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Long-term measurements of atmospheric peroxyacetylnitrate (PAN) at rural sites in Ontario and Nova Scotia; seasonal variations and long-range transport

By K. A. BRICE[1], J. W. BOTTENHEIM[2]*, K. G. ANLAUF[2] and H. A. WIEBE[2],
[1]*Concord Scientific Corporation, Downsview, Ontario, Canada*; [2]*Atmospheric Environment Service, Downsview, Ontario, Canada*

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ABSTRACT

The atmospheric behaviour of PAN at locations well-removed from major urban areas has been studied over extended periods using highly sensitive, automated gas chromatographic techniques at two sites in eastern Canada; Longwoods in southern Ontario (February–October 1983), and Kejimkujik in Nova Scotia (May 1984 onwards). In addition, data have also been obtained from more limited measurement programs in northern Ontario at Chalk River (November–December 1983) and North Bay (January–February 1984). The variations in PAN mixing ratios observed at these sites have been examined with reference to available data for other atmospheric components, such as O_3, HNO_3, particulate nitrate and sulphate. Air mass back-trajectory calculations have been performed for Kejimkujik to relate observed periods of elevated PAN mixing ratio to specific source regions for precursor NMHC and NO_x. For the sites studied, periods of enhanced PAN mixing ratio are observed to be possible throughout the yearly cycle, indicating that significant photochemical activity can occur even during wintertime. This contrasts with the available data for ozone, where photochemical formation in polluted air masses appears to be suppressed in winter. Seasonal patterns of PAN behaviour are probably site-dependent, but the observations suggest that the highest PAN maxima are favoured during fall and late winter/early spring. The long-term data from Kejimkujik also reveal an underlying seasonal variation in the typical background value of PAN observed at this site; this background value maximizes in late winter/early spring and minimizes in summer. In general, the magnitude of the observed PAN maxima appears to decrease with distance from the source region of influence. PAN accounts for a significant fraction of the observed oxidized nitrogen species at all the sites studied, and appears to make an increasing contribution as the transport time from the source region increases. In background tropospheric air, the contribution of PAN may be as high as 80–90%.

1. Introduction

Photochemical air pollution is now known to result from the action of sunlight on hydrocarbons and oxides of nitrogen. Elevated levels of undesirable secondary pollutants may be formed, such as ozone, peroxyacetylnitrate (PAN) and aerosols, with identifiable effects on human health, vegetation and amenity. PAN, the principal member of a family of organic nitrogen compounds (peroxyacylnitrates) was first measured in the Los Angeles atmosphere during the late 1950's at concentrations of up to 100 ppb(v) (Stephens et al., 1956; Stephens, 1987).

PAN has since been detected as a constituent of sunlit urban atmospheres throughout the world, with concentrations in excess of 10 ppb(v), and is clearly an important photochemical pollutant (Temple and Taylor, 1983). Observations of PAN in rural areas indicate the possibility of PAN formation and transport in urban plumes on a regional scale (Brice et al., 1984; Spicer et

* Corresponding author.

al., 1979). Measurements of PAN at remote locations where anthropogenic influences should be minimal, such as the high Arctic (Bottenheim et al., 1986) and the upper troposphere over the Pacific Ocean (Singh et al., 1986), provide justification for the consideration of PAN as a ubiquitous global trace species.

The underlying processes leading to the formation and decay of PAN in the atmosphere are now generally understood. The reaction of atmospheric hydrocarbons with hydroxyl radicals (HO) can generate peroxyacetyl radicals, which then combine with NO_2 to form PAN (Demerjian et al., 1974). Since hydroxyl radicals are almost exclusively formed from photochemical reactions in the atmosphere, the mere presence of PAN is an indication of the occurrence of photochemistry. In contrast, tropospheric ozone is also a product of the hydrocarbon photo-oxidation sequence, but may have a substantial non-photochemical source from intrusions of ozone-rich stratospheric air (Mukammal et al., 1985).

PAN undergoes thermal decomposition (rapidly increasing with temperature) and so exists in equilibrium with NO_2 (Hendry and Kenley, 1977; Cox and Roffey, 1977).

$$CH_3CO_2NO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3CO_2 + NO_2.$$

Reaction of peroxyacetyl radicals with other atmospheric species (primarily NO) constitutes irreversible removal of PAN. Other sinks for PAN include reaction with HO radical (Wallington et al., 1984), dry deposition to surfaces (Garland and Penkett, 1976), photolysis (Senum et al., 1984) and washout (Lee, 1984). Overall, under typical conditions, the lifetime for PAN in the lower atmosphere can be calculated to range from a few hours to several days (Singh, 1987). PAN may therefore constitute an important part of the global odd nitrogen cycle, acting as a temporary reservoir for atmospheric NO_2 (Crutzen, 1979; Singh and Hanst, 1981) and effectively extending its lifetime (Fig. 1).

The PAN measurement program conducted by the Atmospheric Environment Service has been stimulated by the need to acquire an improved understanding of atmospheric processes, providing the necessary knowledge by which specific air quality issues can be rationally addressed. In particular:

(1) Extensive modelling studies during the last two decades have suggested a significant role for nitrogen oxides in the chemistry of urban polluted atmospheres (McRae and Seinfield, 1983), during long range transport of pollutants (Bottenheim et al., 1984) and in the remote unpolluted troposphere (Logan et al., 1981). Of primary importance, is the influence of nitrogen oxides upon the levels of oxidant species (OH, HO_2, O_3) present in these situations. A major question in the NO_x chemistry is the identity, and the distribution between the ultimate products in the atmosphere. It is apparent that PAN can play an important role in this distribution. However, actual observations of oxides of nitrogen and product species that can be used to test the model predictions are scarce, except for studies conducted within urban areas.

(2) Precipitation acidification involves a substantial contribution from nitrogen species, especially during the winter (Summers and Barrie, 1986). In order to correctly simulate the underlying chemistry, it is necessary to take into account the formation and behaviour of the main oxides of nitrogen, including PAN, to realistically

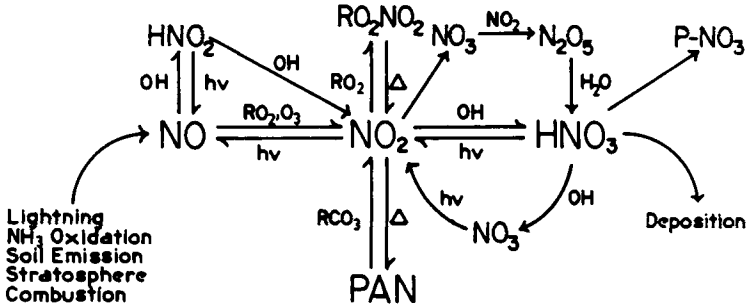

Fig. 1. Simplified conceptual outline of tropospheric odd nitrogen cycle.

represent NO_x conversion and transport. Validation of atmospheric models requires representative (i.e., long-term) field data.

The behaviour of PAN has been determined over extended periods using highly sensitive automated gas chromatographic techniques at two sites in Eastern Canada: Longwoods in southern Ontario (February–October 1983), and Kejimkujik in Nova Scotia (May 1984–present). In addition, data from more limited duration studies at other sites in Ontario are available: Chalk River (November–December 1983) and North Bay (January–February 1984). All the sites studied can be considered essentially free of significant influence from local emissions of precursor species for PAN, providing a unique opportunity to investigate the occurrence of long-range transport. The variations in PAN concentrations at these sites can be examined with reference to available data for other atmospheric components, such as O_3, HNO_3, particulate nitrate and sulphate, to reveal some significant features of atmospheric PAN behaviour, during both clean and polluted conditions. Furthermore, the use of air mass back-trajectory calculations permits the identification of possible source regions contributing to periods of elevated PAN concentrations at individual receptor sites.

2. Experimental procedures

2.1. Sampling site locations

All sampling sites used to obtain the PAN measurements discussed here are located in rural regions of eastern Canada (Fig. 2) well removed from major urban areas. With the exception of North Bay, all sites belong to the Canadian Air and Precipitation Monitoring Network (CAPMoN), operated routinely for the collection of daily air and precipitation data (Barrie et al., 1980; Wiebe et al., 1985). Fig. 2 also shows gridded annual NO_x emission densities for eastern North America. Calculated emission densities for reactive hydrocarbons have previously been shown to be highly correlated with those for NO_x (Bottenheim et al., 1984); as an approximation, the spatial distribution of hydrocarbon emissions can also be represented by Fig. 2. Longwoods can be considered to be under the influence of medium-range transport of polluted air masses during southerly to south-westerly flow from major source regions such as the US Midwest, and in particular the Detroit area (approximately 100 km away). Chalk River and North Bay are more remote from these source regions. Kejimkujik is well removed from the source regions affecting the other sites, but lies within the possible influence of high emission sources of hydrocarbons and nitrogen oxides located in the Boston–Washington corridor of the US east coast.

2.2. Determination of PAN in the ambient atmosphere

2.2.1. Automated gas chromatography. PAN was measured by means of an automated gas chromatograph employing electron capture detection (GC-EC). Fig. 3 shows diagrammatically the major components of the system.

Every 30 min, ambient air was drawn through a Teflon filter via a stainless steel sample line (5 m × 0.3 cm o.d. × 0.2 cm i.d.) and a 6-port sampling valve (Carle) to a 5 cm^3 sample loop, made from 0.3 cm o.d. × 0.2 cm i.d. stainless steel tubing. (Note: losses of PAN in the sampling line have been shown to be insignificant, by comparison with samples injected directly by syringe.) Pumping continued for 2 min, after which the pump was isolated by switching a solenoid valve and turned off, allowing the air in the sample loop to equilibrate to ambient pressure for 30 s. The sampling valve was then switched and the ambient air sample swept on to the GC column by the carrier gas stream. A commercial isothermal GC (Pye Unicam PU 4500) was selected for this application, employing injection port and oven temperatures of 40°C and a detector temperature of 60°C. A glass column (50 cm × 0.6 cm o.d. × 0.4 cm i.d.) packed with 5% Carbowax 400 on Chromosorb G-AW, (DMCS, 100–120 mesh) was used for the separation. Ultra High Purity nitrogen (Linde) was used as supplied (i.e. without attempts to trap oxygen or other impurities), and served as the carrier gas (60 cm^3 min^{-1}). The signal from the EC detector was continuously recorded using a chart recorder, and also fed to a HP 3390 integrator during each chromatographic run, lasting about 8 min. Fig. 4 shows typical integrator output for an ambient air sample

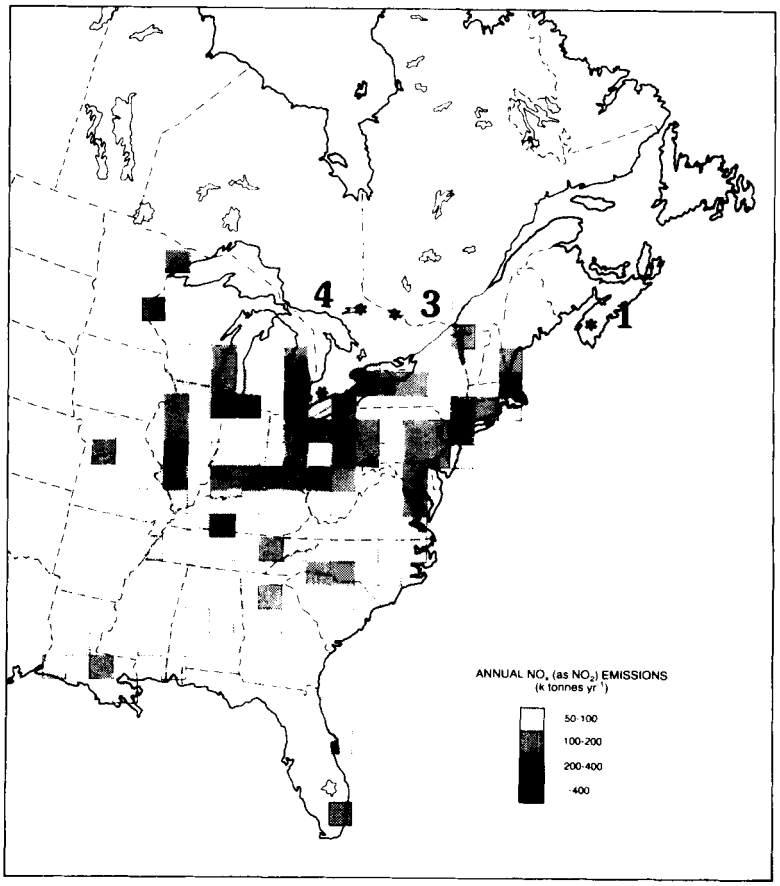

Fig. 2. Annual NO_x emissions for NE North America, and CAPMoN sampling site locations (1, Kejimkujik; 2, Longwoods; 3, Chalk River; 4, North Bay).

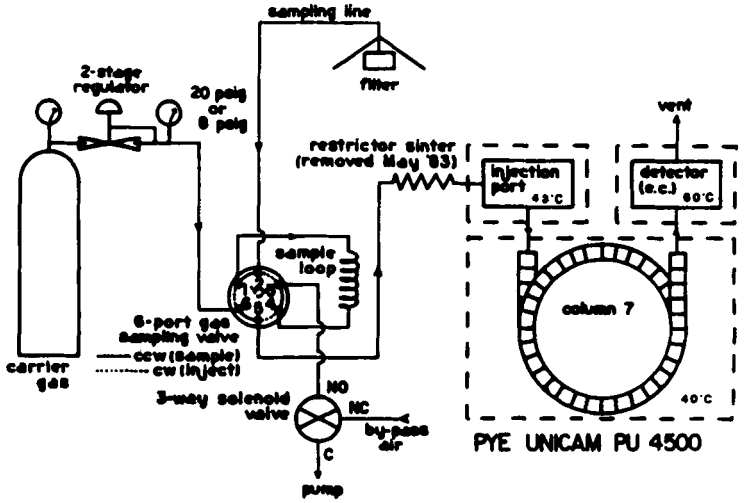

Fig. 3. Flow schematic of AES PAN Monitor No. 1.

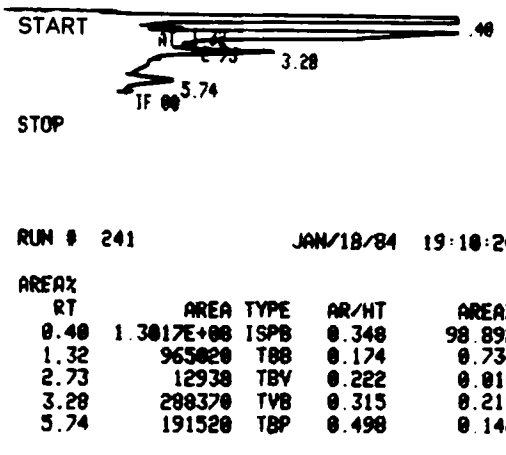

Fig. 4. Typical chromatogram and integrator output for a 5 cm^3 ambient air sample obtained using AES GC-EC PAN Monitor No. 1. Pye Unicam PU4500 chromatograph and ECD detector. Hewlett Packard 3390 integrator. For analytical conditions see text. Integrator attenuation change from 2^7 to 2^3 at run time 1.50 mins. Peak identities and retention times (in minutes) are as follows: O_2 (0.40), CCl_4 (1.32), C_2HCl_3 (2.73), C_2Cl_4 (3.28), PAN (5.74).

(containing about 250 ppt(v) of PAN) analyzed on this unit; PAN elutes at about 5.7 min, well resolved from interfering peaks.

Integrated data were stored on magnetic tape with an HP 85 microcomputer. The overall procedure of switching valves and pump, integrator start-up etc., was controlled by a mechanical timer (Carle Model 4150). The system was visually inspected daily by a local operator, and the chart records and data tape mailed weekly to our laboratories in Toronto.

2.2.2. Calibration procedure. The preparation of gaseous standards of PAN at levels typical of ambient concentrations presents many difficulties due to its inherent instability. Essentially, the method employed here follows that outlined by Stephens (1969) and Penkett et al. (1977) but with some important improvements and modifications. Photolysis of ethylnitrite vapour in an oxygen atmosphere by UV black lights was used to produce an impure product mixture containing appreciable quantities of acetaldehyde, methylnitrate, ethylnitrate and PAN. The products were subjected to cryogenic trapping and concentration, and separated by preparative GC. In this manner, pure gaseous samples of PAN at mixing ratios of 200–400 ppm(v) in nitrogen were prepared at our laboratories in Toronto in 250 cm^3 borosilicate glass flasks, and their concentration determined by gas chromatography with flame ionization detection. The response of the FID was standardized against a calibrated mixture of benzene in air (Scott). The absolute response of the FID, and hence the benzene/PAN response ratio was established by preparing a pure PAN sample in a 9 cm IR cell and measuring the PAN concentration with a Perkin Elmer 1330 IR spectrometer. For calibrations in the field, the concentration of PAN in one of the storage flasks was redetermined, using the same procedure, i.e., GC-FID analysis of the PAN sample and benzene standard, with a second column and FID detector, incorporated in the same GC unit used for the ambient analysis. Aliquots of the PAN standard were then diluted in 50 dm^3 Teflon bags, previously filled with (humidified) zero air, and the diluted mixtures (ppb(v) range) analyzed with the GC-EC system via the ambient air sample line. To allow for the observed instability of PAN in the bags, a time series over at least three hours was developed. The response extrapolated to the time of spiking the bag was then taken as the true initial response to the prepared PAN mixture. The original volume of the bag was determined by evacuation after each set of calibration runs with an integrating mass flow meter inserted in the pumping line.

The analytical system described above has been operated since July 1982 virtually on a continuous basis. Calibration has been performed regularly, normally every 2–3 months. Such a calibration schedule might be considered sparse, however, experience has shown the system to be remarkably stable, but with evidence of a slow but steady upward drift in sensitivity. The accuracy of the calibration is estimated to be $\pm 30\%$, due to systematic uncertainties in several of the calibration steps.

2.2.3. Linearity and detection limit. Extensive calibration studies of the GC-EC system show good response linearity over the range 0.5 to 11 ppb(v). Routine field calibration at mixing ratios below 0.5 ppb(v) present difficulties with the present static dilution calibration procedure. The FID response to PAN at mixing ratios below

~200 ppm(v) cannot be easily verified by short-path IR, transfers of <0.1 cm^3 of such PAN standards cannot be performed with certainty, and Teflon bags at volumes >50 dm^3 are not readily available or easily accommodated at a remote field monitoring site. Consequently, response linearity to lower mixing ratios is assumed for the data sets presented here. However, experience by one of the authors (KAB) with similar PAN monitoring systems suggests no major problems with such an assumption down to 20 ppt(v) (Brice et al., 1984). The minimum detection limit (2 × noise level) for the present system based upon peak height considerations is better than 10 ppt(v). At these levels, the peak identification ability of the HP 3390 is unreliable; on an area basis, values below 20 ppt(v) are typically considered to be below reliable detection limit (BDL).

2.3. *Measurements of ozone, sulphur dioxide, nitric acid and atmospheric particulate matter*

The determination of particulate nitrate and sulphate, HNO_3 and SO_2 was performed at all sites using a triple filter pack technique (sampling rate ~15–20 dm^3 min^{-1}); aerosols were collected on Teflon filters (1 μm pore size), gaseous HNO_3 was collected by absorption on a nylon filter, and SO_2 was collected by a Whatman 41 filter impregnated with K_2CO_3/glycerol solution. The filters were subsequently extracted and analysed using ion-chromatography (Anlauf et al., 1986a). For Longwoods, Chalk River and Kejimkujik, the filter packs were routinely exposed for 24-h periods (12 GMT–12 GMT). For the North Bay study, integrated samples on a six-hourly basis were obtained, using higher flow rates (~35 dm^3 min^{-1}). During day-time, improved resolution down to less than 3 hours was frequently obtained.

Ozone data reported for Kejimkujik were provided by Environment Canada's Environmental Conservation and Protection Service as part of the routine NAPS network (EPS, 1986), using a Dasibi photometric monitor.

2.4. *Air mass back-trajectory analysis during episode days*

In order to correlate the PAN observations with air mass origin, back-trajectories were obtained for each of the monitoring locations from the AES Lagrangian trajectory model (Olson et al., 1978). Five-day back-trajectories at 3 altitude levels are routinely available (1000 mb, 925 mb and 850 mb) at 6-h intervals (0 GMT, 6 GMT, 12 GMT, 18 GMT). Haagenson et al. (1987) have shown that wind flow corresponding to the low to middle boundary layer is the most appropriate for simulating the transport of boundary layer pollutants. Consequently, the 925 mb trajectory has been selected for consideration in this study.

3. Results

Figs. 5, 6, and 7 show available air quality data from Kejimkujik, Longwoods and Chalk River, respectively. Ambient mixing ratios for PAN, HNO_3 and p-NO_3^- are plotted as daily averages (12 GMT–12 GMT, assigned to the first day). Based upon these daily averages, a plot is also shown for each site of the PAN molar ratio (PMR), which is defined as:

$$\mathrm{PMR} = \mathrm{PAN}/(\mathrm{PAN} + \mathrm{HNO_3} + \mathrm{p\text{-}NO_3^-}).$$

This ratio reflects the contribution of PAN to the observed nitrogen secondary product sum. PAN and ozone (for Kejimkujik only) data are also plotted as the daily maximum mixing ratio over the same 24-h period; this provides a clearer representation of the magnitude and occurrence of periods of elevated mixing ratio. Both PAN and ozone have been shown to undergo surface deposition (Garland and Penkett, 1976), often leading to significant overnight depletion within a shallow inversion layer. The calculation of a daily average mixing ratio based upon ground level observations incorporates these depleted values, yielding an estimate that is not fully representative of conditions within the well-mixed atmospheric boundary layer.

The long-term data from Kejimkujik are also summarized in Table 1 on a monthly basis. For each of the parameters, values are provided for the median, 25 and 75 percentile points of the cumulative frequency distributions.

Fig. 8 shows data for PAN, HNO_3 and p-NO_3^- for the North Bay site. Because of the greater resolution in the data, these are shown as 6-h averages. The PMR is also plotted on a similar basis. (Full data records for all species are available in tabular form on request from the authors).

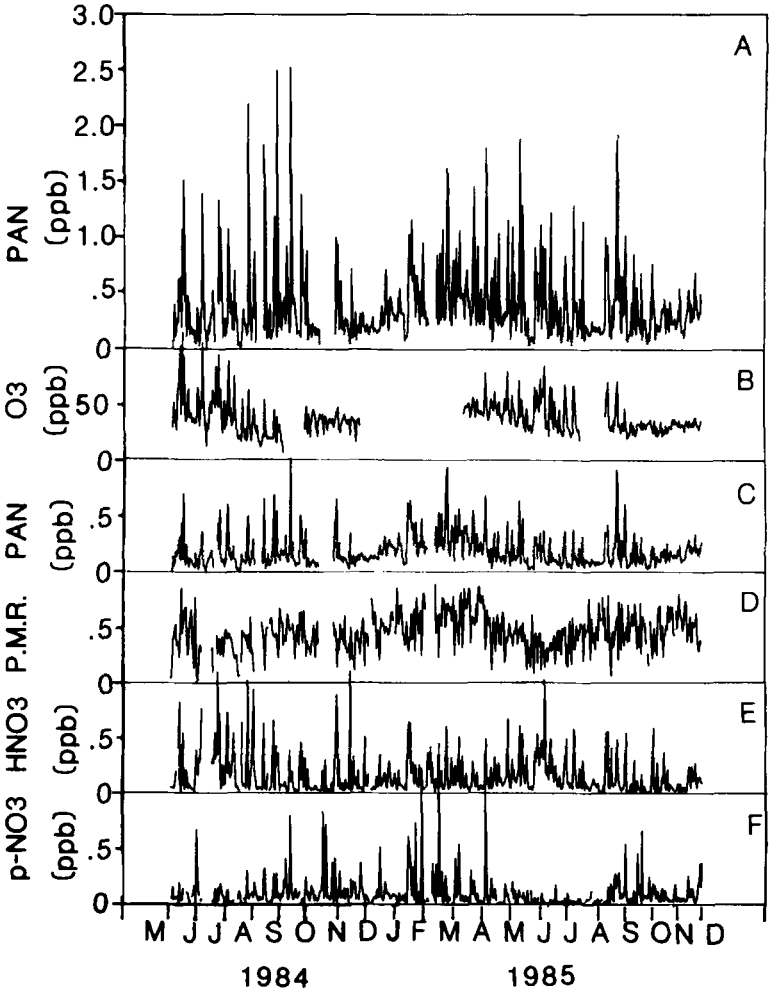

Fig. 5. Kejimkujik air quality data; June 1984 to December 1985: (a) PAN daily maximum mixing ratio; (b) Ozone daily maximum mixing ratio; (c) PAN daily average mixing ratio; (d) PAN molar ratio (PMR) using daily average mixing ratio values; (e) HNO_3 daily average mixing ratio; (f) Particulate nitrate ($p\text{-}NO_3^-$) daily average mixing ratio.

4. Discussion

Most measurements of PAN to date have tended to focus on the behaviour during summer months, when PAN concentrations would be expected to be highest; analytical sensitivity has often been inadequate for routine monitoring below 200–300 ppt(v). The AES PAN monitor possesses detection limits that make the study of clean air PAN levels a real possibility. Whilst some very high sensitivity PAN measurements have been reported by other workers these have usually been confined to short-term measurements at a particular site, or occasional measurements at different times of the year (Singh et al., 1985; Singh et al., 1986). Consequently, an examination of aspects such as seasonal variations, or changes in episode frequency from year to year, has not been really feasible.

The extended data sets reported here for Kejimkujik and Longwoods represent an opportunity to examine some important features of

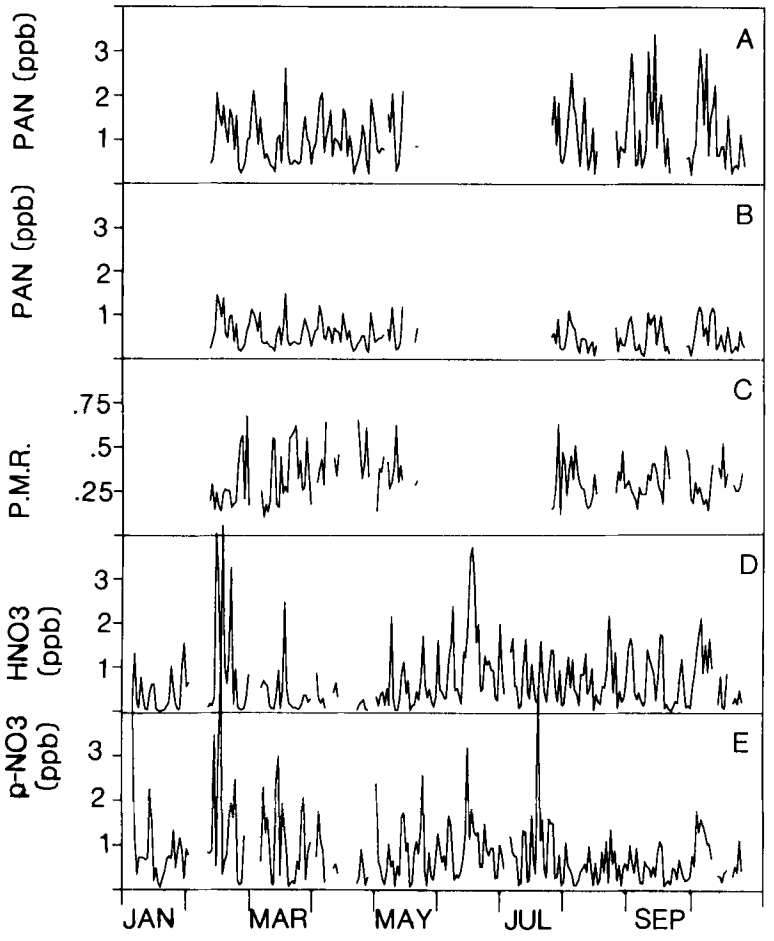

Fig. 6. Longwoods air quality data; February 1983 to October 1983: (a) PAN daily maximum mixing ratio; (b) PAN daily average mixing ratio; (c) PAN molar ratio (PMR), using daily average mixing ratio values; (d) HNO_3 daily average mixing ratio; (e) Particulate nitrate ($p\text{-}NO_3^-$) daily average mixing ratio.

atmospheric PAN behaviour during both clean and polluted situations, and under different seasonal conditions. The wider applicability of such identified elements of PAN behaviour can also be investigated using the more limited data sets for North Bay and Chalk River.

4.1. Temporal and spatial variations in ambient PAN concentrations

The extended data set for Kejimkujik provides strong evidence for a definite seasonal dependence in atmospheric PAN behaviour. Daily maxima (Fig. 5a) of >0.5 ppb(v) are potentially possible throughout the yearly cycle. Highest PAN maxima are observed during spring and early fall, rather than summer, with the winter months displaying marginally lower peak PAN levels. Furthermore, Fig. 5a clearly shows that the PAN episodic behaviour is superimposed on an underlying seasonal variation in the typical baseline, or background value of PAN observed at the site—this background value maximizes in late winter/early spring (~300 ppt(v)), and minimizes in summer (~100 ppt(v)). This pattern is also evident in the monthly summary data of Table 1 for this parameter, where the 25 percentile PAN mixing ratio clearly maximizes during late winter/early spring.

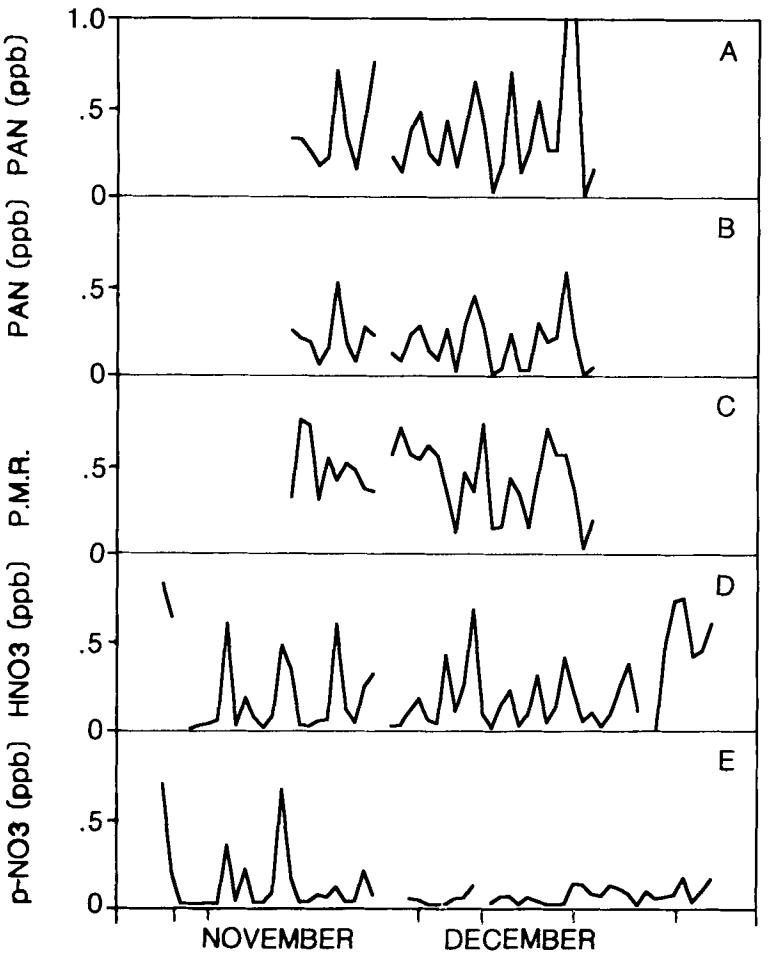

Fig. 7. Chalk River air quality data; November to December 1983. (a) PAN daily maximum mixing ratio; (b) PAN daily average mixing ratio; (c) PAN molar ratio (PMR), using daily average mixing ratio values; (d) HNO_3 daily average mixing ratio; (e) Particulate nitrate ($p\text{-}NO_3^-$) daily average mixing ratio.

PAN data from Kejimkujik up to August 1986 have been presented previously (Bottenheim et al., 1987). Data for 1986 are not dealt with here in detail because, at present, fully verified supporting data for $p\text{-}NO_3^-$, HNO_3 etc. are not available beyond the end of 1985. However, this additional eight months of PAN data clearly shows the existence of a further late winter/early spring high in the underlying PAN background for 1986. This type of behaviour is similar to that discussed previously by Penkett and Brice (1986) for a rural site in the UK, using $CFCl_3$ as a sensitive tracer to identify periods of background air, unaffected by recent contact with anthropogenic sources.

Ozone behaviour at Kejimkujik (Fig. 5b) contrasts with that seen for PAN, with the highest mixing ratios being observed during summer months. These observed ozone maxima are well correlated in time with corresponding peaks in the PAN levels. However, during winter, very few deviations from a constant ozone level are observed suggesting that photochemical formation of ozone is suppressed. The absence of ozone data during early 1985, precludes any definite statements regarding patterns in the underlying background values.

The maximum PAN values observed at Longwoods (Fig. 6a) are noticeably higher than those typically seen at Kejimkujik. Peak PAN

Table 1. *Kejimkujik air quality data; June 1984 to December 1985. Monthly summaries of cumulative frequency distributions (25, 50, 75 percentile points)*

	PAN—daily maximum, ppb			O_3—daily maximum, ppb			PAN—daily average, ppb			HNO_3—daily average, ppb			p-NO_3^-—daily average, ppb			PAN molar ratio (PMR)		
Month	25%	50%	75%	25%	50%	75%	25%	50%	75%	25%	50%	75%	25%	50%	75%	25%	50%	75%
June 84	0.11	0.19	0.48	34	40	61	0.05	0.09	0.17	0.03	0.07	0.16	0.04	0.06	0.10	0.25	0.40	0.57
July 84	0.17	0.29	0.48	34	47	60	0.08	0.12	0.19	0.17	0.30	0.45	0.03	0.04	0.13	0.28	0.31	0.41
Aug. 84	0.11	0.23	0.36	21	30	46	0.06	0.09	0.15	0.06	0.16	0.35	0.02	0.06	0.11	0.24	0.31	0.42
Sept. 84	0.14	0.24	0.53	17	20	26	0.07	0.11	0.21	0.03	0.05	0.19	0.03	0.06	0.09	0.40	0.48	0.54
Oct. 84	0.14	0.25	0.59	28	34	39	0.07	0.12	0.26	0.03	0.06	0.19	0.05	0.09	0.14	0.34	0.41	0.51
Nov. 84	0.13	0.18	0.19	33	36	41	0.07	0.09	0.12	0.02	0.03	0.07	0.05	0.07	0.13	0.35	0.41	0.48
Dec. 84	0.13	0.18	0.25	31	36	37	0.07	0.10	0.13	0.03	0.05	0.09	0.06	0.09	0.14	0.30	0.38	0.48
Jan. 85	0.17	0.21	0.33				0.12	0.14	0.23	0.05	0.07	0.16	0.05	0.06	0.10	0.45	0.50	0.57
Feb. 85	0.26	0.33	0.62				0.14	0.23	0.41	0.06	0.09	0.25	0.03	0.07	0.11	0.40	0.54	0.64
Mar. 85	0.26	0.30	0.84				0.20	0.23	0.40	0.05	0.09	0.22	0.03	0.07	0.17	0.51	0.62	0.72
Apr. 85	0.32	0.45	0.66	42	47	51	0.20	0.29	0.37	0.05	0.08	0.20	0.03	0.06	0.09	0.50	0.61	0.73
May 85	0.21	0.30	0.59	40	44	52	0.11	0.17	0.25	0.06	0.08	0.18	0.01	0.03	0.09	0.40	0.56	0.67
June 85	0.12	0.30	0.45	30	40	46	0.07	0.11	0.20	0.07	0.13	0.21	0.02	0.06	0.12	0.34	0.41	0.48
July 85	0.17	0.35	0.61	34	44	62	0.07	0.11	0.22	0.12	0.24	0.39	0.01	0.02	0.04	0.26	0.35	0.42
Aug. 85	0.12	0.19	0.42	23	27	42	0.06	0.07	0.14	0.05	0.09	0.22	0.01	0.03	0.04	0.31	0.46	0.50
Sept. 85	0.14	0.19	0.38	29	35	58	0.07	0.08	0.11	0.04	0.08	0.09	0.01	0.03	0.09	0.36	0.45	0.56
Oct. 85	0.13	0.26	0.55	25	31	32	0.07	0.12	0.25	0.02	0.04	0.09	0.03	0.07	0.10	0.38	0.51	0.59
Nov. 85	0.14	0.23	0.33	24	29	32	0.06	0.12	0.15	0.02	0.04	0.11	0.03	0.06	0.10	0.35	0.46	0.60
Dec. 85	0.22	0.29	0.39	30	32	34	0.12	0.17	0.22	0.03	0.08	0.14	0.03	0.06	0.14	0.38	0.51	0.60

mixing ratios in excess of 2 ppb(v) frequently occur during the Longwoods monitoring period, with the highest maxima occurring during the fall. The absence of data during mid-summer and winter prevents any conclusive statement regarding a seasonal variation in background values for this site.

The limited data set for Chalk River (Fig. 7a) shows PAN daily maxima to be substantially reduced compared to Longwoods. However, these winter maxima are comparable to those seen at Kejimkujik at an equivalent time of year. The data set for North Bay (Fig. 8a), in contrast, shows PAN mixing ratios rising to >1.5 ppb(v) on several occasions during January–February 1984. The PAN values shown here are 6-h averages, and examination of the complete data set shows that the observed PAN maxima actually exceed this smoothed value by about 25% in most cases.

These results suggest that, for a given time of year, the potential maximum PAN value observed is strongly site dependent, with the ranking:

Longwoods > North Bay
> Chalk River ≥ Kejimkujik.

Reference to Fig. 2 shows that this reflects the differing source–receptor relationships existing for each site, with the highest and lowest PAN maxima corresponding to sites closest and furthest removed from the source region of influence, respectively.

The observed temporal and spatial variations implied by these data sets can be qualitatively explained with respect to current understanding of PAN chemistry. The level of a secondary pollutant such as PAN in the atmosphere represents the competition between photochemical production and destruction processes:

HO + hydrocarbon
→ secondary pollutant → sink process.

Since all the sites being considered are well removed from local sources of precursors, all observations of elevated PAN levels must result from the transport of photochemically aged air masses originating from distant source regions. Consequently, the actual transport time between source and receptor becomes an important parameter in determining the balance in the production and destruction processes. The observed decline in typical PAN maxima with

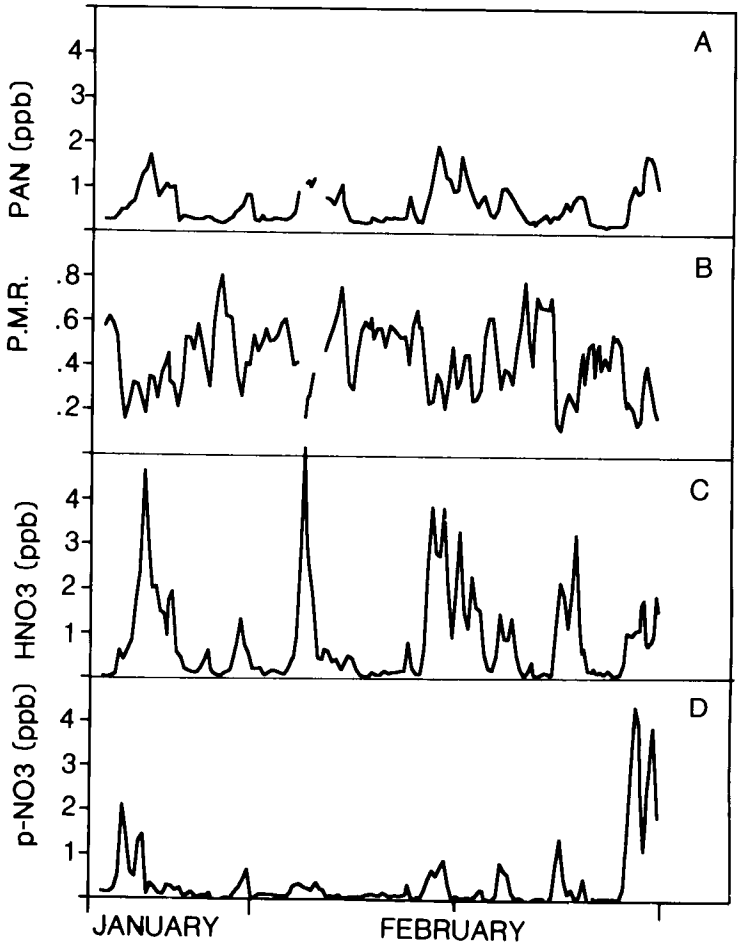

Fig. 8. North Bay air quality data; January to February 1984. (a) PAN mixing ratio (six-hourly average); (b) PAN molar ratio (PMR), using six-hourly average mixing ratio values; (c) HNO_3 mixing ratio (six-hourly average); (d) Particulate nitrate ($p\text{-}NO_3^-$) daily average mixing ratio.

increasing transport time from appropriate source regions appears qualitatively reasonable, and suggests that the time scale for PAN formation is much shorter than the time scale for destruction.

The seasonal variation in the magnitude of the observed PAN maxima can be accounted for as follows; during summer, the average concentration of HO radicals is increased by the greater solar intensity and duration. However, the accompanying increased temperatures also produce a rapid increase in the rate of thermal decomposition for PAN. Other sinks for PAN, such as surface dry deposition, are also probably at a maximum during the growing season. Hence, although photochemical conditions conducive to PAN formation may be less frequent and of lower intensity during spring, fall and winter, the increased thermal stability at lower temperatures and reduced surface dry deposition may lead to higher maxima being observed at a distant receptor site. At Kejimkujik, the observation of peak values in spring and fall suggests that the increasing production potential during summer is effectively nullified by the reduced lifetime caused by the higher temperatures. For a site substantially closer to the sources, a different pattern might be expected with the PAN maxima

more dependent upon the formation rate. Extended measurements in the UK (Brice et al., 1984) at a rural site west of London showed that PAN maxima at this site were greatest during summer months, although very significant periods of elevated PAN were observed to be possible during late winter/early spring and fall. Similarly, urban measurements by Tsalkani et al. (1987) in France during the months of October and February clearly demonstrate the considerable potential for PAN production at these times of the year. Such a site, however, is heavily influenced by local emissions of PAN precursor species, although long-range transport of photochemically-aged air masses can contribute to the observations. Long-term studies of seasonal PAN behaviour at an urban site would be expected to demonstrate somewhat different patterns to those observed in the present study at rural sites.

The underlying seasonal variation in the typical background PAN level observed at Kejimkujik can be explained in an analogous fashion. Available evidence suggests that background continental air contains all the precursors required for PAN production at all times of the year, i.e., NMHC, NO_2 and HO radicals (Kasting and Singh, 1986). The decrease of solar radiation and HO radical concentration in winter is offset by an increase in the background NMHC (Tille et al., 1985; Lightman et al., personal communication) and NO_2 levels (maximizing in early spring) and hence the decreasing photochemistry need not lead to an equivalent drop in PAN formation rate. Combined with a reduced loss rate during winter and early spring, such a production rate dependence could well drive the chemistry to give the observed late winter/early spring PAN maximum background. In fact, modelling studies by Kasting and Singh (1986) predict this seasonal pattern for PAN in both background continental and maritime situations.

4.2. Relationships among pollutant species

The photochemical processes leading to the production of PAN and ozone are also involved in the formation of gaseous nitric acid, and particulate sulphate and nitrate. Consequently, the observed temporal trends of these secondary pollutants are expected to show well-defined inter-relationships.

For Kejimkujik, the peaks in the PAN record can be seen to correspond with simultaneous observations of elevated HNO_3. Though not shown here, the peaks in p-SO_4^{2-} are also well matched in time, confirming the presence of a relatively well-aged, polluted air mass.

Note that HNO_3 is more abundant than p-NO_3^- during summer, but these components become comparable during winter and early spring (Figs. 5e, 5f and Table 1). Possible reasons for such observations have been discussed previously (Anlauf et al., 1986b).

The removal pathways for atmospheric nitrogen oxides (NO_x) involve both physical (e.g., deposition) and chemical (homogeneous and heterogeneous) processes. Chemical conversion of NO_x leads to the formation of PAN, nitric acid and particulate nitrate, along with trace levels of gaseous and particulate organic nitrates and other oxygenated nitrogeneous compounds, as shown schematically in Fig. 1. Lagrangian-type modelling studies predict that nitric acid formation in a polluted air mass should initially proceed faster than the production of PAN (Derwent and Hov, 1982). However, with increasing transport time, the higher removal rate for nitric acid (dry deposition, aerosol formation, wet removal) should increase the relative importance of PAN as a carrier of atmospheric NO_x.

The PAN molar ratio (PMR) is shown in Fig. 5d, and the daily average PAN values in Fig. 5c. The PMR value shows appreciable scatter reflecting the dependence of this ratio on the exact air mass origin, transport time and precipitation history. Some interesting features are discernible from the monthly summary data listed in Table 1. A central value of ~0.4–0.5 appears typical for the ratio at this site, and there is evidence for a summer minimum and a late winter/early spring maximum. Detailed examination shows that the upper values seen for this ratio (0.8 to 0.9) are obtained during periods when the ambient PAN mixing ratios are actually low, and the air is relatively clean. This can be accounted for on the basis of the previously discussed long lifetime of PAN; for an aged, near background air mass, the HNO_3 and p-NO_3^- originally formed would have been more effectively removed than PAN by deposition processes (dry and wet).

For Longwoods, the peaks in the PAN record

are also seen to correspond with periods of elevated HNO_3 mixing ratio. HNO_3 and p-NO_3^- values at Longwoods are more evenly matched over the study period (Figs. 6d and 6e). In contrast to the pattern seen at Kejimkujik, HNO_3 does not appear to be more abundant than p-NO_3^- during the summer months. This probably reflects the presence of elevated ambient NH_3 levels in the fertile agricultural region surrounding the Longwoods site, enhancing the production of particulate ammonium nitrate (from $HNO_3 + NH_3$).

Fig. 6c shows the temporal variation in the PMR value for the Longwoods site, and the observed average PAN mixing ratio is given in Fig. 6b. As seen previously at Kejimkujik, there is appreciable scatter in the data, but the central value of this ratio appears to be slightly lower ($\sim$0.35). Once again, the periods of maximum PAN mixing ratios do not coincide with the observation of the highest fraction of PAN in the overall nitrogen balance. Furthermore, the upper values seen for this ratio ($\sim$0.6) are certainly lower than those seen at Kejimkujik. For the Longwoods site, the observation of clean, well aged background air is less likely because of the proximity of precursor source regions; the reduced average transport time produces an increased contribution from HNO_3 and p-NO_3^- to the ratio.

For Chalk River and North Bay, effectively spanning the period November 1983 to February 1984, the data patterns for p-NO_3^- and HNO_3 show that episodes of either or both species are possible, depending upon the exact conditions (Figs. 7d, 7e, 8d, 8e). Once again the elevations in PAN also track the observations for HNO_3 in time.

Figs. 7c and 8c show the variations in PMR for Chalk River and North Bay, respectively. The expanded scale of the plots demonstrates very clearly the tendency of this ratio to maximize during those periods when the PAN mixing ratio attains the lowest, or background values, and to actually decline during periods when the observed PAN levels are highest. The absolute value of the ratio at both sites is consistent with those observed at Longwoods and Kejimkujik—at North Bay, the value appears centred at $\sim$0.4, whereas for Chalk River the ratio may be slightly higher.

In summary, PAN consistently appears to be a very significant component of the oxidized nitrogen species at all the sites studied. The PMR values reported are in good agreement with those from short-term observations obtained during summer 1982 in southern Ontario and northern Ontario (Anlauf et al., 1985, 1986b; Bottenheim et al., 1984). In these previous investigations, however, high values of PMR were not always associated with the influx of background air, but could also be caused by a preferential removal of HNO_3 and particulate nitrate from a polluted air mass due to extensive rainfall.

At locations away from NO_x/NMHC source areas, the PMR value emerges as a potentially useful indicator of air mass age. Values below 0.5 indicate an air mass that has experienced recent contact with source regions (on a time scale of 1–2 days) and subsequent photochemistry producing significant quantities of HNO_3 and p-NO_3^-. With increasing transport distance and time, this value steadily rises, and may increase rapidly in instances of rainfall within the polluted air mass. For very well-aged air, approaching background composition, the highest values of PMR are attained. Measurements at other remote locations reported by Singh et al. (1985), Fahey et al. (1986) and Bottenheim et al. (1986) support this interpretation.

4.3. Air mass origin and PAN maxima at Kejimkujik

For all the sites considered, it is possible to perform air mass back-trajectory calculations to relate observed periods of elevated PAN mixing ratio to a particular source region for precursor NMHC and NO_x. Three examples of this procedure will be discussed for Kejimkujik to indicate some typical features of the long range transport impact upon this site for fall, summer and early spring episodes.

4.3.1. 8 October 1984 (Julian Day 282). This episode exhibited the highest PAN mixing ratio (2.52 ppb(v)) experienced during the 19 months of data reported here. Examination of Fig. 5a shows that this episode was typical of many seen at Kejimkujik—relatively sharp on a temporal basis, with a well-defined onset and conclusion. Fig. 9 provides a more detailed description of the PAN data pattern for the period 7–9 October 1984, where the data collected every half hour are

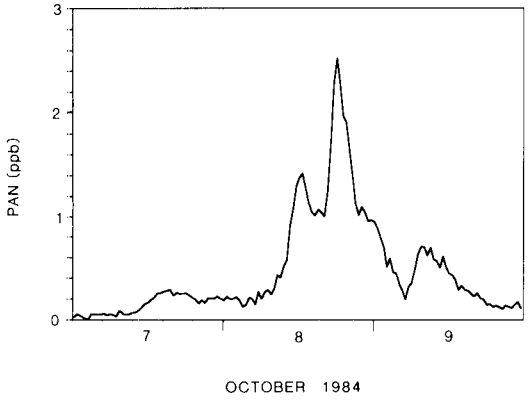

Fig. 9. PAN mixing ratios at Kejimkujik, 7–9 October 1984; grab samples every 30 min (times are local, ADT).

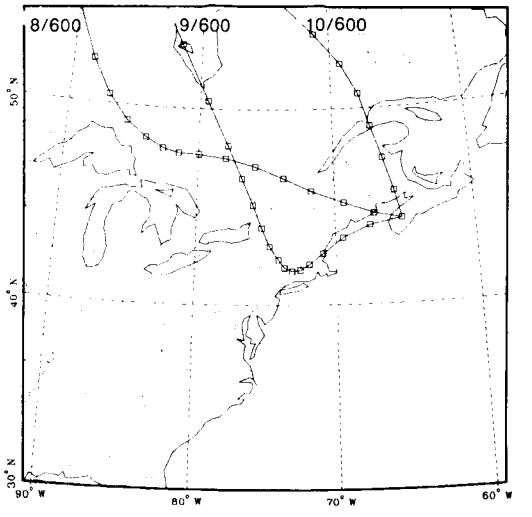

Fig. 10. Calculated 925 mb air parcel 120-h back-trajectories ending at Kejimkujik, Nova Scotia for the period 8–10 October 1984. The arrival time of each trajectory is labelled according to day/hour (GMT). Points on trajectories are 6 h apart.

plotted. PAN levels were low (~200 ppt(v)) throughout 7 October and during the early morning of 8 October. After about 0800 ADT (11 GMT), the PAN levels rose rapidly to nearly 1.5 ppb(v) by noon, decreased slightly, and then rose again in mid-afternoon to reach a maximum of 2.5 ppb(v) at ~1800 ADT (21 GMT) on 8 October. A rapid decay then followed during late evening and throughout the night, reaching a minimum of ~200 ppt(v) at ~0600 ADT (9 GMT) on 9 October. Fig. 10 shows representative 120-h air mass back trajectory calculations for Kejimkujik at the 925 mb level for 8, 9 and 10 October 1984. The points shown on the trajectory represent the calculated air mass positions at intervals 6 h apart.

The trajectory for 8 October, at 6 GMT shows a westerly to north-westerly flow, shifting to westerly at 12 GMT, and becoming westerly to south-westerly at 18 GMT. The 6 GMT trajectory on 9 October shows that the air mass originated in Northern Quebec, initially as a strong north-westerly flow which avoided other major pollution sources before reaching the Boston region and changing into a slower, south-westerly flow towards Kejimkujik. Thus, the period of maximum PAN is observed to correspond to air flow that had passed over the high emission sources around Boston approximately 24 h previously. Subsequent trajectories for 6 GMT, 12 GMT and 18 GMT on 9 October show the air flow to shift back to westerly and then north-westerly, paralleled by a marked decrease in the PAN mixing ratios seen at Kejimkujik. By 6 GMT on 10 October, the trajectory shows north to north-westerly air flow to Kejimkujik, and correspondingly low PAN mixing ratios are observed.

The synoptic situation giving rise to this highly source-specific pattern of air mass back-trajectories has also been examined. At the start of this period on 8 October, conditions were dominated by a high centred off the Atlantic coast near New York, and a low moving eastward across northern Hudson Bay, combining to give the westerly to north-westerly flow. Through 8 October, the high moved slowly eastwards, with its circulation becoming elongated along an east–west axis as the low pushed through Hudson Strait. By 18 GMT on 8 October, the flow had become mainly south-westerly as the high receded eastwards, with the approach of a slow-moving cold front. The cold front moved through the site at 6 GMT on 9 October, bringing a return to a north-westerly flow around the eastern side of a high centred over Western Quebec.

4.3.2. 23 August 1984 (Julian Day 236). This episode exhibited the highest summer PAN mixing ratio (2.19 ppb(v)) seen at Kejimkujik to date.

Fig. 11 shows the detailed temporal behaviour of PAN over the period 22–24 August 1984, indicating a well-defined onset and conclusion for the episode on 23 August. PAN levels were low at ~200 ppt(v) during most of 22 August but began to increase steadily after sunset, and reached a peak at ~1.2 ppb(v) early in the morning (~0300 ADT, 6 GMT). Following a decline, another increase occurred after about 0800 ADT (11 GMT), reaching a maxima of 2.19 ppb(v) at ~1300 ADT (17 GMT) on 23 August. A marked decline then took place, so that by ~0000 ADT on 24 August, PAN levels had essentially returned to baseline values.

Fig. 12 shows representative 120-h air mass back-trajectory calculations at the 925 mb level for 22, 23 and 24 August 1984. The trajectory for 18 GMT on 22 August, shows a north to north-westerly flow, shifting to westerly early on 23 August; this trajectory strongly suggests a possible influence from Quebec in the first pollution peak. As 23 August progressed, the flows became more south-westerly in nature, with the 12 GMT and 18 GMT trajectories (shown) passing directly over Boston and New York, respectively. The trajectory for 18 GMT on 24 August shows the air flow to now have a long oceanic fetch, missing the source regions completely, and effectively ending the episode.

The synoptic situation for this period shows that a high moving slowly eastward off the Atlantic Coast combined with a deep trough following behind, to produce the westerly flows

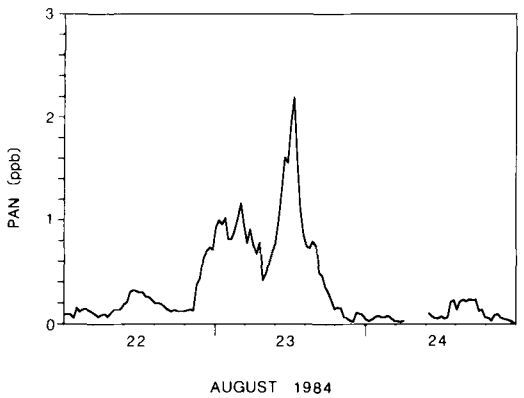

Fig. 11. PAN mixing ratio at Kejimkujik, 22–24 August 1984; grab samples every 30 min (times are local, ADT).

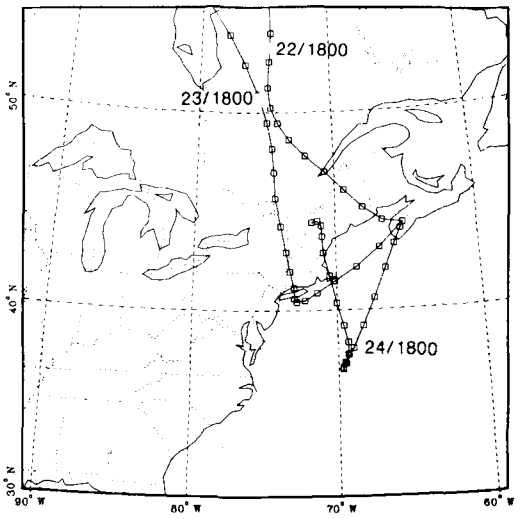

Fig. 12. Calculated 925 mb air parcel 120-h back-trajectories ending at Kejimkujik, Nova Scotia for the period 22–24 August 1984. The arrival time of each trajectory is labelled according to day/hour (GMT). Points on trajectories are 6 h apart.

indicated in the trajectories during 22 August. The flows became essentially south-westerly by 18 GMT on 23 August as the low intensified and moved eastwards towards the north-eastern seaboard. As the movement continued, the flow became more southerly, giving a more oceanic fetch to the air flow reaching the site.

4.3.3. 26 April 1985 (Julian Day 116). Fig. 13 shows the detailed temporal behaviour of PAN from 25–27 April 1985; the PAN maxima observed (1.45 ppb(v)) at ~1300 AST (17 GMT) is fairly typical of many observed during early spring conditions, being well-defined and superimposed upon a background level of PAN that is slightly elevated compared to the previous two cases.

PAN levels began to rise rapidly on 26 April from overnight values of ~100 ppt(v) around 0600 AST (10 GMT), peaked at 1300 AST (17 GMT), and then dropped to about 350 ppt(v) by late afternoon. This value persisted overnight until after local noon on 27 April.

Fig. 14 shows representative 120 h air mass back-trajectory calculations at the 925 mb level for 25, 26 and 27 April 1985. The trajectory for 18 GMT on 25 April shows a north to north-westerly flow, essentially bringing clean air to the site. By

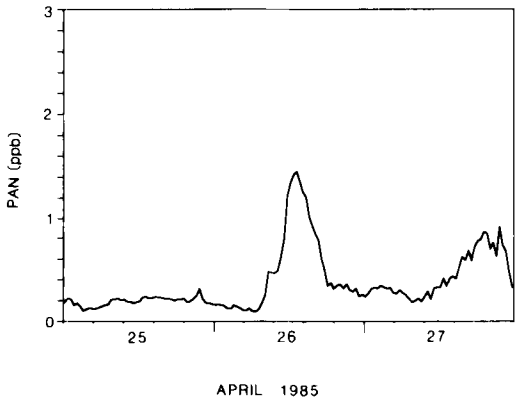

Fig. 13. PAN mixing ratios at Kejimkujik, 25–27 April 1985; grab samples every 30 min (times are local, AST).

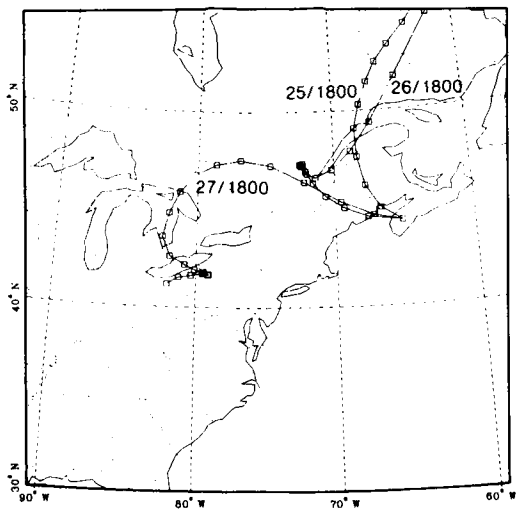

Fig. 14. Calculated 925 mb air parcel 120-h back-trajectories ending at Kejimkujik, Nova Scotia for the period 25–27 April 1985. The arrival time of each trajectory is labelled according to day/hour (GMT). Points on trajectories are 6 h apart.

18 GMT on 26 April, the flow is west to north-westerly, passing directly over Quebec (actually looping) and implicating this as the source region for the precursors. Subsequently trajectories for 27 April at 6 GMT, 12 GMT and 18 GMT (shown) indicate the west to north-westerly flow to be maintained, but now pass to the south of Quebec, bringing the site under the influence of air flow from Ontario north of Lake Huron.

The synoptic situation in this instance, was significantly different to that seen for the two cases previously examined. The dominant feature was a compact low centred over southern Newfoundland bringing cyclonic flow to the site. As the low slowly filled, this resulted in a westerly shift for the trajectories causing the Kejimkujik site to come under the influence of the Quebec source region.

5. Conclusions

The measurement of atmospheric PAN over extended periods at remote sites in eastern Canada, using a highly sensitive analytical technique, has been shown to be a feasible exercise. These studies have revealed features of PAN behaviour that would not necessarily be evident from short-term studies. These include:

(1) For all sites studied, periods of elevated PAN mixing ratio are possible throughout the year, indicating that significant photochemical activity can occur even during wintertime.

(2) The exact seasonal patterns for PAN are probably site-dependent, but the observations suggest that the highest PAN maxima are favoured during fall and late winter/early spring.

(3) The magnitude of the observed PAN maxima at a given time of year appears to decrease with distance from the source region of influence.

(4) For Kejimkujik, the data reveal a definite indication of an underlying seasonal variation in the typical background value of PAN. This background value maximizes in late winter/early spring, and minimizes in summer.

(5) For all sites studied, PAN accounts for a significant fraction of the observed oxidized nitrogen species, and appears to make an increasing contribution as the transport time from the source region increases. In typical background air, the contribution of PAN may be as high as 80–90%. PAN must be accounted for in any realistic representation of nitrogen oxide transport.

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