

# ATMOSPHERIC CONCENTRATIONS AND TEMPORAL VARIATIONS OF C<sub>1</sub>-C<sub>3</sub> CARBONYL COMPOUNDS AT TWO RURAL SITES IN CENTRAL ONTARIO

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**Abstract**—Measurements of formaldehyde, acetaldehyde, acetone and propionaldehyde concentrations were made at two rural sites in central Ontario. One site (at Egbert, Ont.) is located  $\approx$  60 km northwest of Toronto, while the other site (at Dorset, Ont.) is  $\approx$  150 km northeast of the Egbert site. Measurements were made using a modified version of a derivatization technique in which sample air is pumped through Teflon tubes packed with silica gel that is coated with 2,4-dinitrophenylhydrazine (DNPH). The product hydrazones were separated and quantified using HPLC. Quantitative determinations of formaldehyde, acetaldehyde and acetone were made for 49 and 47 samples at the Dorset and Egbert sites, respectively, between 25 July and 30 August 1988. The average concentrations determined at the Dorset site for formaldehyde, acetaldehyde, and acetone were 1.6, 0.46 and 1.8 ppb, respectively, and for the Egbert site the corresponding averages were 1.8, 0.57 and 1.6 ppb. A set of 10 samples from the Egbert site were analysed for propionaldehyde yielding an average concentration of 0.03 ppb. The formaldehyde measurements were compared with measurements made at the same time using Tunable Diode Laser Absorption Spectroscopy. The observed concentrations reported here are compared with previously reported measurements of these species and interpreted in terms of atmospheric variables (e.g. meteorology, concentrations of precursor hydrocarbons) influencing their concentrations.

**Key word index:** Formaldehyde, acetaldehyde, propionaldehyde, acetone, carbonyl, atmospheric, measurements, DNPH, derivatization, oxidant.

## INTRODUCTION

An important objective of atmospheric chemists is to formulate computer models to enable simulation of processes occurring between emission and ultimate deposition of various pollutants, such as those associated with 'acid rain'. There are currently two Eulerian long-range transport regional air quality models being developed in Canada and the U.S.—the Acid Deposition and Oxidant Model (ADOM), described by Venkatram *et al.* (1988) and the Regional Acid Deposition Model (RADM), described by Chang *et al.* (1987). To provide data to evaluate and test these models, a major 2 year field study is being conducted in the eastern U.S. and Canada at several air sampling sites and from aircraft. Among the key chemical species that need to be accurately measured to provide input to the model evaluation are the carbonyl compounds.

Aldehydes and ketones are known to play a critical role in the oxidative photochemical processes that

occur in the troposphere. Their photolysis represents a significant source of atmospheric free radicals, formaldehyde being a principal source of HO<sub>2</sub> and thus ultimately HO (Calvert and Stockwell, 1983). In addition, aldehydes and ketones are products of the atmospheric oxidation of both natural and anthropogenic hydrocarbons. Thus the atmospheric carbonyl compound concentrations and their variability can be an indication of the extent of photochemical activity for a particular air mass. The relative concentrations of carbonyl compounds in ambient air could also be indicative of the nature of the hydrocarbon precursors. For example, whereas some aldehydes such as benzaldehyde are derived largely from the oxidation of anthropogenic hydrocarbons, others, e.g. methacrolein and methyl vinyl ketone are the result of the atmospheric oxidation of isoprene, an important natural hydrocarbon (Lloyd *et al.*, 1983).

A variety of carbonyl compounds are known to be precursors to formation of peroxyacetyl nitrate (PAN), an important atmospheric oxidant and bac-

terial mutagen (Kleindienst *et al.*, 1985, 1990) that is also intimately linked in the transport and fate of global NO<sub>x</sub> (Singh and Hanst, 1981). For both urban impacted and clean air masses, a variety of carbonyl compounds including acetaldehyde, acetone and methyl glyoxal can contribute significantly to PAN production. There is also considerable interest in measurement of higher molecular weight peroxyacyl nitrates (Singh and Salas, 1989), such as peroxypropionyl nitrate (PPN). PPN is believed to arise solely through oxidation of anthropogenic hydrocarbons, whereas PAN has both natural and anthropogenic sources. Thus measurements of PAN and PPN in conjunction with their carbonyl precursors (e.g. acetaldehyde and propionaldehyde) can provide valuable information regarding the source and nature of the air mass containing them.

It is thus clear that measurements of atmospheric carbonyl compounds are important in general terms with regard to development of our understanding of atmospheric oxidative processes, and also in the present specific case of the need for a database to test the Eulerian models. A number of analytical methods have been developed for measurement of atmospheric levels of formaldehyde, including Differential Optical Absorption Spectroscopy (DOAS [Platt and Perner, 1980]), Tunable Diode Laser Absorption Spectroscopy (TDLAS [Harris *et al.*, 1989]), and a Continuous Scrubbing Fluorometric Detection technique (CSFD [Lazrus *et al.*, 1988]). These techniques all have detection limits of 0.1 ppb or better for formaldehyde and provide good time resolution. A recent intercomparison of the latter two techniques indicated a correlation coefficient of 0.93 for a comparison of ambient measurements in the 1–10 ppb HCHO range (Kleindienst *et al.*, 1988). Although all three techniques are sensitive and selective for formaldehyde, they do not afford determinations of the higher molecular weight carbonyls. In addition, the DOAS and TDLAS techniques are not readily accessible to many atmospheric researchers and are not easily deployed at remote sites or on aircraft. Thus there is a need for a reliable, accurate, sensitive and selective technique that can be utilized for quantitative determinations of various carbonyl compound concentrations under a range of ambient conditions. Over the past few years determination of carbonyl compounds in air by derivatization with 2,4-dinitrophenyl hydrazine (DNPH) followed by HPLC separation and detection of the hydrazone products (Kuwata *et al.*, 1979; Grosjean and Fung, 1982) has come into widespread use. In the standard method using micro-impingers for sample collection, the detection limit is  $\approx 1$  ppb for a 1 h sample. This technique offers the advantage of relative simplicity and low cost, and enables determination of various aldehydes and ketones. The micro-impinger method is, however, cumbersome for field studies requiring large numbers of samples, or for those conducted at remote sites. An alternative approach has been described by Tejada (1986) that

involves use of commercial silica gel cartridges (Waters Sep-Pak) that are coated with the DNPH reagent. This technique offers the advantage that samples are in a much more convenient form for field work, and that slightly higher sample flow rates are possible. The work of Tejada indicated equivalent results for the impinger and silica gel cartridge techniques.

Although the method of Tejada offers important advantages over the impinger technique, sample acquisition at the maximum possible flow rate with the cartridges leads to a detection limit for formaldehyde, for a 1 h sampling time, of  $\approx 0.5$  ppb. This is adequate for urban environments, but it is necessary to achieve detection limits that are considerably lower than this for measurements at rural sites such as those to be discussed here. We describe the results obtained for a series of ambient air samples acquired at two rural sites in central Ontario in July and August 1988, using a modification of the DNPH coated silica gel cartridge technique. The measurement effort focused on the predominant atmospheric carbonyls present at such sites, i.e. formaldehyde, acetaldehyde and acetone. These measurements were conducted as part of the Eulerian Model Evaluation Field Study. Therefore one purpose of the effort was to obtain ambient measurements of these carbonyl compounds that could be used as a part of the model evaluation effort. The results are discussed in terms of the local and regional photochemical and meteorological variables that may influence the observed carbonyl concentrations and compared with previously reported carbonyl measurements at other sites.

## EXPERIMENTAL

Ambient air samples were obtained between 25 July and 30 August 1988 at Environment Canada's Centre for Atmospheric Research Experiments (CARE) at Egbert, Ontario (44°14'N, 79°47'W) and at the Ontario Ministry of the Environment's monitoring station at Dorset, Ontario (45°13'N, 78°56'W). (A series of samples was also obtained from aircraft flying between the two sites; these data are not presented here.)

The Egbert air monitoring site is located on a grassy moderate hill, elevation 220 m. It is surrounded by farmland with a patch of forest (predominately deciduous) roughly 1 km to the north. This site is  $\approx 60$  km to the northwest of Toronto, and is  $\approx 8$  km to the northeast of the town of Alliston, population  $\approx 5000$ . A major (north-south) highway passes  $\approx 5$  km to the east. Thus depending on the air trajectory there can be significant relatively local sources of hydrocarbons and NO<sub>x</sub>.

The Dorset site is an APIOS (Acid Precipitation in Ontario Study) monitoring site, located in a rural forested area of central Ontario, elevation 320 m. A small town (Dorset), population  $< 1000$ , is located 4 km to the northeast. There are no significant local point sources of anthropogenic hydrocarbon or NO<sub>x</sub> input. The monitoring site is in a valley, with a hill that is 100 m to the southwest, elevation 387 m. The site is also surrounded by hilltops  $\approx 500$  m to the northwest (elevation 385 m),  $\approx 500$  m to the northeast (elevation 401 m), and  $\approx 1000$  m to the south (elevation 409 m). The local land is 88% forested (75% deciduous, 25%

coniferous) and 10% water. A map indicating the relative locations of the sampling sites is shown in Fig. 1.

A wide variety of additional atmospheric measurements were made at both sites during this period including measurements of  $O_3$ ,  $NO$ ,  $NO_x$ ,  $NO_2$ ,  $NO_y$ , PAN,  $HNO_3$ ,  $SO_2$ ,  $H_2O_2$ , hydrocarbons, particulate nitrate and sulfate, CO, major ions in precipitation, radiation flux, and micrometeorology measurements. (Much of this information is to be published in separate papers.) HCHO measurements were conducted at both sites by TDLAS, employing methodology previously described by Harris *et al.* (1989). Samples for carbonyl compound determination were obtained by pumping ambient air through a 5  $\mu m$  Teflon filter, followed by a small Teflon manifold and then through one of 12 pairs of  $\frac{1}{2}$ " OD  $\times$  3" long Teflon tubes (front and back) packed with 45/60 mesh silica gel that had been coated with acidified DNPH reagent. Only one of the pairs of sample tubes was connected to the pump and flow meter at a given time, as determined by the position of a 12-port Teflon valve. The valve was automatically advanced through the 12 positions using a mechanical timer. Sample inlets were located at a height of  $\approx 5$  m above ground and  $\approx 1$  m above the top of the respective sample buildings. Sample flow rates were typically 3–3.5  $l\ min^{-1}$ , as measured with Hastings mass flow meters calibrated with a dry test meter. The relatively higher sample flow rates achieved with this method are largely the result of use of coarser mesh silica gel relative to that used in the Waters Sep-Pak cartridges. For all samples, air was drawn through two sample tubes in series, both to ensure that adequate collection efficiency was achieved, and to provide realistic blank values. For acetaldehyde and formaldehyde the collection efficiency at these flow rates is near 100% (see below). In such a case we feel that the backup sample provides the most representative blank, since air containing all components of the actual sample not collected in the front tube is drawn through the backup tube. This is potentially important to account for the possibility of reactions of other pollutants on the surface of the silica gel (either with DNPH or between various pollutants) to yield carbonyl products. Subtraction of the amount of hydrazone product on the backup tube from that on the front thus enables correction for either this type of 'artifact' or for contamination during sample handling that may differ from that for the blanks. As found by others, the detection limit of this technique is limited largely by the blank levels of the analyte carbonyl compounds. We estimate the detection limit for formaldehyde and acetaldehyde to be  $\approx 0.15$  and 0.10 ppb, respectively, for 3 h integrated samples.

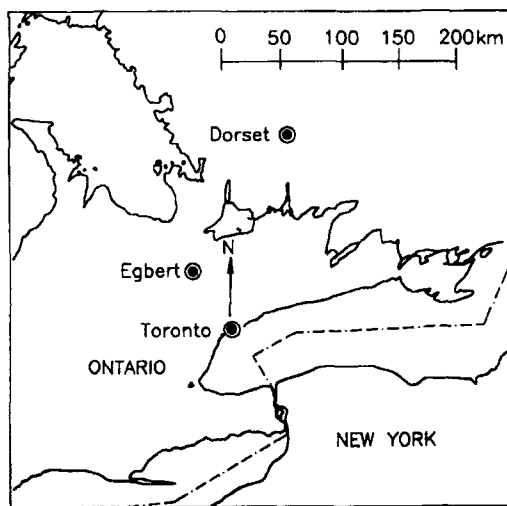


Fig. 1. Map of sampling locations.

DNPH used for these measurements was from Aldrich (30% water) that was twice recrystallized in acetonitrile (Burdick and Jackson). The silica gel coating solution was prepared by 1:20 dilution of a saturated solution of DNPH in acetonitrile (ACN) which was then acidified with concentrated HCl (1:1000 dilution). A 5 cm length of the tube was packed with 45/60 mesh silica Gel (Chromatographic Specialties Ltd.), held in place with perforated TFE Teflon disks. Before coating with the DNPH reagent the tubes were washed with three 10 ml portions of ACN. The tubes were then coated by slowly forcing 7 ml of the solution through the tube using a repetitive dispenser. Excess ACN was blown out of the tubes with  $\approx 0.5$   $l$  of prepurified nitrogen. The tubes were stoppered with glass plugs until needed for sampling. After sampling the tubes were restoppered and returned to the laboratory. The sampled tubes were eluted with an accurately measured aliquot of ACN immediately prior to analysis. It was found that 5–10 ml ACN resulted in elution of  $\geq 99\%$  of the hydrazones from the tube. Exposed sample tubes remained stable for up to 3 weeks but once eluted they needed to be analysed within 1 to 2 days to avoid contamination.

The hydrazones in the eluted samples were separated and detected using a Varian 5000 HPLC, with detection by absorption at 366 nm. The hydrazones were separated using two Supelcosil LC-18 5  $\mu m$  25 cm  $\times$  4.6 mm columns (Supelco) connected in series. The mobile phase used was a mixture of methanol/water, solvent programmed from 60 to 90% methanol. A chromatogram of a sample obtained on 29 August 1988 at the Egbert site is shown in Fig. 2. The  $CH_3CHO$  concentration measured for this sample was 0.2 ppb. We found that the peak at  $\approx 12$  min eluted simultaneously with the formaldehyde hydrazone when ACN/ $H_2O$  was used as the solvent system. The observation of a co-eluting formaldehyde interference has also been reported by Guenier *et al.* (1984). In addition, using ACN/ $H_2O$  we were unable to separate the propionaldehyde and acetone hydrazones. Thus for these reasons methanol/ $H_2O$  seemed to be the preferred solvent system. The peak at  $\approx 4$  min appears to be a DNPH decomposition product. As has been reported by others, double peaks were observed for acetaldehyde and propionaldehyde, presumably due to the *syn* and *anti* forms of the hydrazones (Smith and Drummond, 1979). The detector output was sent to an HP3393 integrator equipped with an HP9114B disk drive to enable re-analysis of chromatograms. Since for small peaks greater accuracy was achieved by manual measurement of peak heights rather than use of integrator areas, all data reported here were obtained by manual peak height measurement. Instrument

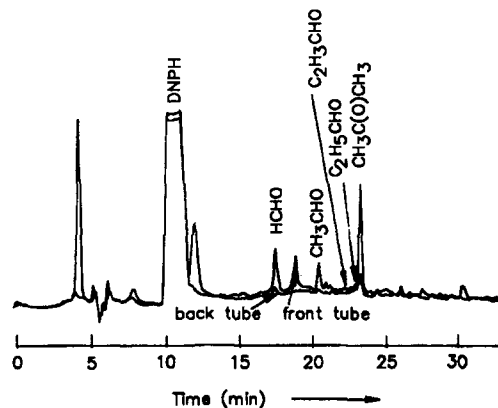


Fig. 2. HPLC chromatogram of 3 h sample taken at Egbert, Ont.

calibration was conducted using solutions of freshly synthesized hydrazones in ACN. The hydrazones were twice recrystallized from ethanol. To assess the collection efficiency for the  $\frac{1}{2}$ " tubes we conducted a brief series of experiments involving gas-phase samples prepared by dilution of pure carbonyl samples with clean air in Teflon bags. Although it was not possible in these experiments to determine the absolute accuracy of the technique (because of the difficulty in determining wall losses of the carbonyls in the bags), it was found that the 'collection efficiencies' for acetaldehyde, and propionaldehyde were both  $100 \pm 5\%$ , as measured by the fraction of the carbonyls that carry over into a second tube in series. These experiments are useful to the extent that there is a reduced possibility (using Teflon bag samples) for artifact formation in determination of the collection efficiency. The concentrations ranged from 50 to 100 ppb for these experiments and the flow rates were  $\approx 4 \text{ l min}^{-1}$ . Bag experiments using the  $\frac{1}{2}$ " tubes were not conducted for acetone. A limited set of bag experiments with acetone using the commercial Sep-Pak cartridges was conducted in which we found that the collection efficiency was  $90 \pm 10\%$ . Since the acetone experiments were conducted at sample flow rates of  $1 \text{ l min}^{-1}$  and the flow rates for the measurements reported here were  $\approx 3\text{--}3.5 \text{ l min}^{-1}$  it was anticipated that the collection efficiency for acetone using the  $\frac{1}{2}$ " tubes was less than that found for the Sep-Pak cartridges (see below).

There are several possible sources of error for the DNPH technique, including contamination of the cartridges, and differences in the degree of contamination for the front and back cartridge. It is also conceivable that the hydrazones will react with components of the air during sampling, thus leading to results that are low. It has recently been shown by Arnts and Tejada (1989) that  $\text{O}_3$  can react with both the DNPH reagent and with the product hydrazones, leading to a significant negative interference. For example, in the presence of 120 ppb  $\text{O}_3$ , the measured formaldehyde concentration were 34% low, at formaldehyde concentrations that were in the range 20–40 ppb. It should be noted that the Dorset site is normally fairly clean with respect to  $\text{O}_3$ , i.e. concentrations were typically  $\approx 20\text{--}40$  ppb.

## RESULTS

### Data reliability

Sample tubes for this study were prepared, sampled and analysed in lots of 26:12 each for front and back tubes, and two blanks. The blank samples were tubes prepared exactly as those used for ambient sampling and taken to the sites with the samples, but were not sampled. Formaldehyde, acetaldehyde and acetone were by far the dominant carbonyl compounds present in all samples. As described above, for each sample collected both front (F) and back (B) sample tubes were used. Since the collection efficiencies for formaldehyde and acetaldehyde are  $\approx 100\%$  the back tubes were used as the most representative blank, as discussed above. Thus for these two aldehydes (and propionaldehyde) the total number of moles collected was calculated by subtracting the amount measured in the back tube from the front. For acetone the total quantity of acetone hydrazone present on the back tubes was substantially larger than present in the blank tubes. As discussed above, this was interpreted as due to non-perfect collection efficiency. Because of this, for acetone the total number of moles collected was calculated as  $(\text{moles}_F - \text{blank}) + (\text{moles}_B - \text{blank})$ .

The blank values used in the above calculation were the average of two blank tubes used for each set of 12 samples. The average blank values for formaldehyde, acetaldehyde, and acetone were  $4 \pm 3$ ,  $3 \pm 4$  and  $5 \pm 1$  nmol tube $^{-1}$ , respectively. The average numbers of total moles collected (after blank correction) for these three compounds were 81, 20 and 71 nmol, respectively. From the calculated number of moles per tube and the integrated sample air volumes the gas-phase carbonyl concentrations in ppb (V/V) can be calculated. The calculated concentrations for both the Egbert and Dorset sites are presented in Tables 1 and 2. The data in these tables are all presented to two decimal places, for consistency. This is not meant to imply anything about the analytical uncertainty or sampling precision. The measurement uncertainty is discussed in more detail below. The mode of calculation for formaldehyde and acetaldehyde is intended to account for artifact formation or contamination. However, the method of acetone concentration calculation assumes no artifact formation and no contamination other than that experienced by the blank samples. Thus to the extent that such artifact formation or contamination does exist for acetone, then the acetone concentrations may be somewhat systematically high.

Formaldehyde measurements were also made at both sites using the TDLAS technique. The TDLAS data were obtained as 5 min averages, and for comparison have been averaged over the same time frame as used for the DNPH sampling (i.e. 3 or 6 h). These TDLAS averaged data are plotted against the DNPH data for 78 points in Fig. 3. A plot of  $([\text{HCHO}]_{\text{DNPH}} - [\text{HCHO}]_{\text{LASER}})$  vs the mean  $[\text{HCHO}]$  did not yield a slope significantly different from zero, indicating an absence of a statistically significant bias between the two methods. Nor was there a statistically significant difference in the slopes for the Egbert and Dorset measurements. In addition a linear regression of the data does not yield an intercept significantly different from zero. Thus the line in the figure represents the linear regression best-fit line  $([\text{HCHO}]_{\text{DNPH}} = 1.05 \times (\pm 0.07) \times [\text{HCHO}]_{\text{LASER}})$ , forced through the origin. The uncertainty represents the 95% C.L. for the slope. As can be seen in Fig. 3, there are three points at relatively high  $[\text{HCHO}]$  that are statistical outliers. Thus although they were included in the plot, they were not included in the regression. Including them in the regression did not, however, yield a slope significantly different from unity. The correlation coefficient is 0.79 for both data sets regressed together. The average difference between HCHO measurements for the two techniques is 31%.

To test for the possibility of interference from  $\text{O}_3$ , the ratio  $[\text{HCHO}]_{\text{DNPH}}/[\text{HCHO}]_{\text{LASER}}$  was plotted against  $[\text{O}_3]$  in Fig. 4 using data from both sites. Shown in this figure are the best-fit linear regression line along with the 95% confidence limits of the regression line. The indicated confidence limits indicate that the slope of the line is not significantly different from

Table 1. Carbonyl concentrations, ppb—Egbert, Ont., 1988

Sample start*	Sample stop	[HCHO]	[CH <sub>3</sub> CHO]	[CH <sub>3</sub> C(O)CH <sub>3</sub> ]	[C <sub>2</sub> H <sub>5</sub> CHO]	Sector†
7/25/16:05	7/26/09:36	NM	0.54	0.61	—	SW
7/26/09:40	7/26/14:10	2.04	0.82	2.04	—	SW
7/26/15:10	7/26/17:15	1.47	0.58	2.14	—	SW
7/26/17:21	7/27/09:13	1.15	0.50	1.11	—	NW
7/27/09:19	7/27/15:19	NM	0.54	1.43	—	NW
7/27/16:21	7/27/23:22	1.85	0.79	2.05	—	NW
7/27/23:22	7/28/05:22	1.75	1.92	3.69	—	NW
7/28/05:22	7/28/11:22	1.76	0.58	1.47	—	NW
7/28/11:22	7/28/17:22	3.02	0.40	2.04	—	NW
7/28/17:22	7/28/23:22	4.00	NM	0.97	—	SW
7/28/23:22	7/29/05:22	4.25	0.43	1.58	—	SW
7/29/05:22	7/29/11:22	3.57	0.74	1.41	—	SW
7/29/12:55	7/29/18:55	1.95	0.73	3.07	—	SW
7/29/18:55	7/30/00:55	NM	0.93	3.26	—	SW
7/30/00:55	7/30/06:55	NM	0.81	2.30	—	SW
7/30/06:55	7/30/12:55	3.04	1.03	3.25	—	SW
7/30/12:55	7/30/18:55	NM	0.64	2.35	—	SW
7/30/18:55	7/31/00:55	2.01	0.81	2.30	—	SW
7/31/00:55	7/31/06:55	1.71	0.47	1.91	—	SW
7/31/06:55	7/31/12:55	NM	0.75	2.44	—	SW
7/31/12:55	7/31/18:55	2.63	0.88	2.33	—	NW
8/01/00:55	8/01/06:55	1.62	0.75	2.44	—	NW
8/01/06:55	8/01/12:55	2.07	0.73	1.98	—	NW
8/15/09:53	8/15/12:45	1.43	1.39	1.18	—	NW
8/15/12:45	8/15/15:45	1.49	1.42	0.92	—	NW
8/15/15:45	8/15/18:45	1.70	0.48	1.15	—	NW
8/15/18:45	8/15/21:45	1.60	0.55	1.37	—	NW
8/15/21:45	8/16/00:45	1.59	0.71	1.58	—	NW
8/16/00:45	8/16/03:45	1.72	0.88	1.62	—	NW
8/16/03:45	8/16/06:45	1.93	1.00	1.73	—	NW
8/16/06:45	8/16/09:45	1.84	1.16	1.37	—	NW
8/16/09:45	8/16/12:45	3.14	0.94	1.84	—	NW
8/16/12:45	8/16/15:45	2.06	0.76	2.43	—	NW
8/16/15:45	8/16/18:45	2.80	1.01	2.41	—	NW
8/16/18:45	8/16/21:45	2.74	1.17	3.26	—	NW
8/28/14:57	8/28/17:57	0.92	0.40	0.94	0.027	NW
8/28/17:57	8/28/20:57	1.58	0.55	1.14	0.016	NW
8/28/20:57	8/28/23:57	1.17	0.27	1.75	0.021	NW
8/28/23:57	8/29/02:57	0.94	0.39	1.00	0.027	NW
8/29/02:57	8/29/05:57	0.76	0.28	0.70	0.017	NW
8/29/05:57	8/29/08:45	0.71	0.23	0.81	0.012	NW
8/29/08:45	8/29/11:45	1.06	0.34	2.05	0.020	NW
8/29/11:45	8/29/14:45	1.41	0.28	1.60	0.004	NW
8/29/14:45	8/29/17:45	0.97	0.42	1.38	0.055	NW
8/29/17:45	8/29/20:45	0.68	0.37	1.59	0.067	NW
8/29/20:45	8/29/23:45	0.71	0.20	0.39	—	NW
8/29/23:45	8/30/08:05	1.06	0.16	1.06	—	NW

NM Not measured.

\* Sample times in month/day/h:min.

† Air mass origin according to 48 h back trajectory.

zero, i.e. there is no apparent trend with increasing O<sub>3</sub> concentration. This is expected since the Arnts and Tejada (1989) study indicated that the effect is small below 100 ppb O<sub>3</sub>, and is within the scatter of the measurements. The scatter in the plotted ratio increases with decreasing O<sub>3</sub>, since O<sub>3</sub> correlates with the HCHO concentration and we would expect greater scatter in the DNPH measurements at low concentration. The TDLAS is calibrated with gas-phase formaldehyde standards introduced at the system inlet using a formaldehyde permeation source calibrated against chromotropic acid. It is estimated that the absolute uncertainty in the TDLAS measure-

ments was  $\pm 15\%$ . For many of the individual sets of samples collected, the agreement between the two was much better than that observed over the entire study. For example for the period 4–7 August, the average difference between the two techniques at Dorset was 24%. These data are plotted in Fig. 5, where the vertical error bars represent the 95% confidence limits of the back cartridge loading (relative to the front cartridge). This is appropriate since we are assuming that the back cartridge represents the best blank. Thus the error bars represent the 95% confidence limits of the blank concentration. (The horizontal bars for all figures with error bars represent the range of the

Table 2. Carbonyl concentrations, ppb—Dorset, Ont., 1988

Sample start*	Sample stop	[HCHO]	[CH <sub>3</sub> CHO]	[CH <sub>3</sub> C(O)CH <sub>3</sub> ]	Sector†
7/28/18:00	7/29/00:00	2.40	0.85	3.29	SW
7/29/00:00	7/29/06:00	1.75	0.56	2.95	SW
7/29/06:00	7/29/12:00	2.40	0.82	2.89	SW
7/29/12:00	7/29/18:00	2.15	1.19	3.67	SW
7/30/00:00	7/30/06:00	2.57	0.74	3.34	SW
7/30/06:00	7/30/12:00	3.87	NM	1.12	SW
7/30/12:00	7/30/17:00	2.31	1.11	3.10	SW
8/04/12:30	8/04/18:30	3.06	1.49	4.15	SW
8/04/18:30	8/05/00:30	1.74	0.49	3.62	SW
8/05/00:30	8/05/06:30	1.74	0.66	2.57	SW
8/05/06:30	8/05/12:30	4.41	1.66	3.52	SW
8/05/12:30	8/05/18:30	3.55	1.11	3.81	SW
8/05/18:30	8/06/00:30	1.47	0.53	2.33	SW
8/06/00:30	8/06/06:30	1.37	0.13	1.37	SW
8/06/06:30	8/06/12:30	1.61	0.70	1.81	SW
8/06/12:30	8/06/18:30	1.52	0.68	1.93	NW
8/06/18:30	8/07/00:30	1.02	0.32	1.42	NW
8/07/00:30	8/07/06:30	0.89	0.42	1.24	NW
8/07/06:30	8/07/12:30	0.61	0.24	1.09	NW
8/15/18:00	8/15/21:00	1.20	0.38	1.78	NE
8/15/21:00	8/16/00:00	1.30	0.39	0.65	NE
8/16/00:00	8/16/03:00	0.80	0.24	1.12	NE
8/16/03:00	8/16/06:00	1.05	0.14	0.76	NE
8/16/06:00	8/16/09:00	0.97	0.44	0.72	NW
8/16/09:00	8/16/12:00	3.20	0.58	2.71	NW
8/16/12:00	8/16/15:00	4.12	1.15	4.30	NW
8/23/15:00	8/23/18:00	1.45	0.51	1.24	SE
8/23/18:00	8/23/21:00	1.78	0.60	1.34	SE
8/23/21:00	8/24/00:00	2.11	0.53	1.34	SE
8/24/00:00	8/24/03:00	1.43	0.41	1.66	SE
8/24/03:00	8/24/06:00	0.86	0.95	1.60	SE
8/24/06:00	8/24/09:00	1.09	0.82	1.30	SE
8/24/09:00	8/24/12:00	2.06	0.98	1.96	SE
8/24/12:00	8/24/15:00	2.57	0.80	1.64	SE
8/24/15:00	8/24/18:00	1.95	0.56	1.81	SE
8/24/18:00	8/24/21:00	0.61	0.11	1.18	SE
8/24/21:00	8/25/00:00	0.94	0.27	0.82	SE
8/28/14:15	8/28/18:00	1.01	0.09	1.03	SW
8/28/18:00	8/28/21:00	1.44	0.34	0.99	SW
8/28/21:00	8/29/00:00	0.50	0.26	1.01	SW
8/29/00:00	8/29/03:00	0.90	0.17	0.80	NW
8/29/03:00	8/29/06:00	0.85	0.19	0.66	NW
8/29/06:00	8/29/09:00	1.23	0.27	1.02	NW
8/29/09:00	8/29/12:00	1.11	0.29	1.41	NW
8/29/12:00	8/29/15:00	1.18	0.34	1.24	NW
8/29/15:00	8/29/18:00	1.36	0.30	2.02	NW
8/29/18:00	8/29/21:00	0.99	0.38	1.17	NW
8/29/21:00	8/30/00:00	0.63	0.16	0.84	NW
8/30/00:00	8/30/03:00	0.63	0.17	1.21	NW

NM Not measured.

\* Sample times in month/day/h:min.

† Air mass origin according to 48 h back trajectory.

sampling interval.) The data for the two techniques correlate well, but there is some systematic difference between them near the end of the period. We estimate that the absolute uncertainty (i.e. including any possible systematic errors) in the formaldehyde and acetaldehyde measurements for this study was  $\pm 30\%$ . For acetone we estimate  $\pm 40\%$ , due to the uncertainty in the collection efficiency.

An intercomparison study of formaldehyde measurement techniques was recently conducted (Kleindienst *et al.*, 1988) in which the DNPH technique using

Waters Sep-Pak cartridges was compared to the TDLAS technique, for 10 ambient samples ranging from  $\approx 1$  to 8 ppb. When the DNPH results are plotted on the ordinate, the slope and intercept were  $0.95 \pm 0.36$  and  $0.9 \pm 2.5$  ppb, respectively, with a correlation coefficient of 0.906. Although the correlation coefficient is better for the Kleindienst *et al.* data the concentrations measured in that study were significantly higher. Another comparison between the DNPH technique using the Sep-Pak cartridges and several other spectroscopic techniques for ambient HCHO

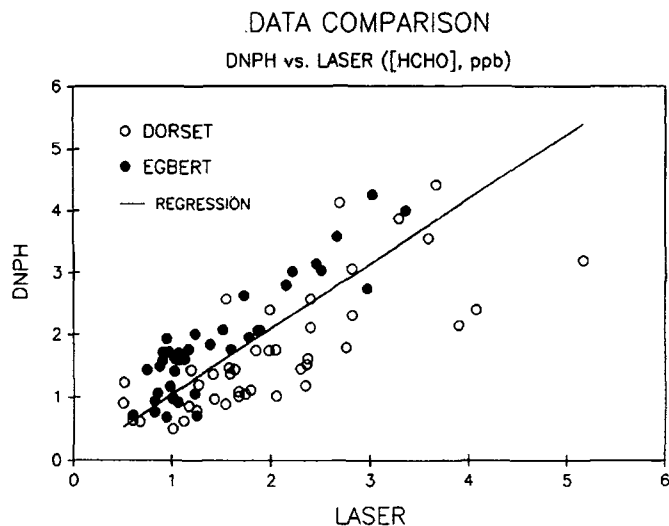


Fig. 3. Comparison of HCHO concentrations measured using TDLAS and DNPH techniques.

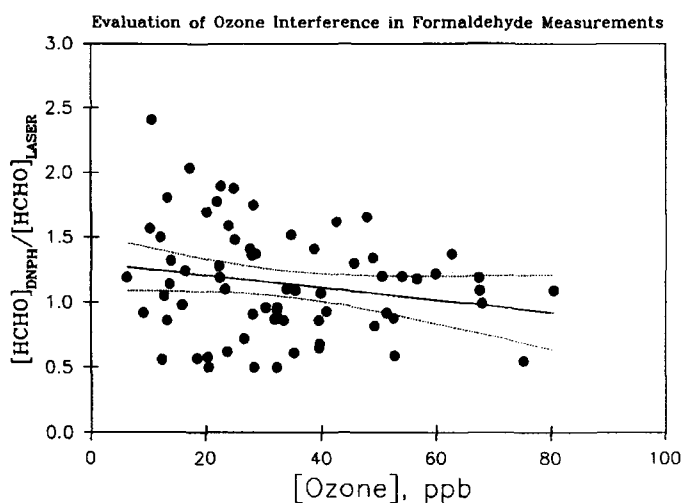


Fig. 4. Plot of the ratio of HCHO determinations (DNPH/LASER) vs the measured ozone concentration.

measurements (FTIR, TDLAS, DOAS and two fluorometric methods) was recently performed at a site 35 km east of Los Angeles (Lawson *et al.*, 1991). The ambient formaldehyde concentrations were typically between 5 to 15 ppb. For a set of 16 DNPH samples, when evaluated against the mean of the spectroscopic techniques, the DNPH technique yielded a slope and intercept of  $0.81 \pm 0.30$  and  $0.64 \pm 0.82$  (indicated errors are 95% C.L.) ppb, respectively, with a correlation coefficient of 0.85. We note that the peak  $O_3$  concentrations for that study were near 200 ppb, and thus, as discussed by Arnts and Tejada (1989), interference from  $O_3$  could offer an explanation for the DNPH method yielding results that were 15–20% low. It

would thus appear that the quality of results obtained in this study using the DNPH technique compare well with others, particularly considering that the formaldehyde concentrations prevalent at these two rural sites were typically a factor of five lower than, for example, in the Lawson *et al.* (1991) study.

#### Measurement results

This data set represents the first measurements of these three carbonyl compounds in a rural environment in Canada. Not all of the samples obtained during this study were obtained simultaneously at the two sites. However, 26 pairs of samples were acquired with sample time midpoints for the two sites that were

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DNPH and Laser HCHO Measurements

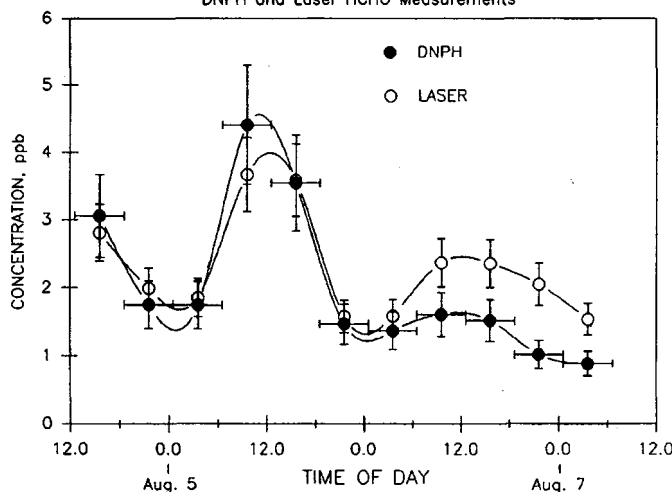


Fig. 5. Comparison of HCHO measurements at Dorset, Ont., 4-7 August 1988.

the same to within 1 h. The average concentrations for this set of 'simultaneous' data are presented in Table 3 below. It was found that there is no significant difference in averages for the complete and simultaneous data sets. The average ratio for measurement of each of the three compounds (for simultaneous samples) at Egbert vs Dorset is presented in the Table as E/D. Also presented in Table 3 are the analogous averages for simultaneous samples obtained under conditions of air trajectories that were from the southwest (see Discussion).

In principle this technique could be used for ambient measurements of nearly all carbonyl compounds. However, as indicated in Fig. 2, formaldehyde, acetaldehyde and acetone are by far the principal carbonyls present. The determination of higher molecular weight carbonyls is complicated by their low concentrations and the increased problems with unambiguous identification due to coeluting isomeric compounds. Although the  $C_3$  aldehyde acrolein is well resolved from the other carbonyls (see Fig. 2) our limited laboratory studies using samples of acrolein in air in Teflon bags yielded results that were low (relative to the calculated bag concentrations); Tejada (1986) has indicated that the acrolein hydrazone may be unstable. In cases where the blank levels are low, however, it is possible to quantitatively determine propionaldehyde concentrations. For illustrative purposes we present in Table 1 data from 29 and 30 August at Egbert for propionaldehyde. For this data set the average ratio  $[C_2H_2CHO]_{FRONT}/[C_2H_2CHO]_{BACK}$  was 1.82, i.e. these samples were at or near the limit of detection. It can be seen from these data that the propionaldehyde levels are very low relative to the other carbonyls. For example, for this data set, the average ratio  $[CH_3CHO]/[C_2H_5CHO]$

$= 21$ . This is most likely a reflection of the fact that propionaldehyde is associated with anthropogenic hydrocarbon precursors, whereas the other carbonyl compounds have both anthropogenic and natural hydrocarbon precursors. For this particular set of days the 48 h back trajectories were from the northwest, that is the air was relatively clean and free of anthropogenic pollution. This ratio can be compared with that observed by Grosjean (1982) for polluted Los Angeles air of  $\approx 1$ . Thus it appears that the ratio  $[CH_3CHO]/[C_2H_5CHO]$  may serve as an effective indicator of the presence of anthropogenic pollution.

Since these carbonyl compounds are products of atmospheric hydrocarbon photooxidation, we might expect the concentration data to exhibit a diurnal profile. We have calculated the average concentration for each of the three carbonyls for both sites as a function of time of day, in 3 h intervals, e.g. all samples whose midpoints fall between 00:00 and 03:00 were averaged and taken as the average concentration at 01:30. The result of these calculations are presented in Figs 6 and 7 (Dorset and Egbert, respectively). For clarity of presentation we have included only the error bars ( $\pm 1\sigma$ ) for the formaldehyde measurements. Figure 6 indicates that there is a strong diurnal variation in all three carbonyls for the Dorset site, with the maximum concentration for all three species being between noon and 3:00 pm. There also seems to be a smaller night-time maximum for the 3-6 a.m. period. We do not believe that this is an artifact as it was also visible in the TDLAS data for several days. In contrast, however, the corresponding plot for the Egbert site (Fig. 7) shows a minimal diurnal variation, with the exception of a slight decrease in concentration between 3:00 and 6:00 a.m. which is also apparent in the Dorset data for HCHO and  $CH_3C(O)CH_3$ .



Table 3. Average carbonyl concentrations determined at Egbert (E) and Dorset (D), ppb (simultaneous samples)

	HCHO	CH <sub>3</sub> CHO	CH <sub>3</sub> C(O)CH <sub>3</sub>	HCHO/CH <sub>3</sub> CHO	HCHO/CH <sub>3</sub> C(O)CH <sub>3</sub>
E	1.8(1.0)*	0.57(0.28)	1.6(0.7)	3.4(1.8)	1.3(0.8)
E(SW traj.)	2.8(1.2)	0.67(0.19)	1.9(0.8)	4.2(2.6)	1.9(1.2)
D	1.6(1.0)	0.46(0.32)	1.8(1.1)	4.0(1.9)	1.0(0.6)
D(SW traj.)	2.2(0.8)	0.71(0.35)	2.5(1.0)	4.0(2.8)	1.0(0.9)
E/D, avg.: (all)	1.3(0.5)	1.7(1.8)	1.1(0.6)		
E/D, avg.: (SW traj.)	1.3(0.5)	1.4(1.3)	1.0(0.7)		

\* 1 std. dev.

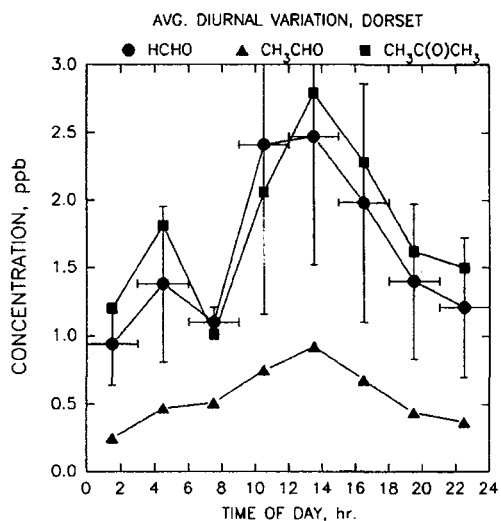


Fig. 6. Average diurnal variation in carbonyl compound concentrations measured at Dorset, Ont.

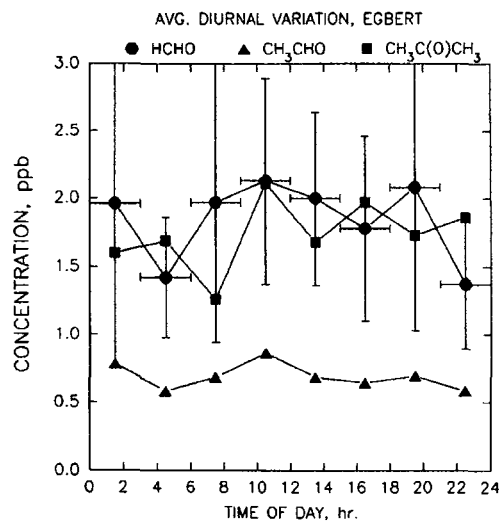


Fig. 7. Average diurnal variation in carbonyl compound concentrations measured at Egbert, Ont.

#### DISCUSSION

There have been relatively few ambient measurements of carbonyl compounds in rural areas against which to compare our data. Formaldehyde measurements over the mid-Atlantic using a DNPH method (Lowe and Schmidt, 1983) yielded concentrations typically in the range of 0.1–0.3 ppb. In contrast, daytime urban formaldehyde concentrations are typically in the range 10–30 ppb (Lawson *et al.*, 1991; Grosjean, 1982; Tanner *et al.*, 1988; Schulam *et al.*, 1985). The measurements of Lowe and Schmidt (1983) reflect the range of background formaldehyde concentrations resulting from oxidation of methane and light NMHCs in clean air. A limited set of acetaldehyde measurements (Schulam *et al.*, 1985) in August at Whiteface Mountain, New York, yielded concentrations typically in the 0.3–0.7 ppb range. Both acetaldehyde and acetone have been measured (Cavanagh *et al.*, 1969) at Point Barrow, Alaska, using a gas chromatographic technique, where acetaldehyde and acetone were found typically at levels of 0.2–0.3 and 0.5–1.5 ppb, respectively. As discussed by Chatfield *et*

*al.* (1987), recent tropospheric acetone measurements range from 0.2 to 1.8 ppb, with mean values of 0.5 ppb in the remote Northern Hemisphere. Thus the levels observed at Dorset are significantly above the marine background, whether due to impact from natural hydrocarbons or transport from anthropogenic sources.

We note that the average carbonyl compound concentrations (see Table 3) are very similar for the two sites, even though the Egbert site (under southerly flow) is more likely to be subject to transport from urban sources. For acetone this observation can be reconciled taking into account the relatively slow rates for its formation and removal processes. As discussed by Chatfield *et al.* (1987), OH reaction with propane can account for perhaps half of the acetone production in the troposphere. The effective rate constant (at 298 K) for production of the appropriate precursor radical is  $9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , corresponding to a 'lifetime' for acetone formation by this route of  $\approx 13$  days (assuming an OH concentration of  $1 \times 10^6 \text{ cm}^{-3}$ ). There are two known principal sinks for acetone: photolysis and reaction with OH. As discussed by Chatfield *et al.* rainout and washout are

of negligible importance for acetone due to its high vapor pressure and moderate Henry's Law coefficient ( $30 \text{ M atm}^{-1}$ ). The deposition velocity for acetone to ground is not known. The lifetimes for acetone for removal by photolysis and OH reaction are approximately 40 and 20 days, respectively. It thus seems reasonable to expect that acetone concentrations should not vary considerably over time scales corresponding to a typical air parcel transit time between Egbert and Dorset (for wind speeds of  $15 \text{ km h}^{-1}$  the transit time would be  $\approx 10 \text{ h}$ ). In contrast, both formaldehyde and acetaldehyde can be produced from very reactive hydrocarbons, and their atmospheric lifetimes for reaction with OH are roughly one half to one day. The fact that the concentrations for these aldehydes are similar at the two sites could be reconciled assuming that natural hydrocarbon chemistry is more dominant for the Dorset site, as discussed below.

As indicated in Table 3, the typical measured ratio for  $[\text{HCHO}]/[\text{CH}_3\text{CHO}]$  is 3–4. The relatively high values for this ratio observed in this study may reflect the local participation of natural reactive hydrocarbons whose oxidation yields more formaldehyde than acetaldehyde. For example, isoprene, which is a major reactive hydrocarbon for both sites yields formaldehyde as a principal atmospheric photooxidation product (Lloyd *et al.*, 1983). A computer simulation of isoprene photooxidation was shown to yield a  $[\text{HCHO}]/[\text{CH}_3\text{CHO}]$  ratio of 10 (Jacob and Wofsy, 1988). Recent measurements of formaldehyde and acetaldehyde (conducted by H. Westberg, Washington State University) at Scotia, PA, a forested (deciduous) site at which isoprene chemistry often plays a dominant role indicated a  $[\text{HCHO}]/[\text{CH}_3\text{CHO}]$  ratio of typically 10 (Shepson, 1989). We note that for the 'simultaneous' data set this ratio was slightly higher at Dorset (a more forested site) than in Egbert (4.0 vs 3.4, respectively). This can be compared with a typical ratio of these two compounds in Southern California sites of  $\approx 2$  (Grosjean, 1982; Singh and Salas, 1986). Tanner and Meng (1984) have reported seasonal variations in this ratio for samples obtained on Long Island, i.e. 4.1 in the winter and 1.9 in the summer. It is not clear why this should be the case. As discussed above, one might expect considerably higher ratios in the summer, due to oxidation of natural hydrocarbons such as isoprene which leads to HCHO. It is interesting to note that Tanner *et al.* (1988) have found ratios of  $[\text{HCHO}]/[\text{CH}_3\text{CHO}]$  in Rio de Janeiro of 0.85, presumably due to substantial use of ethanol-containing fuel in that area. Thus since the  $[\text{HCHO}]/[\text{CH}_3\text{CHO}]$  ratio can vary between  $\approx 1$  (urban) and 10 (deciduous forested) this ratio could be used as a measure of the possible impact of natural hydrocarbons in the photochemistry of a particular air mass.

Since these two sites are located along a line from southwest to northeast (a trajectory which may be

expected to represent relatively polluted air), we analysed these data with respect to the existing wind fields. Average concentrations were calculated for the entire period according to air mass origin using the 48 h back trajectories (925 mbar). The averages were segregated into four quadrants, i.e. NE, SE, SW and NW, and are presented in Fig. 8 (where the error bars represent  $\pm 1\sigma$ ). The air mass sector for each sample obtained is indicated in Tables 1 and 2. Because of the limited nature of the data set a complete set of sectorized averages could only be obtained for the Dorset site. As expected, the average concentrations are significantly higher when the air mass is from the southwest for the Dorset site (for formaldehyde and acetaldehyde), indicating that pollutant transport to the site is important. For nine of the 'simultaneous' samples the trajectory was from the SW. Averages for these samples for Egbert and Dorset are presented in Table 3. Although the average concentrations are higher for these conditions, there is not a significant difference in the ratios of concentrations determined in Egbert vs Dorset relative to the ratios for the full set of 'simultaneous' samples. This may be a reflection of the complexity of conditions that influence carbonyl concentrations at these sites. For example, although the air transported to both sites may contain relatively high carbonyl concentrations, the ambient temperature was considerably higher under southwesterly flow, and thus emission rates of natural hydrocarbons would be expected to be higher, particularly for the Dorset site.

As indicated in Figs 6 and 7, there is a strong diurnal dependence of the carbonyl concentrations at the Dorset site, but not at the Egbert site. The diurnal profile is very similar for all three carbonyls at the Dorset site. There is frequently a sharp rise in the concentrations of these carbonyls as well as for other

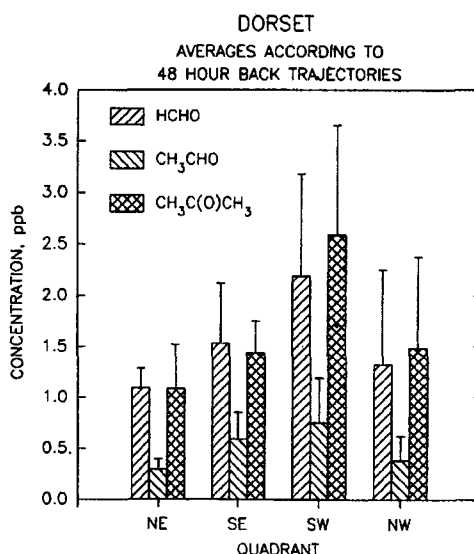


Fig. 8. Average carbonyl compound concentrations measured at Dorset, Ont., according to air mass origin.

pollutants such as PAN, O<sub>3</sub> and particulate matter at ≈9:00 a.m. These pollutant concentrations rise too fast and too early in the day for this to be entirely of photochemical origin. In Fig. 9 we present as an example 5 min averaged O<sub>3</sub> (Dasibi) and half hour averaged HCHO (TDLAS) data from 5 August, indicating a substantial increase in the concentrations of these species between 8:00 and 10:00 a.m. Because of the time of day and the rapid increase in concentration this is likely to be at least partly a physical process. The Dorset site is in a valley which is conducive to the formation of a low nocturnal inversion layer that breaks up early in the day, i.e. between 6 and 9 a.m. Thus during the night there is dry deposition of pollutants to the surface which significantly depletes the concentrations under this inversion layer, as apparent for example in the O<sub>3</sub> data in Fig. 9. When the inversion layer rises (from solar heating), more polluted air from aloft can mix downward causing the surface level concentrations to rise. Such a diurnal pattern influenced by night-time radiation inversions has been previously observed (cf. Colbeck and Harrison, 1985; Fehsenfeld *et al.*, 1983). The most convincing evidence for this may be in the fact that the profiles for acetone and formaldehyde are very similar for the Dorset site (Figs 6 and 10). This is not what would be expected if chemical processes were dominant, in light of their very different formation and removal rates, as discussed above.

It is also interesting to note that there is often a local maximum in the early morning hours for these carbonyls (i.e. for the 3–6 a.m. averages in Fig. 6), centered typically around 3:00 a.m., which has also been observed in the formaldehyde (TDLAS) and O<sub>3</sub> data. It would seem most likely that this is caused by a purely meteorological process, i.e. a similar downward mixing of more polluted air from aloft.

A stagnant air event with back trajectories from the southwest occurred for the samples obtained at Dorset on 4–7 August. Various key chemical species as well as the carbonyl compounds for this time period are plotted in Fig. 10. We also present here data for HCHO (TDLAS), PAN and O<sub>3</sub> at Egbert for the purpose of comparison. These data illustrate clearly the strong diurnal variation with substantial night-time losses, and a sharp early morning increase for all compounds at the Dorset site. In contrast to this it can be seen in Fig. 10 that the diurnal variation is less pronounced at the Egbert site (e.g. for HCHO and O<sub>3</sub>). See Fig. 9 for the Dorset TDLAS HCHO data on 5 August. This is most likely due in part to greater losses at the surface during the night-time in Dorset under the low lying nocturnal inversion layer. It should be noted, however, that shallow night-time inversions are common at the Egbert site (Hoff *et al.*, 1989). For 5 August the inversion height in the early morning hours was ≈300 m. On 5 August the 48-h back trajectory (925 mb) indicated wind flow in a line from Egbert to Dorset but by 7 August the back trajectories were from the northwest. The diurnal variation at Dorset during this period (i.e. 4–6 August) seems to be reasonably consistent with an early morning break-up of the nocturnal inversion layer resulting in more polluted air from aloft mixing down to ground level. By 7 August the air aloft was relatively clean. It should be noted, however, that although the Egbert air had higher concentrations of ozone and PAN than observed for daytime samples at Dorset, the formaldehyde concentrations during this period (e.g. 5 August) were significantly higher at Dorset, as shown in Fig. 10. Thus formaldehyde was to some extent either produced as a result of local photochemistry at Dorset, or within the air mass in transit between the two sites.

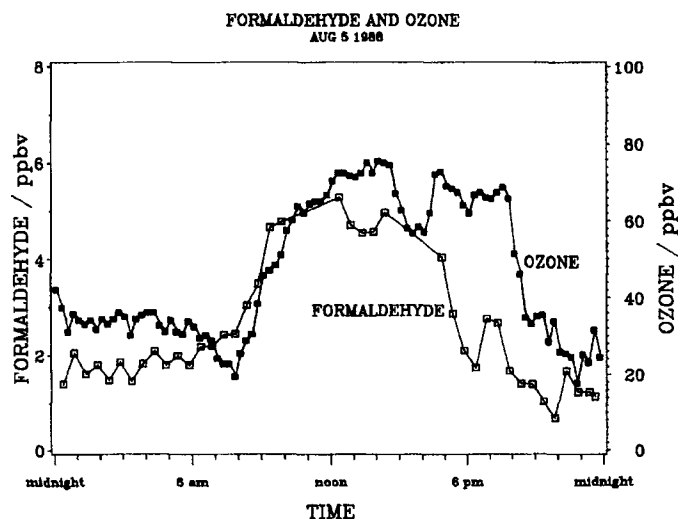


Fig. 9. Ozone and HCHO (TDLAS) measurements conducted 5 August 1988 at Dorset.

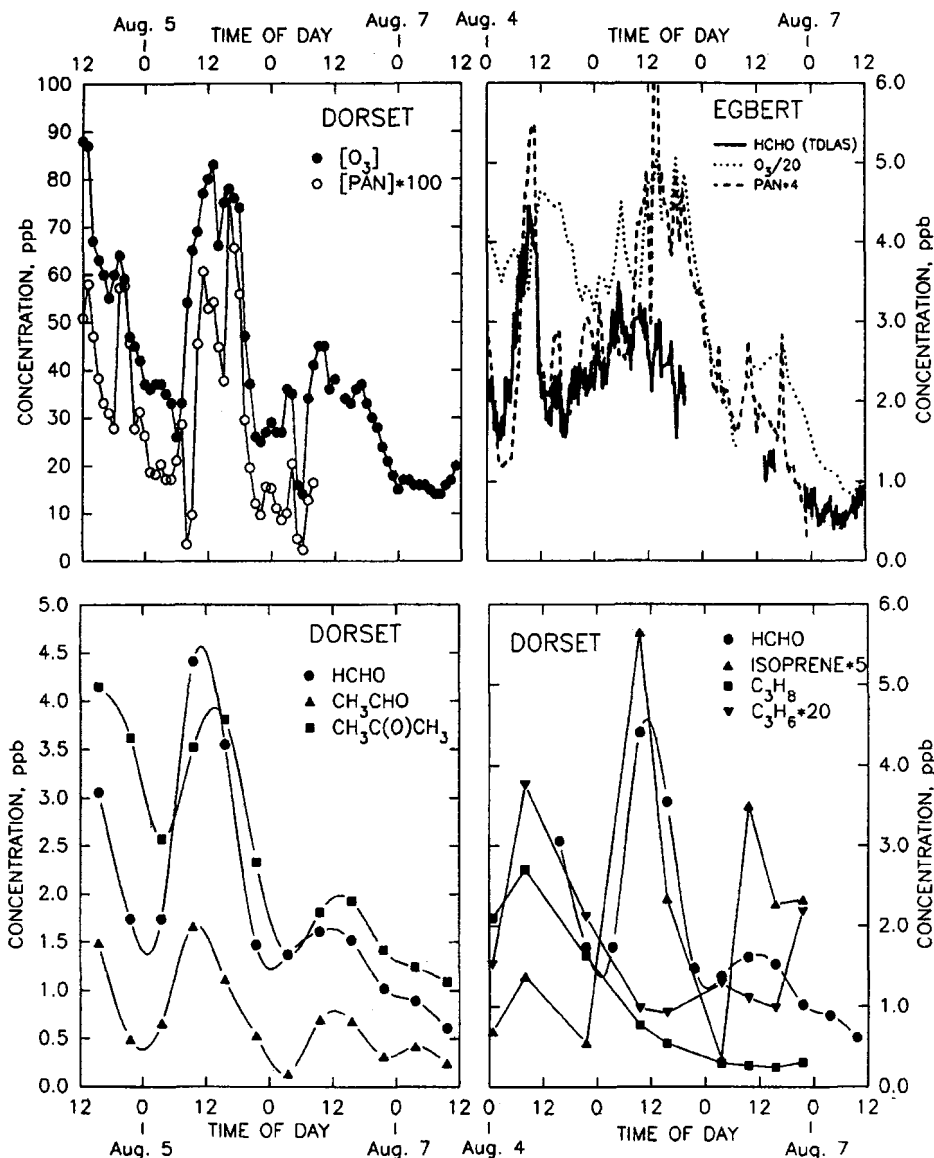


Fig. 10. Selected species concentrations at Egbert and Dorset, 4-7 August 1988.

Since the carbonyls are products of hydrocarbon oxidation it is instructive to examine hydrocarbon profiles in the same time period. Figure 10 shows propane, propene and isoprene data obtained at the Dorset site for the period 4-7 August. Propane and propene were chosen because they represent a range of atmospheric lifetimes; for propene the lifetime for reaction with OH is  $\approx 10$  h, whereas for propane it is closer to 10 days. In addition OH reaction with propene is one (of many) source of formaldehyde and acetaldehyde, and as stated above, propane is an important source of acetone. It seems clear from inspection of Fig. 10 that local photochemistry involving these anthropogenic hydrocarbons is not the source of the increased carbonyl concentrations on 5 August. Although there were only three hydrocarbon

samples per day the carbonyl and the isoprene concentrations seem to be correlated. Given the relatively high ratio  $[HCHO]/[CH_3CHO]$ , the relatively higher HCHO present at Dorset (in this time period), and the isoprene data, it appears that there may have been a significant contribution to the carbonyl production (and other secondary pollutants) from local photochemistry involving natural hydrocarbons. With this in mind, it is interesting to note that double peaks were observed in the ozone and particularly the PAN profile on 5 August with maxima at  $\approx 4:00$  p.m. This is consistent with local photochemistry contribution as there was increased cloud cover in the early afternoon at Dorset followed by a local maximum in irradiance near 4:00 p.m. It is difficult (in the absence of a detailed modelling study) to delineate the possible

contribution to the observed profiles from meteorological and photochemical effects. These measurements, however, illustrate the need for measurements of the products of natural hydrocarbon oxidation, i.e. in the case of isoprene, methyl vinyl ketone and methacrolein measurements would have been particularly instructive. Isoprene was one of the most important reactive hydrocarbons present in terms of the product of hydrocarbon concentration and its OH reaction rate constant (Bottenheim *et al.*, 1990). Thus the DNPH technique should be further evaluated in terms of application to higher molecular weight carbonyl compounds.

As stated above the averaged data from Egbert exhibits little diurnal variation. However there are some cases where there is strong diurnal variation at the Egbert site, e.g. the period 28–30 August (Fig. 11 for both Egbert and Dorset), which shows a strong diurnal variation in the formaldehyde and acetone concentrations, particularly for the Egbert site. This diurnal pattern is also apparent in the Egbert O<sub>3</sub> data for this period, where for example the O<sub>3</sub> varied between 8 ppb at 8:00 a.m. and a maximum of 39 ppb at 3:00 p.m. on 29 August. Throughout this period the back trajectories indicated flow from the west to northwest, and levels of all pollutants were relatively low for both sites (the O<sub>3</sub> reached a maximum at Dorset at 3 p.m. of  $\approx 38$  ppb). For this period the HCHO and CH<sub>3</sub>C(O)CH<sub>3</sub> profiles are very similar, even for the Egbert site. It is unclear why this should

be the case, unless there is also a significant meteorological impact on the acetone profiles for Egbert as well. Under conditions of W–NW flow, the two sites should be identical in terms of chemical inputs from transport, assuming regional representativeness for these sites. In addition, there is little diurnal variation in the acetaldehyde data for this period, in contrast to that observed for the other two species. Of the three species the detection limit and the precision for acetaldehyde measurement is better than for the other two species (cf. Fig. 2) because of consistently low blank values for acetaldehyde. The very low levels of propionaldehyde, shown in Table 1, are consistent with expectations for relatively clean rural air. The data in Fig. 11 indicate a much more distinct diurnal variation for formaldehyde than observed by Lowe and Schmidt for the mid-Atlantic data. The chromatogram presented in Fig. 2 (taken from a sample from Egbert on 29 August) indicated that for these concentrations the front tube levels are substantially above the detection limit, for 3 h integrated samples. Thus, this data set clearly indicates that this method can provide adequate time resolution to make it a viable technique for examining relatively short-term fluctuations in carbonyl concentrations in clean air. With further optimization of this technique it could provide useful data in terms of interpretation of the contribution of natural hydrocarbons to photochemistry at rural sites.

## CONCLUSIONS

In this paper we have presented the results of measurements of C<sub>1</sub>–C<sub>3</sub> carbonyls that were made at two sites in central Ontario. The measurements of formaldehyde conducted using a modified DNPH technique exhibited reasonable agreement with the TDLAS technique, but with considerable scatter. Improvement could possibly be achieved using an ozone scrubber on the sample inlet that is inert towards the carbonyls, but this is likely to be useful only for very polluted air. Overall, the technique did yield reasonable data for the carbonyls measured at levels as low as 0.1 ppb for 3 h integrated samples. By far the dominant carbonyl compounds in this environment are formaldehyde, acetaldehyde and acetone. Measurements of propionaldehyde indicate that the ratio [CH<sub>3</sub>CHO]/[C<sub>2</sub>H<sub>5</sub>CHO] may be a useful indicator of the presence of anthropogenic photochemical pollutants. Although the formaldehyde and acetaldehyde concentrations were on average slightly higher at the Egbert site, this was not the case for acetone, probably reflecting its longer atmospheric lifetime and slower formation rates. Under conditions of southwesterly flow the Dorset carbonyl concentration data are consistent with a significant contribution from transport. The Dorset data also exhibit a strong diurnal variation that appears to be significantly driven by the formation of a nocturnal inversion layer influenced by the local topography. This conclusion is supported by

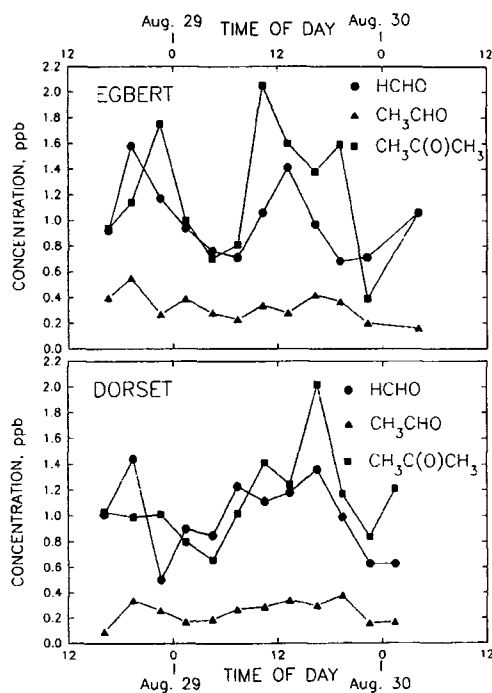


Fig. 11. Measured carbonyl compound concentrations at Egbert and Dorset, 28–30 August 1988.

the similarity in the formaldehyde and acetone profiles. However, from comparison with other measurements of carbonyls and from limited hydrocarbon data it appears that there may well be significant photochemical activity involving natural hydrocarbons that influences the levels of carbonyl compounds and other secondary products, e.g. O<sub>3</sub> and PAN. The relatively high ratios of formaldehyde to acetaldehyde and propionaldehyde are consistent with contribution to its formation from natural hydrocarbons, e.g. isoprene. The ratio [HCHO]/[CH<sub>3</sub>CHO] may be a useful indicator of the impact of natural hydrocarbons in local scale photochemistry. Further measurements of other carbonyls (e.g. methyl vinyl ketone and methacrolein) at this site using the DNPH technique could provide valuable information regarding the relative contribution of natural and anthropogenic hydrocarbons to local photochemical processes.

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