurements shown (5) are averages (±1σ) of all values measured during the entire period; these σ's are significantly higher than the inherent TDLAS precision as a result of the atmospheric variability over the same time period.

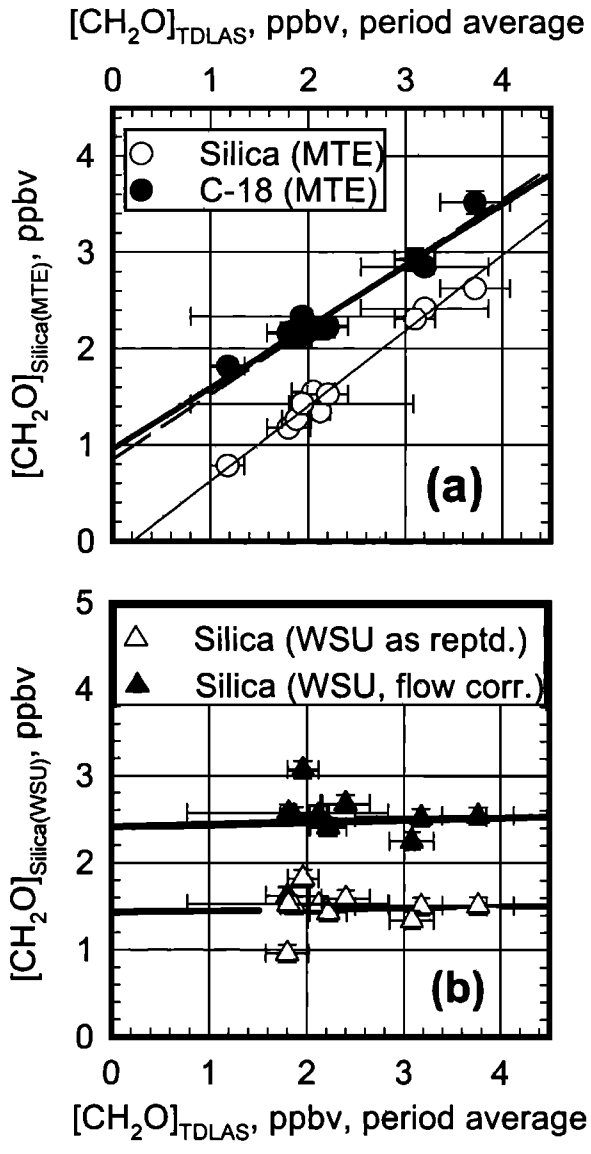

Figure 9. Regressions of the DNPH-cartridge data from the ambient air measurements of MTE and WSU versus those measured for matched time periods by the TDLAS system of NCAR. The lines shown are the bivariant least squares fits of the data. The two regression lines shown for the C-18 DNPH cartridge data of MTE (Figure 9a) correspond to fits using all of the 11 measurement periods (thick solid line; $y = 0.96 \pm 0.13 + (0.64 \pm 0.06)x$) and a fit in which the lowest data point (last measurement period) was discarded (dashed line; $y = 0.85 \pm 0.17 + (0.68 \pm 0.07)x$). The regression line for the silica DNPH cartridge data of MTE (thin line) is given by $y = -0.16 \pm 0.12 + (0.78 \pm 0.05)x$. In Figure 9b the open triangles are the silica DNPH-cartridge data as originally reported by WSU, while the solid triangles are the same data as recalculated to remove a flow rate measurement problem which was detected after the original report to the referees. The thin horizontal lines through the data points show the range of [CH_2O] values observed by the TDLAS during each of the cartridge measurement time periods. The thick solid line and the dashed line are, respectively, the weighted, bivariant, least squares fits to the data as originally reported and with the corrected airflow through the cartridges ($y = 2.40 \pm 0.12 + (0.029 \pm 0.049)x$).

ratio = 1.10 ± 0.18. The C-18 data also track the TDLAS data reasonably well, as seen in Plate 2a (blue squares and lines), but there is a significant deviation (factor of 2.25) seen during the last measurement period. This final measurement period is coincident with a rain event that occurred during the sampling periods 13.82-17.62 June 2 and 17.92-20.92 June 2. An examination of Plate 2 shows, according to the TDLAS (NCAR) data, a precipitous drop in the CH_2O concentration between 38 and 40 hours (i.e., 1400-1600 June 2). However, an examination of the ozone profiles during this same period shows the ozone concentration to remain within the range 45 and 60 ppbv. The plot in Figure 8 suggests that under these conditions ([O_3]/[CH_2O] (≈60), the C-18 measurements should be 50-60% higher than the TDLAS values during the last ambient measurement period. From the data in Table 5, the CH_2O value from the C-18 cartridge was 54% higher than that from the NCAR TDLAS. Thus even under ambient conditions the ozone interference in C-18 system is apparent. Conceivably, the results of Figure 8 could be used to generate correction factors to account for this interference and the calibration issue. However, more work is required to investigate the effect of cartridge loadings and differences in the octadecylsilica substrate before one can make meaningful generalizations concerning the effects observed with other C-18 cartridges.

With the exclusion of the data from the last ambient measurement period (17.92 to 20.92 hours June 2), all other C-18 DNPH cartridge data (MTE) using the hydrazone calibration are within 20% of the TDLAS average. The reported data from the cartridge experiments, plotted versus the average [CH_2O] observed over the same period by the TDLAS (NCAR) in Figure 9a, tell a different story. The C-18 data (MTE) show a reasonably good correlation with the TDLAS measurements, but the small slopes and large intercepts in the regression plot in Figure 9a suggest that there are some problems with this measurement technique, probably related to the effect of ozone: $[CH_2O]_{C\text{-}18(MTE)} = 0.96 \pm 0.13 + (0.64 \pm 0.06)[CH_2O]_{TDLAS}$. This slope is much smaller than that found in the regression of the spike data. It should be noted, however, that the single lowest point in the MTE C-18 versus TDLAS plot (Figure 9a), has an inordinate influence on the slope and intercept in this case. If one removes this point, the remaining data give the regression: $[CH_2O]_{C\text{-}18(MTE)} = 0.85 \pm 0.17 + (0.68 \pm 0.07)[CH_2O]_{TDLAS}$. For this scenario the slope compares somewhat better with that found from the spike data (0.78 ± 0.02).

The ambient data measured by the MTE silica cartridge (with O_3 scrubber) using the hydrazone calibration tracks the data from the TDLAS (black curves) reasonably well in Plate 2b (blue circles and lines), but they are significantly lower than the TDLAS data. In this case, the average ratio $[CH_2O]_{silica(MTE)}/[CH_2O]_{TDLAS} = 0.70 \pm 0.04$; the regression gives $[CH_2O]_{Silica(MTE)} = -0.16 \pm 0.12 + (0.78 \pm 0.05)[CH_2O]_{TDLAS}$. These data are highly consistent with the manifold measurements using the hydrazone calibration.

However, if the data are corrected using the CH_2O gas-phase calibration given above, values shown under column 5 of Table 5 are determined. In this case, the average ratio $[CH_2O]_{silica(MTE)}/[CH_2O]_{TDLAS} = 0.95 \pm 0.05$. Although the O_3/CH_2O ratio changes considerably during the ambient measurements, the tight standard deviation by either the hydrazone calibration or the NCAR gas phase calibration

suggests that there is no interfering influence from ozone. These data are shown graphically in Plate 2b (red points and lines). An examination of Plate 2a indicates that the C-18 data using the gas-phase calibration (red curves) are systematically higher than the TDLAS (NCAR) CH_2O data (black curves). Again, the greatest deviation of more than a factor of 2 occurs for the last ambient period where the O_3/CH_2O ratio is approximately 60. By contrast, the silica gel cartridge data, corrected by the NCAR gas-phase standards, gives agreement with the integrated TDLAS measurements to within ± 5% during the measurement periods.

The scatter in the silica cartridge data of WSU in the regressions for the spike experiments (Figure 6c) rendered meaningless similar recalculation of the ambient data based upon the NCAR standards. The WSU silica cartridge data from the ambient measurements (as originally reported and as corrected for the original error in the flow measurements) are compared with the TDLAS (NCAR) in Table 4 and Plate 2c and Figure 9b. Although the average ratio for the corrected data appears to be reasonable, $[CH_2O]_{silica(WSU)}/[CH_2O]_{TDLAS}$ = 1.06 ± 0.29, the regression of the measurements against the TDLAS time-matched ambient data shows no correlation, the slope of the regressions is near zero, and there are large positive intercepts for both the original and the corrected silica(WSU) ambient data: $[CH_2O]_{silica(WSU)\text{-}corrected}$ = 2.40 ± 0.12 + (0.029 ± 0.049)$[CH_2O]_{TDLAS}$. As in the spike comparisons, the reasons for this are unclear. The results can be rationalized qualitatively if some contamination of the KI scrubber for O_3 and/or small leaks around the cartridge seals existed during these measurements which allowed trailer air to be pulled into the cartridge.

5. Conclusions

The intercomparison of six different formaldehyde method techniques has been carried out using both spiked samples of CH_2O in Aadco zero air and in ambient air near NCAR in Boulder, Colorado. The CH_2O reference method was the TDLAS system of NCAR, and the standards employed were verified using four independent methods. Mixtures of CH_2O with added trace gases (NO_2, SO_2, isoprene, O_3, H_2O) were prepared to test for possible interferences in the analyses. Blind analyses of the samples were made using three very different, rapid response (minute), continuous methods of measurement which were compared with the results of the TDLAS system and the NCAR source inputs: the Brookhaven National Laboratory coil 2,4-dinitrophenylhydrazine (CDNPH) system; the Texas Tech University cyclohexadione-diffusion scrubber (CHDDS) method; and the University of Rhode Island coil enzyme (CENZ) method. The analytical results from the spike results as reported to the referee showed strong correlations with the TDLAS measurements. However, the absolute values of the [CH_2O] were about 21 ± 1% below the TDLAS data in one case (CDNPH), 34 ± 1% above in another (CHDDS), and 27 ± 1% below in the other (CENZ).

For ambient measurements at matched times during the first measurement period, the average ratios $[CH_2O]_X/[CH_2O]_{TDLAS}$ (± 1σ) were 0.89 ± 0.12 (CDNPH), 1.30 ± 0.15 (CHDDS), and 0.63 ± 0.06 (CENZ, first period). Again the different data sets tracked one another quite well. The results of analyses of a blind liquid phase CH_2O standard by each group gave very similar results, so the differences seen in the gas-phase CH_2O

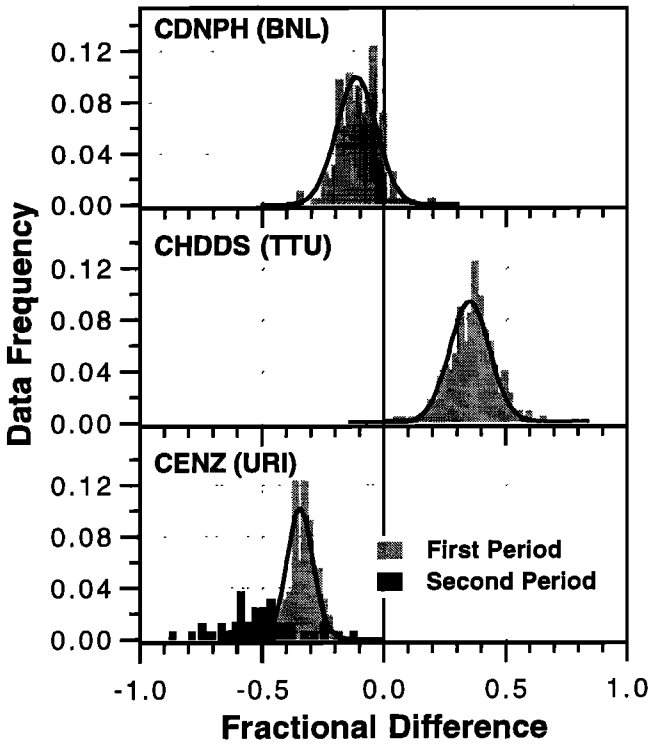

Figure 10. Histograms of the fractional differences, δ = ($[CH_2O]_{Group}$ - $[CH_2O]_{TDLAS}$)/$[CH_2O]_{TDLAS}$ for the periods of ambient CH_2O measurement. The statistics of the Gaussian fits for the CDNPH versus TDLAS, CHDDS versus TDLAS, and CENZ versus TDLAS data for the first period are, respectively, average, -0.11, 0.36, -0.34; σ, 0.08, 0.09, 0.06; median, -0.11, 0.36, -0.34; mode, -0.12, 0.35, -0.35; pairs of points, 194, 224, 113. For the δ distribution of the CENZ versus TDLAS data during the second period, average = -0.53, σ = 0.14, median = -0.53, mode = -0.54, number of pairs of points = 49. These CENZ versus TDLAS second period results were corrected for TDLAS calibration spikes.

measurements seemed to arise largely from uncertainty in the collection efficiency of the coils (CDNPH, CENZ) or diffusion scrubber (CHDDS) used in the instruments. Two of the ambient measurements (CDNPH, CHDDS) compared reasonably well with the TDLAS data when the blind standard samples data were used to correct for calibration differences. The third set of measurements (CENZ) was improved significantly, but on the average, it still remained significantly lower than the TDLAS. For measurements at matched time periods during the 12-42-hour period (Plate 1), the average ratios $[CH_2O]_X/[CH_2O]_{TDLAS}$ are 1.04 ± 0.14 (CDNPH), 1.00 ± 0.11 (CHDDS), and 0.82 ± 0.08 (CENZ, first period).

The agreement between measurements of the continuous measurement methods and TDLAS data is summarized well in histograms (Figure 10) that show the fractional differences, δ = ($[CH_2O]_{group}$ - $[CH_2O]_{TDLAS}$)/$[CH_2O]_{TDLAS}$. The results are shown for CDNPH (BNL) and CHDDS (TTU) in the first period and CENZ (URI) results for the first and a subsection of the second period from 42 to 56 hours (1800 June 2 to 0800 June 3) with the data frequency normalized to 161 coincident data pairs. This second period was characterized by persistent rain, and it was well after the shutdown period of the other

instruments. The plot shows the histograms of the data (shaded bars) and a fitted Gaussian function (black curve). The statistical information is given in the caption. The CDNPH and CHDDS histograms show standard deviations (σ) of 8 and 9%, respectively. The near collocation of the average, the median, and the mode (i.e., the most probable value) suggests symmetry in the distributions and therefore mostly random differences. For the URI histogram in the first period of measurement the distribution is also symmetric but is more peaked than the CDNPH and CHDDS distributions with a σ = 6%.

After eliminating the TDLAS calibration spikes, the δ-distribution for the CENZ histogram from the second period shows a degradation of the agreement seen in the first period with a shift to more negative values, the average, median, and mode are no longer collocated, and the σ is increased by a factor of 2.3. The cause of the decreased level of agreement is not clear. With only two instruments operating, it is not possible to ascertain which instrument experienced a change, or even if both instruments changed. The second measurement period constitutes a more stringent test than the first since the concentrations of formaldehyde are about a factor of 4 lower than those of the first period, and it was a period of persistent rain. Conceivably, such conditions could magnify significantly differences in the two inlet systems. Clearly, this study leaves unanswered issues concerning the influence of moisture on inlet systems during the analysis of low CH_2O concentrations in moist air.

In view of these results it is highly recommended to those who measure ambient formaldehyde concentrations in the future that their instruments be calibrated at the measurement site using gas-phase standards introduced at the instrument air inlet, even though liquid standards are used as well to follow the liquid-phase portion of the instrument performance.

Two different DNPH cartridge techniques were also used in the intercomparison to determine average concentrations over long sampling periods (hours): silica gel DNPH cartridges with a KI O_3 scrubber (Washington State University) and both the silica gel DNPH cartridges (with O_3 scrubber) and the C-18 DNPH cartridges (with no O_3 scrubber) (ManTech Environmental). With the use of the CH_2O hydrazone calibration, the MTE C-18 and silica gel cartridge measurements showed a reasonable correlation with the TDLAS measurements, although the results from the MTE silica cartridges were about a factor of 2 below the standards in the synthetic matrix experiment, and in the ambient data they were 35% below the TDLAS measurements. The present data suggest that much of the difference between the MTE silica gel cartridges and the TDLAS results can be attributed to differences in the calibration. When the NCAR gas-phase spike data are employed to calibrate the ambient measurements, the results from the silica gel cartridges and the TDLAS are the same within statistical uncertainty. When the same gas-phase calibration was used with the C-18 cartridges, the results showed a positive bias of approximately 60%, presumably reflecting a positive ozone interference in this case (no O_3 scrubber was used). The WSU silica cartridge results were highly scattered and showed no significant correlation with the TDLAS measurements. Contamination of the O_3 scrubber and/or leakage of trailer air into the cartridge flow may have been a problem with the WSU instrument. In view of these results alone, it is recommended that even for integrated long-time (hours) ambient [CH_2O] measurements, specific validation tests for flow integrity, collection efficiency, O_3-scrubber efficiency, and possible contamination of the KI scrubber be conducted during the study. Unlike the continuous CH_2O methods used in this study, the cartridge techniques are blind during the collection process, and rapid analysis of selected samples would be beneficial to ensure system integrity. In addition, questions remain about the origin of positive interferences in [CH_2O] measurements by the C-18 technique by O_3. Also, it is clear that the information which these cartridge techniques can provide on the time dependence of the [CH_2O] is seriously limited, especially for ambient concentrations in the high part per trillion by volume to low part per billion by volume range. The time resolution, sensitivity, and precision of the cartridge systems are less than that possible with any of the four continuous methods used in this study. The accuracy of the cartridge techniques (for integrated, long time periods of hours) may not be inherently worse than that of the continuous methods.

The intercomparison program has demonstrated that a field gas-phase calibration is essential for accurate CH_2O determinations. Each of the monitoring systems utilized specific collection, separation, and/or derivatization procedures that cannot be assumed to be 100% efficient, especially when not previously validated under the exact field conditions.

We recognize that uncertainties in measurements of trace gases can result from both instrument error and operator error, as well as from fundamental biases of the technique (such as interferences). Although it may be presumptive to judge whether a given technique is sound and appropriate from the results of a single intercomparison, the participants in the current intercomparison are experienced in the use of their measurement techniques; their results are probably representative of those which would be determined by other experienced investigators using the same techniques, and the problems observed here are probably representative of those which will be encountered by others.

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