

ATMOSPHERIC CONCENTRATIONS AND TEMPORAL VARIATIONS OF C₁–C₃ 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 ≈ 60 km northwest of Toronto, while the other site (at Dorset, Ont.) is ≈ 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 HO₂ 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_x (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 ≈ 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 ≈ 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 ≈ 60 km to the northwest of Toronto, and is ≈ 8 km to the northeast of the town of Alliston, population ≈ 5000 . A major (north-south) highway passes ≈ 5 km to the east. Thus depending on the air trajectory there can be significant relatively local sources of hydrocarbons and NO_x.

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_x 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 ≈ 500 m to the northwest (elevation 385 m), ≈ 500 m to the northeast (elevation 401 m), and ≈ 1000 m to the south (elevation 409 m). The local land is 88% forested (75% deciduous, 25%

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