RELATIONSHIPS BETWEEN PAN, PPN AND O_3 AT URBAN AND RURAL SITES IN ONTARIO

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Abstract—PAN concentrations were determined during the summer of 1989 and the winter of 1990 at three sites in Ontario representing urban (Toronto), suburban downwind (Stouffville) and rural (Dorset) locations. PAN concentrations were found to reach levels of $\approx$4 ppb in Toronto under conditions of stagnant southerly air flow. Observed PAN concentrations were compared with concurrent measurements of PPN and O_3. PPN concentrations were found to be, on average, between 8 and 11% of those of PAN, with slightly higher PPN/PAN ratios found for air masses that were relatively anthropogenic-pollution impacted. For the Dorset site, however, the dependence on air-mass origin was small. The slopes of regressions of ozone vs PAN were found to increase substantially from urban to rural air masses, with typical O_3/PAN ratios for a mid-range ozone concentration of 50 ppb being 50, 110 and 330, for Toronto, Stouffville and Dorset, respectively. Analysis of the data for Toronto and Stouffville under varying meteorological conditions indicates significant potential for oxidant production in the absence of transport of pollutants from other sources.

Key word index: PAN, PPN, ozone, nitrogen oxides, oxidant, troposphere, photochemistry.

1. INTRODUCTION

Recently there has been renewed interest in the importance of peroxyacetyl nitrate (PAN) in tropospheric photochemistry. PAN has long been known to be a potent lachrymator (Stephens *et al.*, 1961; Heuss and Glasson, 1968) and phytotoxicant (Taylor, 1969; Mudd, 1975; EPA, 1978; Temple and Taylor, 1983). There has also been increasing concern with regard to the role of PAN in human health effects due to exposure to ambient air, particularly in the presence of elevated O_3 (Horvath *et al.*, 1986). PAN has been shown to react with bacterial DNA and with nucleic acid bases (Peak and Belser, 1969), and Lovelock (1977) has speculated on the possible role of PAN in the incidence of skin cancer in photochemically active areas. PAN has since been found to be a bacterial mutagen (Kleindienst *et al.*, 1985, 1990). There is thus a need for understanding of the conditions leading to elevated levels of PAN for both urban and rural areas. In addition to being a product of photochemical smog, PAN's thermal decomposition to yield free radicals can result in acceleration of the development of photochemical smog (Carter *et al.*, 1981). The strong temperature dependence of the thermal decomposition of PAN (Cox and Roffey, 1977; Hendry and Kenley, 1977) has a substantial impact on its role in global tropospheric photochemistry. At low temperatures, PAN can represent an important reservoir for atmospheric odd nitrogen (Singh and Hanst, 1981; Singh and Salas, 1983). Numerous studies indicate the potential for long-range transport of reactive nitrogen as PAN (Nielsen *et al.*, 1981; Hov, 1984; Brice *et al.*, 1984). This is supported by recent observations of high PAN/NO_x ratios in the cool middle free troposphere (Ridley *et al.*, 1990a), and the dominance of PAN as the major odd nitrogen compound in the Arctic (Bottenheim *et al.*, 1986; Bottenheim and Gallant, 1989).

There have been relatively few measurements of PAN at either urban or rural sites in Canada. PAN measurements have been reported for the Canadian Prairie cities of Edmonton (Peake *et al.*, 1988) and Calgary (Peake and Sandhu, 1983). Daytime PAN concentrations reaching as high as 7 ppb were reported for these cities during stagnant summertime conditions, and as high as 1–2 ppb in winter. These cities are relatively isolated with respect to transport of PAN precursors, thus these data indicate clearly the potential for photochemical production of PAN on a local scale for even these relatively north-latitude (51°N) cities. This conclusion is supported by the recent modelling study of Gladstone *et al.* (1992). The study of Corkum *et al.* (1986), in which PAN measurements were conducted on the north shore of Lake Erie, indicates that transport of PAN from the U.S.

midwest into southern Ontario can result in ambient PAN concentrations as high as 1–2 ppb. Anlauf *et al.* (1985) found that periods of elevated oxidant in southern Ontario correlate with southwesterly air-mass trajectories. PAN measurements at rural sites in Ontario, reported by Bottenheim *et al.* (1984) and Brice *et al.* (1988), indicate that PAN represents a significant fraction of the total reactive odd nitrogen, this fraction increasing with distance from precursor sources. The Brice *et al.* data also indicate the potential for maximum PAN concentrations in late winter/early spring, in contrast to seasonal variations in ozone.

There have been no reported measurements of PAN concentrations in the Toronto area. However, ozone measurements indicate a significant oxidant formation potential for this urban environment, with ozone concentrations in summer often exceeding twice the National Ambient Air Quality Objective of 82 ppb for 1 h (Anlauf *et al.*, 1975; Canadian Council of Ministers of the Environment, 1990). The observed ratios of $[O_3]/[PAN]$ of $\approx 14:1$ reported by Altshuller (1983) for urban North American environments, the measurements discussed above for other relatively north-latitude cities, and the possibility for long-range transport all indicate the potential for elevated PAN concentrations for this urban area. To assess the potential for PAN production in various environments in Ontario, a series of PAN (and PPN) measurements were conducted at three sites in Ontario between May 1989 and February 1990 representing urban, suburban downwind and rural locations. In this paper we discuss the chemical and meteorological factors that can lead to elevated PAN concentrations, and describe in quantitative terms the relationships between measured concentrations of PAN, PPN and O_3 in these environments.

2. EXPERIMENTAL

PAN and PPN measurements were conducted at Ontario Ministry of the Environment air-monitoring stations in Toronto, Stouffville and Dorset, Ontario, the locations of which are shown in Fig. 1. The Stouffville site was located ≈ 100 m from a main road passing through the town of Stouffville, pop. $\approx 20{,}000$. The Stouffville site can be significantly impacted by the Toronto (and southern Ontario) plume when air flow is from the S or SW. However, with northerly flows the air at Stouffville would be relatively clean. The Dorset site is in a rural environment, with relatively insignificant local sources of anthropogenic VOCs or NO_x. The site is in a valley, in a mixed deciduous/coniferous (75%/25%) forested area. Photochemical oxidant formation at this site has been studied in some detail (Shepson *et al.*, 1991; Lin *et al.*, 1992). Data are reported here for the following dates: Toronto—25 May to 31 August 1989 and 2 January to 7 February 1990; Stouffville—25 May to 31 August 1989; Dorset—5 July to 31 August 1989 and 2 January to 7 February 1990. PAN and PPN were measured at each site by gas chromatography with electron capture detection (GC/ECD). The three GC/ECDs were essentially identical, and used glass columns (6.3-mm o.d., 105-cm length) packed with 10% Carbowax 400 on Chromosorb G-AW, and 5% CH_4 in Ar carrier gas, at a flow rate of

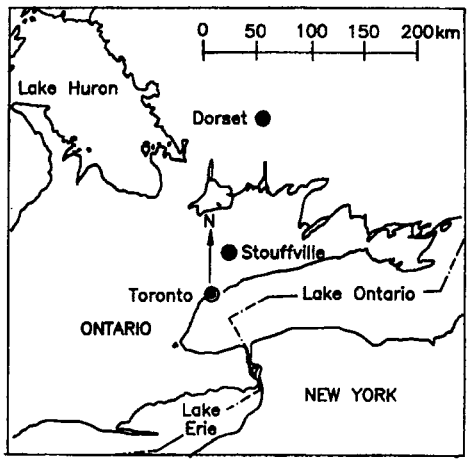

Fig. 1. Map of the measurement site region.

≈ 65 cm^3 min^{-1}. The columns were maintained at 35 °C while the detector temperatures were 50 °C. The ECD detectors were identical Valco model 140BN ECD detectors. Injections of ≈ 5 cm^3 air samples were effected every hour (every 40 min for Dorset) using a six-port valve (Valco) equipped with a conditioned stainless-steel sample loop. The PAN retention time was ≈ 4 min and the PAN peaks were integrated with HP 3390 integrators. GC/ECD calibrations were conducted (monthly) against known concentrations of PAN, generated using a solution of PAN in dodecane that was purified by preparative GC, in a flowing mixture of zero air. The PAN concentration was quantified using a chemiluminescence NO_x monitor (Monitor Labs model 8840) as described in Blanchard *et al.* (1990). A sample of this PAN/air standard was simultaneously injected into the GC/ECD instruments for calibration. Calibration for PPN (retention time ≈ 5 min) was conducted in an identical manner. The estimated uncertainties in the concentrations reported here for PAN and PPN are $\pm 20\%$ for cases where the concentrations were more than three times the detection limits of 0.01 and 0.03 ppb, respectively.

Air samples at the Toronto monitoring site were obtained from a glass manifold through which air was drawn from ≈ 1 m above the roof of a three-storey building in the Toronto city centre. There was relatively good ventilation at the level of sampling. For the Dorset and Stouffville sites air was drawn through similar glass manifolds from ≈ 1 m above the roofs of small one-storey buildings. For each site the air sampled by the PAN GC/ECDs was drawn through a 5-μm Teflon filter to remove particulate matter.

Ozone was measured at each site using a Dasibi u.v. absorption ozone monitor (Model AH-1008), with a detection limit of 2 ppb. Nitrogen oxides were measured at all sites using unmodified Monitor Labs Model 8840 chemiluminescence monitors that contain molybdenum-based converters for NO_2 measurement. Although the configuration of these instruments does not allow the measurement of NO_y as per the commonly accepted definition (Fahey *et al.*, 1985), they do quantitatively detect most components, namely NO, NO_2, HNO_3, organic nitrates and PAN. These monitors were calibrated monthly with NTIS NO standards. The detection limit was 5 ppb.

3. RESULTS AND DISCUSSION

The lifetime, transport and fate of PAN are tied to its temperature-dependent (Hendry and Kenley, 1977)

thermal decomposition (Reaction -1), and the subsequent reactions of the peroxyacetyl radicals, as shown in Reactions (2)–(4).

$$CH_3C(O)OO + NO_2 \rightleftarrows CH_3C(O)OONO_2 \quad (1, -1)$$

$$CH_3C(O)OO\cdot + NO \rightarrow CH_3C(O)O\cdot + NO_2 \quad (2)$$

$$CH_3C(O)OO\cdot + RO_2 \rightarrow CH_3C(O)O\cdot + RO\cdot + O_2 \quad (3)$$

$$CH_3C(O)OO\cdot + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (4)$$

PAN can also be removed through dry deposition, but wet deposition is unlikely to be important given the small Henry's Law coefficient (Kames *et al.*, 1991). Ambient PAN concentrations are thus dependent on a variety of factors affecting its production and removal, including light intensity, the concentrations of reactive hydrocarbons and nitrogen oxides, the ratio NO_2/NO and meteorological variables including temperature, wind speeds and the height of the mixed layer. In this section we will discuss the observed PAN and PPN concentrations for the three sites discussed here in light of these factors.

3.1. *Observations of PAN concentrations*

The observed PAN concentrations are presented graphically in Fig. 2 for all three sites for both the summer and winter measurement periods. In the summer the concentrations measured at Toronto and Stouffville were generally within a factor of two of each other (depending in part on wind direction), while those measured at Dorset were considerably lower. As shown in the figure, the maximum PAN concentrations were 3.97, 2.44 and 0.92 ppb, at Toronto, Stouffville and Dorset, respectively. The data for all sites show a strong diurnal variation with significantly lower concentrations at night. Averaged diurnal PAN concentration profiles generated by averaging all the measurements for each hour over the summer measurement period, for each of the three sites are shown in Fig. 3. Representative error bars are shown for each site as the 95% confidence limits (CL) of the mean [PAN]. To facilitate comparison, the Dorset PAN concentrations were multiplied by 3. The average PAN concentrations for each site exhibit a distinct diurnal profile, very similar in shape and magnitude to those observed by Singh and Salas (1989) for northeastern U.S. cities. The minimum concentrations occur between 0300 and 0600 and a broad maximum exists between 1200 and 1500, shortly after the solar irradiance maximum. The relationship between PAN concentration and solar radiation suggests that local photochemical PAN production is important at all sites. The nighttime minimum in PAN can be attributed to the presence of a nocturnal boundary layer (NBL) which isolates the lowest 100–200 m of the atmosphere from the rest of the planetary boundary

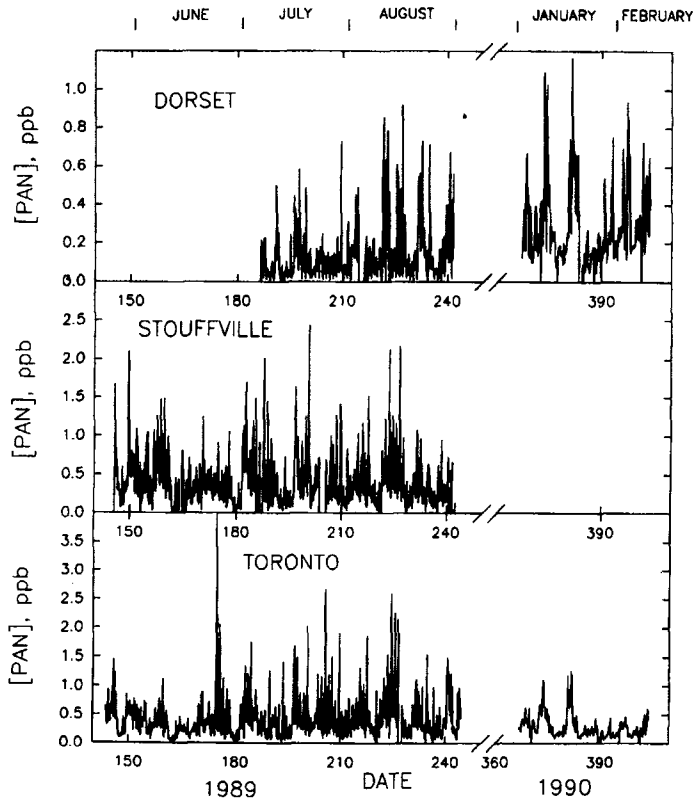

Fig. 2. Hourly PAN concentrations measured at Toronto, Stouffville and Dorset. Date refers to number of days from 31 December 1988.

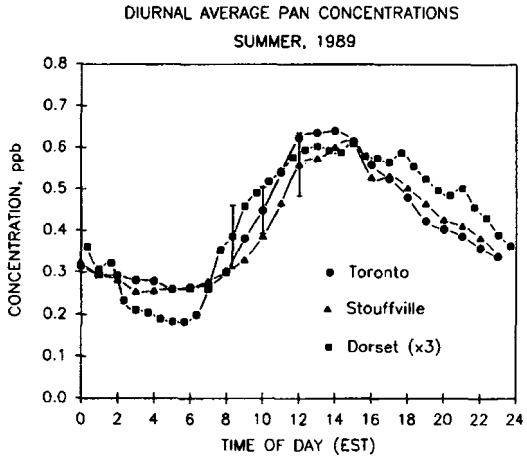

Fig. 3. Diurnal average PAN concentrations for Toronto, Stouffville and Dorset, summer 1989.

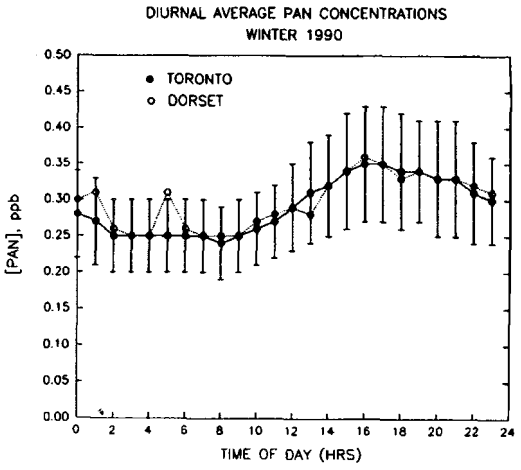

Fig. 4. Diurnal average PAN concentrations for Toronto and Dorset, winter 1990.

layer thus allowing the depletion of reactive species through surface deposition or by thermal decomposition followed by loss through Reaction (2). The latter is, however, likely to be much less important for Dorset. The rapid rise in the PAN (and other photochemical pollutant) concentrations between 0600 and 0900 at Dorset (accounting for 65% of the average morning increase), and the somewhat slower and delayed rise at the other sites, is attributed to the break-up of the NBL allowing the downward mixing of the undepleted air above the inversion. Thus the NBL meteorology can dominate the observed profiles and photochemical production of PAN can only be inferred from data between 1000 and 1800 h.

PAN concentration measurements were also made for the Toronto and Dorset sites for 5 weeks in the winter of 1990. The maximum concentrations observed for Toronto and Dorset were 1.27 and 1.17 ppb, respectively. Thus, the maximum concentrations observed at Dorset were in the winter. The winter measurements were characterized by relatively long periods (i.e. several days) of stable concentrations with only a very weak diurnal variation (see Fig. 2). Diurnal average PAN concentrations are presented in Fig. 4 (we note that for Fig. 4 the Toronto and Dorset data are on the same scale). The similarity in absolute concentration along with the temporal correspondence in profiles for Toronto and Dorset, shown in Fig. 2, indicate that PAN concentrations are relatively homogeneous on regional (hundreds of kilometres) scales in the winter. This is due to the combined effects of lower photochemical activity (i.e. production), fewer or weaker nocturnal inversions, the much longer thermal lifetime of PAN, and (probably) a much lower deposition velocity of PAN to snow.

3.2. *Meteorological influences*

The distances between these sites ($\approx$150 km Toronto–Dorset) make them well suited for studies of regional-scale pollution episodes and of the dependence of oxidant chemistry on air-mass origin. There are almost no anthropogenic sources north of Dorset, and few north of Stouffville. Thus air from the north is expected to be relatively clean continental air, whereas air from the south will come from regions of high population densities in the U.S. and Canada. In addition, measurements at Stouffville, which is 50 km northeast of Toronto, provide opportunities for studies of oxidant formation downwind of a major urban source region. For southerly trajectories the Stouffville and Dorset sites are downwind of Toronto; in contrast, the back trajectories show little connection between the three sites for most cases of northerly flow. Sectoring the PAN data using the back trajectories indicates that, on average, PAN concentrations are higher for all sites (both summer and winter) when the air mass originates from the south, showing the importance of the anthropogenic sources.

The most significant oxidant episode recorded for summer 1989 was for 23–27 June. The PAN measurements for this period are presented in Fig. 5, for the Toronto and Stouffville sites (no Dorset data is available). The maximum concentrations of ozone and PAN measured at Toronto were 139 and 4 ppb, respectively, at 1400 on 23 June. The meteorology was dominated by a high-pressure system generating slow flow from the south with wind speeds of $\approx$7 km h^{-1} and 48-h back trajectories originating from the Ohio/West Virginia area connecting Toronto with Stouffville. The most distinctive feature in the Stouffville data is the presence of two PAN peaks, one at $\approx$1200, and a later (often higher) afternoon peak, at $\approx$2000. This double maximum is also occasionally observed in the ozone data, although it is much less pronounced. For example, for 25 June at Stouffville, O_3 reached maxima of 57 and 52 ppb at 1500 and 2200 (resp.), with a 40-ppb local minimum at 1900. The first PAN peak appears to be due to local production as it occurs well after the break-up of the NBL and near the solar u.v. irradiance maximum (1200) and is probably

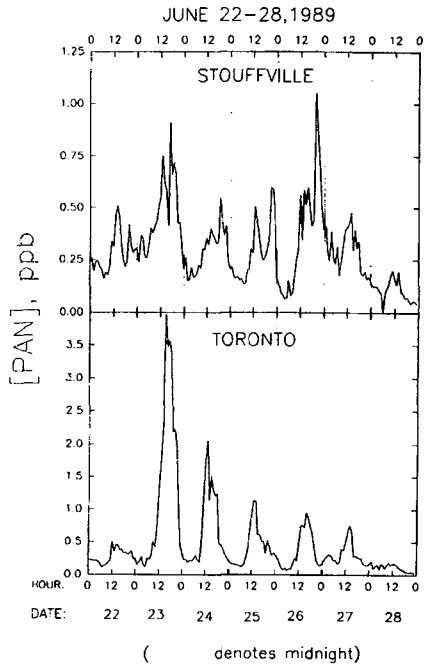

Fig. 5. PAN concentrations measured at Toronto and Stouffville during oxidant episode, 22–28 June, 1989.

typical of the production over a wide area since precursor sources are widely dispersed to the south. The second peak occurs at around 2000 h and cannot be locally generated as the solar radiation intensity was much lower. This must be due to transport from Toronto (and/or other source regions SW of Stouffville) and reflects both the PAN remaining in the midday Toronto peak and the additional PAN produced in transit. This is consistent with an 8-h airmass transit time for a 7 km h^{-1} wind moving air from Toronto to Stouffville. If the PAN levels observed for Stouffville at 1200 do represent regional-scale production, then the Toronto data indicate that most of the PAN produced in Toronto was from the local urban NMHC and odd nitrogen inputs. Although there is clear evidence for PAN transport, the Stouffville PAN maxima were much smaller than those in Toronto. Therefore, for this case, PAN loss must dominate over production in transit from Toronto to Stouffville. Under high NO_x conditions PAN loss occurs primarily via Reactions (−1) followed by (2). Thus under these conditions the effective thermal lifetime for PAN, for a temperature of 299 K and an observed $[NO]/[NO_2]$ ratio of 0.3, is $\approx$2.2 h (uncertain to $\pm$50% due to the nitrogen data). Thus in the 8-h transit time there can be substantial loss by thermal decomposition, which in this case dominates production. These observations indicate that transport of PAN itself (i.e. in the absence of photochemical production) over moderate distances (>100 km) at summer temperatures is unlikely to contribute to significantly elevated surface PAN concentrations at more rural sites.

In contrast, there were cases during which PAN concentrations were considerably higher in Stouffville. This can occur under conditions of high-pressure stagnant flow, with Toronto and Stouffville receiving polluted air from SW Ontario, but where the trajectories are from the W or SW, with Toronto and Stouffville not meteorologically connected. An example case, 5–9 June, is shown in Fig. 6, which indicates that the Stouffville PAN concentrations were consistently higher than those measured in Toronto, and higher than for the period 23–27 June. In this case there was little evidence of a second peak from the Toronto plume. That the PAN concentrations are higher in Stouffville than in the previous case where Stouffville receives air directly from Toronto, suggests that regional production of PAN from the widely distributed precursors is dominant. The lower PAN concentrations in Toronto during this period are related to the relatively much higher NO concentrations in Toronto, causing a net local PAN loss. These high levels of NO also suppressed local ozone concentrations as on 6 June the ozone maximum was 106 ppb at Stouffville but only 48 ppb in Toronto.

Under conditions of northerly flow, where there are few upwind sources of anthropogenic NMHC and NO_x, the situation for these three sites is quite different. Figure 7 shows the PAN data for a sample period of northerly flow, 12–16 July 1989. On 12 July the maximum PAN concentrations were 1.4 ppb at Toronto but only 0.7 ppb at Stouffville and 0.1 ppb at Dorset. Thus there is significant PAN production in Toronto from the local inputs, even under these well-ventilated conditions. For the next 2 days PAN levels

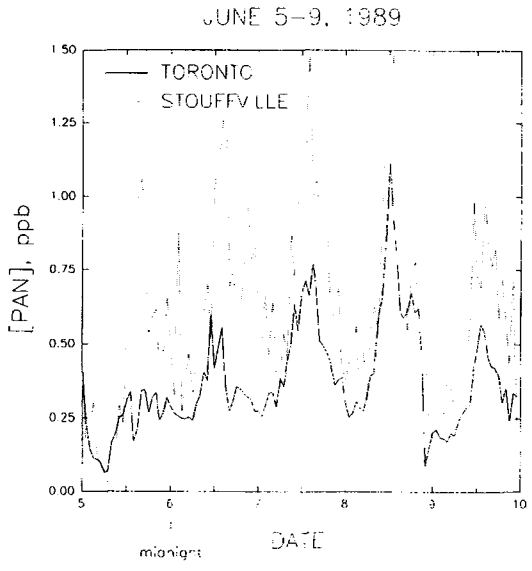

Fig. 6. PAN concentrations measured at Toronto and Stouffville, 5–9 June 1989.

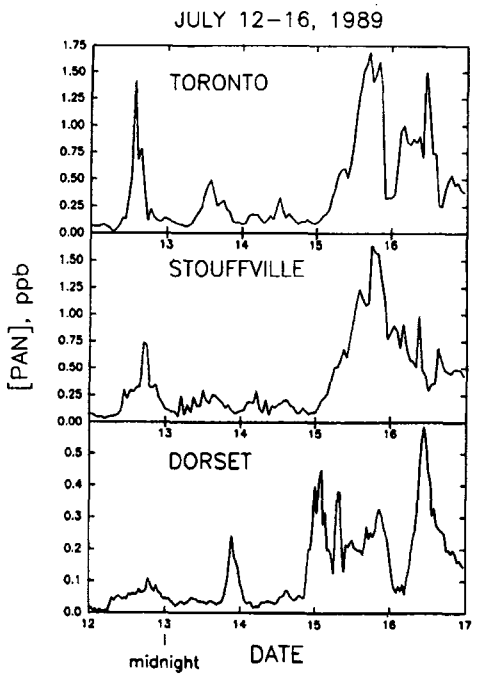

Fig. 7. PAN concentrations measured at Toronto, Stouffville and Dorset, 12–16 July 1989.

were quite low for all three sites, except for a short-lived peak at Dorset before midnight on 13 July (when ozone also reached a maximum of 51 ppb). Although this is physically consistent with an instability in the nocturnal boundary layer, daytime levels when measurements were made from the fully developed boundary layer were much lower, and thus the origin of the elevated PAN and ozone is unclear. The sampled air mass became more polluted on a regional basis for 15 and 16 July. There were no changes in the calculated back trajectories compared to 12–14 July, although measured wind speeds dropped from 15–20 to 5–10 km h^{-1}. Ozone concentrations reached 71 ppb at Dorset at 1230 on 16 July, the highest level for this period. Radiometer data indicates the absence of cloud but radiation intensities were slightly lower ($\approx$20%) at noon on the 15 and 16 July, indicating relatively hazier conditions. It is unclear exactly why oxidant levels were relatively high for 15–16 July but it is clear that significant oxidant levels can exist in this environment in the absence of transport of precursors from more polluted anthropogenic source regions.

In contrast to the situation in summertime, PAN concentrations for Toronto and Dorset appear homogeneous and transport-dependent in the winter. As shown in Figs 2–4, winter daytime PAN concentrations are 50% below summer levels at Toronto, but a factor of two higher at Dorset. The data presented in Fig. 2 show close temporal correspondence of PAN concentrations at Toronto and Dorset. Since there is lower irradiance there is less PAN production, and the longer thermal lifetime of PAN (5.2 days at a typical January temperature in Ontario of 268 K) and probable small dry-deposition velocity to snow (<0.01 cm s^{-1} to water; Kames *et al.*, 1991) leads to relatively spatially uniform concentrations on a regional scale.

3.3. *Relationships between PAN and* O_3

The net production of ozone requires the photochemical conversion of NO to NO_2 to occur through organic peroxy radical oxidation. A participant in this process is the peroxyacetyl radical, which can alternatively produce PAN. Thus in photochemically active air masses we expect a positive correlation between these species. Plots of O_3 vs PAN (1000–1800 data only) for the three sites for the summer of 1989 are shown in Fig. 8. For this analysis the complete set of PAN and O_3 measurements were sorted according to PAN concentration and divided into ten equally occupied bins of data. The corresponding average $[O_3]$ and 1σ deviations are plotted against the average [PAN] for each bin. The slopes and intercepts of the best-fit regression lines for each plot are shown in Table 1. As shown in the table, the slopes increase moving from urban to less locally polluted sites. The intercepts (which represent "background" O_3) are lower for Stouffville, and particularly Toronto, due to the impact of the NO–O_3 titration. That urban environments can act as local sinks for ozone has been discussed by Angle and Sandhu (1989).

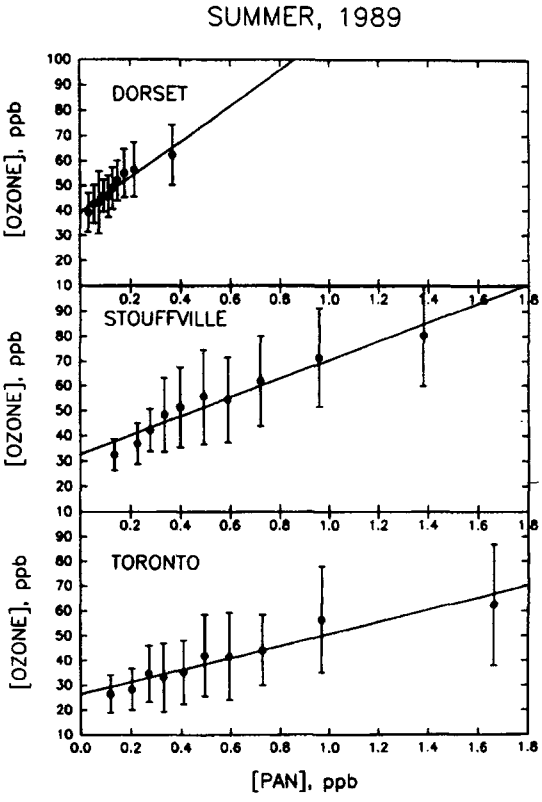

Fig. 8. Regressions of O_3 vs PAN for Toronto, Stouffville and Dorset, summer 1989.

Table 1. Slope and intercept for the regression $[O_3] = m[PAN] + c$

Site	Slope (m)	Intercept (c)
Toronto	24.3	26.4
Stouffville	37.8	32.7
Dorset	70.6	39.2

The relationship between PAN and ozone for predominantly urban atmospheres has been reviewed by Altshuller (1983). The average ratio O_3/PAN for a number of U.S. cities (mostly southern California), was reported as 14, with a wide range of variability (unfortunately slopes and intercepts are not reported). For remote sites in the continental U.S. this ratio was found to be much higher, the average ratio for six sites being 120. Similar results have been reported for the Netherlands (Nieboer and Van Ham, 1976), where relatively low $[O_3]/[PAN]$ ratios, i.e. ≈ 14, were found for air masses impacted by anthropogenic pollution, but much higher ratios, i.e. ≈ 30–50 for clean, e.g. marine, air. Recently, an extensive study was conducted (Roberts *et al.*, 1992) of the PAN–O_3 relationship for various (mostly rural) sites in eastern North America. For daytime (i.e. 1300–1800) measurements the data at five sites were fitted to the following equation: $[O_3] = 15.2*[PAN] + 42.7$. Ridley *et al.* (1990b) found a slope of 21 for measurements at Niwot Ridge, CO, under conditions of anthropogenic impact. In contrast, recent measurements in the free troposphere (Singh *et al.*, 1990) indicated a slope of over 200. The trend in the data reported here is consistent with the above observations, however, whether considering the slope or the ratio, the Toronto results are quite high relative to those observed for other urban areas. The data are consistent with the idea that the increasing ratio for air masses removed from sources is due to two principal factors: the decreasing concentrations of the PAN precursors, and the increased opportunity for PAN loss due to thermal decomposition. For typical daytime conditions ($NO_2/NO = 2$), $\tau_{PAN} = 50$ min at 303 K, while τ_{ozone} (from photolysis) is of the order of several days, depending on humidity. The PAN lifetime, however, can be $[NO_x]$ dependent, since at low $[NO_x]$ Reactions (3) and (4) can become more important. These points are exemplified by the data of 10 August 1989 where the 48-h back trajectory indicated relatively slow SW flow, essentially through Toronto and Stouffville to Dorset. The observed PAN and ozone concentrations and the calculated ratio $[O_3]/[PAN]$ are presented in Fig. 9. Considering only the daytime data, we see that as the air mass moved downwind from the source region the $[O_3]/[PAN]$ ratio increased; the ratios shown in Fig. 9 are 25–75, 50–100 and 100–150 for Toronto, Stouffville and Dorset, respectively. Even these Dorset ratios were much lower than for days with relatively clean-air (low $[NO_x]$) trajectories. For example the $[O_3]/[PAN]$ ratio at noon on 13 July (PAN data is shown in Fig. 7),

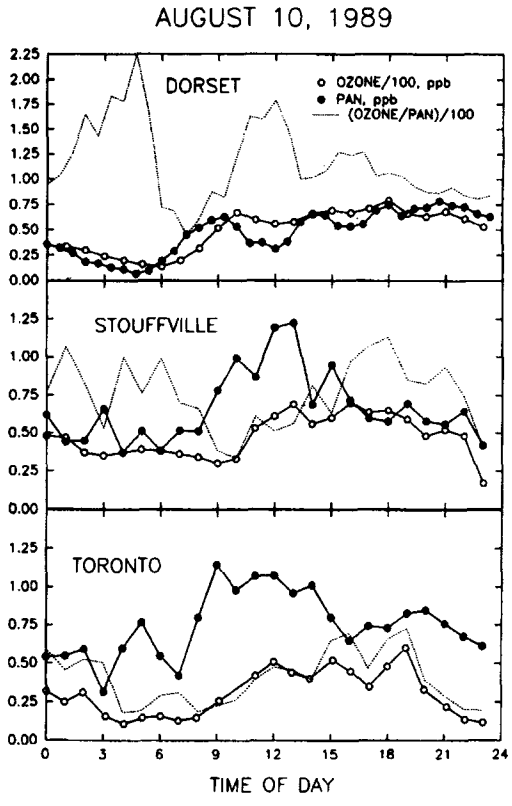

Fig. 9. Plots of O_3, PAN and O_3/PAN for Toronto, Stouffville and Dorset, 10 August 1989.

with trajectories from the north was 840. It can also be seen from Fig. 9 that the $[O_3]/[PAN]$ ratio increases throughout the night and early morning under the NBL, and then decreases dramatically at the break-up of the NBL at around 0600. The nighttime soil NO emissions at Dorset are very low ($\leq 2\,\mu g\,m^{-2}\,h^{-1}$) and so under the NBL the nighttime NO_2/NO ratios are generally very large (≥ 30) thus preventing net thermal decomposition. Thus the only process removing ozone and PAN is dry deposition, and the data imply that the deposition velocity for PAN at Dorset (at night) is significantly greater than for ozone. This is in contrast to the published values of Garland and Penkett (1976), who reported a ratio $V_d(O_3)/V_d(PAN) \approx 2$. A series of measurements at this and other sites in Ontario are consistent with lower values for this ratio of deposition velocities, but with considerable variability (Shepson *et al.*, 1992).

The O_3–PAN plots for the daytime winter data are shown in Fig. 10. Unlike the summer data, the O_3 levels at Toronto were on average less than half those measured at Dorset. Figure 10 shows that these two species are anticorrelated, for both sites. This likely is a consequence of the much lower photochemical production of ozone and PAN in the winter, coupled with the large NO sources in Toronto which act as a local sink for ozone, but much less so for PAN because of the enhanced thermal stability at winter temperatures.

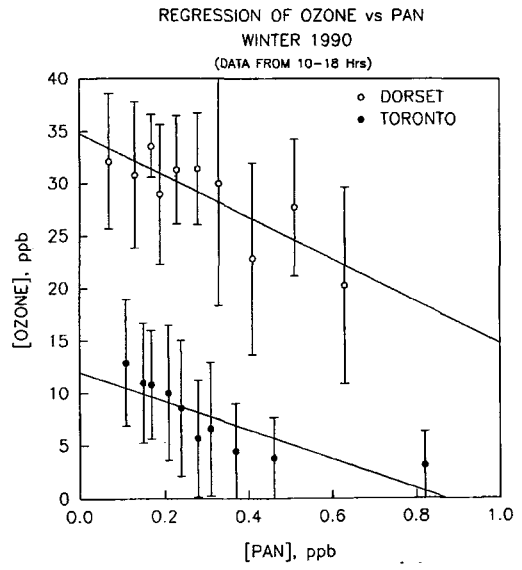

Fig. 10. Regressions of O_3 vs PAN for Toronto and Dorset, winter 1990.

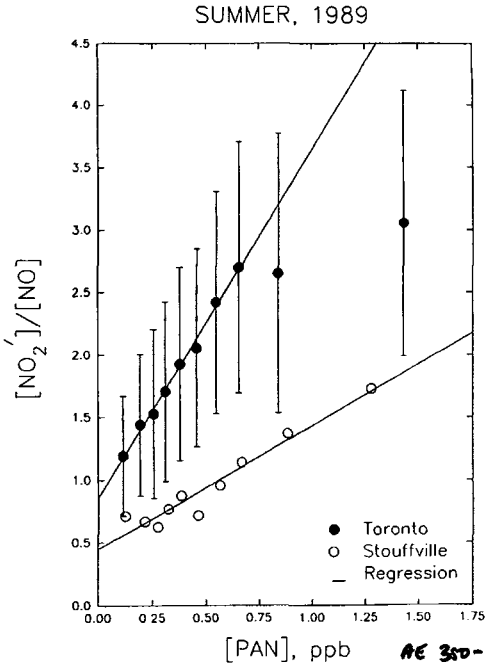

Fig. 11. Regressions of NO_2'/NO vs PAN for Toronto and Stouffville, summer 1989.

Episodic concentrations for PAN occur under southwesterly trajectories. Under these conditions the ozone concentrations become very low, while for northerly trajectories in the winter the ozone concentrations were relatively higher. Thus the anti-correlation exists either because higher NO_x concentrations under southerly flow conditions result in ozone loss from reaction with NO, or because background ozone concentrations (possibly from stratospheric injection) are higher when air is from the north.

3.4. *Relationships between PAN and measured nitrogen oxides*

As indicated by Reactions (−1) and (2), the formation and stability of PAN are dependent on the relative concentrations of NO and NO_2. The commercial nitrogen-oxide monitors used in this study do not measure NO_2 specifically but rather NO_2 plus a variety of nitrogen species, including PAN. However, in an urban environment with a strong NO input the NO_2 channel would likely be dominated by NO_2. This is the case for Toronto and Stouffville as the measured PAN was always less than 2% of the total nitrogen oxides (which are typically 20–50 ppb). For Dorset, the NO_y levels were normally below the instrument detection limit. We therefore use NO_2', the difference between the converter channel and the NO channel, as an estimate of the actual ambient NO_2.

Figure 11 shows a plot of the daytime (1000–1800) ratio $[NO_2']/[NO]$, against the PAN concentration as described for the ozone data in Fig. 8. This ratio is a function of the concentration of oxidants (i.e. ozone and peroxy radicals) in the air mass, and shows a strong correlation with the PAN concentration at both Toronto and Stouffville. The slope of the Toronto line is 2.5–3 times greater than for Stouffville indicating there is less PAN production for the same amount of oxidant production. This points to the fact that the initial hydrocarbon oxidation in Toronto will produce peroxy radicals that oxidize NO, ultimately yielding carbonyl compounds that are PAN precursors (e.g. acetaldehyde, methyl glyoxal), but little direct production of acetyl radicals. It is not until further carbonyl compound oxidation (or photolysis) occurs in the air mass, in this case after moving downwind from Toronto toward Stouffville, that PAN is produced.

3.5. *Relationships between PAN and PPN*

Since PAN and PPN are both produced from the oxidation of carbonyl compound precursors we would expect their concentrations to be correlated, especially in areas experiencing anthropogenically enhanced photochemical activity. Figure 12 shows a plot of [PPN] against [PAN] for the entire summer 1989 Toronto data set (error bars are 1σ deviations). The data represent daytime averages for 10 bins, as described for the O_3–PAN plots. The concentrations are highly correlated ($r^2 = 0.995$), with a slope of 0.089. Corresponding plots for Stouffville and Dorset showed equally good correlations with slopes of 0.112 and 0.081, respectively. These values are in agreement with the recent measurements of Singh and Salas (1989) and Ridley *et al.* (1990b), who report ratios for both urban and rural sites ranging from 0.03 to 0.15 with an average of 0.08. Both these studies found that the ratio was smaller for clean continental or rural air. For this data set, the data for each site were sectored

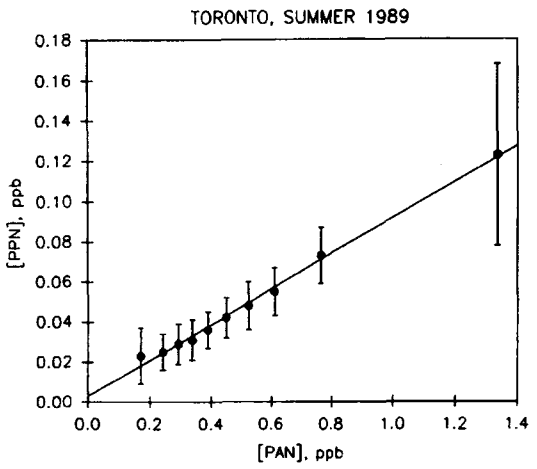

Fig. 12. Regression of PPN vs PAN for Toronto, summer 1989.

into four quadrants (NE, SE, SW and NW) according to the air-mass origin as determined from the 48-h back trajectories. The average measured PPN/PAN ratio for the three sites are presented in Table 2. The PPN/PAN ratios are higher for trajectories representing air masses more impacted by anthropogenic pollution (i.e. from the south) but the differences are, although statistically significant, rather small. This is particularly surprising for the cases of NW and SW flow for Dorset and Stouffville where we would expect significant differences in the air mass composition.

Our averaged data show no dependence of the ratio on [PAN], in contrast to the observations of Singh and Salas (1989) and Ridley *et al.* (1990b). We do, however, observe significant variability in the ratio on short time scales. In fact for some oxidant episodes an anti-correlation between [PPN]/[PAN] and [PAN] was apparent. For the data presented in Fig. 13 (10–13 August), the 48-h back trajectories showed a weak flow from the southwest so that Stouffville was directly downwind of Toronto. It is clear that whereas the [PPN]/[PAN] ratio for Toronto is near the average value of 0.089, the corresponding ratio for Stouffville is considerably higher, i.e. $\approx$0.15–0.20, implying that PPN production becomes relatively more important as the air mass ages. The ratio also appears to be a minimum at the daily PAN maximum. The thermal lifetime of PPN is slightly shorter than that for PAN (Roberts, 1990) so the variation must be due to differences in the production rates. In many cases the ratio increases at night when surface deposition under the inversion layer is a dominant removal mechanism, and it thus may be that the deposition velocity is larger for PAN than for PPN.

Ridley *et al.* (1990b) have attributed their lower [PPN]/[PAN] ratio for clean air to a combination of three factors: (a) the PPN precursors (e.g. 1-butene) have a shorter lifetime than the PAN precursors; (b) PPN has a shorter reactive lifetime with respect to OH; and (c) PAN, but not PPN, can be produced from the oxidation of isoprene. The small variation in the [PPN]/[PAN] ratios reported here leads us to examine reasons why these factors may not apply in this situation. Under flow from the southwest, Dorset can be significantly impacted by anthropogenic hydrocarbons from the U.S. and SW Ontario. However, there are no major anthropogenic sources north of the site, so under northerly flow conditions isoprene may be the dominant reactive hydrocarbon. Daytime concentrations of up to 5 ppb isoprene have been reported for this site (Bottenheim *et al.*, 1990). The absence of a substantial difference in the PPN/PAN ratio for Dorset implies that either reactive alkenes such as 1-butene are not a significant source of PPN, there is not sufficient transit time for (b) above to affect the PPN/PAN ratio, or that isoprene oxidation is not a relatively more important source of PAN under flow from the north. This last possibility is feasible since under northerly flow conditions the temperature is relatively low, and isoprene emission rates under such conditions would be substantially reduced.

The principal precursor to PPN formation is normally assumed to be propionaldehyde, which is believed to arise nearly entirely from oxidation of anthropogenic hydrocarbons. In contrast, for PAN there are a number of precursors including acetaldehyde, acetone (produced from propane and alkene oxidation) and methyl glyoxal (produced from isoprene and aromatics oxidation). The relative importance of these depends on the nature of the air mass, e.g. the relative contribution of natural and anthropogenic hydrocarbons to the photochemistry. Thus the similarity in the PPN/PAN ratio between Toronto and Dorset implies either that local photochemical production of PAN and PPN is not the principal source of these compounds at Dorset, or that there are comparable natural sources of precursors for both species. We recently reported ratios of [propionaldehyde]/ [acetaldehyde] for northerly flow conditions of $\approx$0.05

Table 2. PPN/PAN ratios as a function of air-mass origin

	Toronto		Stouffville		Dorset	
Sector	PPN/PAN	95% CL (N)	PPN/PAN	95% CL	PPN/PAN	95% CL
NW	0.077	0.004 (145)	0.129	0.007 (153)	0.095	0.007 (29)
NE	0.058	0.008 (5)	0.101	0.025 (7)	—	—
SE	0.100	0.006 (15)	0.156	0.011 (13)	—	—
SW	0.088	0.003 (544)	0.127	0.004 (463)	0.106	0.005 (63)

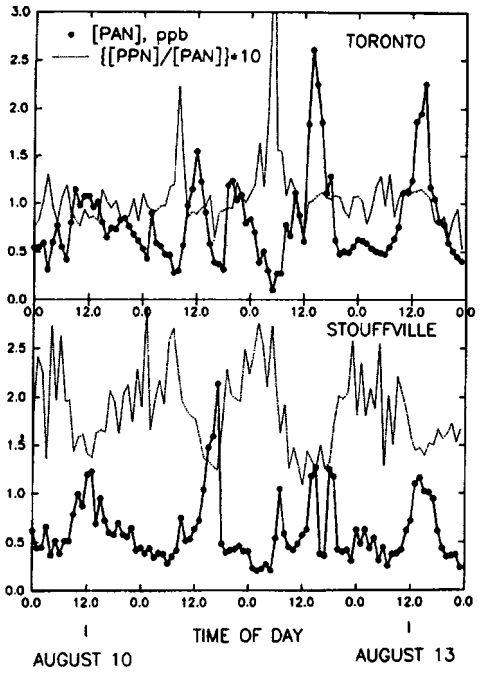

Fig. 13. Plot of PAN concentrations and the PPN/PAN ratio at Toronto and Stouffville, 10–13 August 1989.

(Shepson *et al.*, 1991) indicating relatively fewer sources of propionaldehyde relative to acetaldehyde. In urban areas this ratio is much higher (Grosjean, 1982). It thus seems clear that detailed measurements of carbonyl precursors in both anthropogenic and natural hydrocarbon-impacted environments are necessary to understand PAN and PPN formation at these sites.

4. CONCLUSIONS

The PAN measurements reported here indicate that PAN levels in urban and rural environments in Ontario are typically in the range 0.1–0.6 ppb, for both summer and winter, with substantial diurnal variability in summer. Oxidant episodes, typically under conditions of southwesterly flow where hydrocarbon and NO_x precursors can be transported from other source regions, can lead to PAN concentrations as high as $\approx$4 ppb. However, PAN concentrations in Toronto under northerly flow conditions can still reach levels as high as $\approx$2 ppb. For Toronto, fresh inputs of NO can result in local suppression of oxidant levels. As the NO_2/NO ratio increases with the movement of the urban air mass downwind, e.g. toward Stouffville, levels of PAN and O_3 can be significantly elevated, relative to those nearer the urban source. Data from Dorset imply that significant oxidant concentrations (O_3 as high as 70 ppb) can exist under conditions where anthropogenic inputs are relatively low. For rural sites such as Dorset, a complete understanding of the nature of PAN precursors is necessary. The measured ratios of PPN/PAN, which do not seem to vary substantially with the nature of the air mass, indicate that it is unclear what the PPN (and PAN) precursors are. The measured ratios of O_3/PAN were found to increase for cleaner air masses, in agreement with other studies. However, the O_3/PAN ratios observed at these sites were found, in general, to be relatively higher than those observed at other North American sites. Some of the variability in the surface level O_3/PAN ratio may be significantly influenced by the relative deposition velocities, which seem to be quite different from published values at the Dorset site.

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