

ATMOSPHERIC MERCURY IN THE ATLANTIC REGION

CHAPTER 3

ENVIRONMENT CANADA ATLANTIC REGION MERCURY SYNTHESIS REPORT

DRAFT (NOT TO BE CITED OR QUOTED)

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3.0. MERCURY IN THE ATMOSPHERE

3.1 Introduction

Mercury is problematic to study from several perspectives. Firstly, it is ubiquitous in the natural environment but is not uniformly distributed. Secondly, mercury is a multi-hop species in that it is volatile and when deposited can be re-volatilized only to be re-deposited again elsewhere (the grasshopper effect or global distillation). Thirdly, mercury in the atmosphere exists in all three phases (solid/particle, liquid and gas) with most mercury (~ 98%) present in the gas phase as elemental (Hg^0) mercury (Mason *et al.*, 1994). Historically, the difficulties in measuring mercury are due to its relatively low concentration in the atmosphere (1.5 ng/m^3), the ease in which contamination can occur, its propensity to exist in 3 phases and its ability to react with other chemical species (Schroeder *et al.*, 1991). Technological advancements have provided an improved capacity for conducting accurate and precise total gaseous mercury measurements in the environment on broader spatial and finer temporal scales.

There is still uncertainty concerning the role of mercury derived from the atmosphere and the relative importance of natural versus anthropogenic mercury within the overall issue of elevated mercury in biota. A substantial body of literature exists which shows increased mercury deposition during post-human settlement (Hermanson, 1998) and post-industrialization (Swain *et al.*, 1992; Lockhart *et al.*, 1995). Although the precise amount of natural versus anthropogenic mercury remains to be quantified, it is apparent that human activity has added to the global mercury burden mercury (Mason *et al.*, 1994).

Concern regarding the potential for substantial atmospheric contribution of anthropogenic mercury to ecosystems in the Atlantic regional is based upon past experience with other pollution issues involving the atmosphere such as acid deposition, ground level ozone and air toxics. Research into these issues has been able to establish linkages with known anthropogenic emission sources upwind of the Atlantic region. It is probable that mercury in the Atlantic region is derived from both natural and man made sources locally as well as through medium and long range transport in the atmosphere. The question is one of relative amounts or proportions.

Although the question of natural versus anthropogenic mercury is important, it is not the only issue to be resolved. The national atmospheric mercury science program is based on a number of science and policy related questions as follows:

- what portion of the mercury in the atmosphere is of natural vs. anthropogenic origin?
- what portion of the mercury in the atmosphere is new emissions vs. re-emitted
- what is the spatial (3-D) and temporal distribution of atmospheric mercury (3 phases)?
- what are representative background mercury concentrations?
- what causes deviations from these levels?

- what proportion of mercury in the atmosphere is derived from local sources vs. long range transport?
- how do Canadian ambient mercury concentrations and deposition levels compare on a global scale?
- how is mercury transformed in the atmosphere?
- what relationships exist between mercury and other pollutants?
- what are the major processes regulating air-surface mercury exchange?
- are regional ecosystems a net source or sink for atmospheric mercury?
- are mercury concentrations in the atmosphere and deposition responding to changes in anthropogenic emissions?

The national and regional atmospheric mercury programs are attempting to address these issues. This chapter is intended to present some of the preliminary results of the first 2 years of atmospheric mercury measurements conducted in the Atlantic region under this program.

3.2 Total Gaseous Mercury (*Beauchamp, Tordon, Schroeder, Witte*)

Total gaseous mercury (TGM) was measured using a Tekran™ Model 2537A continuous mercury vapor analyzer with dual gold traps. Amalgamated mercury is thermally desorbed and detected at 253.7 nm using cold vapor atomic fluorescence spectrometry (CVAFS). Total gaseous mercury monitoring sites in Canada are illustrated in Figure 3-1. TGM has been measured at 2 sites in the Atlantic region and 1 site in Maine as shown in Table 3-1.

Table 3-1: Locations, sampling dates and measurement frequency for TGM measurements at 2 sites in the Atlantic region and 1 site in Maine.

Site	Lat./Long	Start	End	Frequency
Kejimkujik	44° 26' 10" 65° 12' 20"	July 1995	ongoing	5 min
St. Andrews	45° 05' 12" 67° 04' 30"	Nov 1995	ongoing	5 min
Acadia (Me)	44° 22' 26" 68° 15' 38"	July 1996	Sept 1997	5 min

3.2.1. Daily Total Gaseous Mercury (TGM)

TGM concentrations ranged from approximately 0.50 to 3.97 ng/m³ over the measurement period listed for the 3 sites listed in Table 3-1. Although average TGM concentrations at all 3 sites were in the 1.5 -1.8 ng/m³ range (Table 3-2), there were differences in diurnal variability between 3 sites. Kejimkujik TGM concentrations

showed a daily or diurnal range with an amplitude of approximately $0.5\text{--}1.0\text{ ng/m}^3$ rarely going below 1.0 or above 2.0 ng/m^3 during the summer months. The lowest TGM concentrations at the Kejimikujik site, those $< 1.0\text{ ng/m}^3$, were also measured in the summer months, usually during the overnight period. Strong TGM depletion episodes were unusual and may be related to depletion processes such as heavy dew formation.



Figure 3-1: Long term continuous total gaseous mercury monitoring sites in Canada using Tekran CVAFS analysers as of November 1997.

At Kejimikujik National Park, the marked diurnal cycle occurred only during the summer months as is illustrated in Figure 3-2. This illustration depicts a warm dry period in between August 17 and August 23 1995. Although the diurnal variability illustrated in Figure 3-2 is typical for the June to August period, the exact profile can vary widely day to day depending on temperature, cloud cover, precipitation and solar insolation. The TGM diurnal profile was significantly correlated ($p < 0.001$) with the diurnal temperatures during the summer, on overcast days when the solar insolation was less, TGM diurnal ranges were more limited even under similar temperature regimes.

St. Andrews TGM showed a degree of diurnal variability but this occurred less frequently than observed at Kejimikujik and the amplitude of the diurnal curve was lower in magnitude ($\sim 0.5\text{ ng/m}^3$) under similar meteorological conditions. TGM concentrations at Acadia showed little or no diurnal cycle during the summer. The reasons for these

between site differences are not known. All of the sites are rural, sparsely populated with mixed forest cover. Forest types are similar consisting of mixed coniferous and hardwood. One of the few contrasts between the sites is that Kejimikujik National Park is more inland than the other 2 sites and has abundant wetlands within its boundaries while the other 2 sites are coastal and have limited freshwater wetlands in the immediate vicinity.

Table 3-2. Comparison of mean total gaseous mercury (TGM) concentrations at selected sites. Means for the 3 study sites are for the 1996 calendar year. Note that monitoring at Acadia covers only July-Dec 1996. TGM ranges shown for the 3 sites include data from the start of measurements (see Table 3-1) through to September 1997.

TGM (ng/m ³)		Location	Source
Mean	Range		
3.22	1.3-13.3 (Mar-May 90)	Egbert (ON)	Schroeder 1994
2.3	1.3-4.9	Lake Michigan (MI)	Keeler et al. 1994
2.21	1.4-3.6	Pt. Petre (ON)	Schroeder 1990
2.0	1.2-4.2	Underhill (VT)	Burke et al 1995
2.0	1.8-1.4	South Haven (MI)	Keeler et al 1994
1.79	0.28-3.97	Acadia (ME)	this study
1.77	1.47-2.17	North Central Pacific	Fitzgerald et al. 1991
1.64	0.45-5.05	Florida	Gill et al. 1995
1.56	0.49-3.36	St. Andrews (NB)	this study
1.49	0.13-3.40	Kejimikujik (NS)	this study
1.57	1.00-2.45	Wisconsin	Fitzgerald et al. 1991
1.47	0.79-5.51	St. Anicet (QE)	Poissant 1996
0.55	0.02-1.85	Ross I. Antarctic	de Mora et al. 1993
Polluted			
12	3.4-36	W-2 soil storage	Lindberg et al. 1991
8.7	1.8-62	Chicago (IL)	Keeler et al. 1994
5.9	0.8-16	Walker Branch (TN)	Lindberg et al 1991

It has been suggested that the summer diurnal cycle in TGM may simply be a function boundary layer dynamics and vertical mixing. However, under overcast conditions, flux measurements (see section 3.5 below) has indicated that direct solar radiation may play an important role in TGM dynamics (see also Poissant and Casimir 1998). Therefore, the diurnal pattern at Kejimikujik may not be due to simple boundary layer dynamics, especially since strong depositional processes which could deplete TGM during the night on a regular basis, have not been measured. It is possible that the increase in TGM during the daylight period is, at least in part, related to evasion and air-surface

interactions (Amyot et al., 1994, Poissant and Casimir 1998). By fall (September), the magnitude of the diurnal range diminishes and is absent by late October and throughout the winter and early spring period.

3.2.2 Mercury Transport

In industrial and urban regions of North America mercury emissions from nearby point sources such as incinerators or fossil fueled power generating facilities are well documented. However, there is limited evidence concerning the long range transport and transboundary flow of mercury, especially into the Atlantic region. Although several mercury emission sources do exist in the Atlantic region (Dorion *et. al.*, 1998), it has been shown in various studies that elevated pollutant levels can occur on an episodic basis and these episodes can often be traced back to transport from distant emission source regions.

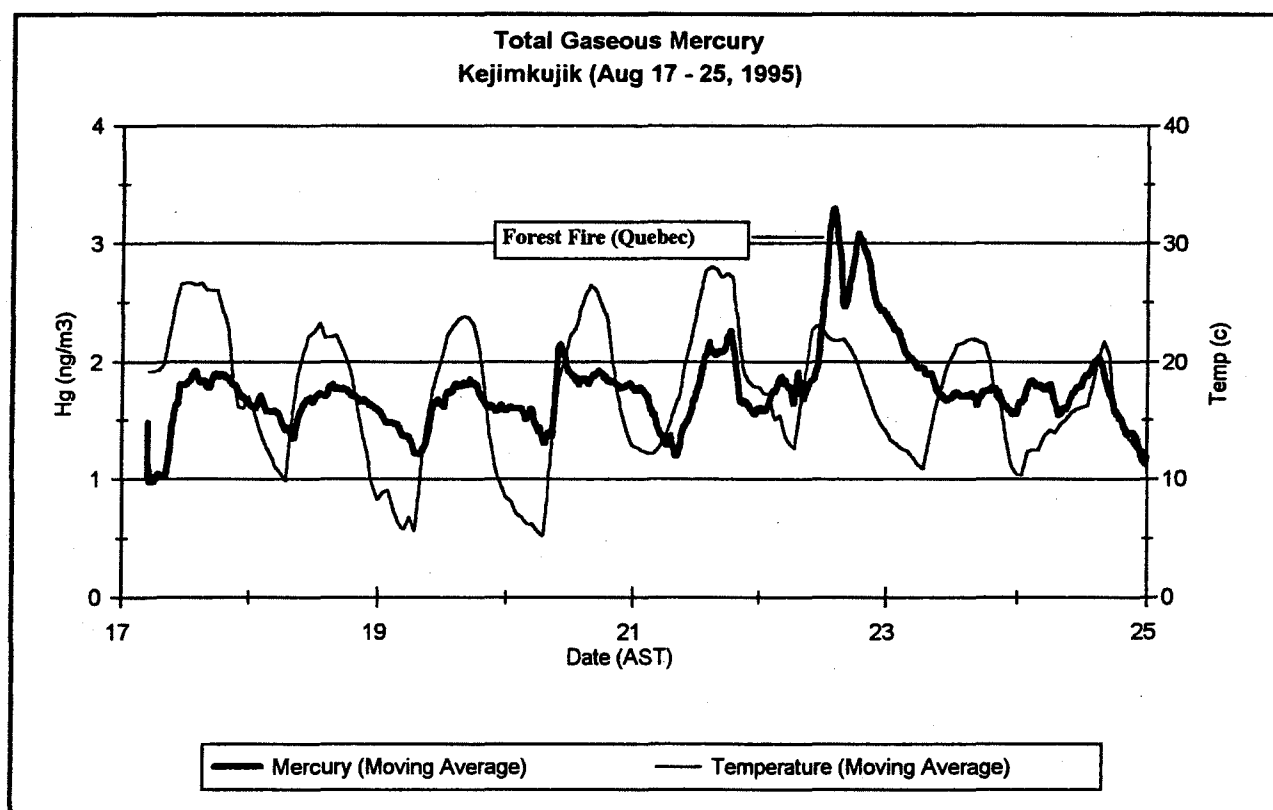


Figure 3-2: Diurnal TGM concentrations at Kejimkujik National Park during August 1995.

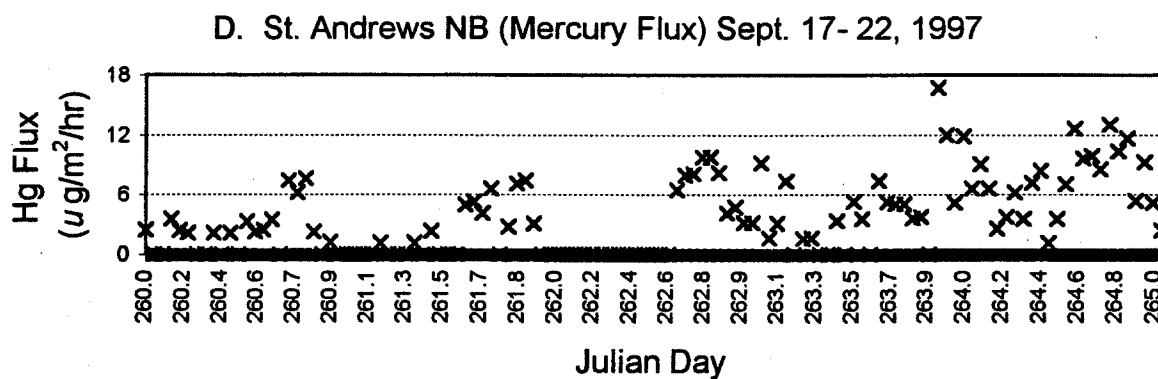
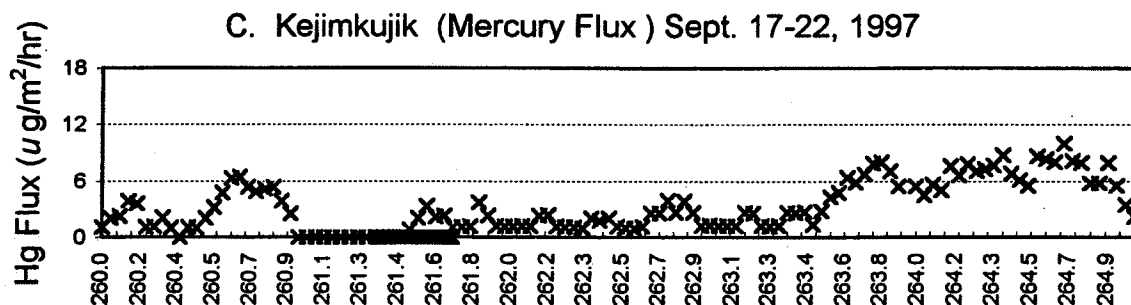
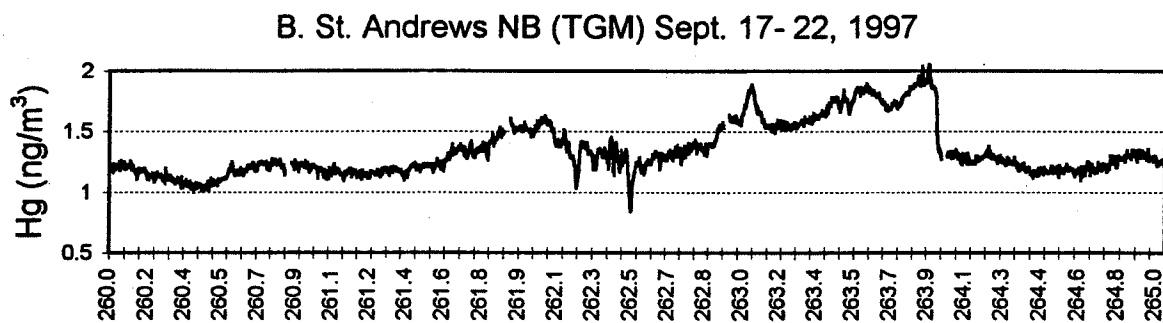
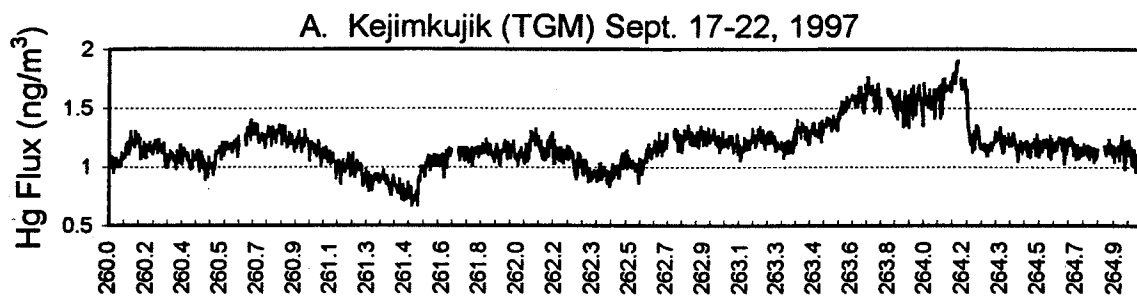
Studies of pollutants in the Arctic (which has no substantial local anthropogenic mercury emission sources) have indicated that pollutants are transported relatively long distances from industrial regions in North America and Europe. The Atlantic region lies downwind of major industrial and populated mercury emission source regions in the United States northeast, the Great Lakes basin and the Windsor-Quebec corridor region of Canada. Previous studies of atmospheric pollutant transport suggest that the Atlantic region can be strongly influenced by emissions transported from these regions. One important objective of the mercury program is to study source-receptor relationships to determine if there is a link between periods of elevated ambient TGM and transport over known emission sources or source regions.

Ambient TGM monitoring data from Kejimikujik, St. Andrews and Acadia were reviewed for periods in which exceptionally high mercury levels occurred for short periods of time. One such period occurred on August 22-24 1995. TGM concentrations at Kejimikujik National Park climbed rapidly throughout the morning and mid-day reaching a peak concentration of 3.36 ng/m^3 on the late afternoon of August 22. TGM concentrations then declined slowly during the night and early morning of August 22-23 and had returned to normal levels by August 25 (Figure 3-2). The Kejimikujik TGM analyser was the only instrument operating at that time so the spatial extent of this episode is not known.

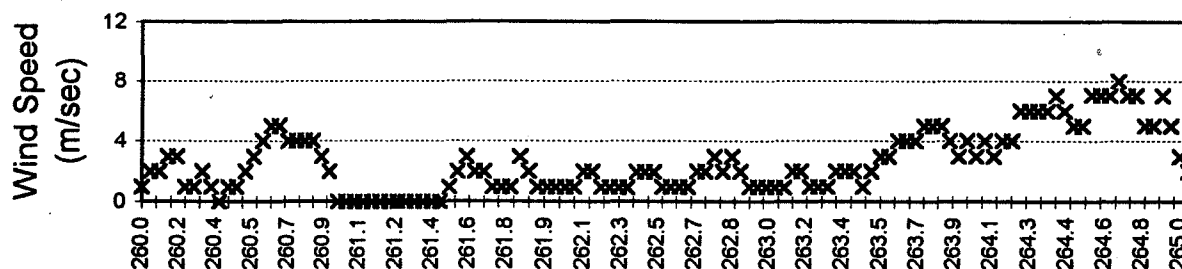
Aircraft, media reports as well as satellite imagery and casual observation clearly indicated the source of the elevated TGM. Extensive forest fires in Quebec coupled with a westerly flow and vertically stable meteorological conditions over eastern Canada restricted vertical mixing and confined dense concentrations of wood smoke within the boundary layer during this period. Vertical and horizontal visibility and sunlight were markedly restricted. The resulting wood smoke and possibly volatilization of mercury from forest soils led to the elevated mercury concentrations measured at ground level and probably throughout the lower troposphere.

Another period of elevated TGM concentration occurred on September 20-21 1997. At this time there were 3 TGM analysers operational in the region and all 3 showed a similar pattern over an extensive area. Figure 3-3 (A&B) depict TGM concentrations at Kejimikujik and St. Andrews (Acadia is not shown but was similar) during the September 17-21 1997 period. TGM concentrations increased throughout the day on Sept 20 reaching a maximum concentration at Kejimikujik National Park of approximately 1.8 ng/m^3 during the overnight period on Sept 21 (Julian day 264).

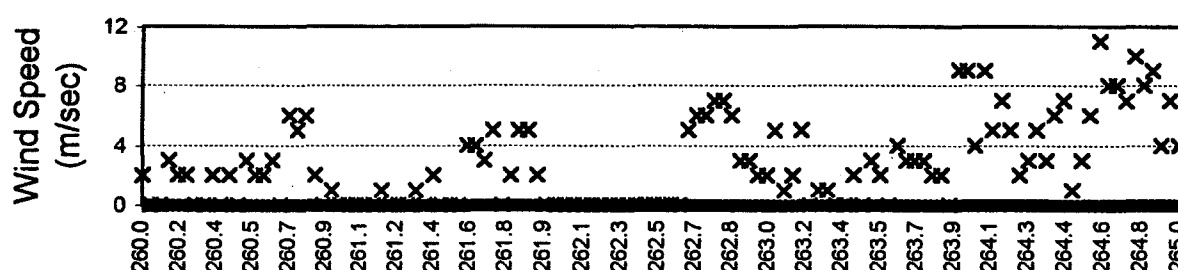
The buildup in TGM concentrations at the 3 sites occurred over a 2 day followed by a sudden and rapid drop to normal (background) concentrations in the early morning of September 21. The TGM maximum occurred several hours earlier at St. Andrews and Acadia indicating that the mercury was transported from the southwest. This was confirmed using trajectory analyses.



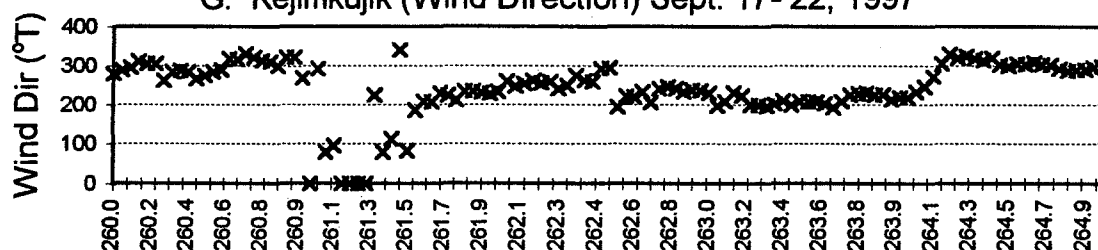
E. Kejimikujik (Wind Speed) Sept. 17- 22, 1997



F. St. Andrews NB (Wind Speed) Sept. 17- 22, 1997



G. Kejimikujik (Wind Direction) Sept. 17- 22, 1997



H. St. Andrews NB (Wind Direction) Sept. 17- 22, 1997

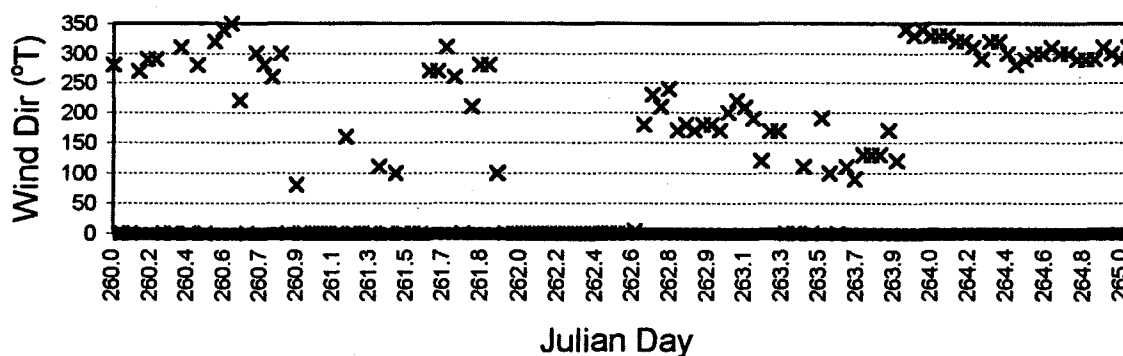


Figure 3-3: TGM concentration, horizontal flux, wind speed and wind direction at Kejimikujik National Park, NS and St. Andrews, NB for September 17-22 1997 showing the period before, during and shortly after a mercury LRTAP event.

This pattern of gradual buildup in pollutant concentrations followed by a rapid shift back to "background" levels is typically found in ozone episodes (CCME 1997). Ozone episodes in the Atlantic region are commonly initiated by either a high pressure system offshore (e.g. Bermuda high) or an approaching cold front associated with a low to the west of the region. Either synoptic pattern or the two in combination place the Atlantic region in a southwesterly flow originating over the northeastern US and the Windsor-Quebec corridor (both known emission source regions). A review of the synoptic meteorological conditions during this period showed an approaching low pressure system with its center to the west, atmospheric transport conditions were conducive to elevated pollutant levels. The recent history of air passage was plotted using air parcel trajectory analysis (Figure 3-4; [A&B]).

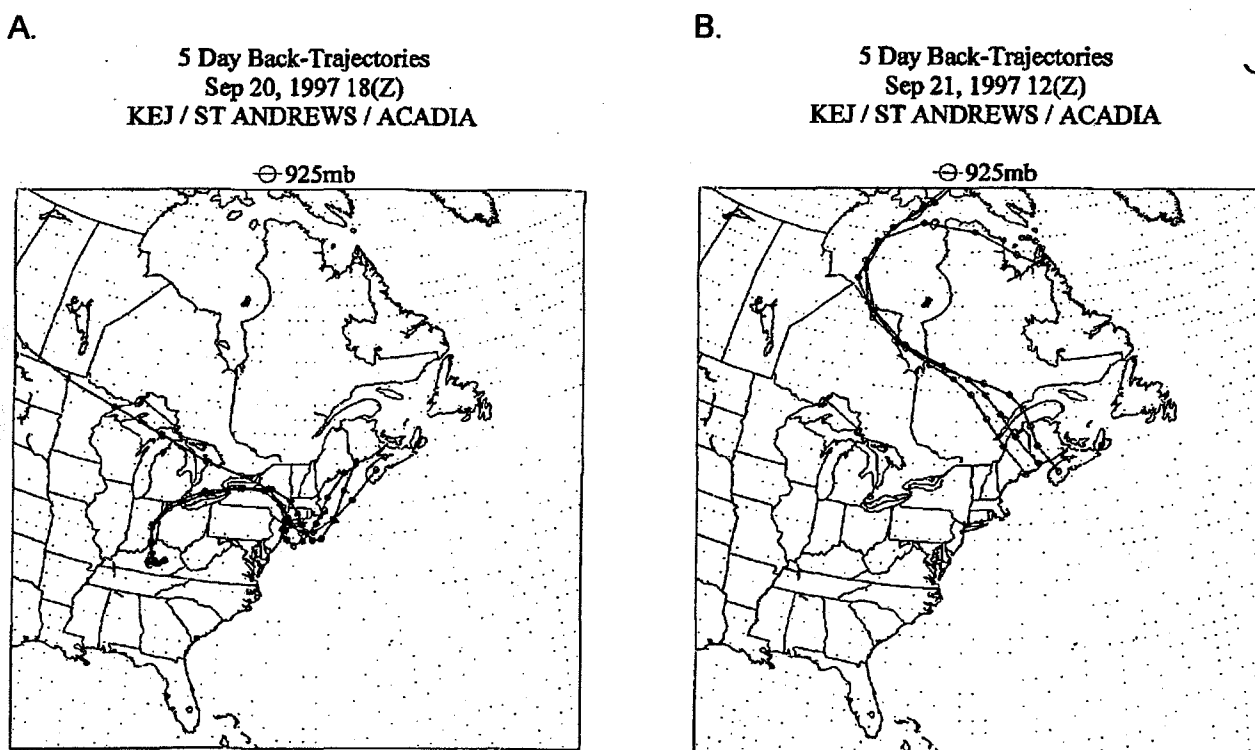


Figure 3-4: 925 mb air parcel trajectories during the buildup of TGM at the Kejimikujik, St. Andrews and Acadia monitoring sites (A) in comparison to air parcel trajectories after the passage of the cold front and the return of TGM concentrations to background levels (B).

After passage of the cold front, the airmass changed and pollutant levels returned to lower "background" TGM concentrations in the resulting northwesterly flow behind the front (Figure 3-3; G&H).

Horizontal mercury flux increased at both sites during the period of elevated TGM concentrations and wind speeds (Figure 3-3 [C&D]). Flux at Kejimikujik increased from less than $6 \text{ ug/m}^2/\text{hr}$ to approximately $10 \text{ ug/m}^2/\text{hr}$ compared to an increase from 6 to over $12 \text{ ug/m}^2/\text{hr}$ at St. Andrews. Flux at both sites remained high after TGM levels returned to normal due to persistently high wind speeds (Figure 3-3 [E&F]) behind the front but returned to normal values within days as winds diminished.

3.2.3. Seasonal Trajectory Climatology

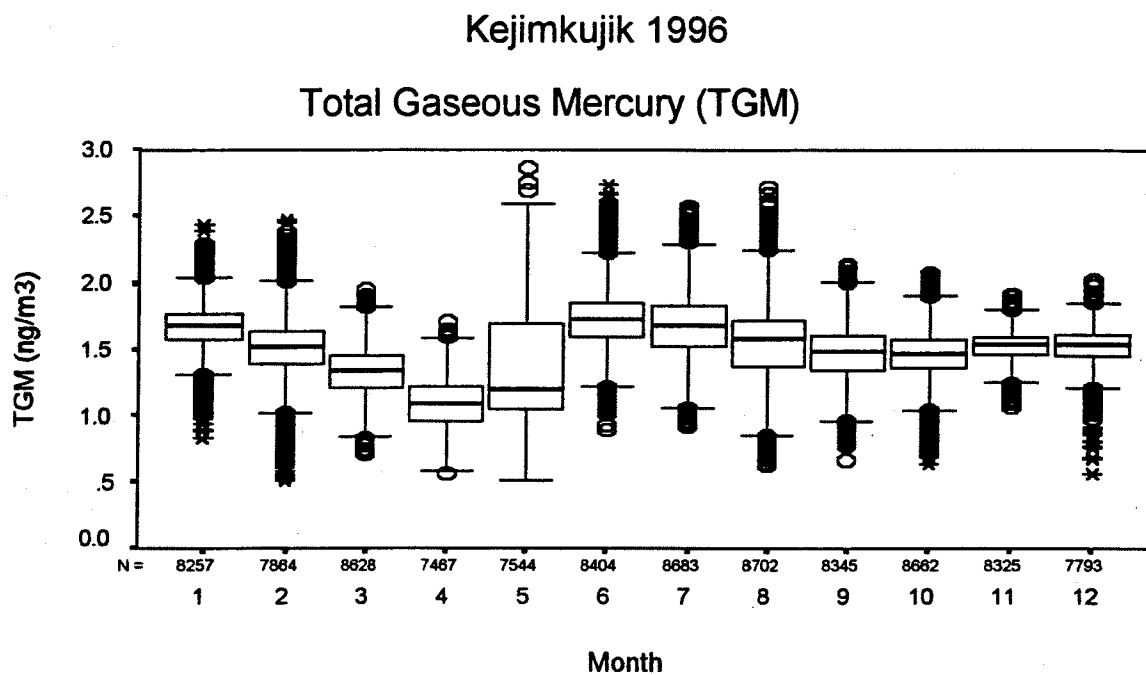
Elevated TGM concentrations were defined using monthly box plots as the high outlier data points. These data points are shown in Figure 3-5 (A, B & C) by a circle (near outliers) or an asterisk (far outliers) located above the horizontal bar at the uppermost tip of the upper whisker in each monthly box plot (these TGM values are "high" outliers as opposed to "low" outliers located at the bottom of the box and whisker plots).. This non-parametric analysis is somewhat analogous to outliers defined using standard deviation criterion.

Monthly high outlier TGM data was put in 3 month bins to provide a seasonal view of the data. Air parcel trajectories describing the transport pattern over the previous 5 days (similar to those in Figure 3-4) were produced for periods during which elevated TGM occurred. The same 3 month bins were used to provide a seasonal view of transport patterns associated with elevated TGM concentration. Summer is defined as June-August, fall as September-November, winter as December-February and spring as March-May. The plotted trajectories provide an approximation of the seasonal transport climatology for elevated TGM and possible source-receptor relationships.

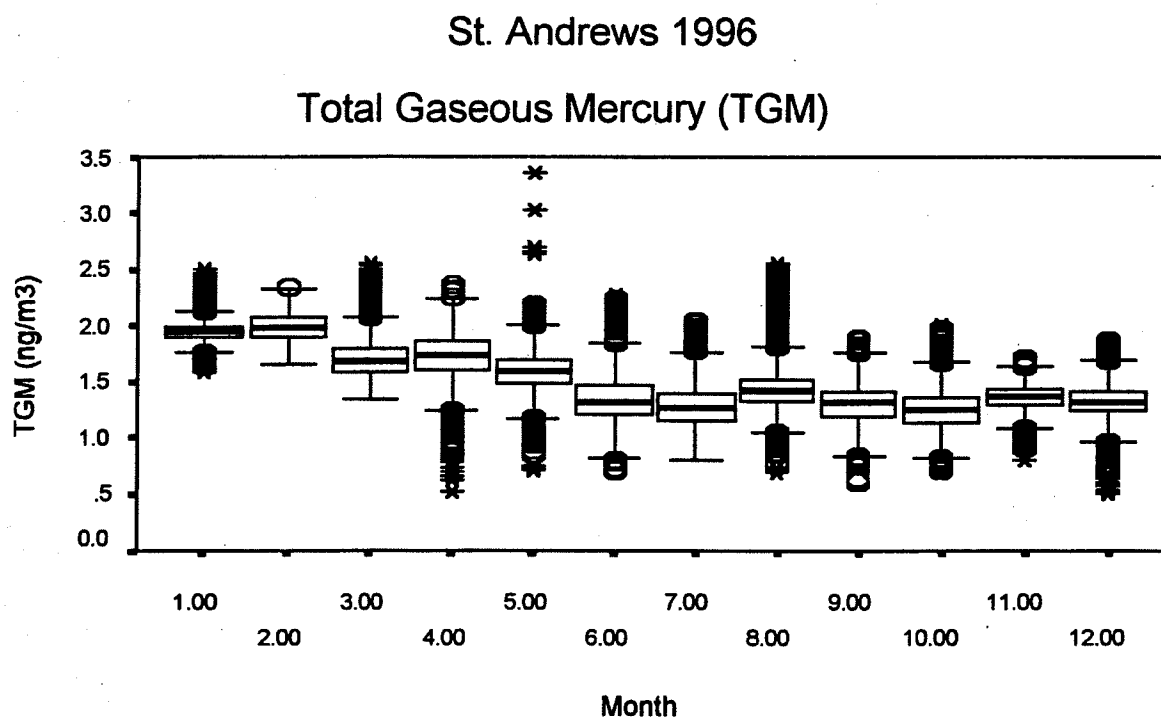
Figure 3-6 (A) illustrates 925 mb trajectories for elevated TGM concentration at Kejimikujik National Park for the winter (December 95 to February 96) period. It is apparent that, in this period, there are no consistent transport patterns. In the winter months the trajectories appear to be random and may reflect the influence of small localized sources in the immediate vicinity. Possible sources might include wood stoves, oil furnaces or other combustion sources commonly used in colder weather. Similarities between sites were also apparent. Between Dec 95 and Feb 96, trajectory climatologies for St. Andrews (not shown) also indicated arrivals of air parcels from all directions. Data was not available for Acadia National Park in the winter of 95-96.

Analysis of seasonal trajectory climatologies for Kejimikujik National Park in 1997 showed some differences from the previous year likely due to variations in meteorological conditions. In the winter of 1996-97 all of the trajectories originated from the southwest to northwest quadrant which includes the Great Lakes region and.

A.



B.



C.

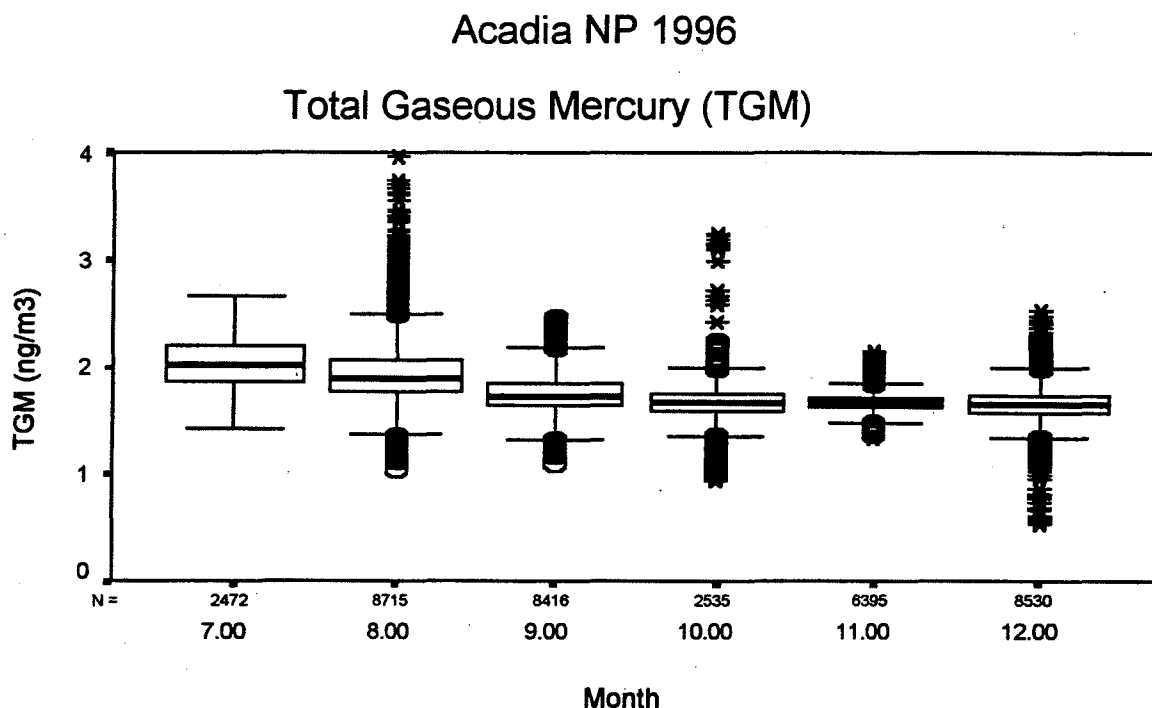


Figure 3-5: Box and whisker plots of the seasonal distribution of TGM concentrations at A) Kejimikujik National Park; B) St. Andrews and C) Acadia National Park in 1996 (circles and asterix' are outliers).

northeast US states. The random pattern observed in the winter of 1995-96 was not apparent in 1996-97 (Dec-Feb). Winter 925 mb trajectory patterns at Acadia and St. Andrews in 96-97 were similar to that of Kejimikujik where transport from the southwest to northwest sector dominated.

In spring (March-May) of 1996 the occurrence of elevated TGM at Kejimikujik is relatively infrequent compared to the winter period. During the previous winter there were approximately 600 five minute TGM values classed as outliers (although many of these may be consecutive values and not separate events) compared to only 50 in the spring of 1996. Spring trajectories, although fewer in number, show a more consistent pattern with flow from the north (Figure 3-6; [B]). TGM concentrations in the Arctic atmosphere in winter are within the range of values recorded at Kejimikujik National Park in the spring of 1996 (Schroeder 1998).

It is difficult to determine where an emission point or area source may lie along a trajectory pathway. There are candidate mercury emission sources to the north of Kejimikujik including power generating facilities in New Brunswick, the city of Saint John

and others which lie within the Atlantic region. However, it is also possible that elevated TGM coincides with the breakdown of the Arctic vortex and pollutants from North America and Europe which have built up in the Arctic over the winter period begin to mix southward in a process referred to as the Arctic spring outbreak.

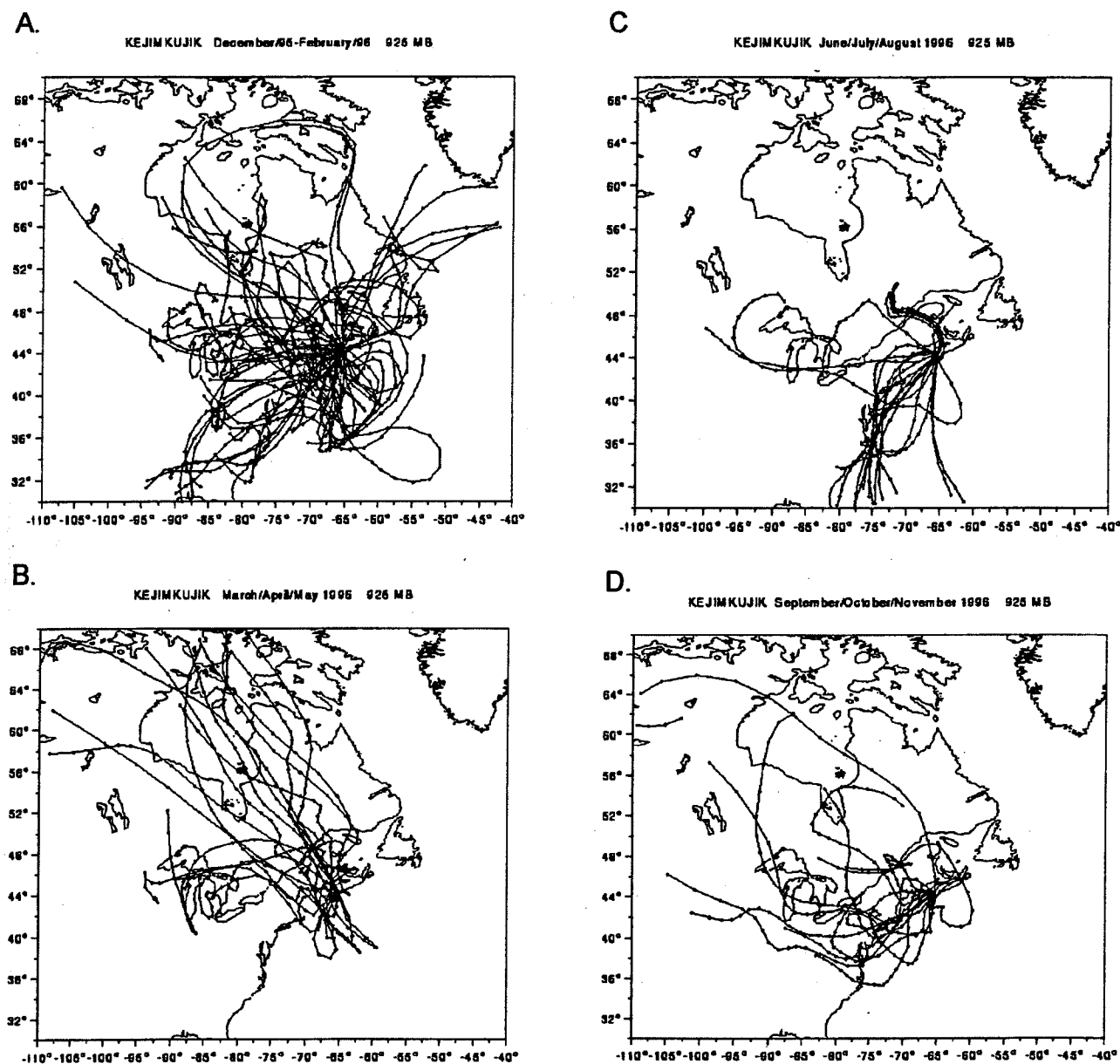


Figure 3-6 Seasonal 925 mb trajectory climatology for elevated TGM in ambient air at Kejimikujik National Park (see text for explanation).

Spring transport patterns in 1996 at St. Andrews also showed transport from the north on several occasions but, unlike those for Kejimikujik, many of these trajectories also passed over urban centers in the Great Lakes and Windsor Quebec corridor. Some of the trajectories trace backward from the south and traveled northeastward along the east coast of the US over the 5-day trajectory history. Data for Acadia was not available until July 1996 thus cannot be compared.

Spring 1997 trajectories at Kejimikujik indicated transport from the north as was the case in 1996 but trajectories also arrived at the Kejimikujik site from the west and southwest. At Acadia, trajectories in the spring of 1997 were few in number but also showed a tendency to come from the north. In the spring of 1997, transport to St. Andrews was more westerly in nature although, on a few occasions, trajectories arrived from a northerly direction.

It is possible that trajectory climatologies associated with elevated TGM simply reflect overall seasonal transport patterns since both elevated and overall transport (all trajectories) in the spring time show a dominant north-westerly direction. Further analysis is required to more fully assess differences between seasonal transport patterns versus those patterns associated exclusively with elevated TGM concentrations.

In the June-August 1996 period, trajectories associated with elevated TGM at Kejimikujik showed a pattern dominated by transport along the northeast corridor (Figure 3-6; [C]), an area associated with large point sources of anthropogenic mercury emissions in the US (Pai et al., 1998). Although the US northeast corridor was the most frequent contributor to elevated TGM concentrations at Kejimikujik National Park during this period, a distinctive feature of the trajectory climatology in the summer of 1996 was the cluster of 4-5 trajectories passing over northern New Brunswick. These trajectories passed within the vicinity of a large power generating facility, a mining and smelting operation and a chlor-alkali plant. These are all potential sources of mercury emissions (Dorion et al., 1998).

Trajectories which originate in the Great Lakes basin and transit some major urban centers including Chicago, Detroit, Windsor, Hamilton and Toronto can also be observed. There are 2 summer trajectories which originate over the ocean and do not transit any anthropogenic sources (except possibly shipping), over the 5 day trajectory. Trajectory patterns for St. Andrews in 1996 showed arrival of air parcels from the northeast corridor and the Great Lakes region with no particular source region dominating.

In 1997, summer trajectory pathways at Acadia were predominantly from the west and southwest. Transport conditions were similar at St. Andrews although north-northwesterly flows occurred on several occasions.

Fall trajectories in 1996 at Kejimikujik (Figure 3-6; [D]) and St. Andrews were relatively few in number and distributed in a more random pattern over the southwest to northeast quadrants. Some trajectories also traverse mining and smelting operations as far away as Quebec and Manitoba although the contribution of these potential sources relative to other sources along the trajectory pathway remain uncertain.

In general, trajectory patterns for elevated TGM concentrations at Kejimikujik National Park and the other 2 sites showed differences in transport patterns on a seasonal basis as well as differences within season between the 2 years. However, there are similarities between sites and between years at individual sites. On an annual basis, elevated TGM concentrations were most commonly associated with transport from the southwest through to the northwest quadrant which is coincident with the direction weather patterns most frequently travel. However, the association with elevated TGM may not simply reflect the dominant meteorological patterns. This is also the quadrant which would have the most anthropogenic influence with respect to mercury emissions. It is feasible that the overall trajectory climatology at the various sites reflects anthropogenic influences and, as indicated above, may also reflect a mix of long range atmospheric mercury transport from outside the region in addition to transport related to emission sources within the Atlantic region.

Given the relatively long atmospheric lifetime (~1 yr.; Hall, 1995) of TGM in the atmosphere, it is possible that a combination of local (Nova Scotia), medium range (Atlantic region), long range (eastern Canada/northeastern US) and global (European) sources may impact the Atlantic region. These data support the contention that mercury is a global pollutant and mitigation may have to be dealt with by all levels of industry and government from the local to the international level.

3.2.4 Seasonal TGM

The overall seasonal distribution of all TGM data at the 3 study sites did not vary substantially between years at sites where multiple year data was available. Data for all 3 sites in 1996 is presented in Figure 3-5 (note: sampling at Acadia only began in July of that year).

Both Kejimikujik and St. Andrews showed an annual range for median TGM concentrations of approximately 0.8 ng/m^3 . However, the Kejimikujik site seasonal TGM distribution differed from the pattern found at St. Andrews. Kejimikujik TGM exhibited summer and winter maximum compared with a single winter maximum at St. Andrews. The summer growing season TGM distribution in Kejimikujik appeared to follow a solar and temperature seasonal profile whereas TGM concentrations at the St. Andrews site were highest in January and declined steadily throughout the spring and remained relatively stable in the summer-fall period (Figure 3-5;[B]). Acadia followed a July-Dec pattern similar to the other 2 sites.

3.2.5 Annual TGM

Mean annual TGM concentrations were highest at Acadia National Park compared to the Kejimikujik and St. Andrews sites (Table 3-2) but all 3 sites exhibited mean and median concentrations which were generally close but slightly greater than the global background level of approximately 1.5 ng/m^3 . Higher mean TGM values for Acadia may be related to its proximity emission source regions distributed along the US northeast corridor (Washington, Baltimore, New York and Boston). Overall ranges in TGM concentrations were similar to those measured in other North American locations where minimum concentrations rarely went below 0.5 ng/m^3 (which is probably related to methodological limitations) or above 3 ng/m^3 . Maximum TGM concentrations at polluted sites were considerable higher.

3.3 Vertical Distribution of Total Gaseous Mercury in the Atmosphere (Banic, Beauchamp, Tordon, Schroeder)

Few continuous direct measurements of total gaseous mercury (TGM) in the atmosphere have been made at more than a few meters above the earth's surface and into the free troposphere. During the Radiation, Aerosol and Cloud Experiment (RACE) conducted in August and September 1995, TGM was measured over Nova Scotia, the Bay of Fundy and the Gulf of Maine at altitudes up to 5 km using a Tekran™ TGM analyser. The sampling period of the analyser was shortened from 5 min to 2.5 minutes to improve the horizontal and vertical resolution during the flights. The aircraft made transects in level flight as well as a number of rapid ascents and descents over a period of 2 weeks. Operational details are given in Banic et al. (1998). Mercury in cloud water and particulate mercury was also sampled during RACE but the data is not yet available and is not discussed in this report.

Results of the TGM profiling are being analyzed and final results are pending. Laboratory testing of the mercury analyser indicated that the instrument was affected by pressure changes during flight. The pressure response was quantified and a correction applied to the ambient TGM measurements. The corrected TGM data set is not yet available and specific results cannot yet be shown. However, some preliminary conclusions can be made based on preliminary analysis of the data.

The vertical distribution of TGM in the atmosphere over eastern Canada appears to be relatively uniform up to 5 km ranging from $1\text{--}1.7 \text{ ng/m}^3$ over a total of 12 flights with an average of approximately 1.5 ng/m^3 . Although TGM concentrations at or near surface may show slight variability, these data indicate that total gaseous mercury throughout much of the planetary boundary layer (PBL) and free troposphere remains at concentrations similar to the global background ($\sim 1.5 \text{ ng/m}^3$). This may partially explain the lack of variability in average TGM values shown in Table 3-2. This also indicates that there is a large reservoir of TGM in the atmosphere over the region and probably globally

Preliminary findings also indicate that mercury in cloud water (eventually precipitation) may not be derived from TGM but is more likely derived from particulate scavenging in-cloud and below cloud (Banic et al. 1998).

When completed, the aircraft based studies conducted during RACE will provide important information concerning the mercury burden in the troposphere regionally and globally, the direction and magnitude of transport in the troposphere and, when compared to estimates of anthropogenic emission estimates, better estimates of natural versus anthropogenic emissions and their relative contribution regionally and globally. This study will also provide relevant information on atmospheric mercury interactions with other pollutants and processes in cloud which will support atmospheric mercury modeling efforts.

3.4 Mercury in Precipitation (Beauchamp, Tordon, EMAN, MDN)

Mercury concentrations in precipitation were measured at all of the sites listed in Table 3-1. However, the Acadia site is operated and maintained by staff at Acadia National Park and the Maine Department of the Environment (MEDEP) and those data are not presented or discussed further.

Both sites located in Atlantic Canada (Kejimikujik and St. Andrews) are part of the National Atmospheric Deposition Program (NADP) Mercury Monitoring Network (MDN). The locations of the Atlantic region sites and other MDN sites in North America are shown in Figure 3-7.

3.4.1 Total mercury concentration in precipitation.

Total mercury concentrations in precipitation measured at Kejimikujik and St. Andrews between July 1996 and July 1997 were similar with annual averages of 9.4 and 10.3 ng/l, respectively (Table 3-3). The difference is not considered to be statistically significant. It is likely the mean for St. Andrews is slightly higher due to 2 high concentration samples collected in December 1996 and March 1997.

Concentrations in precipitation are frequently expressed as volume weighted means to reduce the effects of small samples with high concentrations and thus providing a more representative overall concentration. Volume weighted average mercury concentration in precipitation is provided in Table 3 for the 2 study sites. The volume weighted average concentrations for Kejimikujik and St. Andrews (6.6 and 7.1 ng/l) were similar to the median values for the two sites (5.7 and 6.7 ng/l, respectively).

Kejimikujik had the highest weekly mercury concentration recorded in any of the precipitation samples with over 90 ng/l measured in August of 1996. This sample was from a trace amount of precipitation which may account for the exceptionally high

Mercury concentrations in precipitation exhibited a clear seasonal pattern of lowest concentrations in the winter and highest concentrations in the summer with the spring and fall as transition between these two periods (Figure 3-9). The reasons for the pattern is not clear but may be regulated simply by temperature and volatility. It does not appear that local heating fuel combustion during colder periods has a substantial impact on mercury concentrations in precipitation.

3.4.2. Mercury Wet Deposition

Total annual mercury wet deposition (deposition via precipitation) at Kejimikujik and St. Andrews were estimated to be 8.7 and 8.3 $\mu\text{g}/\text{m}^2/\text{yr}$. Figure 3-10 shows that seasonal mercury deposition follows a pattern similar to that shown for mercury concentration with generally higher deposition in the summer and minimum weekly mercury deposition measured in the winter period.

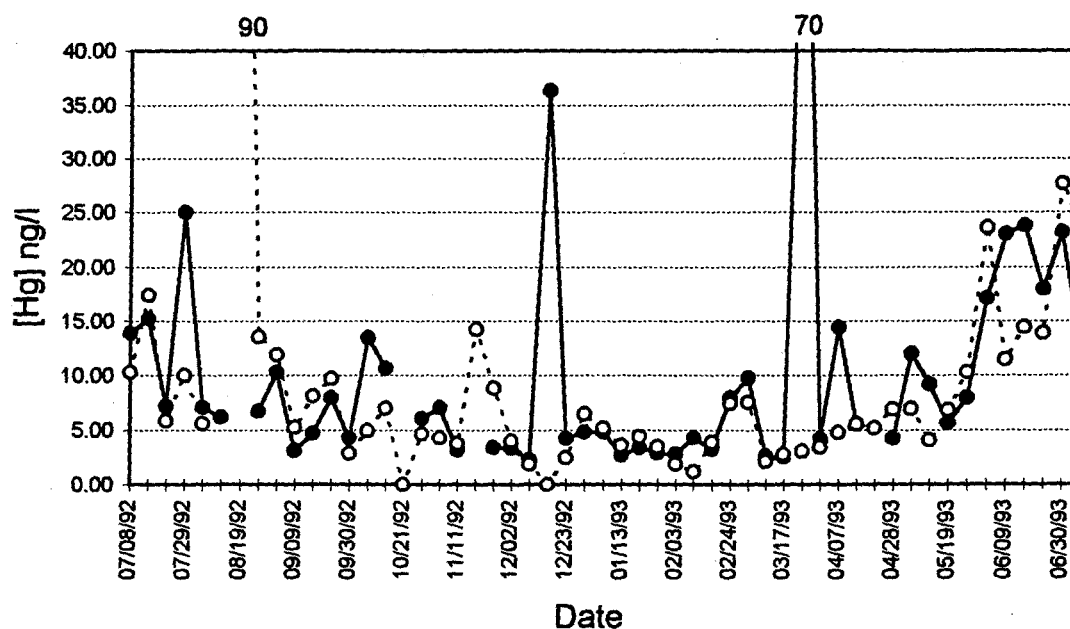


Figure 3-9: Seasonal distribution of total mercury concentration in precipitation at Kejimikujik National Park (open circles, dashed line) and St. Andrews (dark circles, solid line) between July 1996 and July 1997.

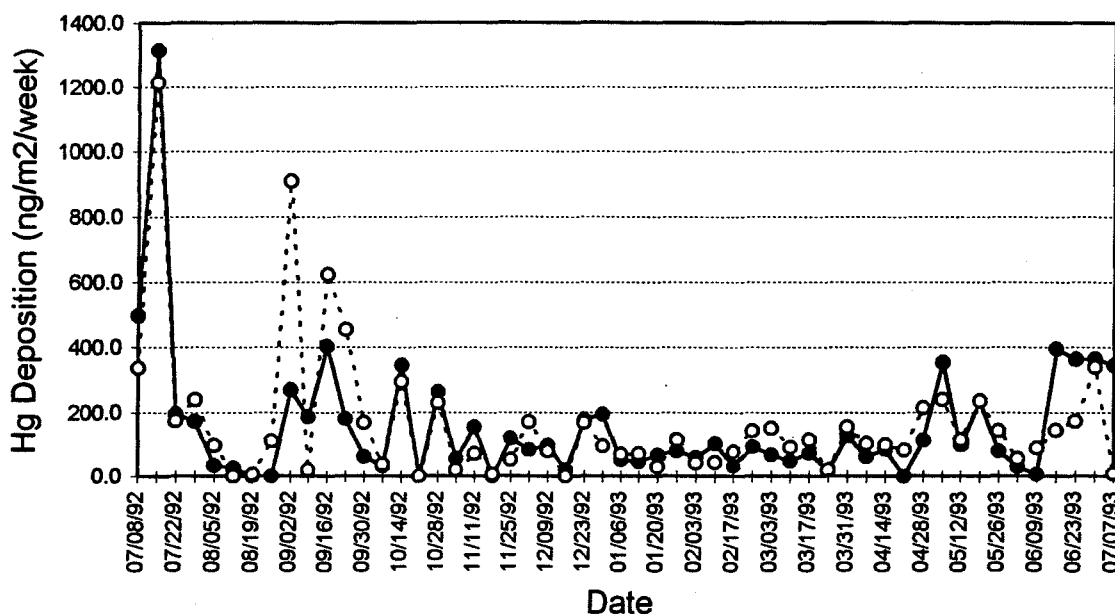


Figure 3-10 : Seasonal distribution of weekly total mercury deposition via precipitation at Kejimikujik National Park (open circles) and St. Andrews (dark circles) between July 1996 and July 1997.

Deposition during the 96-97 study period was strongly influenced by the passage of extratropical storm systems which deposited relatively large volumes of precipitation over short time periods (1-3 days). Hurricane Bertha deposited over 1200 ng/m² of mercury at Kejimikujik and over 1300 ng/m² at St. Andrews during the week ending on July 16 1996. Another event following in just over a month, hurricane Edouard, deposited ~900 ng/m² on Kejimikujik on September 3 1996. These 2 events at Kejimikujik accounted for 24% of the annual total mercury deposition. Thus, it is probable that annual variability in meteorological conditions, particularly in the frequency and severity of various tropical, extra tropical or other intense low pressure systems can strongly influence overall mercury deposition patterns.

Total annual mercury deposition is similar in magnitude when compared to other sites in North American as shown in Table 3-4. Kejimikujik and St. Andrews have the largest precipitation volumes of the various sites which increase deposition assuming concentrations remain similar. At Kejimikujik National Park, mean mercury concentrations in precipitation were somewhat lower than most other sites based on a similar comparison (Table 3-3). Lower concentrations are offset with higher recorded precipitation volume giving similar annual mercury deposition. A similar comparison showed that mercury concentrations in precipitation at St. Andrews were similar in magnitude to those of other North American sites even though higher volumes were not reflected by substantial higher annual deposition amounts. The similarity in total mercury deposition at St. Andrews may be related to the distribution of mercury concentration in relation to precipitation volume in weekly samples as illustrated in

Figure 3-9 (B). These 2 components were somewhat different in Kejimikujik National Park in comparison to the site at St. Andrews, N.B.

Table 3-4: Comparison of annual total mercury deposition via precipitation at the 2 Atlantic region study sites with other North American estimates.

Hg Deposition ug/m²/yr	Precipitation mm/yr. (year)	Location	Authors
12.7	1160 (93-94)	South Haven (MI)	Hoyer et al. 1995
9.4	890 (92-93)	South Haven (MI)	Hoyer et al. 1995
9.3	1119	Underhill (VT)	Burke et al. 1995
9.1	880 (93-94)	Dexter (MI)	Hoyer et al. 1995
8.7	-	Wisconsin	Fitzgerald et al. 1994
8.7	872 (92-93)	Dexter (MI)	Hoyer et al. 1995
8.7	1545 (96-97)	Kejimikujik (NS)	this study
8.3	1205 (96-97)	St. Andrews (NB)	this study
6.8	-	Wisconsin	Fitzgerald et al. 1994
5.8	730 (93-94)	Pellston (MI)	Hoyer et al. 1995
5.5	710 (92-93)	Pellston (MI)	Hoyer et al. 1995

3.5 Air-Surface Mercury Flux (Boudala, Folkins, Beauchamp, Tordon)

In order to complete a watershed mercury mass balance, a clear understanding and detailed quantification of the fluxes of constituents both internal and external to the watershed must be known. Only when the individual components of the mass balance are identified, quantified and tallied can the relative contribution of individual components be weighed. Metals can enter or leave a watershed through a number of pathways. Input can occur through groundwater and surface flow while losses can occur through stream outflow and sedimentation (Niragu and Wong, 1989). It is also important to understand exchange processes between the atmosphere and the surface (soil and water) including process such as dry and wet deposition. In the case of mercury it is also necessary to understand processes regulating gas exchange.

The atmosphere may play an important role in the redistribution of mercury in the environment through the process of gas exchange between the atmosphere and soil or water surfaces. Gas exchange is a bi-directional process in that mercury can leave soil and water surfaces in a process referred to as evasion (volatilization) in addition to the more commonly measured input pathway of mercury deposition via precipitation. Air-water and air-soil exchange of TGM has been measured and analyzed at selected sites in the Kejimikujik National Park but the spatial and temporal magnitude of gas exchange, as well as the physical-chemical factors regulating exchange processes of mercury between the atmosphere and the watershed, are still not well understood.

Between June and August 1997 a preliminary study of air-water and air-soil mercury exchange (flux) was undertaken at selected sites in Kejimikujik National Park including North Cranberry and Big Dam West Lakes; two watersheds selected for mass balance studies. Flux measurements were made using a dynamic flux chamber constructed of Teflon film measuring 20W x 20H x 60L cm. Concentrations in ambient air were compared with concentrations measured within the flux chamber with Hg evasion or deposition based on differences between these measurements. A constant flow rate of 1.5 L/min was maintained through the chamber for the duration of the measurement period. TGM within and outside the chamber was measured for a 5 min sampling interval on both channels consecutively resulting in an ambient and a chamber measurement every 20 min. The chamber was blank tested before and after measurements by placing the chamber on top of a Teflon sheet.

The number of flux measurements conducted over water and soil at each site were limited due to restricted access during an unusually severe dry period in the summer of 1997 and the subsequent forest fire hazard. At least one flux measurement varying in duration from 19 to 52 consecutive hours was made over soil and water at each of the 2 sites as well as another experiment over soil at the AES air chemistry monitoring site. Preliminary results of the mercury flux measurements showed that both evasion and deposition of gaseous mercury can occur depending on a number of environmental factors including temperature, wind speed, solar insolation and mercury speciation in the substrate.

The range of flux values at the various locations over differing surface types is summarized in Table 3-5. Mercury flux was measured over soil and water at North Cranberry Lake and Big Dam West Lakes, as well as over soils at the Kejimikujik CAPMoN site. Big Dam West and North Cranberry Lakes are shallow (mean depth < 4 meters), acidic (pH < 5.5) and colored (organic) although Big Dam West is much more colored than North Cranberry.

Negative flux was measured over water at North Cranberry Lake and soils at Big Dam West Lakes as well as over soils at the Kejimikujik CAPMoN site. These negative (deposition) values are small in comparison to evasion rates which was the dominant direction of transfer. These findings are consistent with those of Poissant and Casimir (1998) for sites in Quebec. Deposition typically occurred overnight and into mid-morning although flux measurements over soil were negative throughout most of the 39 hours of measurement at Big Dam West. Measurements in the Big Dam area were made under a dense canopy of mature hemlock over natural forest litter. Therefore, very little sunlight penetrated the canopy and conditions were cool and cloudy throughout much the measurement period.

Table 3-5: Summary of locations, surface type, date, time, duration and range of mercury flux based on measurements made at Kejimikujik National Park sites during 1997. Negative flux indicates deposition while positive flux indicates evasion from surface to air.

LOCATION	SFC TYPE	DATE	START TIME	END TIME	DURATION (Hours)	FLUX (ng/m ² /hr)	
			(GMT)	(GMT)		Min.	Max
KEJ. CAPMoN	SOIL	27-Jun-97	4:00	23:00	19	-0.67	3.79
BIG DAM WEST	SOIL	09-Jul-97	23:00	24:00	1	-0.17	-0.08
BIG DAM WEST	SOIL	10-Jul-97	0:00	16:00	16	-1.45	1.76
BIG DAM WEST	SOIL	11-Jul-97	1:00	23:00	22	-1.22	0.23
BIG DAM WEST	WATER	10-Aug-97	18:00	22:00	4	1.8	10.73
BIG DAM WEST	WATER	11-Aug-97	0:00	24:00	24	0.74	43.82
BIG DAM WEST	WATER	12-Aug-97	0:00	24:00	24	0.16	6.22
NORTH CRANBERRY	WATER	21-Aug-97	22:00	24:00	2	0.23	0.83
NORTH CRANBERRY	WATER	23-Aug-97	0:00	24:00	24	-0.26	13.48
NORTH CRANBERRY	SOIL	24-Aug-97	19:00	23:00	4	2.49	3.78
NORTH CRANBERRY	SOIL	25-Aug-97	0:00	23:00	23	1.16	2.99
NORTH CRANBERRY	SOIL	26-Aug-97	0:00	18:00	18	1.1	2.78

Mercury flux generally exhibited a strong diurnal cycle correlated with solar radiation and soil temperature or water temperature depending on the location of the measurements and the surface type. This relationship is illustrated in Figure 3-11 (A-C) for Big Dam West Lake measurements made over water in mid August. In this example it was also apparent that mercury evasion was also influenced by wind speed. Maximum measured flux from the water surface at Big Dam Lake on August 12 (6.2 ng/m²/hr) was only a fraction of the flux measured the previous day (43.8 ng/m²/hr) even though air and water (not shown) temperatures and solar insolation were similar. The difference between these 2 days was primarily in the much lower wind speeds on Aug 12 compared to the previous day. It is possible that mercury evasion is lower on calm days due to the rapid loss and depletion of dissolved gaseous mercury in the surface micro layer of the lake. It is speculated that increased winds leads to greater mixing in the surface layer of the lake. This exposes more organic mercury from the overall mercury reservoir beneath the lake surface layer which can be photoreduced to dissolved gaseous mercury (DGM) for eventual evasion.

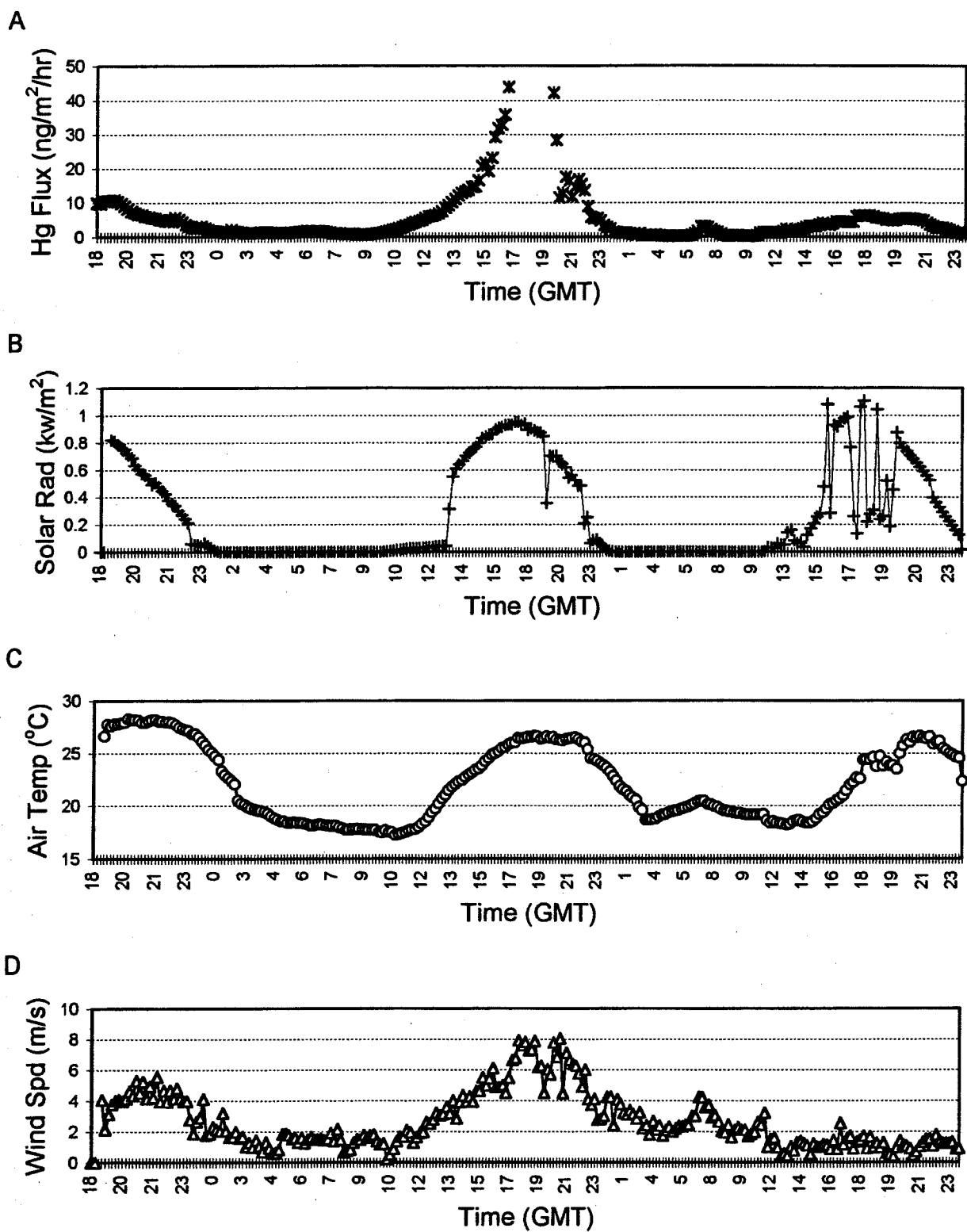


Figure 3-11: Mercury flux (A), solar radiation (B), air temperature (C) and wind speed (D) over water at Big Dam West Lake from August 10-12, 1997.

Colored lakes tend to have more total mercury available for photoreduction which may account for higher fluxes measured in Big Dam West Lake. Big Dam West Lake is highly colored by dissolved organic (humic) compounds (DOC) which bind with metals including mercury. North Cranberry Lake has clearer water and comparatively lower DOC.

Although the mercury air-water and air-soil exchange results are preliminary in nature and based on a limited data set, it appears that terrestrial and aquatic systems are dynamic in terms of the movement of mercury. Mercury flux can vary widely between sites even within the same watershed if soils or surface waters have different physical or chemical characteristics. Within a site there are large diurnal differences in the direction and magnitude of mercury exchange between the surface and the atmosphere as well as large differences from day to day or seasonally depending on meteorological factors. Knowledge of the spatial and temporal variability in factors affecting flux, some of which are discussed above, are limited in scope. More needs to be done on speciation of mercury in various compartments as well as interactions with other physical and chemical characteristics (e.g. ozone).

4.0 Conclusions

In the 2 year study period thus completed, increased knowledge of spatial and temporal distribution of TGM has been obtained. TGM concentrations in the Atlantic region are close but somewhat greater than the global average of 1.5 ng/m^3 yet are similar to concentrations elsewhere in eastern North America. Differences between sites exist with one of the main differences being a strong diurnal cycle in TGM at the Kejimikujik National Park site during the summer months.

In addition to TGM concentrations at the surface, data collected during RACE (96) indicate that TGM concentrations are relatively constant throughout the planetary boundary layer (PBL) and the free troposphere. This means that there is a large atmospheric reservoir of mercury.

Seasonal transport patterns for TGM vary year to year and more data is required before consistent patterns are discernible over the annual cycle. However, there is empirical data which indicates that many possible sources contribute to TGM levels in the Atlantic region from local sources to LRTAP from North American and European source regions. The relative influence of these different sources may vary seasonally and the precise magnitude of the contributions from the various regions cannot be determined from these data.

In some cases elevated TGM levels have been associated with natural events as in the case of forest fires in Quebec. Other periods of elevated TGM appear similar in nature to pollution episodes associated with elevated ground level ozone which are largely anthropogenic in origin and have been closely associated with long range transport of air pollutants (LRTAP) from industrial emission source regions in Canada and the northeastern US. The association between elevated TGM and other anthropogenic pollutants needs further investigation. In addition to LRTAP, it is possible that inter-provincial transport of TGM from sources within the Atlantic region may be occurring.

With respect to the question of anthropogenic vs. natural sources of mercury in the atmosphere, it can be said that both are sources of mercury emissions but their relative contributions to the atmosphere and the receiving environment cannot be quantified.

Little is known about particulate mercury in the region and efforts should be made to measure this form of mercury. Also little is known about mercury speciation in air in any phase.

Studies have been initiated which examines exchange processes between the atmosphere and the surface. Mercury deposition via precipitation has been quantified for one full annual cycle and, like TGM concentrations, total mercury concentration in precipitation and mercury wet deposition are similar in magnitude to other sites in eastern North America. Mercury concentration and wet deposition are greatest in the summer and lowest in the winter.

Mercury deposition via precipitation is only one exchange mechanism between the atmosphere and the surface. Mercury is volatile and evasion can occur in addition to deposition. Preliminary studies at Kejimikujik in the summer of 1997 indicated that gas exchange occurs over both soil and water surfaces. Depositional fluxes were very small compared to evasion from these surfaces although the method used may not fully quantify depositional processes. Evasion over water tended to be substantially larger than evasion from soils especially where the water was high in dissolved organic matter (DOM). Evasion from soils and water were correlated with solar insolation, temperature and wind speed. These measurements indicated that flux is important in overall mercury dynamics and additional research is required to better understand spatial and temporal variability in flux and factors regulating this process. The goal of closing a watershed mass balance will require more experiments over soils, lakes, wetlands and vegetation and a strategy to scale various process. Temporal and spatial scaling is a major problem which needs to be addressed and model developers need to be consulted in all phases of this work.

Although TGM and mercury in precipitation have been addressed in part, there are no measurements of particulate mercury in the region nor have there been adequate assessments of mercury speciation in any of the 3 phases in which mercury is found in the atmosphere. The lack of particulate mercury data introduces uncertainty into estimates of dry deposition. The absence of data concerning mercury speciation makes

the understanding of exchange processes more difficult. Both of these can affect the accuracy and precision of model output. Transformation process for mercury in air including physical and chemical interactions with other compounds which affect environmental pathways are also largely unknown.

Atmospheric research and monitoring to date has largely been focused at natural, regionally representative sites. There remains a lack knowledge concerning emissions from contaminated sites such as mine tailings landfills or at the tailpipe and smokestack.

In spite of these shortcomings it is time to begin to construct an integrated (ecosystem) mercury model starting by building a framework and filling in the blanks. Models will be an integral tool for predicting how the atmosphere will respond to emission controls and how these changes will manifest themselves at the ecosystem level.

5.0 Recommendations

- * continue measurements of TGM concentrations
- * continue measurements of total mercury in precipitation
- * continue estimates of mercury wet deposition.
- * initiate measurements of particulate mercury.
- * design/implement studies of mercury speciation in all 3 phases.
- * design/implement experimental studies to determine interactions of mercury with other chemical compounds.
- * expand aircraft based studies of mercury distribution and interactions in the atmosphere.
- * expand spatial and temporal data set of mercury flux over soils and water.
- * expand mercury flux measurements to contaminated sites.
- * examine mercury flux in coastal marine systems (with DFO).
- * continue development of mercury transport/transformation models.
- * gauge streams at Big Dam and North Cranberry for mass balance work.

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