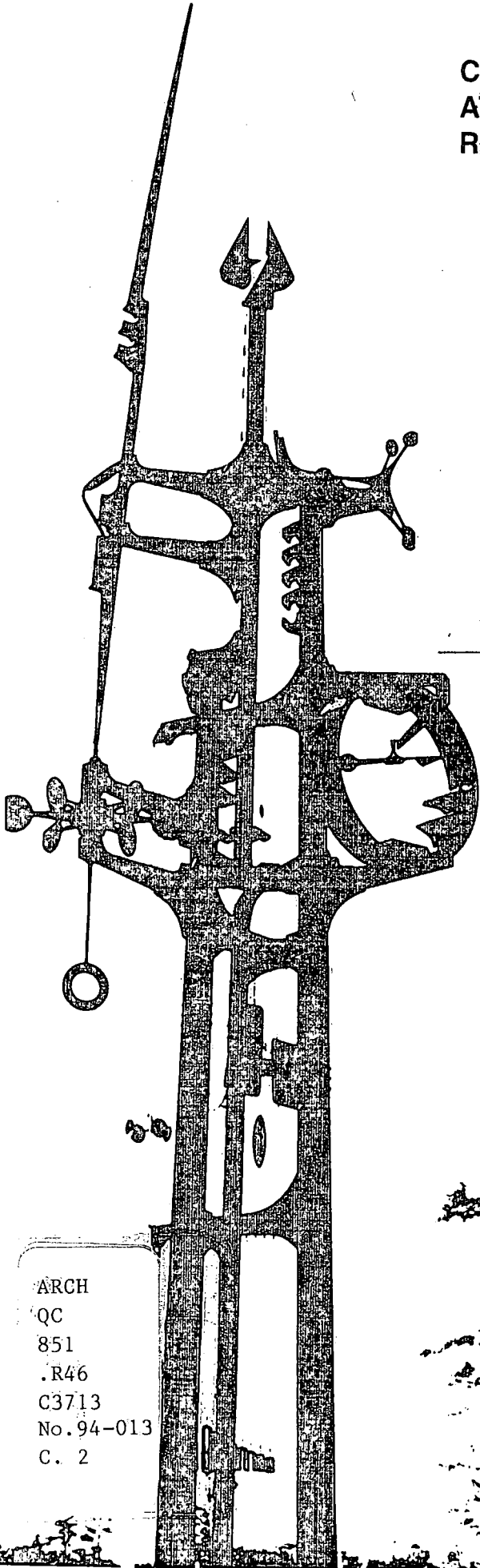# CLIMATE AND ATMOSPHERIC RESEARCH

RECHERCHE ATMOSPHÉRIQUE ET CLIMATIQUE

Environment Canada

Environnement Canada

Atmospheric Environment Service

Service de l'environnement atmosphérique

CARD REPORT NO. 94-013

**The Canadian Acid Aerosol Measurement
Program 1992-93 Report**

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Acknowledgments

Abstract

The Canadian Acid Aerosol Measurement Program (CAAMP) was established in 1992 to support an assessment of the health effects of acid-rain-related air pollutants. The main objectives of CAAMP are: determine the annual and seasonal average concentrations, peak levels (12-24 hr) and day to day variations in the concentration fine particle strong acidity (H^+), fine mass ($PM_{2.5}$) and coarse mass (PM_{10}); estimate the Canadian population's exposure to H^+, $PM_{2.5}$ and PM_{10} to assess the significance of the results of ongoing particulate health effects research and to provide daily concentration time series for acute health effects studies. CAAMP is a joint effort of the Atmospheric Environment Service and the Environmental Protection Service of Environment Canada and the Air Quality Health Effects Research Section of Health Canada.

In 1992 and 1993 measurements were taken in Surrey, BC, Windsor, Ont., Egbert, Ont., Toronto, Ont., Montréal, Que., Sutton, Que., Saint John, NB and Kejimkujik National Park, NS. This report describes the field and laboratory methods involved in collecting these measurements and summarizes the results of these activities.

Mean fine particle sulphate concentrations (SO_4^{2-}) were highest in Windsor, followed by the other Ontario sites. Concentrations were lowest in Surrey and second lowest at Kejimkujik. Fine particle strong acidity was found to behave differently. The highest mean concentrations were at the two Maritime sites, in particular in Saint John, where the mean level was a factor of two higher than in Kejimkujik (the second highest site). Acidities were lower in areas where the sulphuric acid component of the fine particles experienced greater neutralization from reaction with gaseous ammonia. Thus, H^+ concentrations tended to be lower in the major urban centres (i.e., Toronto and Montréal) and in areas with greater amounts of agricultural activity, such as Egbert. On average, ambient concentrations of particulate mass ($PM_{2.5}$ and PM_{10}) were larger in the urban areas and at locations with higher SO_4^{2-} levels. Daily time series plots show that elevated concentrations of all the particulate components are episodic. Compared to SO_4^{2-}, $PM_{2.5}$ and PM_{10}, episodes of H^+ tended to be less frequent and of shorter duration. Consistent with the higher mean concentrations, H^+ episodes (24 hour concentration > 100 nmoles m^{-3}) were most frequent in Saint John. Sulphate episodes (>100 nmoles m^{-3}) tended to be more frequent in Windsor. Compared to previous years, air pollutant levels in 1992 and 1993 were below average. Preliminary results from 1994 indicate that concentrations were higher at many of the sites, but the differences among sites observed in 1992-93 continued to persist.

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1.0 Introduction

Over the past 10 to 15 years a significant amount of research has focused on the acid deposition issue. Knowledge of the sources of acidifying pollutants and the atmospheric processes affecting their fate has improved substantially. There is now substantial information on the temporal and spatial variability in acidic deposition in North America. Concerns over ecological effects have generally resulted in more emphasis being placed on studying the potential damage due to *acidic deposition*. Consequently, less attention has been paid to the impact of acidic pollutants while still in the atmosphere where they have the potential to adversely affect human health (deposition in the respiratory tract) and they will contribute to visibility degradation. These two issues are currently receiving more attention. In Canada, the health effects of acid rain-related air pollutants and the possible subsequent need for additional future emission controls (i.e. beyond those required by the Canada - U.S. Air Quality Agreement and the U.S. Clean Air Act) are being examined in accordance with the requirements of the Green Plan.

The Canadian Acid Aerosol Measurement Program (CAAMP), which formally began in 1992, aims to assist in the study of the health effects of acid rain by meeting each of the following objectives:

1. Collect data on fine particle acidity and particle mass in the fine and coarse mode at multiple Canadian locations.

2. Determine annual and seasonal averages, peak levels (12-24 hr) and temporal variability of particle acidity and fine and coarse masses.

3. Estimate the exposure to fine particle acidity of the Canadian population.
    *   to assess the significance of the results of ongoing health effects research in a Canadian context
    *   insure that the data are appropriate for incorporation into future health studies.

CAAMP is a joint effort of the Atmospheric Environment Service and the Environmental Protection Service of Environment Canada and the Air Quality Health Effects Research Section of Health Canada. The main features examined by CAAMP are:

*   Fine particle strong acidity (H^+).

*   The fraction of mass in the fine and coarse modes ($PM_{2.5}$ and PM_{10}).

*   The concentrations of the major inorganic constituents (ions and metals) on the particles.

*   Ambient NH_3 and HNO_3 concentrations.

At two Canadian Air and Precipitation Monitoring (CAPMoN) sites (Egbert, Ont and Sutton, Que) and one Ontario Ministry of the Environment site (Windsor) particulate measurement equipment began operating in June 1991 or before. During May, June and July of 1992 measurements at Toronto, Montréal, Kejimkujik and Saint John were initiated. The locations where measurements were made in 1992 and 1993 are shown in Figure 1. Sites in urban areas

reflect CAAMP's interest in estimating the human exposure to particles. Concentrations measured at rural sites are expected to be a better indication of the concentrations within larger, regional-scale air masses thereby providing information on the broad spatial distribution in particle acidity.
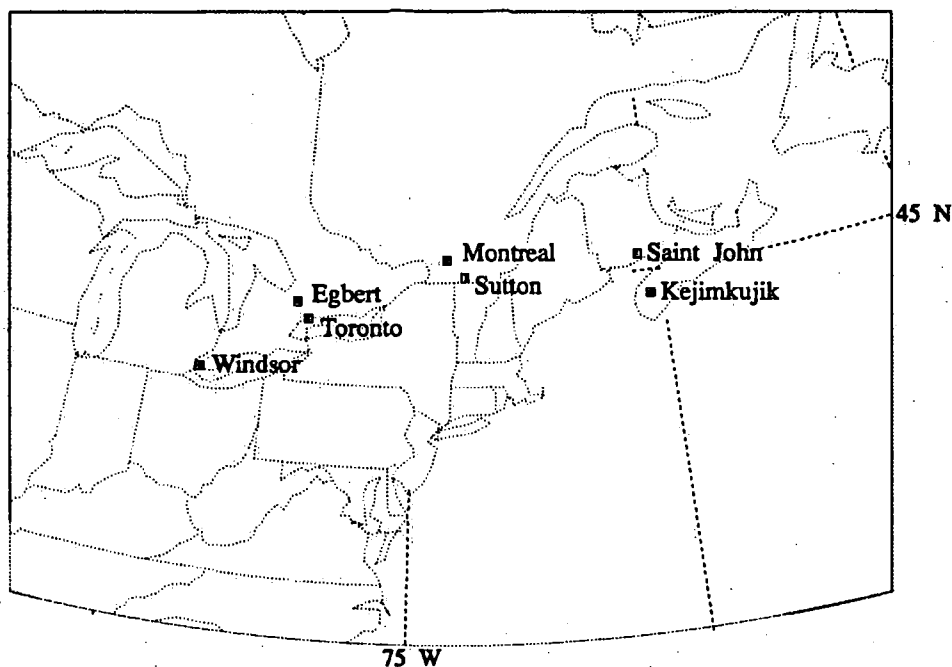
Figure 1   The locations of the 1992-93 Canadian Acid Aerosol Measurement Program sites. The Surrey East site is not shown.

The rural sites are generally in close proximity to the urban sites. This configuration will provide some information on the amount of variability in concentrations over relatively small distances and will provide information on the effect of urban emissions on particle acidity.

This CAAMP report includes details on the field and laboratory methods, including the relevant quality assurance procedures. Also included in this report are the measurement results from the Spring of 1992 to the end of 1993. In the next section a brief background on the acid aerosol issue along with information on previous Canadian measurements of fine particle strong acidity are presented.

2.0 Background

Acidic aerosols are heterogeneous mixtures of several classes of pollutants. They contain strong and weak acids in the form of particles, liquids and gases, and while the particles are predominantly below 2.5 µm in diameter, they can grow to relatively large sizes (i.e., acid fog). This discussion focuses entirely on acidic sulfates which are the species of most concern to CAAMP.

It is well known that in eastern North America, sulphur is a major component on the fine particles and that owing, to their slow deposition velocity these particles can spread relatively homogeneously over large regions. What is not known is the exact chemical formulation of the sulphur-containing molecules. Oxidation of SO_2 emissions leads to aerosols containing H_2SO_4 which, when exposed to gaseous NH_3, reacts rapidly to form partially and fully neutralized NH_4^+ salts (e.g. NH_4HSO_4, $(NH_4)_2SO_4$). Relatively little information on the partitioning between the various forms of sulphur compounds in the atmosphere over North America is available. However, the fraction of the aerosol that is acidic (H^+ concentration) tends to exhibit more spatial variability (horizontally and vertically) than SO_4^{2-} and the availability of NH_3 is the main factor influencing this fraction.

Tanner et al. (1981) and Kitto et al. (1992) provide good reviews of measurements of particle acidity that have been made in the past. There have been some measurements taken over Canada. Smith-Palmer and Wentzel (1986) reported 24 hour acidity values of up to approximately 186 nmoles m^{-3} in central Nova Scotia. These measurements were made using dichotomous samplers, without the use of NH_3 denuders, and were taken over separate 2-4 week periods in the summers of 1984 and 1985. Waldman et al. (1990) observed a maximum 24 hour H^+ level of 190 nmoles m^{-3} in Metropolitan Toronto. The mean 24 hour acidity during the July to August time period (in 1985) ranged from 18-24 nmoles m^{-3}, depending upon location in metro Toronto. From measurements taken near Dunnville, Ont., in the summer of 1984, Keeler et al. (1990) reported some of the highest surface H^+ concentrations measured to date. During the period, which extended from June 29 to August 9, a 12 hour concentration of close to 550 nmoles m^{-3} was observed. There were nine 12 hour periods with H^+ concentrations above 100 nmoles m^{-3}. Keeler et al. (1990) reported mean day and night H^+ concentrations during the study of 56 and 39 nmoles m^{-3}, respectively.

Table 1 is a summary of the fine particle H^+ and SO_4^{2-} concentrations measured at the six Canadian locations involved in the Health Canada/Harvard School of Public Health 24-Community Study (Spengler et al., 1993). In Ontario there was a clear warm season peak in concentrations with the highest levels in June-September. The Dunnville and Pembroke observations indicated that there was a N-S gradient in H^+ concentrations. The SO_4^{2-} measurements shown in Table 1 and those from other networks (i.e. CAPMoN and Ontario Provincial SO_4^{2-} measurements) exhibit the same behaviour. Note that the data were collected in a different year at Leamington. It is not known how much of the differences between Leamington and Dunnville are a result of interannual variability as opposed to spatial variability. However, the CAPMoN site of Longwoods, Ont., measured a small *increase* in SO_4^{2-} between the

summer of 1988 and 1989. Thus, the decrease from Dunnville in 1988 to Leamington in 1989 could be a reflection of an actual gradient in ambient H^+ and SO_4^{2-} over southwestern Ontario. Concentrations of H^+ and SO_4^{2-} were considerably lower in Saskatchewan and British Columbia and did not exhibit a strong seasonal pattern.

Similar to the behaviour of SO_4^{2-}, H^+ episodes can influence large areas. In Figure 2 the H^+ and O_3 concentrations at Dunnville and Pembroke during July and August of 1988 are shown. There are 2 or 3 instances when both locations experienced simultaneous increases in H^+. On Aug. 9-13 the episode, which probably originated from large emissions in the Midwest U.S., did not penetrate far enough north to be detected at Pembroke.

Table 1 Summary of fine particle H^+ and SO_4^{2-} concentrations measured in Canada during the Health and Welfare/Harvard School of Public Health 24-Community Study. Warm season=May-Sept. Cold season=Oct.-Mar.

	Leamington, Ont. 1989-90			Pembroke, Ont. 1988-89			Dunnville, Ont. 1988-89		
	n	H^+	SO_4^{2-}	n	H^+	SO_4^{2-}	n	H^+	SO_4^{2-}
Annual	166	19.28	50.14	100	24.91	40.46	119	28.72	61.87
Winter	43	12.21	34.62	17	16.41	22.47	30	8.6	35.17
Spring	41	15.15	49.73	20	8.40	25.30	23	14.35	47.43
Summer	41	39.08	79.20	32	39.53	62.47	35	54.82	104.86
Fall	41	11.02	37.76	31	25.13	37.38	31	29.39	49.87
Cold	84	11.63	36.15	48	22.04	32.10	61	19.16	42.64
Warm	82	27.11	64.46	52	27.56	48.17	58	38.77	82.09

	Yorkton, Sask. 1990-91			Penticton, B.C. 1989-90		
	n	H^+	SO_4^{2-}	n	H^+	SO_4^{2-}
Annual	183	0.64	6.9	106	9.7	9.5
Winter	45	0.14	1.68	19	10.44	11.75
Spring	47	0.76	12.01	29	8.8	10.68
Summer	46	1.53	7.58	26	10.72	8.05
Fall	45	0.12	6.08	32	9.26	8.14
Cold	90	0.13	3.88	51	9.70	9.49
Warm	93	1.14	9.82	55	9.71	9.44

As indicated in Table 1 above, the concentrations tended to be higher at Dunnville during the period. However, on July 30 and August 5 they were higher in Pembroke. While this is entirely possible, the higher concentrations at Pembroke on these 2 days could have been a result of the every-other-day resolution of the H^+ measurements. That is, the peaks associated with the particle-laden air masses were experienced on July 29 and August 4 at Dunnville, but were missed because the samplers were not operated. The daily maximum hourly O_3 concentrations at Dunnville (see Figure 2) do suggest that the peak H^+ concentrations may have occurred on these days. The peaks were captured at Pembroke because an extra day of transport was needed to advect the particles further north. Thus, the high H^+ levels in Pembroke on July 30 and August 5 could have been exceeded in Dunnville on the previous days and the concentrations were already decreasing at Dunnville when the concentrations peaked at Pembroke.

The short time series in Figure 2 indicates that there are similar atmospheric processes leading to elevated H^+ and O_3 concentrations. The correspondence in O_3 and H^+ peaks was driven, to a large extent, by a similar dependence on the meteorological processes leading to high concentrations. However, the main precursor for H_2SO_4 is SO_2, while for O_3 it is NO_x and hydrocarbons and the spatial distribution of the sources of these species differs. In addition to meteorology, the chemical production of O_3 and H^+ are related since H_2SO_4 formation also depends upon intermediate photochemical species (e.g., OH, H_2O_2). The H^+ and O_3 behaviour exhibited in Figure 2 suggests that there is the potential for large sections of southern Ontario to simultaneously experience elevated O_3 and H^+ concentrations (i.e., it is likely that concentrations were high over areas between Dunnville and Pembroke and these areas sustain a large number of people). Given the large number of people who may therefore be exposed to elevated H^+ and/or O_3 levels there is cause for concern regarding the potential risk to public health.

The direct health effects associated with H^+ exposure are discussed in detail in the NAPAP report on the health effects of acid deposition (NAPAP, 1990). It was concluded that, while substantial uncertainty exists, the body of data raises concern that acidic aerosols, alone or in concert with other pollutants, may be contributing to health effects in exposed populations. However, it was stated that the precise magnitude and full nature of the health risk remains somewhat speculative. Spengler et al. (1990), Lippmann (1985) and Lipfert (1989) also provide good summaries of the current state of knowledge regarding the health effects of exposure to fine particle strong acidity. These papers point towards the need and justification for more research into the health effects arising from exposure to acidic aerosols and to respirable particles in general.
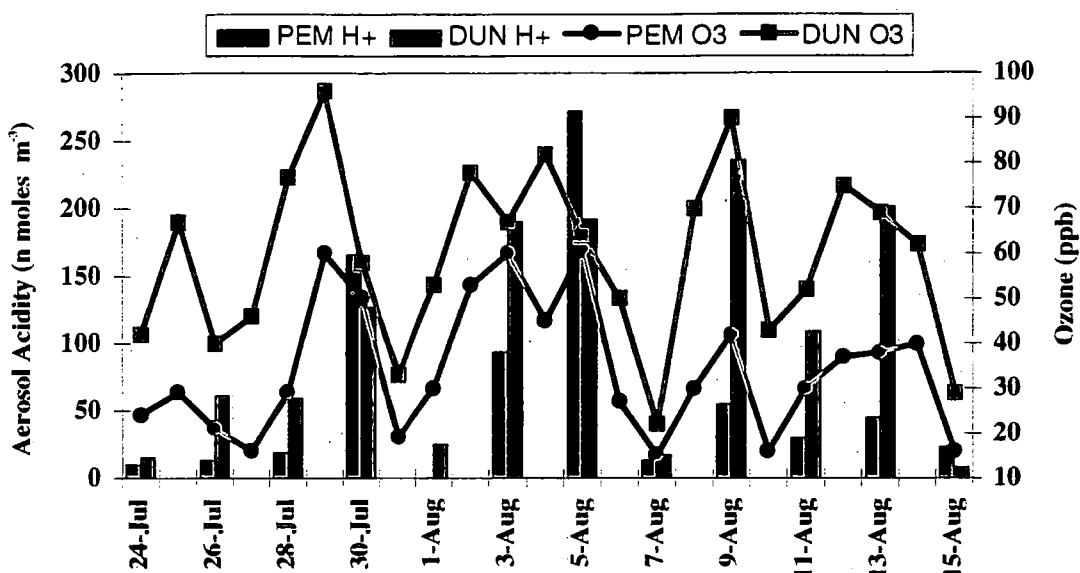
Figure 2 Time series of Dunnville and Pembroke, Ontario, 24 hour mean H⁺ and O₃ concentrations measured in the summer of 1988.

3.0 Methods

3.1 Field Measurements

Table 2 lists the various measurements that were collected at each site and the sampling frequency. Four different types of sampling apparatus were used. Both annular denuder systems (single and double denuder) and the fine and coarse mass particle sampling units (Air Diagnostics and Engineering 10 l min^{-1} 10 and 2.5 μm cut size inertial impactors) use a MKS 1159B-20,000SV mass flow controller, calibrated for 1 atm and 0° C, to regulate the flow rate. The dichotomous samplers (dichotomous sampler model 241, Anderson Instruments/General Metal Works) rely on their own pump and flow controller systems which maintain a total flow rate of approximately 16.7 l min^{-1}.

Chart recorders are attached to the flow controller power supply/readout device to continuously monitor flow rates. The chart traces and the information on the log sheets are used to calculate the total volume of air sampled over the 24 hr period. Not all dichots have operable chart recorders and thus the volume of air sampled is usually determined from the log sheet reports of the start and stop rotometer readings and elapsed time. For the denuder/filterpack systems (annual denuder system [ADS]) and the impactors the volume is referenced to 0° C and 1 atm. In contrast, for the dichotomous samplers (dichots) the total volume fluctuates with variations in ambient temperature and pressure. Therefore, there are small differences in the masses obtained from the impactors and the dichots. Although the flow controllers used with the denuder systems and impactors are expected to provide relatively trouble-free regulation of the

flow, they have been found to malfunction when exposed to moisture and contaminants from the filters. To avoid this occurrence the filterpacks are kept covered and moisture traps (Cole Parmer compressed 22 scfm air filters #G-02917-10) have been installed in the sample lines. In addition, the site operators are periodically instructed to vary the rate of flow from 0 l min^{-1} to full scale to insure that the flow controller is responding. Under normal circumstances the flow controllers are calibrated and dichots are overhauled 1 to 2 times per year.

The supplies necessary to collect one week of samples and one blank (i.e. filterpacks, filters, impactor plates and denuders) are shipped to each site and stored at room temperature (~22° C). After all the supplies in a shipment have been used they are shipped back to the laboratory. Filterpacks are shipped and stored on site in sealed plastic bags and are only removed during the sampling period. Similarly denuders are kept capped except during sampling.

The site operators are trained in the assembly of the denuder systems, impactors and dichots. The field protocols, which the operators have been instructed to follow, are included in Appendix A. It is most important that the operators insure that compete 24 hour samples, commencing at approximately 0800 EST, are collected using the proper flow rate. Field log sheets (sample history forms) are used by the operators to record all the sampling parameters. The operators are also instructed to test the denuder systems and dichotomous samplers for possible leaks and to record the results on the log sheet. These procedures, as well as those for taking blank samples, are outlined in the protocols in Appendix A.

Shown in the Appendix are schematics (Fig. A.1 and A.2) of the single and double denuder systems. Size-selective inlets are attached to both systems to remove particles greater than approximately 2.5 µm in diameter. In the single denuder system, a 10 l min^{-1}, 2.5 µm cut FEP coated aluminum cyclone (URG-2000-30EN) is used with a 150 mm 3-channel stainless steel denuder (URG-2000-30X3CSS). Coarse particle removal in the double denuder system is accomplished with the use of an elutriator with an acceleration jet (URG-2000-30K) attached to a 265 mm glass impactor denuder (URG-2000-30DI). These are attached to a 242 mm glass denuder (URG-2000-30B). Both systems include a denuder for the collection of gaseous NH_3 which is coated with a 1:1 mixture of 4% citric acid in de-ionized water and 2% glycerol in methanol. In the double denuder system a second denuder is attached upstream of the NH_3 denuder to capture ambient HNO_3, HONO (not reported in the CAAMP data) and SO_2. It is coated with a 1:1 mixture of 2% sodium carbonate in de-ionized water and 2% glycerol in methanol.

The filterpacks are loaded with a Gelman Zeflour, supported PTFE, 2µm pore size Teflon filter which is situated immediately downstream of the denuders, followed by a nylon filter (Gelman Nylasorb) and a citric acid coated Whatman 41 filter. The Teflon filters collect the fine particles and the citric acid coated filters capture NH_3 resulting from the revolitization of NH_4NO_3 particles. In the double denuder system the nylon filter captures HNO_3 also resulting from the revolitization of NH_4NO_3 particles. Thus, an H$^+$ correction due to neutralization from NH_3 liberated from the NH_4NO_3 particles (Keeler et al., 1989) is possible with the double denuder system. This is not possible with the single denuder system because HNO_3 is not removed upstream and thus the nylon filter provides a measure of both ambient HNO_3 and

HNO_3 from the NH_4NHO_3 particles. Consequently, the nitrate concentrations from the nylon and Teflon filters are summed and reported as total nitrate.

Table 2 Particulate and gaseous species measured at the Canadian Acid Aerosol Measurement Program sites, the sampling frequency and the sampling equipment used to collect the samples.

SITE	Particulate	Gas	Frequency	Equipment
Windsor, Kejimkujik	$H^+, SO_4^{2-}, NH_4^+, NO_3^-$	HNO_3, SO_2,	daily (May-Sept.) 1 in 3 (Oct.-Apr.)	3-stage filterpack with 2 denuders
	$PM_{2.5}, PM_{10}$	NH_3	daily (May-Sept.) 1 in 3 (Oct.-Apr.)	dichotomous sampler (dichot)
	trace elements		1 in 6	dichotomous sampler
Egbert, Sutton	$H^+, SO_4^{2-}, NH_4^+, NO_3^-$	HNO_3, SO_2,	daily (May-Sept.) 1 in 3 (Oct.-Apr.)	3-stage filterpack with 2 denuders
	$PM_{2.5}, PM_{10}$	NH_3	daily (May-Sept.) 1 in 3 (Oct.-Apr.)	Air Diagnostics Impactors dichot from May 1993
	trace elements		1 in 6	Air Diagnostics Impactors dichot from May 1993
Toronto, Montréal, Saint John	$H^+, SO_4^{2-}, NH_4^+, NO_3^-$	Total Nitrate	daily (May-Sept.) 1 in 3 (Oct.-Apr.)	3-stage filterpack / 1 denuder
	$PM_{2.5}, PM_{10}$		daily (May-Sept.) 1 in 3 (Oct.-Apr.)	dichotomous sampler
	trace elements		1 in 6	dichotomous sampler
Surrey East	$H^+, SO_4^{2-}, NH_4^+, NO_3^-$	HNO_3, SO_2, NH_3	daily from July 1 to Sept. 8, 1994	3-stage filterpack with 2 denuders

* From Sept. 20 to Dec. 31, 1993, all samples (except Saint John) were collected with a 1 in 6 frequency.

Samples were collected for 24 hour periods starting at 0800 EST. From May 1, 1992, or whenever sampling commenced to approximately Sept. 20, 1992, measurements were taken every day. From Sept. 20 to April 31 samples were collected every third day. All samples were analyzed for the species shown in Table 2 with the only exception being that elemental analysis using X-Ray Fluorescence (XRF) was only carried out on every sixth sample, however, the remaining filters have been archived for future reference.

3.2 Laboratory Procedures

3.2.1 Sampling apparatus

Two separate laboratories are involved in providing the field sites with sampling equipment and in chemical analyses and mass determination. Measurement activities at Egbert, Sutton and Kejimkujik are supported by an Atmospheric Environment Service lab operating at the Centre for Atmospheric Research Experiments in Egbert, Ont. (CARE). The urban sites are maintained by the Environmental Protection Service Chemistry Division laboratories at the Environmental Technology Centre in Glouchester, Ont. (RRETC; RR=River Road). The filterpacks, denuders, filters and impactor plates/pins are prepared for sample collection by each of the labs and shipped to the sites on a routine basis. Enough equipment to collect one week of samples and one blank are included in each shipment. The ambient concentrations of the gases collected using the double denuder system are being measured; hence unexposed denuders are used for each sample period. This requires that 16 denuders be included in each shipment. Ambient NH_3 concentrations at the sites operating the single 3-channel denuders are not being quantified. These denuders have a large capacity for NH_3 collection so the field operators use each denuder for one week before replacing. Thus, each shipment to the field includes 2 denuders (1 spare).

Prior to shipment to the field, clean denuders are coated with the citric acid and sodium carbonate solutions, dried and capped. Eight filterpacks are cleaned, dried and loaded with the Teflon, nylon and citric acid coated filters and assembled. To minimize filterpack leakage they are threaded to a tightness of 30 lb in^{-2}. Pure Teflon filterpacks designed to meet CAPMoN specifications are utilized at all sites except Sutton where triple-stage URG filterpacks (URG-2000-30F) are used. The 37 mm Teflon filters used for mass determination (Gelman Teflo 2.0 μ m pore size) are weighed under controlled climatic conditions (T$\approx$22° C, RH$\approx$40%), fixed in rigid plastic rings (lexan) and placed securely in small plastic petri dishes before shipment to the field. Technical staff from the C&P Pollution Measurement Division (PMD) are responsible for all aspects of the mass measurements.

The field operators ship, via courier, the exposed filterpacks, impactor pins and plates, denuders and 37 mm filters to the laboratories as soon as all the supplies are exhausted. The filterpacks are disassembled and the filters are removed with tweezers and quickly placed in 12 ml polyethylene tubes, which are sealed tightly (polyethylene caps). The tubes are stored at room temperature (~22° C) until extraction and subsequent analysis. Only the denuders used with the double denuder system are extracted for chemical analysis. The extracts are poured into the 12 ml polyethylene tubes and are kept refrigerated (5° C) until chemical analysis. The single 3-channel denuders are then cleaned and prepared for subsequent sampling.

3.2.2 Chemical analyses

The main objective of CAAMP is to study fine particle acidity and thus, the most important chemical parameter is strong acidity measured from the particles collected on the Teflon filters. Acidity is determined by pH measurement of the filter extracts. Both laboratories are using Hach electrodes and Fisher Scientific pH meters. To insure that there is no interference from

weak acids, which are known to exist in the particle phase, the particles on the Teflon filters are extracted in 10 ml of a 10^{-4} N perchloric acid solution (pH≈4). Consequently, standards for anions and for particle ammonium IC analysis are also prepared in 0.1 mN $HClO_4$. The filter and extract solution are placed in a sonic bath for at least 30 min prior to chemical analysis. The difference between the concentration of H^+ in the original extract solution ([H+]≈10^{-4} nmole ml^{-1}) and the extract solution containing the contents of the Teflon filter provides a measure of the amount of strong acid (in n moles ml^{-1}) on the fine particles. This is calculated using:

$$H^+[10^{-6} \text{ nmole ml}^{-1}] = 10^{-pH_s} - 10^{-pH_e} \qquad (1)$$

where pH_e corresponds to the pH of the extract solution, which is measured repeatedly during the pH measurement of the sample, pH_s. After pH measurement the particulate extracts are analyzed by ion chromatography (Dionex* 2020i at CARE and Dionex DX-300 at RRETC) for SO_4^{2-}, NO_3^- and NH_4^+.

HNO$_3$ and SO$_2$ captured by the nylon filters are extracted in 10 ml of IC anion eluent (40.0 ml 0.36M Na$_2$CO$_3$ + 60.0 ml 0.34M NaHCO$_3$ + 4.0 l DDW) and analyzed for SO_4^{2-} and NO_3^- using ion chromatography (IC). The standards for the analysis of these extracts are prepared in sodium carbonate/bicarbonate solution as well. HNO$_3$, SO$_2$ and NH$_3$ that have reacted with the denuder coatings are extracted using 10 ml of DDW and analyzed by IC for NO_3^-, SO_4^{2-} and NH_4^+, respectively.

The 37 mm Teflon filters used for the determination of the total mass of particulate matter below 10 μm and 2.5 μm in diameter are returned to the climate-controlled balance room after exposure in the field. They are allowed to equilibrate with the ambient conditions before the final weight is measured. Mass measurements are made using either a Mettler M3 or MT5 microbalance which are equipped with Polonium 210 static elimination bars.

3.2.3   Lab Quality Assurance (QA)

Standard quality control practices and operating procedures are followed to insure that both laboratories are consistently reporting analytical results with a known degree of accuracy and precision. External references (Arafat and Aspila, 1992, 1993) are periodically analyzed by IC to determine if we are within the range of values reported by other laboratories. In addition, a set of in-house quality control samples are included with each IC run. At CARE, 3 separate QC solutions, spanning the range of sample concentrations, plus distilled water are used. If the concentration of any one of these QCs is not within prescribed limits, which are determined through repeated measurements of the QC solutions (used for establishing operational limits and precision), then the results of the run are examined to determine if the samples need to be re-analyzed or if recalculations are necessary. At the C&P laboratory, at least 2 different QCs are included to evaluate the performance of the IC. The RRETC quality control procedures and results are described in more detail in Appendix B.1.

Before determining the additional acidity due to the particle samples the pH meters are calibrated with buffers solutions with pH values of 3.0 and 4.0. The response of the pH meter is then tested against working standards which are made from H$_2$SO$_4$ to prescribed pH levels. pH

measurements of these standards are required to be within ±0.05 units, which corresponds to an H^+ concentration precision of 12% . In the CARE laboratory, three standards with pH values of approximately 3.2, 3.3 and 3.6 are used while in the C&P laboratory four standards with pHs of 3.21, 3.45, 3.80 and 3.90 (±0.02) are used. If the pH measurements of any of these standards do not satisfy the ±0.05 criteria the meter is re-calibrated and the standards are checked again before measuring the pH's of the extracted particulate samples. To calculate the H^+ from a particle sample two separate readings of pH_e and pH_s are taken and averaged. These values are then used in Equation 1 above.

In April 1993 a 4 point calibration, using H_2SO_4 solutions with calculated pH values of 3.54, 3.68, 3.77 and 3.88, was initiated at the CARE laboratory. The pH 3.0 and 4.0 buffers were then used as the QC standards. As described above, the measured pH of these standards were expected to be within ±0.05 pH units of the known value. The effect of utilizing a different calibration procedure is expected to be small, however, it is currently under evaluation. Depending upon the amount of difference resulting from the use of the two methods, the H^+ concentrations determined using the 2 point calibration may be recalculated using the results of the working standard measurements to develop a new calibration curve.

Mass determinations from the 37 mm Teflon filters are done by the Pollution Measurement Division at RRETC. To check that the balance is operating consistently the same three standard filters are weighed after the balance is calibrated and before a series of sampling filters are weighed. The mass of each of these filters must be within ±10 µg of the expected mass. In addition, 10 % of all filters are weighed a second time in order to further assess the precision of the mass determination procedure. Second weighing (QA weighing) of filters must fall within acceptability limits of ±10 µg and ±25 µg for new and exposed (sampled filters), respectively. This corresponds to a PM_{10} acceptability limit of ±2.9 µg m^{-3}. If these limits are exceeded then the entire series of filters, along with QA re-weighs, are weighed again. Additional details of mass determination are outlined in Appendix B.2.

3.2.4   Field Quality Assurance

The field operators have been trained in the operation of the sampling equipment and have been provided with detailed protocols outlining the sampling procedures. The operators record the information necessary to calculate the sampling duration and mean flow rate along with comments detailing problems encountered while preparing the sampling equipment or during sampling. To insure that the reported flow rate is representative of the actual amount of air passing through the denuders and filters a leak check procedure is followed prior to sampling. If the flow rate through the plugged annual denuder system (as described in Appendix A) is not below 0.8 l min^{-1} the equipment is examined, the denuder and filterpack junctions are tightened and the system is checked for leaks again. The operators have been instructed not to proceed until the leak check criterion is satisfied. As described in Appendix A, a similar procedure is followed with the operation of the dichots. No leak check procedure has been implemented for the Air Diagnostics and Engineering impactors. However, periodic inspection of the equipment indicates that there is little possibility of external leaks and thus, deviations from 10 l min^{-1} are not expected.

Blank samples are distributed to field sites on a routine basis to assess the effects of normal sampling and handling on the measured pollutant concentrations. At least once per month (weekly a majority of the time) the operators assemble 2 complete annular denuder systems. One system is prepared for sampling (leak check etc.) while the other system (blank sample) is left exposed to the ambient air (5-10 minutes). When the active system starts sampling the blank system is capped, disassembled and returned to the shipping case.

The overall success of the CAAMP field and laboratory practices is also judged through periodic comparison with the concentrations reported by other networks. The Canadian Air and Precipitation Monitoring Network (CAPMoN) is collocated with CAAMP at Egbert, Sutton and Kejimkujik. Comparisons between the National Air Pollution Surveillance (NAPS) reports of ambient sulphate concentrations, which are measured every 6th day at the urban sites, will also be undertaken as the data become available.

4.0 Results

4.1 Site Set-up

Prior to May of 1992 the sampling activities at Egbert, Sutton and Windsor were managed entirely by the laboratory at CARE. In May 1992, the responsibility for operating the Windsor site shifted to RRETC and sampling equipment was installed at the Ontario Ministry of the Environment site near 880 Bay Street in downtown Toronto. During early June equipment were set-up at Kejimkujik, NS and in the Forest Hill district of Saint John, NB. The Communauté Urbaine de Montréal site at Ontario and Amherst Streets in downtown Montréal and Sutton, Que were also visited in June. All sites were operational by the second week in July, 1992. However, the fine and coarse impactors were not installed at Egbert until mid August. To standardize operations, the impactors at Sutton and Egbert were replaced with dichots in the spring of 1993.

The actual start day for ADS sampling at each site is listed in Table 3. Also shown in Table 3 are the sample capture rates, in percent, for each site. These values indicate what percentage of the possible sampling days (from the start day listed to Dec. 31, 1993) were actively sampled. They do not indicate the percentage of valid samples (i.e., after chemical analysis and examination of the field logs).

4.2 Data Quality

The results of the field and laboratory quality control measures are discussed in detail in Appendix B.3. Data from the field log sheets indicated that there were no major, systematic sampling problems. Leak checks and sampling durations were generally within the prescribed limits. Due to the frequency and amount of rain during the summer of 1992 the mass flow controllers were occasionally rendered inoperable. This problem seemed to occur at sites where the sample line extended downwards from the annular denuder system to the flow controller

(Montréal, Saint John, Egbert and Windsor). This facilitated the flow of moisture, which was penetrating the filterpacks, to the flow controllers. While water itself was not expected to harm the flow controller, the citric acid from F3, which was often dissolved into the water, caused more serious problems. As shown in Table 3, a significant amount of sample days were missed at Saint John during July and August of 1992. At Egbert and Windsor, the problems were fixed relatively quickly and thus, data capture was not affected significantly. Moisture problems were rectified through the installation of moisture traps directly upstream from the flow controllers and by covering the filterpacks.

Table 3 Start-up date for sampling at the CAAMP sites and the sample capture percentage through 1993. $N_{possible}$ is based upon the sampling frequency and the length of time that equipment was installed at the site.

SITE	START DATE	YEAR	ADS $N_{possible}$	ADS %Capture	Mass $N_{possible}$	Mass %Capture
Egbert	May 14	1992	164	96%	35	97%
		1993	201	100%	168	97%
Kejimkujik	July 7	1992	110	98%	111	98%
		1993	201	100%	199	98%
Sutton	June 19	1992	128	101%	128	97%
		1993	185	96%	139	99%
Windsor	May 7	1992	171	93%	133	98%
		1993	201	100%	201	97%
Montréal	June 18	1992	129	100%	110	95%
		1993	201	97%	201	89%
Toronto	June 15	1992	131	98%	132	97%
		1993	201	100%	201	100%
Saint John	July 8	1992	111	40%	124	90%
		1993	218	85%	212	92%
Surrey	June 26	1993	76	99%		
All Sites		1992	944	91%	773	96%
		1993	1484	97%	1321	96%
		Total	2368	94%	2094	96%

At Montréal, a damaged flow controller was utilized unknowingly from early July to late October. After getting wet the controller was dried-out by the operator and appeared to be working properly (i.e. gave a steady flow reading of 9.0 l min^{-1} and a stable zero value), but when the flow controller was calibrated in the field it was found to be working improperly. Subsequent calibration back in Downsview indicated that the reported flow of 9.0 l min^{-1} was actually closer to 13 l min^{-1}. It is not known when during the July to October period the flow rate began increasing from the 9.0 l min^{-1} rate. However, comparison with the SO_4^{2-} concentrations measured by the dichot indicated that the ADS flow rates began to deviate from

the readout values at the beginning of August. From this time until the MFC was replaced in October the dichot SO_4^{2-} concentrations were approximately 20% less than the ADS values. For the affected observations, the flow rates used to calculate the concentrations from the ADS were therefore increased by 20% (to approximately 10.8 l min^{-1}). However, the behaviour of the damaged flow controller from one measurement to the next could not be determined and thus, from August to October there remains some uncertainty in the Montréal ADS concentrations (±10%). Fortunately this problem only affects the magnitude of the concentrations, but not the concentration ratios (i.e. H^+/SO_4^{2-}).

Results of repeated QC analyses, comparison with external standards and the results of the analysis of the blanks are also in Appendix B.3. Through April 1993 precision and accuracy for H^+ and SO_4^{2-} were found to be good. At RRETC there was also good results for NO_3^- and NH_4^+. At CARE, precision for NH_4^+ with $HClO_4$ standards and NH_4^+ and NO_3^- for the H_2O standards were reduced somewhat compared to RRETC, but they were still acceptable. The reasons for the decreased NH_4^+ and NO_3^- precision at CARE are discussed in the Appendix. The QC results for both laboratories for the period from May 1 to Dec. 31, 1993, were found to be well within acceptable limits. For each species and analysis type, 99% (3 times the coefficient of variation) of the repeated QC analyses were within 20% of each other.

CAPMoN data for 1992 and 1993 were compared to the CAAMP observations of SO_4^{2-}, NH_4^+, SO_2 and HNO_3. The results are in Appendix B.3.2.4. Agreement is generally quite good. The NAPS SO_4^{2-} and NO_3^- data are not complete and thus, with the exception of Montreal for 1992, they have not been compared to the CAAMP results. In the following section a summary of the data from the beginning of daily sampling in 1992 to the end of 1993 are presented. Measurements were invalidated when the flow rate and/or sample duration was not acceptable or if other serious field or laboratory problems were noted on the log sheets. They were also invalidated if there was an unreasonable balance between the cations and anions on the Teflon filter. In a few instances, marked discrepancies with CAPMoN have led to the invalidation of an observation. Details of the CAAMP sample validity criteria are listed in Appendix C.

4.3 Particulate and Gaseous Concentrations

During 1992 and 1993 there were few periods when the meteorological conditions were favorable for the build-up of air pollutants. Thus, overall both years are considered to have been "clean" years. There was a measurable amount of variability in the concentrations over time and space and a number of episodes (SO_4^{2-}>100 nmole m^{-3}) were observed. Mean pollutant concentrations based upon all valid measurements in 1992 and 1993 are summarized by site in Table 4a. The 1992 and 1993 data for all the species listed in Table 2, including the trace elements, are available in Microsoft Excel or ASCII files. These can be obtained by writing to:

Dr. Jeff Brook
Atmospheric Environment Service
Air Quality Processes Research Division
4905 Dufferin Street
Downsview, Ontario
M3H 5T4

During the 1992 to 1993 period the number of valid 24 hour measurements ranges from 214 to 340, depending upon site and chemical species. Fewer measurements are available for Saint John due to technical problems in July and August of 1992. All sites were in operation throughout 1993 (Sutton stopped on Sept. 28) and thus there is a similar number of valid measurements across the network. Depending upon site, valid H^+ measurements are available for 90% to 98% of the possible sampling days in 1993.

Overall mean H^+ concentrations ranged from 4 to 32 nmole m^{-3}. Acidities were lowest in Montréal and Toronto. This agrees with the findings of other investigators (e.g., Waldman et al. 1990) who have reported that neutralization of fine particle acidity is greater in large urban areas. The effect of urban activities and/or increased population density can be seen by comparing Egbert to Toronto and Sutton to Montréal. Mean and median SO_4^{2-} concentrations were relatively similar between these two pairs of urban and rural sites, but the H^+ concentrations were lower at the urban locations. The mean H^+ to SO_4^{2-} ratios highlight this difference. They were 0.25 and 0.12 at Sutton and Montréal, respectively, while at Egbert and Toronto they were 0.14 and 0.09.

In agreement with previous estimates (Brook et al., 1992) the highest mean concentrations of H^+ were at the Maritime sites. As can be seen in Table 4a these high levels were due to less H_2SO_4 neutralization, as opposed to higher mean SO_4^{2-} concentrations. As reported by CAPMoN (Sirois et al., 1992), sulphate levels were highest in Ontario, followed by Québec and Saint John. The mean SO_4^{2-} concentration was lowest at Kejimkujik. The smaller amount of neutralization at the Maritime sites, as indicated by an increase in the ratio of H^+ to SO_4^{2-}, is highlighted in Figure 3. In the Fraser Valley (Surrey) and Ontario, H^+ accounted for a relatively small amount of the cations and NH_4^+ a much larger fraction. In contrast, in the Maritimes there was an increase in the amount of H^+ relative to the other ions. This pattern was likely a result of less local NH_3 in the Maritime region and potentially less NH_3 during transport when winds were across the ocean or over sparsely populated areas. The link between local NH_3 and the H^+ to SO_4^{2-} ratio is shown in Table 4a. Mean NH_3 concentrations were lower at Sutton and Kejimkujik relative to Egbert, Windsor and Surrey.

Due to increased levels of human activity and vehicular traffic, the total particle mass ($PM_{2.5}$ and PM_{10}) concentrations tended to be higher at the large urban sites. In 1992 and 1993, Windsor and Toronto had slightly higher levels than Montréal. The mean PM_{10} and $PM_{2.5}$ levels were lowest at the more remote sites of Sutton and Kejimkujik, while concentrations at Saint John and Egbert were in between those observed in the remote and urban areas.
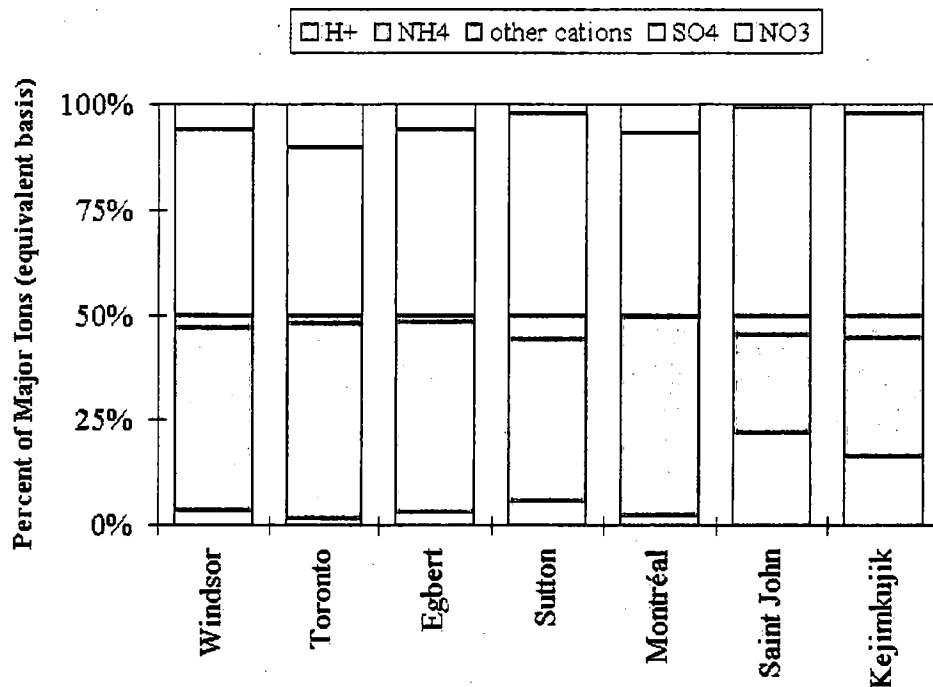
Figure 3 The site to site variation in the mean distribution of the major ions (on an equivalents basis) found on the fine particles collected in eastern Canada from May 1992 to September 1993. H^+ is shown in magenta (pink).

The larger mean SO_4^{2-} at Saint John compared to Kejimkujik was likely a result of local SO_2 sources, assuming that the geographic locations of Saint John and Kejimkujik were similar relative to the main sources of regionally transported SO_4^{2-} and that there were no local sources affecting Kejimkujik. Subtracting the Kejimkujik mean SO_4^{2-} from the Saint John value (Table 4a) indicates that sources near Saint John provided an additional 15 nmoles m^{-3} to the long term average. This represents an enhancement of almost 70% in the mean SO_4^{2-} level. As can be seen in Table 4a, the number of samples at the two sites were substantially different. However, even during the warm season of 1993, when a similar number of samples were collected at each site (135 and 138 at Kejimkujik and Saint John, respectively), Saint John SO_4^{2-} levels were enhanced relative to the regional background. During this period, the mean SO_4^{2-} at Saint John was 41 nmoles m^{-3}, while it was 22 nmoles m^{-3} at Kejimkujik; an enhancement of 86%. Fine particle acidity at Saint John was enhanced even more. For H^+, the enhancements were 120% and 200% for the entire period and the 1993 warm season period, respectively. This suggests that the additional amount of SO_4^{2-} observed at Saint John was highly acidic. For example, during the 1993 warm season the H^+ was 26 nmoles m^{-3} above the regional background, while for SO_4^{2-} it was 19 nmoles m^{-3}. The molar ratio of these two enhancements is 1.37. This high acidity also suggests that the additional SO_4^{2-} observed in Saint John was from local sources (i.e., assuming that neutralization of H_2SO_4 increases with transport distance).

The mean, median and maximum concentrations of the gaseous species are also listed in Table 4a. Measurements of HNO_3, SO_2 and NH_3 were only possible using the double denuder systems (Windsor, Egbert, Kejimkujik, Sutton and Surrey). HNO_3 was collected on the nylon filter included with the single denuder systems (Toronto, Montréal, Saint John), but volatilization of NH_4NO_3 particles collected on the upstream Teflon filters also contributed to nitrate on the nylon filter. Therefore, only total nitrate (nylon NO_3^- + Teflon NO_3^-) is reported from the single denuder measurements. For comparison, total nitrate concentrations were calculated for Windsor, Egbert, Kejimkujik, Sutton and Surrey. Total nitrate, HNO_3, NH_3 and SO_2 concentrations were highest at Windsor. The extremely high SO_2 levels, relative to the other sites are not surprising given the site's proximity to the Rouge River industrial complex and Monroe power generation facilities. The high nitrate levels (HNO_3 and total nitrate) are also consistent with the large NO_x emissions from metropolitan Detroit. The mean total nitrate concentration was also high at Toronto, which is consistent with the amount of vehicular traffic and associated NO_x emissions around metropolitan Toronto. As expected, concentrations of the gaseous pollutants and total nitrate decreased as the monitoring sites became more rural and remote. NH_3 levels were highest at Windsor, Egbert and Surrey (summer only). Agricultural activities (livestock) are relatively intense around Egbert and thus, the observed NH_3 levels are not surprising. Urbanized areas were also a significant source of NH_3. This is indicated by the high levels in Windsor and by the low H^+ to SO_4^{2-} ratios in Toronto and Montréal.

Mean, median and maximum concentrations for the warm season and cold season are listed in Tables 4b and 4c. The differences in mean concentration between seasons were as expected. H^+, SO_4^{2-}, NH_4^+, NH_3, HNO_3 and total nitrate levels were higher in the warm season. As a result of decreased oxidation rates the SO_2 concentrations were higher in the cold season. Relative to the observed differences in SO_4^{2-}, proportionate decreases in $PM_{2.5}$ and PM_{10} concentrations were not observed. This was partially due to increases in the fine particle nitrate concentrations from the warm season to the cold season.

Time series plots of the variations in PM_{10}, $PM_{2.5}$, SO_4^{2-} and H^+ concentrations (μg m^{-3}) are shown in Figures 4a-g. For display purposes the H^+ concentrations are expressed as a fraction of the SO_4^{2-} concentration since they were small relative to the mass and SO_4^{2-} concentrations. This was done according to:

$$H^+_{frac} = \left[SO_4^{2-}\right]\left(\frac{\left[H^+\right]}{2\left[SO_4^{2-}\right]}\right), \qquad (2)$$

where SO_4^{2-} on the left is in μg m^{-3} and the ratio of H^+ to SO_4^{2-} is in nmoles m^{-3}. Thus, equal concentrations of H^+_{frac} and SO_4^{2-} implies that the equivalent ratio of these species was 1.0, which corresponds to H_2SO_4.

Table 4a Mean concentrations of the particulate and gaseous species measured by CAAMP. TN=total nitrate. Concentrations are in nmoles m^{-3} except PM_{10} and $PM_{2.5}$, which are in $\mu g\ m^{-3}$.

	H^+	SO_4^{2-}	NO_3^-	NH_4^+	Ratio	TN	HNO_3	SO_2	NH_3	$PM_{2.5}$	PM_{10}
Egbert											
N	301	315	316	308		291	338	338	340	186	186
MEDIAN	0	24	5	54		25	12	34	86	8	13
MEAN	6	41	11	84	0.14	42	24	70	102	10	16
MAX	92	355	215	586		283	189	703	545	48	77
Kejimkujik											
N	272	270	273	273		256	261	261	276	267	267
MEDIAN	3	11	1	15		8	3	7	16	5	9
MEAN	15	22	2	26	0.68	9	5	15	23	7	11
MAX	326	252	24	189		53	43	193	552	47	60
Sutton											
N	289	290	290	289		261	283	283	281	263	262
MEDIAN	0	18	1	29		12	6	11	47	7	11
MEAN	8	33	3	53	0.25	15	8	23	49	9	14
MAX	115	337	22	400		99	64	234	248	49	97
Windsor											
N	328	328	328	317		305	311	312	328	294	294
MEDIAN	2	33	6	79		58	32	236	97	15	29
MEAN	9	56	15	110	0.17	75	44	270	105	18	31
MAX	279	359	301	587		399	286	1187	447	62	79
Montréal											
N	271	270	270	270		268				268	269
MEDIAN	0	20	3	43		21				11	20
MEAN	4	35	11	76	0.12	29				14	24
MAX	105	430	197	884		229				70	99
Saint John											
N	215	215	215	214		215				268	268
MEDIAN	17	27	1	26		7				9	16
MEAN	33	37	1	35	0.89	9				10	18
MAX	259	191	10	163		34				38	70
Toronto											
N	281	279	279	279		277				296	296
MEDIAN	1	30	10	77		42				14	25
MEAN	4	47	24	109	0.09	52				17	29
MAX	60	321	368	709		386				66	102

Table 4b Mean warm season (May-September) concentrations of the particulate and gaseous species measured by CAAMP.

	H^+	SO_4^{2-}	NO_3^-	NH_4^+	Ratio	TN	HNO_3	SO_2	NH_3	$PM_{2.5}$	PM_{10}
					Egbert						
N	235	249	250	242		228	270	270	273	114	114
MEDIAN	1	25	4	58		25	15	32	100	8	14
MEAN	7	44	9	88	0.16	42	28	62	116	11	18
MAX	92	355	88	586		283	189	363	545	48	77
					Kejimkujik						
N	193	191	193	193		179	183	183	195	201	201
MEDIAN	5	12	1	17		7	3	5	18	6	10
MEAN	19	25	2	28	0.75	10	6	10	27	8	12
MAX	326	252	24	189		53	43	115	552	47	52
					Sutton						
N	226	226	226	225		197	219	219	223	198	198
MEDIAN	2	18	1	30		12	6	9	54	8	12
MEAN	10	36	2	56	0.27	13	8	16	58	10	15
MAX	115	337	14	400		43	41	150	248	49	97
					Windsor						
N	252	252	252	241		232	238	239	252	224	224
MEDIAN	4	37	6	81		63	41	229	108	15	31
MEAN	12	62	10	115	0.19	78	52	265	122	18	33
MAX	279	359	104	578		324	286	1187	447	62	79
					Montréal						
N	201	200	200	200		198				202	203
MEDIAN	1	21	2	43		21				11	21
MEAN	6	39	5	76	0.15	25				14	24
MAX	105	430	109	884		122				70	99
					Saint John						
N	148	148	148	148		148				211	211
MEDIAN	25	32	1	28		7				10	17
MEAN	42	42	1	36	1.01	9				11	19
MAX	259	191	8	163		28				38	70
					Toronto						
N	210	209	209	209		207				229	229
MEDIAN	2	33	6	75		41				15	27
MEAN	6	52	17	108	0.11	50				18	30
MAX	60	321	116	673		215				66	102
					Surrey						
N	70	70	70	70		70	70	70	70		
MEDIAN	4	19	9	45		25	16	60	239		
MEAN	3	16	6	34	0.19	20	13	52	226		
MAX	15	86	44	210		100	64	246	457		

Table 4c Mean cold season (October-April) concentrations of the particulate and gaseous species measured by CAAMP.

	H^+	SO_4^{2-}	NO_3^-	NH_4^+	Ratio	TN	HNO_3	SO_2	NH_3	$PM_{2.5}$	PM_{10}
					Egbert						
N	81	81	81	81		78	83	83	81	51	45
MEDIAN	0	21	9	44		22	6	44	36	7	10
MEAN	1	28	21	69	0.03	39	9	88	44	9	12
MAX	34	110	215	330		264	62	703	174	25	38
					Kejimkujik						
N	70	70	71	71		68	69	69	72	57	57
MEDIAN	0	11	4	15		9	3	14	12	4	7
MEAN	7	16	3	21	0.43	9	3	27	11	6	10
MAX	78	84	11	157		29	20	193	25	32	60
					Sutton						
N	63	64	64	64		62	64	64	58	65	64
MEDIAN	0	17	4	28		15	8	28	14	7	9
MEAN	3	23	5	41	0.14	20	10	46	16	8	10
MAX	80	165	22	262		99	36	234	58	34	34
					Windsor						
N	76	76	76	76		73	73	73	76	70	70
MEDIAN	0	29	16	70		48	12	247	33	14	23
MEAN	2	36	31	97	0.05	65	17	285	47	15	25
MAX	48	126	301	587		399	79	780	261	54	69
					Montréal						
N	70	70	70	70		70				66	66
MEDIAN	0	18	14	46		22				11	20
MEAN	0	25	29	75	0.01	39				12	23
MAX	4	73	197	295		229				37	59
					Saint John						
N	67	67	67	66		67				57	57
MEDIAN	6	16	2	25		7				6	10
MEAN	11	24	2	33	0.46	9				8	13
MAX	89	79	10	112		34				31	41
					Toronto						
N	71	70	70	70		70				67	67
MEDIAN	0	25	29	86		44				13	23
MEAN	0	33	46	111	0.01	58				15	24
MAX	6	152	368	709		386				43	77

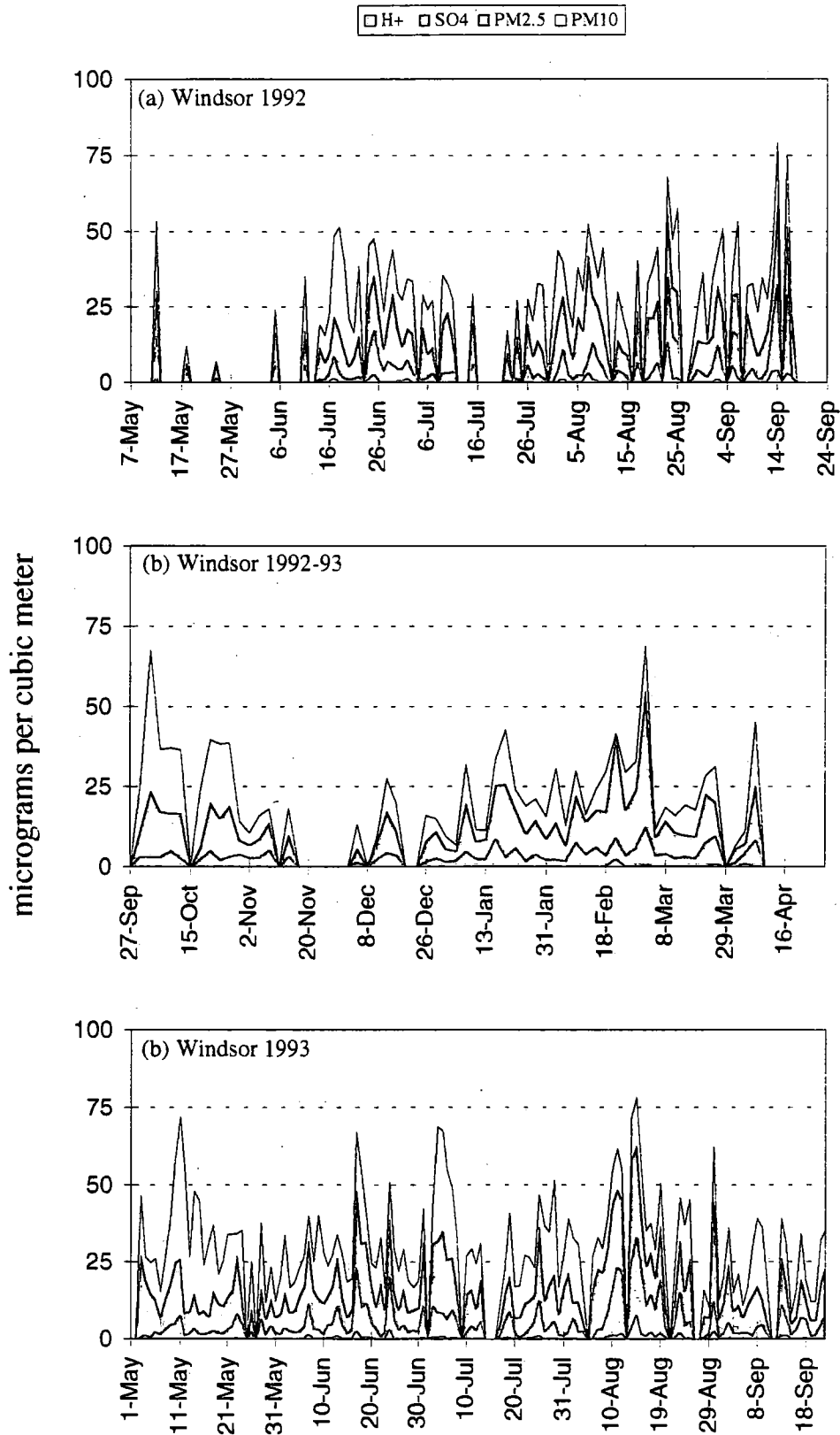Figure 4a Windsor, Ontario. Time series of 24 hour integrated concentrations ($\mu g\ m^{-3}$) of PM_{10}, $PM_{2.5}$, SO_4^{2-} and H^+.

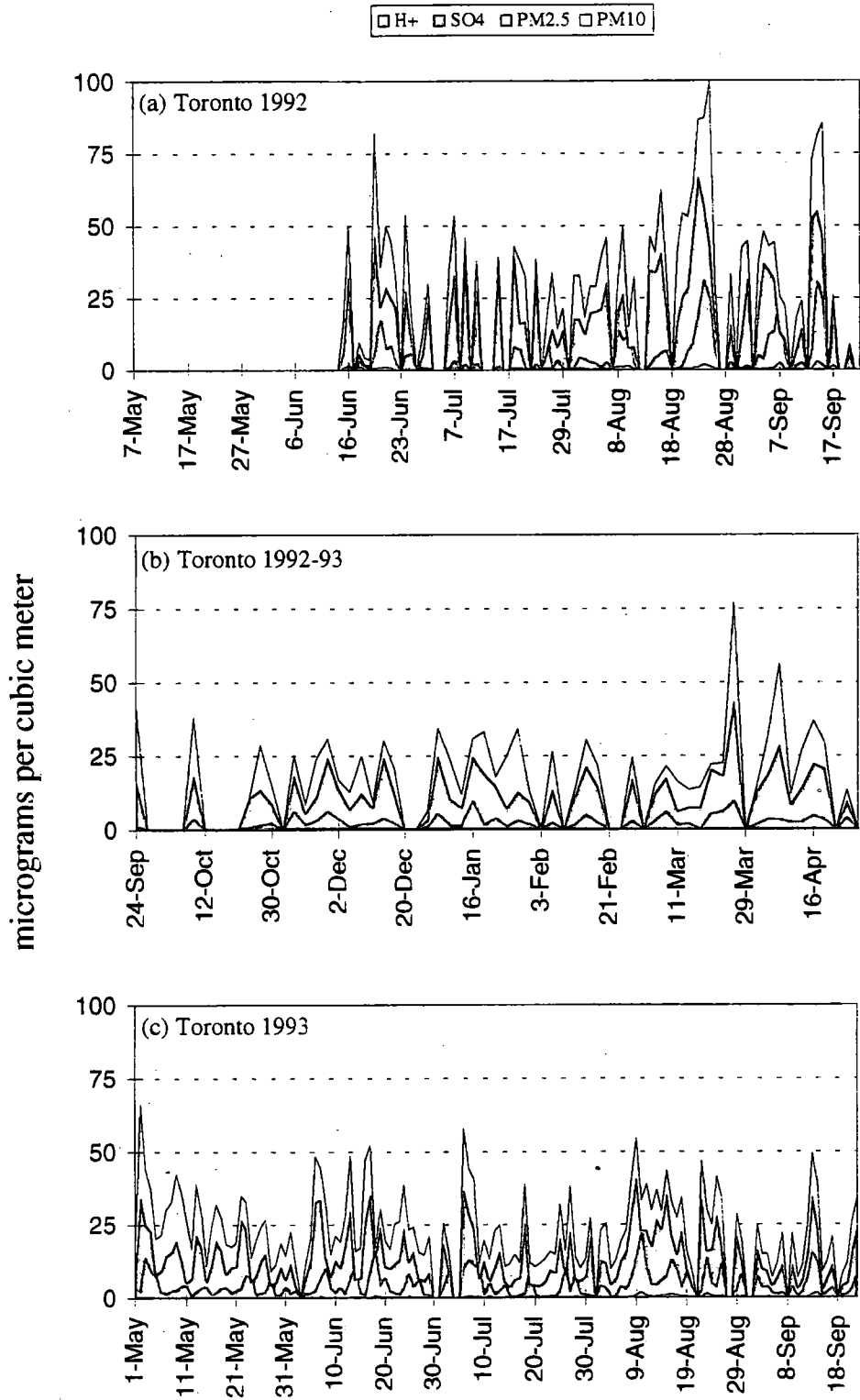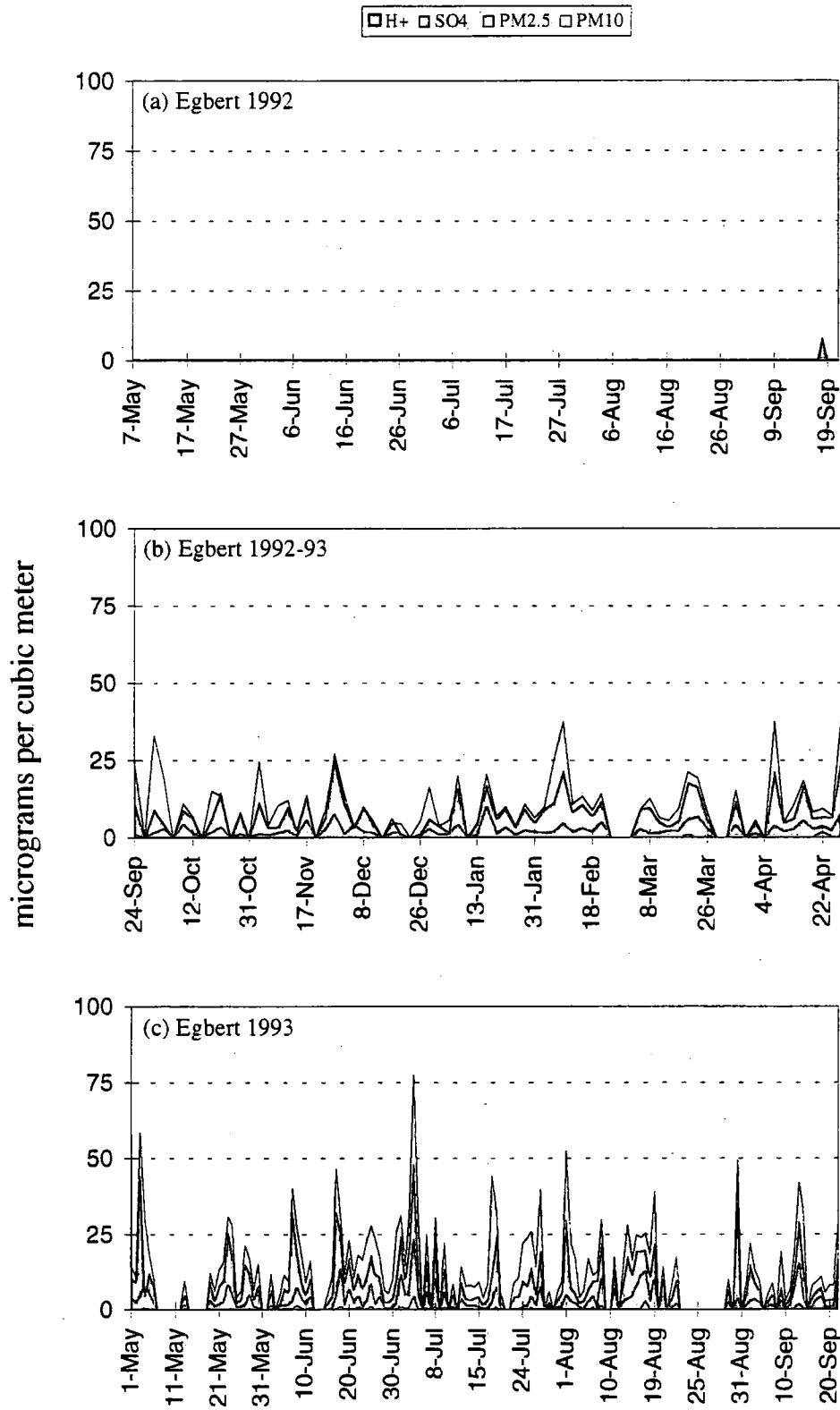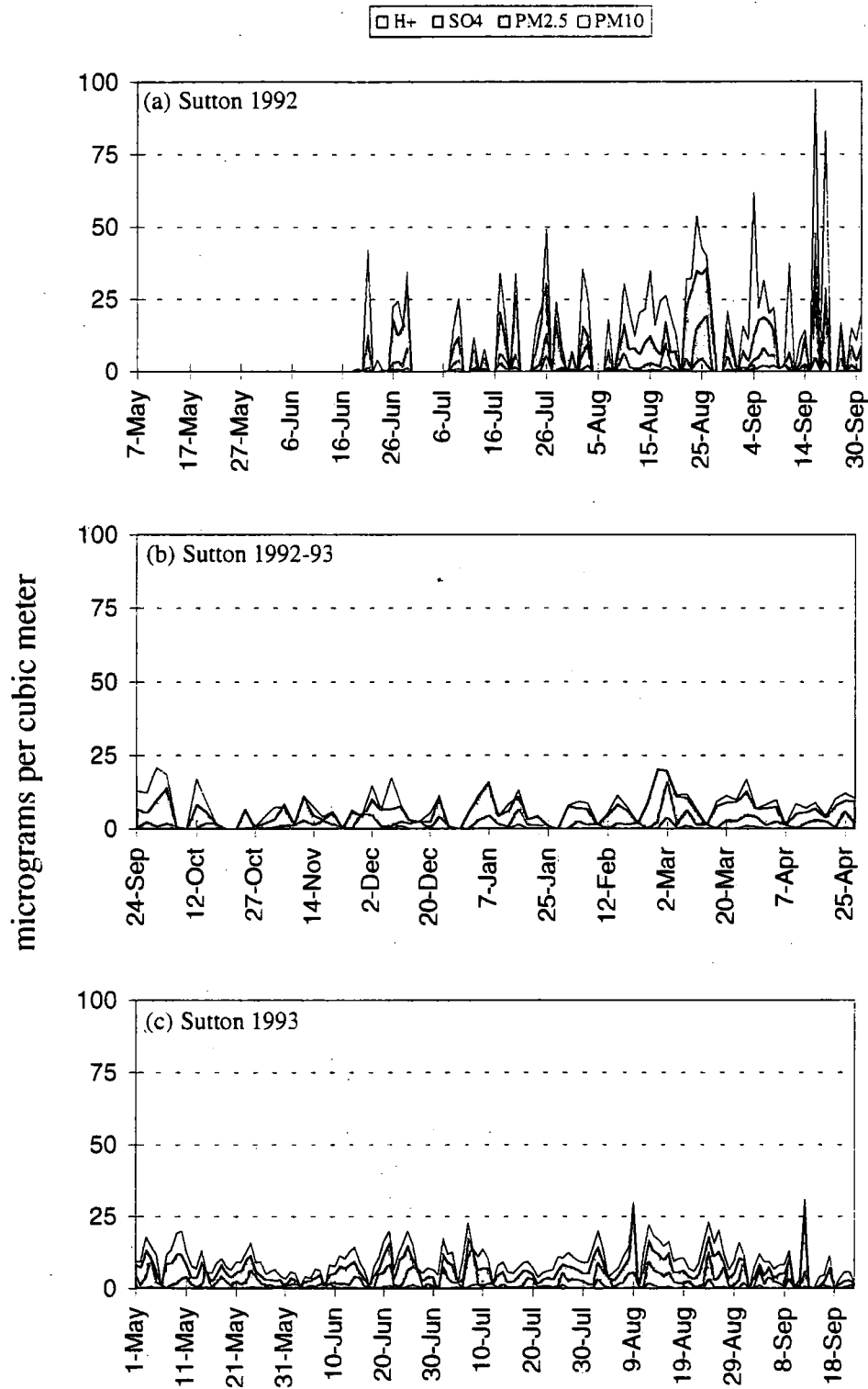Figure 4b Toronto, Ontario. Time series of 24 hour integrated concentrations ($\mu g\ m^{-3}$) of PM_{10}, $PM_{2.5}$, SO_4^{2-} and H^+.

□H+ □SO4 □PM2.5 □PM10

Figure 4c Egbert, Ontario. Time series of 24 hour integrated concentrations ($\mu g\ m^{-3}$) of PM_{10}, $PM_{2.5}$, SO_4^{2-} and H^+.

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Figure 4d Sutton, Quebec. Time series of 24 hour integrated concentrations (μg m^{-3}) of PM$_{10}$, PM$_{2.5}$, SO$_4^{2-}$ and H$^+$.
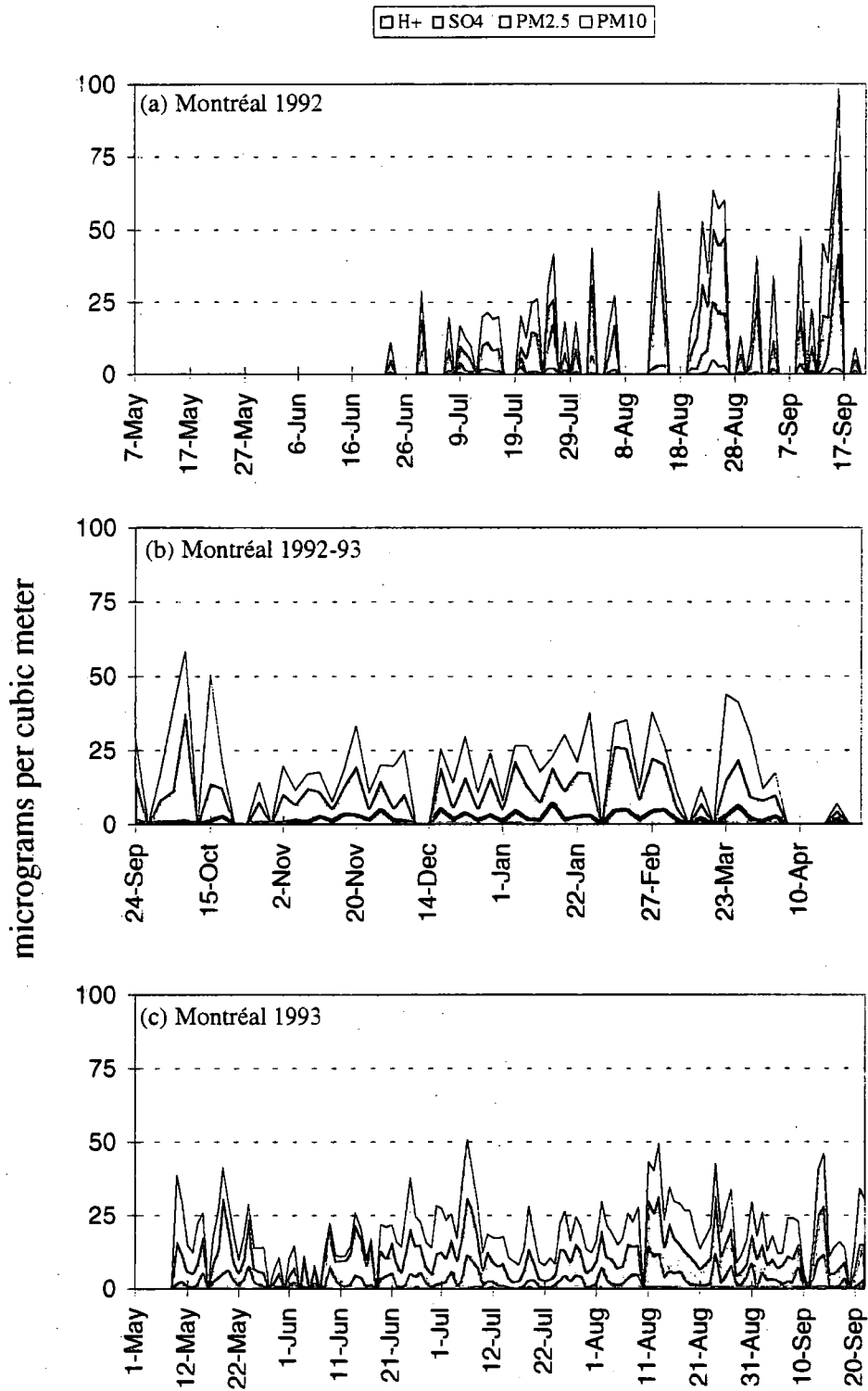
Figure 4e Montréal, Quebec. Time series of 24 hour integrated concentrations (μg m^{-3}) of PM$_{10}$, PM$_{2.5}$, SO$_4^{2-}$ and H$^+$.

☐ H+ ☐ SO4 ☐ PM2.5 ☐ PM10
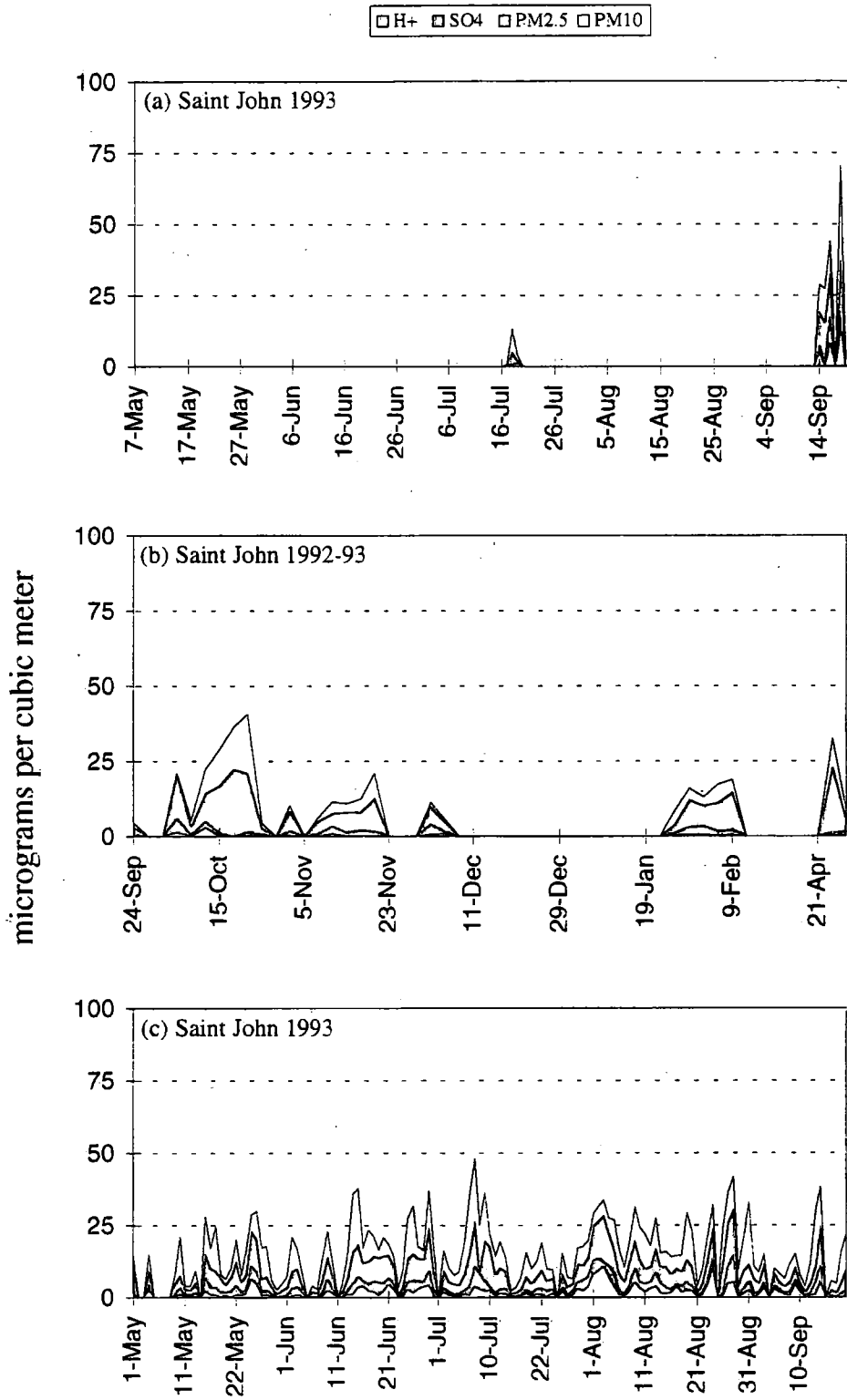
Figure 4f Saint John, NB. Time series of 24 hour integrated concentrations ($\mu g\ m^{-3}$) of PM_{10}, $PM_{2.5}$, SO_4^{2-} and H^+.

☐ H+   ☐ SO4   ☐ PM2.5   ☐ PM10
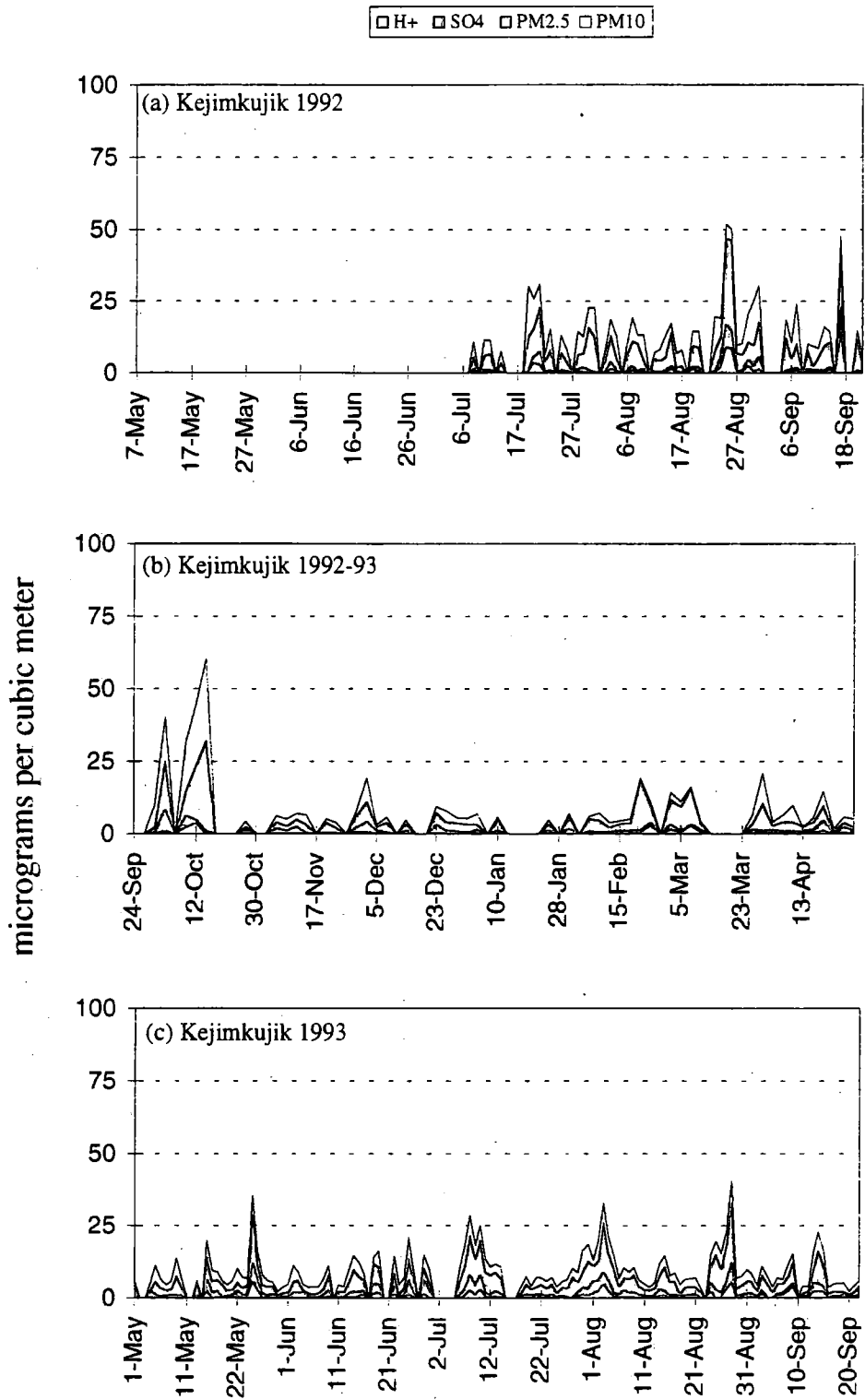
Figure 4g Kejimkujik, NS. Time series of 24 hour integrated concentrations (μg m^{-3}) of PM$_{10}$, PM$_{2.5}$, SO$_4^{2-}$ and H$^+$.

At each site, there was a large amount of variability in the particle concentrations from one 24 hour measurement to the next. All 4 pollutants in Figs 4a-g exhibited episodic behaviour. That is, most of the time the concentrations were relatively low, but within this "baseline level" there were occasional periods of 1 to 3 days with very large concentrations. Observations with this type of behaviour tend to be log normally distributed (note difference between the means and medians in Tables 4a-c). The episodic behaviour of H^+ and SO_4^{2-} were particularly acute, while for mass it was more difficult to distinguish between the baseline and the episodes. Mass concentrations were never zero and this was rarely observed for SO_4^{2-} (days on Figs. 4a-g with $PM_{10}=0$ µg m^{-3} were missing). In contrast, H^+ concentrations were often observed to be zero. The only exception was Saint John where there was usually some H^+ in the ambient air, especially in the warm season. Regardless of season, there were many 24 hour periods with zero acidity values. This suggests that the higher mean levels in the warm season were generally a result of more frequent episodes with higher concentrations.

The relative concentrations of the 4 pollutants shown on Figures 4a-g provides an indication of how much of the PM_{10} was comprised of $PM_{2.5}$ and of how much of the $PM_{2.5}$ was comprised of SO_4^{2-}. On average, SO_4^{2-} accounted for 32% of the $PM_{2.5}$. The ratio of SO_4^{2-} to $PM_{2.5}$ was 0.39, 0.30, 0.35, 0.30, 0.24, 0.36 and 0.27 at Egbert, Kejimkujik, Sutton, Windsor, Montréal, Saint John and Toronto, respectively. On average, the fine fraction accounted for 60% of the PM_{10}. Ratios of the mean mass values in Table 4a shows that this percentage was slightly higher at the rural sites of Kejimkujik, Sutton and Egbert.

As can be seen in Figures 4a-g, the time series for each of the pollutants were correlated. Across all sites PM_{10} and $PM_{2.5}$ were the two most strongly correlated pollutants ($0.66 < R^2 < 0.90$). Not surprisingly, H^+ was most correlated with SO_4^{2-} ($0.50 < R^2 < 0.87$) followed by $PM_{2.5}$ ($0.17 < R^2 < 0.70$) and then PM_{10} ($0.15 < R^2 < 0.53$). The strength of the correlations depended upon site. Site by site linear regression results are summarized in Table 5. Note that non-zero intercepts were possible and thus, they were included in the regressions.

The relationships between H^+ and the other particle measures (i.e., SO_4^{2-}, $PM_{2.5}$ and PM_{10}) were strongest at Kejimkujik, Saint John and Sutton, which are located furthest from the more densely populated areas. SO_4^{2-} and H^+ were found to be least related to particle mass (PM) in Toronto. This suggests that other sources of particulate matter (e.g., vehicles) had a greater influence on $PM_{2.5}$ and PM_{10} in Toronto. The slopes and intercepts of the regressions between SO_4^{2-} and PM and H^+ and PM, which are listed in Table 5, indicate that sulphurous compounds contributed the least to overall PM in Toronto, Montréal, Windsor. This is consistent with the weaker correlations found at these sites and the smaller mean SO_4^{2-} to $PM_{2.5}$ ratios derived from Table 4a.

The difference between the rural and urban sites (mentioned above) in the amount of PM_{10} that was comprised of fine particles ($PM_{2.5}$) was not as obvious from the linear regression of $PM_{2.5}$ vs. PM_{10} (see Table 5). However, large negative intercepts were found for Windsor and Montréal, which were the sites with the smallest mean $PM_{2.5}$ to PM_{10} ratios. The large positive intercept for Sutton indicates that when the concentrations were low ($PM_{10} < 4$ µg m^{-3}) $PM_{2.5}$ was larger than PM_{10}. Obviously, this behaviour is not possible, which suggests that there were

problems with the operation of the Air Diagnostics impactors at Sutton. Regression of PM_{10} and $PM_{2.5}$ for the warm season of 1993 when the dichot was in operation at Sutton yields more reasonable results. The intercept was -1.64 and the slope was 0.83 ($R^2=0.86$).

The number of 24 hour periods with elevated H^+ and/or SO_4^{2-} concentrations are summarized by site in Table 6 (these periods are arbitrarily defined as episodes). According to the frequency of SO_4^{2-} episodes 1993 was "cleaner" than 1992. The only site where there was an increase in episodes was Egbert. Consistent with the mean concentrations in Table 4a-c, SO_4^{2-} episodes were more frequent in Ontario and least frequent at Kejimkujik.

Table 5 Linear regression results relating the particulate pollutants shown in Figures 4a-g. *PM_{10} was the independent variable. *coefficient not significant ($\alpha=0.05$)

				Regression Statistics			
H^+ as the dependent variable				SO_4^{2-} as the dependent variable			
indep. var.	slope	intercept	R^2	indep. var.	slope	intercept	R^2
Egbert							
SO_4^{2-}	0.68	-3.71	0.50	$PM_{2.5}$	0.30	0.12*	0.57
$PM_{2.5}$	0.03	-0.15	0.25	PM_{10}	0.18	0.28*	0.47
PM_{10}	0.02	-0.15	0.23	PM2.5*	0.61	0.46*	0.83
Sutton							
SO_4^{2-}	0.38	-3.96	0.72	$PM_{2.5}$	0.41	-0.74	0.64
$PM_{2.5}$	0.09	-0.48	0.65	PM_{10}	0.25	-0.39*	0.58
PM_{10}	0.05	-0.32	0.49	PM2.5*	0.52	2.07	0.66
Kejimkujik							
SO_4^{2-}	0.9	-7.16	0.87	$PM_{2.5}$	0.34	-0.43	0.75
$PM_{2.5}$	0.18	-0.62	0.70	PM_{10}	0.23	-0.51	0.58
PM_{10}	0.12	-0.64	0.53	PM2.5*	0.72	-0.79	0.90
Windsor							
SO_4^{2-}	0.33	-8.43	0.63	$PM_{2.5}$	0.45	-2.55	0.71
$PM_{2.5}$	0.07	-0.80	0.42	PM_{10}	0.26	-3.00	0.46
PM_{10}	0.04	-0.77	0.24	PM2.5*	0.64	-2.20	0.74
Saint John							
SO_4^{2-}	1.16	-9.60	0.84	$PM_{2.5}$	0.42	-0.59	0.75
$PM_{2.5}$	0.25	-0.79	0.61	PM_{10}	0.24	-0.43*	0.61
PM_{10}	0.13	-0.58	0.45	PM2.5*	0.58	0.20*	0.85
Toronto							
SO_4^{2-}	0.13	-2.00	0.71	$PM_{2.5}$	0.23	0.77*	0.25
$PM_{2.5}$	0.02	-0.04*	0.17	PM_{10}	0.15	0.43*	0.23
PM_{10}	0.01	-0.06*	0.15	PM2.5*	0.63	-0.89*	0.87
Montréal							
SO_4^{2-}	0.18	-1.88	0.55	$PM_{2.5}$	0.40	-1.96	0.70
$PM_{2.5}$	0.03	-0.24	0.34	PM_{10}	0.26	-2.61	0.56
PM_{10}	0.02	-0.27	0.24	PM2.5*	0.68	-2.30	0.86

There were few occurrences of 24 hour H^+ concentrations above 100 nmole m^{-3}. There were no instances when the concentrations surpassed this level in Toronto or Egbert. There were 4 occurrences in Windsor, 2 in Sutton and 1 in Montréal. There were substantially more occurrences at the Maritime sites. Furthermore, there were 5 and 7 days with concentrations above 150 nmoles m^{-3} at Kejimkujik and Saint John, respectively. The number of large episodes at Saint John is more noteworthy given that very few measurements were collected in July and August of 1992. In order to compare sites the percent frequency of episodes is also shown in Table 6.

Table 6 Number and frequency of 24 hour periods (events) with elevated concentrations of H^+ and/or SO_4^{2-}.

SITE	YEAR	H^+ N	SO_4^{2-} N	H^+ events >50 nmoles m^{-3}	H^+ events >100 nmoles m^{-3}	SO_4^{2-} events >100 nmoles m^{-3}
Egbert	92	100	114	5 (5%)	0 (0%)	8 (7%)
	93	216	216	4 (2%)	0 (0%)	18 (8%)
Toronto	92	94	93	1 (1%)	0 (0%)	15 (16%)
	93	187	186	0 (0%)	0 (0%)	19 (10%)
Sutton	92	116	117	8 (7%)	2 (2%)	10 (9%)
	93	173	173	4 (2%)	0 (0%)	4 (2%)
Saint John	92	14	14	2 (14%)	3 (21%)	3 (21%)
	93	201	201	30 (15%)	10 (5%)	11 (5%)
Montréal	92	91	91	4 (4%)	1 (1%)	8 (9%)
	93	180	179	0 (0%)	0 (0%)	7 (4%)
Kejimkujik	92	89	89	4 (4%)	5 (6%)	5 (6%)
	93	183	181	10 (5%)	2 (1%)	2 (1%)
Windsor	92	133	133	5 (4%)	2 (2%)	22 (17%)
	93	195	195	3 (2%)	2 (1%)	25 (13%)

As discussed above, comparison of the time series plots between sites showed that the peaks and valleys in concentrations were correlated across sites. This was due to the regional nature of particulate episodes, which arose from the relatively long lifetime of SO_4^{2-} in the atmosphere and the synoptic scale of the meteorological conditions causing episodes. The two largest and most extensive episodes occurred around August 23 and September 15, 1992. Significant increases in pollutant concentrations were detected at all sites with a slight lag in time of onset due to the west to east progression of the episode-forming meteorological conditions.

The changing nature of the fine particle ionic balance and the spatial correlation in particulate time series can be seen by examining the changes in SO_4^{2-} and H^+ concentration during the Aug. 23-26, 1992 time periods (see Table 7). During this episode a large, slow moving high pressure system moved across the northeast North America. As the southerly winds associated with this system's "back side", advected the pollutants northward, varying

amounts of SO_4^{2-} and H^+ were observed at the sites depending upon origin of the pollutants and the transport path. In Table 6 the concentrations of SO_4^{2-}, H^+ and their ratio as a function of site and day are listed. The nature of the particles changed dramatically as the episode formed further east. Concentrations increased in southwestern Ontario on the 23rd and over Nova Scotia on the 25th of August. While SO_4^{2-} levels tended to be less in the east there was no such pattern in H^+. With the exception of Windsor on the 23rd, the highest acidity was observed at Kejimkujik. This was due to less neutralization. The molar ratios of H^+ to SO_4^{2-} were systematically higher at Kejimkujik attaining a value of about 1. This pattern is typical of the measurements over the summer of 1992 and preliminary results from the summer of 1993 are similar. In the east the molar ratios were close to 1, while in Ontario and Québec they were significantly less than 1.

Table 7 Fine particle sulfate and strong acid concentrations and their molar ratios as a function of location and date during the episode observed on August 23-26, 1992.

	AUGUST EPISODE [H^+] (nmole m^{-3})					
SITE	22	23	24	25	26	27
Windsor	1	279	23	28	5	5
Egbert	6	47	46	30	18	-
Toronto	11	20	40	26	8	0
Montréal	7	19	105	55	58	0
Sutton	13	-	63	104	47	0
Keji	-	8	40	189	176	1

	AUGUST EPISODE [SO_4^{2-}] (nmole m^{-3})					
SITE	22	23	24	25	26	27
Windsor	14	359	158	138	38	31
Egbert	83	275	257	211	57	-
Toronto	94	200	321	256	61	13
Montréal	69	88	260	217	215	21
Sutton	47	-	152	193	201	7
Keji	-	9	58	176	153	7

	AUGUST EPISODE [H^+]:[SO_4^{2-}]					
SITE	22	23	24	25	26	27
Windsor	0.07	0.78	0.15	0.20	0.13	0.16
Egbert	0.07	0.17	0.18	0.14	0.32	-
Toronto	0.12	0.10	0.12	0.10	0.13	0.00
Montréal	0.10	0.22	0.40	0.25	0.27	0.00
Sutton	0.28	-	0.41	0.54	0.23	0.00
Keji	-	0.89	0.69	1.07	1.15	0.14

5.0 CAAMP Activities in 1994

In the fall of 1993 CAAMP measurements were discontinued at Sutton. In the winter of 1994 a single denuder system was set-up with the dichot in Halifax, Nova Scotia (Barrington Street). In the spring of 1994 the Windsor site was moved to downtown Hamilton, Ontario, and the denuder measurements at Kejimkujik were stopped. Monitoring at Sutton and Windsor was stopped because the CAAMP objective of three years of data collection had been satisfied. Measurement of H^+ at Kejimkujik was stopped because the 1992 and 1993 measurements indicated that, on average, the H^+ to SO_4^{2-} ratio was relatively constant and because these data would not be employed in any specific health studies. However, in support of a Health Canada study, three additional sites (3 with H^+ and 2 with $PM_{10}/PM_{2.5}$) were installed around Saint John in June, 1994. Measurements at Egbert, Montréal and Toronto continued throughout 1994. All operational sites (9 sites after June 1) sampled daily from May 1 to September 23. After this time measurements were made every 6th day. The Saint John sites continued daily acid aerosol sampling through October and daily mass sampling through December. Daily dichot measurements were also taken at Kejimkujik through the warm season of 1994.

From late June to early September five additional sites were installed around the Toronto-Hamilton area for H^+ measurement. Daytime (1000 EDT to 1800 EDT) samples were collected on days with elevated particle concentrations. These measurements will provide information on the spatial variability in the H^+ to SO_4^{2-} ratio within a large metropolitan area. One of these additional sites was collocated with the existing Toronto site, which sampled for 24 hour periods. Thus, comparison of the 24 hour and 8 hour daytime measurements at this site will provide information on the diurnal pattern in fine particle acidity. As similar comparison was conducted at Egbert in the summer of 1993 (results not included in this report). Diurnal information is important because a significant diurnal pattern in acidity, with higher levels during the day, has been observed (e.g. Keeler et al., 1990; Waldman et al., 1990). Daytime measurements will also be useful in estimating exposures since people tend to spend more time outdoors during the day.

Measurements from Montréal during 1992-93 are being incorporated in a health study involving emergency room visit statistics. This is the first health study directly using CAAMP data. The 1994 data are expected to be available in March 1995. The 3 year databases from Toronto, Montréal, Windsor and possibly Egbert will be incorporated in a health study in mid 1995. The results of these studies are expected to be included in the 1996 Acid Rain Assessment as per the Green Plan requirements.

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