Chapter 9
Spatial Coverage and Temporal Trends of Land-based Atmospheric Mercury Measurements in the Northern and Southern Hemispheres

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Summary This chapter presents a review of atmospheric mercury measurements (as total and as speciated mercury) conducted at terrestrial sites during the last decade. A large number of activities have been carried out in different regions of the world aiming to assess the level of mercury in ambient air and precipitation, and its variation over time and with changing meteorological conditions. Recent studies have highlighted that in fast developing countries (i.e., China, India) mercury emissions are increasing in a dramatic fashion due primarily to a sharp increase in energy production from the combustion of coal (Chapter 2 by Street et al.; Chapter 3 by Feng et al. in this report). The large increase in mercury emissions in China over the last decade are not currently reflected in the long-term measurement of total gaseous mercury at Mace Head, Ireland between 1996 to 2006, nor in the precipitation data of the North American Mercury Deposition Network (MDN). There are documented recent increases in the oxidation potential of the atmosphere which might account, at least in part, for the discrepancy between observed gaseous mercury concentrations (steady or decreasing) and global mercury emission inventories (increasing). This chapter provides a detailed overview of atmospheric measurements performed at industrial, remote and rural sites during the last decade with reference to the monitoring techniques and location of monitoring sites in most of the continents.

9.1 Introduction

This chapter provides up to date information of currently available data of mercury concentrations (as total and as speciated mercury) observed at terrestrial sites. As elemental mercury is a semi-volatile contaminant it continuously cycles between the atmosphere, ocean and soil. The biogeochemical cycling can be

N. Pirrone and R. Mason (eds.), *Mercury Fate and Transport in the Global Atmosphere*, DOI: 10.1007/978-0-387-93958-2_9, © Springer Science + Business Media, LLC 2009

affected by natural and anthropogenic variables and forcing. Mercury is emitted into the atmosphere from a variety of anthropogenic (e.g. power generation facilities, smelters, cement production, waste incineration and many others) (Pirrone et al., 1996; Pirrone et al. 1998; Pirrone et al., 2001) and natural sources (e.g., volcanoes, crustal degassing, oceans) in different chemical and physical forms (Pacyna et al., 2001; Carpi, 1997). Its cycling between different environmental compartments depends on the rate of different chemical and physical mechanisms (i.e., dry deposition, wet scavenging) and meteorological conditions which affect its fate in the global environment. Both source categories, i.e. anthropogenic and natural, contribute to the global atmospheric pool. It has been suggested that due to intensified anthropogenic release of mercury into the atmosphere since the beginning of industrialization this global pool has increased in the past 150 years. Evidence of long-term changes in the atmospheric mercury burden can be derived from chemical analysis of lake sediments, ice cores and peat deposits (Engstrom and Swain, 1997; Bindler et al., 2001; Biester et al., 2002; Lamborg et al., 2002). A growing number of these records from both hemispheres demonstrate about a threefold increase of mercury deposition since pre-industrial times (Lindberg et al., 2007 and references therein).

In principle, an increase in the global atmospheric pool should also be reflected in the background concentration. Since first reliable measurement data were published about 3 decades ago it is extremely difficult to derive a multidecadal global trend estimate based on these spatially and temporally inchoate air concentration data sets. For example, Asian mercury emissions are suggested to be rapidly increasing at least in the past decade however, this is neither reflected in the long-term measurement of TGM at Mace Head, Ireland covering the period between 1996 to 2006, nor in the precipitation data of the North American Mercury Deposition Network (MDN) (Lindberg et al., 2007 and reference therein).

In 1995, Fitzgerald argued for and defined the basic requirements of an Atmospheric Mercury Network (AMNET). This has partly been accomplished on a regional scale within the Canadian Atmospheric Mercury Network (CAMNet) that may be considered as seminal in this respect. Nevertheless, although atmospheric Hg monitoring stations have increased, the database is sparse, especially in remote locations. Fully aware of these constraints, Slemr et al. (2003) attempted to reconstruct the worldwide trend of atmospheric Hg (TGM) concentrations from long-term measurements of known documented quality at 6 sites in the Northern Hemisphere, 2 sites in the Southern Hemisphere, and multiple ship cruises over the Atlantic Ocean made since 1977. The authors interpreted this information to suggest that the TGM concentrations in the global atmosphere had been increasing since the first measurements in 1977 to a maximum in the late 1980s, after which Hg concentrations decreased to a minimum in 1996 and then remained constant at a level of about 1.7 ng m^{-3} in the Northern Hemisphere. It was also hypothesized that the observed temporal profile was primarily the result of the trends in global Hg use, supply, and emissions.

Lindberg et al. (2007) have pointed out a number of reasons to support the null hypothesis (i.e., there has been little change in TGM since 1977). If one particular monitoring station would be excluded from the evaluation then the data suggest there has been little change in TGM levels in the atmosphere between 1977 and 2002. Additional support for the null hypothesis is provided by TGM measurements for the Southern Hemisphere. TGM results for the Southern Hemisphere do not suggest that there has been much change in TGM levels in the global remote atmosphere over the past 25–30 years. Although it may appear that these competing hypotheses on atmospheric TGM levels in recent times would be disconcerting, this situation is not unusual and often aids the development of research strategies. For example, the value of long-term atmospheric Hg monitoring stations and the need for additional sites is obvious, especially in the remote Southern Hemisphere (Lindberg et al., 2007).

General scientific consensus exists about the current global background concentration that refers to the average sea-level atmospheric Hg^0 at remote sites. The background concentration is currently taken as ca. 1.5 to 1.7 ng m^{-3} in the Northern Hemisphere and ca. 1.1 to 1.3 ng m^{-3} in the Southern Hemisphere (Lindberg et al., 2007).

9.1.1 Quality of Data / Field Intercomparisons

Field intercomparisons of atmospheric mercury measurements have been carried out at different locations and with different objectives:

- an intercomparison at Windsor, ON, an urban site in Canada mainly focussing on the comparability of classical manual methods with newly available automated analysers (Schroeder et al., 1995)
- an intercomparison at Mace Head, a marine background site in Ireland including a comprehensive set of coeval methods for the analysis of different mercury species in air and precipitation (Ebinghaus et al., 1999)
- an intercomparison at Sassetta, a rural site in Tuscany, Italy mainly focussing on the comparability of novel techniques for atmospheric mercury species (Munthe et al., 2001)

All 3 intercomparison exercises have revealed that the measured concentrations of TGM showed good agreement between the participating laboratories. At Mace Head it was additionally demonstrated that the comparability of total mercury concentrations in precipitation was satisfactory as well.

During the Mace Head and the Sassetta intercomparisons it could furthermore be shown, that much higher differences are involved when atmospheric mercury species (namely RGM and TPM) are measured however, it was also demonstrated that the repeatability of similar methodologies increased over time. One major conclusion derived from these studies is that good agreement of TGM concentrations in air determined with different techniques, including manual techniques dating back to the 1970s, makes a combination of data sets from different regions of the world feasible (Ebinghaus et al., 1999).

9.2 Measurements of Air Concentrations in North America

9.2.1 Measurements of Air Concentrations in Canada

Currently, most measurements of gaseous atmospheric Hg in Canada are made using a Tekran 2537A Mercury Vapour Analyser (Tekran Inc., Toronto). This instrument concentrates gaseous phase Hg by amalgamation onto gold cartridges, with subsequent thermal desorption and detection of Hg^0 by cold vapour atomic fluorescence spectrophotometry (CVAFS). This automated measurement system compares well with other manual methods operating on the same principal, commonly used to measure atmospheric Hg (Ebinghaus et al. 1999). A Standard Operating Procedure for detection of TGM in ambient air is available (Steffen & Schroeder 1999). The unit used in Canada to express the concentration of mercury measured by this technique is nanograms per standard cubic metre of air, abbreviated ng m^{-3}, where the volume referred to is at the standard temperature and pressure of 0 °C and 1 atm. The Tekran analysers are operated between a 5 and 30 minute integrated sampling interval, dependent on the site.

Definitions: Hg^0: Gaseous Elemental Mercury, RGM: Reactive Gaseous Mercury, i.e. non-elemental gas phase mercury, PM: mercury bound to particles, MDN: mercury in precipitation (mercury deposition network, only wet deposition measured at this time). The above is the coarsest level of "speciation" that we currently work with. TGM: Total Gaseous Mercury.

9.2.1.1 Remote Locations

Much of the area of Canada is remote from anthropogenic mercury sources. Several of the network sites, described in Sections 9.2.4 below, are situated in remote locations, called background sites; measurements are made at these sites to characterize the mercury present in the atmospheric environment far from anthropogenic inputs. In addition to the network sites and the far Arctic site in Alert, measurements have been made at the two additional sites in remote locations, Kuujjuarapik and Mingan.

9.2.1.2 Urban Locations (Including Mining Areas)

During a brief study in summer 2000, the levels of TGM were measured at two locations in downtown Toronto. The TGM concentrations ranged from 1.3 to 50 ng m^{-3}, with values >3 ng m^{-3} seen more frequently than in rural areas. Local sources affect the urban sites with short periods of high air Hg concentrations. More frequent observations of high concentration episodes of Hg in precipitation (>20 ng L^{-1}) were found at sites closer to urban centres, e.g., Reifel Island which is close to Vancouver, Egbert in close proximity to Toronto and Barrie, and St. Anicet which is close to Montreal, than at more remote locations, e.g., Mingan, Cormak and Kejimkujik Park . The increased anthropogenic activity associated with highly populated areas may result in increased air concentrations of RGM and PM which can be more readily incorporated into cloud water and precipitation, as will be discussed below. The Banic et al. (2003) sampling flight compared the TGM in the urban plume from Montreal to the ambient concentrations; concentrations in the urban plume reached 2.5 ng m^{-3} compared with the ambient background of 1.5 ng m^{-3}. The urban plume was observed at altitudes up to 1.25 km.

The TGM concentration was monitored at 2 mine tailing sites in eastern Nova Scotia, Canada (Beauchamp et. al. 2002). The Caribou Mines and Goldenville tailing sites are remnants of gold mining activities which began in the mid 1800's and continued up to the late 1930's. The gold bearing ore was brought to the surface and crushed in stamp mills located on site then gold was extracted using the mercury amalgamation process. Mercury contaminated tailings were then disposed of in lakes and ponds which now form flat expanses of tailings with surface areas up to a square kilometre and depths up to several meters. The concentrations of TGM in near surface ambient air (10 cm above the mine tailings) at the Goldenville site remained above 2 ng m^{-3} throughout the diurnal cycle reaching a maximum 8.1 ng m^{-3} with a 24 hour average concentration of 3.5 ng m^{-3}. Gaseous elemental mercury concentrations in ambient air at the same height above the Caribou Mine tailings averaged 8.4 ng m^{-3} with minimum and maximum concentrations of 3.2 and 23.0 ng m^{-3}, respectively. Ambient TGM concentrations over legacy gold mine tailings remained well above regionally representative background ambient air concentrations of 1.5 ng m^{-3}. Additionally, measurements of air-surface exchange of mercury from tailings from legacy gold mine activity in Nova Scotia which used mercury amalgamation processes have shown emissions 2 orders of magnitude higher than those observed from undisturbed sites.

9.2.1.3 Temporal Trends at Single Locations

In an example of a model study of processes the comparison of the measured concentrations and simulated Hg concentrations (GRAHM model from Dastoor & 2004) are shown for the CAMNet site Egbert. In this study the natural emissions and re-emissions of Hg were set to zero and the anthropogenic emissions were set to a constant rate throughout the year. The meteorology and surface characteristics varied with season (i.e., seasonal circulation patterns and the seasonal cycles in the boundary layer heights, clouds, precipitation and dry deposition characteristics). The results show the extent to which seasonal variation in the TGM concentrations can be driven by meteorological differences

9.2.1.4 Monitoring Networks and Trends

The Canadian Atmospheric Mercury Measurement Network (CAMNet, www.msc.ec.gc.ca/ arqp/ camnet_e.cfm) was established in 1996 to provide accurate, long-term measurements of TGM concentration and the Hg deposition in precipitation (wet deposition) across Canada. A map of the CAMNet sites is shown in Figure 9.1.

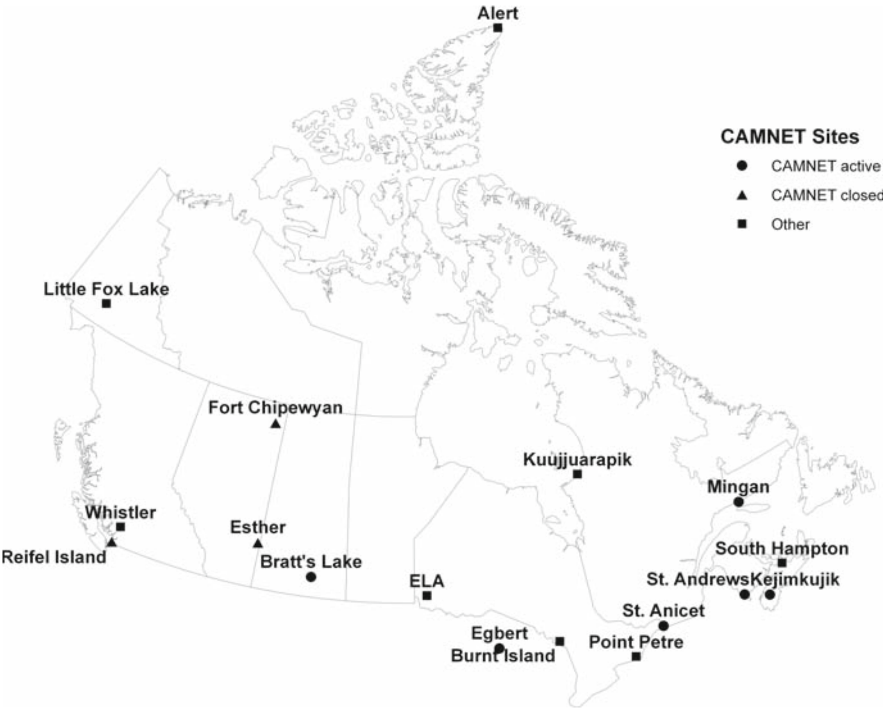


Figure 9.1 Sites in the Canadian Atmospheric Mercury Measurement Network (CAMNet)

The mid-latitude sites will be discussed here, with the Arctic site Alert discussed elsewhere because of different behaviour. The mid-latitude sites are located in background or rural areas, with the latter occasionally impacted by emissions from urban areas. Wet deposition is measured at the CAMNet sites as part of the Mercury Deposition Network (MDN), which includes sites in the United States, Canada and Mexico (http://nadp.sws.uiuc.edu/mdn/). The sampling and analytical methods adhere to the CAMNet Standard Operating Procedure and the USA- National Atmospheric Deposition Network (NADP)-MDN sampling protocol.

An overall average median atmospheric concentration for TGM of 1.60 ± 0.15 ng m^{-3} for the ten Canadian sites was calculated for the years 1997-1999 by averaging together the site medians (Kellerhals et al. 2003). Higher variability of TGM concentrations at the sites in closer proximity to large urban areas appeared to be caused by the alternating exposure of these sites to anthropogenic TGM emissions, depending on wind direction and atmospheric mixing.

Kellerhals et al. (2003) observed that a slight seasonal trend for TGM was seen with higher concentrations observed in winter and spring, and lower concentrations in summer and fall. This is further demonstrated for all years of CAMNet data in Table 9.1. Several factors might contribute to this behaviour (Blanchard et al., 2002), including differences in meteorological conditions and scavenging processes between

Table 9.1 Characteristics of the sampling sites and time periods for the Canadian atmospheric sampling sites

Station	Code	Province	Latitude *(deg)*	Longitude *(deg)*	Altitude (*m* a.s.l.)	Period
Alert	ALT	NU	82.50	-62.33	210	01/95-12/05
Kejimkujik	KEJ	NS	44.43	-65.21	127	01/96-12/04
St. Andrews	STA	NB	45.09	-67.08	80	01/96-12/04
St. Anicet	WBZ	QC	45.12	-74.28	49	01/97-12/05
Point Petre	PPT	ON	43.84	-77.15	75	11/96-12/05
Egbert	EGB	ON	44.23	-79.78	251	12/96-12/05
Burnt Island	BNT	ON	45.81	-82.95	75	05/98-12/05
Bratt's Lake	BRL	SK	50.20	-104.72	577	05/01-12/05
Esther	EST	AB	51.67	-110.20	707	06/98-04/01
Fort Chipewyan	FCH	AB	58.78	-111.12	232	06/00-07/01
Reifel Island	RFL	BO	49.10	-123.17	2	03/99-02/04

a.s.l. above sea level

summer and winter (e.g., reduced mixing heights and higher wind speeds in winter, increased oxidation and larger removal from the atmosphere by wet and dry deposition during warmer months). The seasonal variability observed at the surface will be influenced by changes in the total atmospheric column burden of Hg^0.

Seven of the 10 CAMNet sites experienced a cycle of maximum concentrations near solar noon (1000 to 1400 local standard time (LST)) and minimum concentrations in the early morning hours (0300 to 0700 LST) (Kellerhals et al. 2003). The cycle at the CAMNet sites was attributed to nighttime depletion of TGM in the lowermost atmosphere. Overnight a shallow TGM-depleted layer is formed in the nocturnal inversion layer. Shortly after sunrise there is a rapid increase in near-surface TGM concentration as the nocturnal inversion breaks down and undepleted air is mixed down to the surface. The continued increase in TGM concentration through the morning and into the early afternoon is likely caused by emission of TGM from the surface, which has been observed to increase with increasing solar radiation (Poissant & Casimir 1998).

Long-term monitoring data TGM concentrations from 11 CAMNet sites between 1995 and 2005 were analysed for temporal trends, seasonality and comparability within the network. A statistically significant decreasing trend for TGM concentrations at several rural CAMNet sites was seen for the time period 1995 to 2005 (Table 9.2). The largest declines were observed close to the urban areas of Toronto and Montreal, where levels fell by 17% at Point Petre, and 13% at St. Anicet, respectively. Many of the TGM changes are comparable with the overall trends of total mercury concentrations in precipitation, for similar time periods, at collocated or nearby National Atmospheric Deposition Program's Mercury Deposition Network (NADP-MDN) sites. Results show that these changes are mostly driven by local or regional changes in mercury emissions. Other sites within CAMNet reflect reported changes in hemispherical global background concentrations of airborne mercury, where slight decreases or no statistically significant trend in TGM concentrations exist over the same time period.

Table 9.2 Statistical summary of TGM measurements at CAMNet sites

Station	Days (#)	Mean *(ng m^{-3})*	Median *(ng m^{-3})*	Min *(ng m^{-3})*	Max *(ng m^{-3})*	Lower quartile *(ng m^{-3})*	Upper quartile *(ng m^{-3})*	SD *(ng m^{-3})*
Alert	3603	1.55	1.58	0.03	3.12	1.45	1.73	0.37
Kejimkujik	3168	1.45	1.46	0.54	2.30	1.31	1.59	0.21
St. Andrews	2774	1.42	1.40	0.74	2.46	1.26	1.57	0.23
St.Anicet	3164	1.64	1.60	0.92	16.31	1.44	1.79	0.40
Point Petre	3275	1.78	1.73	0.80	4.26	1.55	1.93	0.34
Egbert	3207	1.67	1.66	0.95	6.90	1.50	1.80	0.27
Burnt Island	2680	1.58	1.58	0.99	2.48	1.43	1.72	0.21
Bratt’s Lake	1424	1.53	1.52	0.79	2.68	1.38	1.64	0.24
Esther	878	1.65	1.65	1.19	2.14	1.54	1.75	0.15
Fort Chipewyan	305	1.36	1.35	0.95	1.77	1.28	1.47	0.15
Reifel Island	1642	1.67	1.67	0.91	2.92	1.56	1.79	0.19
Category (median of stations)								
R-W	2612	1.60	1.60	0.91	2.56	1.48	1.71	0.20
R-E	3263	1.43	1.43	0.88	2.09	1.31	1.56	0.19
R-A	3342	1.68	1.67	1.11	2.99	1.52	1.81	0.22
R-C	2680	1.58	1.58	0.99	2.48	1.43	1.72	0.21
ALL	3959	1.58	1.58	0.21	2.75	1.48	1.68	0.17

R-W = RURAL-WEST (RFL, EST, FCH, BRL);
R-E = RURAL-EAST (KEI, STA);
R-A= RURAL-AFFECTED (WBZ, PPT, EGB);
R-C= RURAL-CENTRAL (BNT)

The following statistical analysis was applied using available daily averaged TGM concentrations from all sites. The application of a seasonal decomposition method was used to isolate a long-term systematic trend, regular seasonal effects, perennial irregular (or cyclical) variations and remaining uncertainties. Detailed information about seasonal decomposition can be found in Temme et al. (2004). This method was performed for all sampling sites with a minimum of five complete years of observations. The regression coefficient and the linear slope were tested for significance using the T-test ($p<0.01$) and if $p>0.01$ then the correlation was marked as non-significant. Daily averages from the year 2000 were chosen for Principal Component Analysis (PCA) because that year offered the most complete spatial information, i.e. data from most stations were available for 2000. Bratt’s Lake is the only CAMNet site which started its measurements after 2000 and is not included in the PCA. The first two principal components explained more than 50% of the total variance in terms of the spatial differences. The components reflect the seasonality in the annual data (factor 1) and the influence of local sources, which can include anthropogenic, natural or re-emission from water surfaces (factor 2). Analysis isolated the sites expected to be most significantly impacted by nearby sources in the Great Lakes Basin and St. Lawrence River Valley (rural-affected sites). Sites were also divided into eastern (RURAL-EAST) and western sites (RURAL-WEST).

The RURAL-AFFECTED category shows the highest overall median TGM concentration (1.67 ng m^{-3}) and the highest variability of all categories for the entire time period. The three corresponding sites Point Petre, Egbert and St. Anicet also showed substantially higher maximum concentrations (4.26 ng m^{-3}, 6.90 ng m^{-3}, 16.31 ng m^{-3} respectively) than all the other sites. Both the categories RURAL-WEST (RFL, EST, FCH, BRL) and RURAL-AFFECTED (WBZ, PPT, EGB) reveal significantly higher overall median concentrations than the RURAL-EAST (KEJ, STA), RURAL-CENTRAL (BNT).

TGM concentrations at all the CAMNet sites (mean = 1.58 ng m^{-3}) were similar to or slightly lower than those observed at European background sites within a comparable time frame. Seasonal variations of TGM concentrations are observed for all sites. Most sites show higher concentrations in winter and spring, and lower concentrations in summer and fall, which is reflected in the corresponding summer/winter (SUM/WIN) and spring/autumn (SPR/AUT) ratios for each station and category. The time series at Fort Chipewyan does not include enough data to support any conclusions about seasonality. The exception to these findings is observed at Point Petre where the SUM/WIN ratio is > 1; although not statistically significant at Point Petre. The differences between summer and winter median concentration ratios are the highest at the RURAL-EAST (SUM/WIN = 0.88) and RURAL-CENTRAL (SUM/WIN = 0.85) sites where a minimum monthly median TGM concentration was observed in September and a maximum in February.

9.2.1.4.1 Trend Analysis

The seasonal decomposition technique was applied to the original daily averages. The same procedure was applied to all other sites and categories containing a minimum of 5 complete years of observations. For sites (e.g. RURAL-WEST) where less than 5 years of data were available, a simple linear regression was applied to the original time series. The resulting overall and annual rates of change in mercury concentration after seasonal decomposition and linear regression are listed in Table 9.3. Missing data in the time series were replaced by interpolation prior to time series analysis. Therefore the number of days in Table 9.3 often exceeds the number of reported daily averages in Table 9.2. Inter-annual and overall changes are given in ng m^{-3} absolute and as a percentage in respect to the starting intercept, respectively. Statistically significant regression coefficients and slopes, i.e. slope and regression coefficients that were significantly different from 0 ($p<0.01$) are indicated in the last column. Sites are marked with an asterisk when seasonal decomposition was not done or the results were uncertain. Trends for the shorter and sometimes incomplete time series for the individual RURAL-WEST sites can not be determined with the same significance as the other sites and were also marked with an asterisk. This also leads to an uncertain overall change for this category. However these time series were incorporated into the "ALL" category.

From the data considered valid within the constraints of the seasonal decomposition and data coverage, five sites showed significant decreases (between −2.2% and −16.6%) in the TGM concentrations over the corresponding time period. The only exception was the slight positive trend at Kejimkujik where an overall +3.3% change is evident between 1996 and 2004. For the first time since continuous automated

Table 9.3 Results from trend analysis after seasonal decomposition

St.	Start *(dd-mm-yy)*	End *(dd-mm-yy)*	Days *(#)*	Intercept *(ng* m^{-3}*)*	Slope *(ng* m^{-3} d^{-1}*)*	Change *(ng* m^{-3} y^{-1}*)*	Change *(% year*$^{-1}$*)*	Change *(ng* m^{-3}*)*	Change *(% overall)*	Signif. ($p<0.01$)
ALT	01-01-1995	31-12-2005	4009	1.58	-0.0000136	-0.0049640	-0.31	-0.05	-3.5	n.s.
KEJ	01-01-1996	31-12-2004	3287	1.43	0.0000144	0.0052560	0.37	0.05	3.3	Yes
STA	01-01-1996	31-12-2004	3288	1.49	-0.0000333	-0.0121545	-0.82	-0.11	-7.4	Yes
WBZ	01 -01-1997	31-12-2005	3286	1.75	-0.0000698	-0.0254770	-1.46	-0.23	-13.1	Yes
PPT	11-05-1996	31-12-2005	3340	2.02	-0.0001000	-0.0365000	-1.81	-0.33	-16.6	Yes
EGB	30-11-1996	31-12-2005	3318	1.69	-0.0000111	-0.0040515	-0.24	-0.04	-2.2	yes
BNT	05-01-1998	31-12-2005	2800	1.62	-0.0000296	-0.0108040	-0.67	-0.08	-5.1	yes
BRL	05-02-2001	31-12-2005	1702							
EST	26-06-1998	22-04-2001	1032							
FCH	17-06-2000	19-07-2001	398							
RFL	03-03-1999	02-11-2004	1807							
R-W	26-06-1998	31-12-2005	2745	1.71	-0.0000755	-0.0275575	-1.61	-0.21	-12.1	n.s.
R-E	01-01-1996	31-12-2004	3288	1.47	-0.0000195	-0.00711750	-0.49	-0.06	-4.4	yes
R-A	11-05-1996	31-12-2005	3343	1.77	-0.0000550	-0.0200750	-1.13	-0.18	-10.4	yes
R-R	05-01-1998	31-12-2005	2800	1.62	-0.0000296	-0.010804	-0.67	-0.08	-5.1	yes
ALL	01-01-1995	31-12-2005	4009	1.61	-0.0000151	-0.0055115	-0.34	-0.06	-3.8	yes

n.s. = not significant, seasonal decomposition not possible (less than 5 years of observations) or questionable
R-W = RURAL-WEST (RFL, EST, FCH, BRL);
R-E = RURAL-EAST (KEI, STA);
R-A = RURAL-AFFECTED (WBZ, PPT, EGB);
R-R = RURAL REMOTE (BNT).

TGM measurements were initiated in North America, Asia and Europe (Kock et al., 2005, Kim et al., 2005), this paper reveals a statistically significant decreasing trend of TGM concentrations from rural locations in Canada between 1995 and 2005. This decreasing trend can be seen with differing intensity at nearly all CAMNet sites and categories, indicating a large spatial distribution of this overall decrease.

9.2.1.4.2 Comparison Between Air Data and Wet Deposition of Mercury in North America

The NADP-MDN network has been operating since 1996 (http://nadp.sws.uiuc.edu/mdn/), with measurements made in Canada as part of CAMNet. The trends of mercury concentration in precipitation from these sites were analyzed using the non-parametric Seasonal Kendall Trend Test (Gilbert, 1987). At the sites that are co-located with, or located in areas near, the CAMNet sites, decreasing trends in MDN concentrations were generally found although there are numerous sites with no statistical significant trends.

Comparisons of the TGM trends and the precipitation concentration trends were made at 4 Canadian sites (St. Andrews, Kejimkujik, St. Anicet and Egbert with site codes NB02, NS01, PQ04 and ON07, respectively) where collocation of TGM and MDN measurements occurs (see Table 9.4). At Kejimkujik where 9 years of MDN data have been collected, concentrations of mercury in precipitation are strongly decreasing (-17.7% overall) whereas TGM is increasing during the same time period (+3.3% overall). At St. Andrews where 7 years of MDN data have been collected, both Hg in precipitation (-13.4%) and TGM (-7.4%) are decreasing. At Egbert, TGM is decreasing slowly, but the co-located and closest MDN sites show no significant change. The co-located MDN site at St. Anicet and nearby MDN stations show good agreement between both the annual and total changes over an 8-year period. St. Anicet has large TGM annual decreases at about -1.5%/year, while three area MDN locations show similar annual changes of between -1.5 to -1.8%. At the other CAMNet sites, there is no co-location with MDN (Burnt Island and Point Petre, Fort Chipewyan) or a data record of less than 5 years (Reifel Island, Bratt's Lake and Esther).

For the MDN sites used in this comparison with significant trends observed (as listed in Table 9.4), the averaged trend is -0.15 ng L^{-1} yr^{-1}. Applying this averaged trend over 10 years (i.e. 1996-2005), with a median total mercury concentration in precipitation of 10 ng L^{-1} (as observed for this time period for these sites), leads to an approximate change of -15%. This observed change in mercury concentration in precipitation is in good agreement with the individual trends in TGM concentrations observed near the major urban areas of Toronto (Point Petre) and Montreal (St. Anicet) for nearly the same time period. We conclude that this agreement indicates that the changes at these stations are most likely driven by local or regional changes in mercury emissions.

In general, the concentration of mercury in precipitation is decreasing at many MDN sites used for comparison in this paper, just as is the TGM at most CAMNet sites. However, some significant differences do exist, particularly at Kejimkujik. At the Canadian MDN sites, the seasonality of Hg concentration in precipitation exhibits an opposite pattern to TGM air concentrations with higher concentrations during the summer months. Two possible factors have been suggested for this seasonal behaviour: increased particle scavenging capacity of rain relative to snow and/or an increase in the oxidation of Hg^0, either in cloud or in the gas phase, during the summer.

Generally, the levels of Hg in precipitation at rural sites in Canada are less than 30 ng L^{-1}, similar to levels observed at border sites in the United States. The lowest median Hg concentrations at the CAMNet sites were found at Cormak (spring, summer, fall and winter concentrations at 4.6, 6.8, 3.0 and 2.9 ng L^{-1}, respectively) and Mingan (summer and winter at 6.6 and 2.9 ng L^{-1}, respectively). Median Hg concentrations in precipitation were higher in the west than in the east in all four seasons. However, sites with the highest observed concentrations do not necessarily have the highest Hg deposition per unit surface area. The deposition is dependent on the precipitation amount as well as on the concentration of Hg in the precipitation. The highest median weekly Hg deposition measured at the Canadian sites on a seasonal basis was at Kejimkujik Park in spring, fall and winter (deposition of 0.120, 0.106 and 0.088 µg m^{-2} $week^{-1}$, respectively), and at St. Anicet in summer (0.166 µg m^{-2} $week^{-1}$). The lowest median weekly deposition was found at Bratt's Lake in the summer and fall (0.083 and 0.036 µg m^{-2} $week^{-1}$, respectively) and at Egbert in winter (0.027 µg m^{-2} $week^{-1}$). For the years 2000 to 2003, the annual wet deposition of mercury at the Canadian sites ranges from 1.9 to 7.9 µg m^{-2} yr^{-1} with the lowest deposition seen at Bratt's Lake and the highest at St. Anicet.

Temporal trends have been developed with the Digital Filtration (DF) technique of Nakazawa for Hg in precipitation at St. Andrews, St. Anicet, Mingan and Kejimkujik Park, each of which have more than 5 years of data. F-tests performed on trends derived by DF have indicated that all correlations are statistically significant with confidence limits of at least 95%. First order half-lives of decline ($t_{½}$) were estimated by dividing –ln 2 with the linearly regressed slope of the trend line (Table 9.5).

The half-life is the time required for the concentration or deposition to decline to half its original value and is estimated by assuming first order decline in concentration and deposition. No significant trends were found for the site of Mingan. From Table 9.5, it can be seen that for the three sites, it will require 14 to 22 years for the concentration of Hg in precipitation to decline to half its current value. However, it will only take ~10 to 13 years for the deposition amount to drop to half. This occurs because the annual precipitation rate has generally decreased between 1996 and 2003 at these locations. For all 3 sites, the r^2 for Hg concentration and deposition are approximately 0.4 and 0.5, respectively, with p-values less than 0.01.

Since Canadian measurements began in 1995, mercury levels in the air have shown only a slight decline throughout most of Canada. The greatest decline of airborne mercury in Canada occurred close to the major urban areas of Toronto and Montreal, where levels fell by about -10% between 1996 and 2005. The largest decreases in TGM were seen at Point Petre, on the north shore of Lake Ontario, near Toronto, where levels declined by -17% and at St. Anicet, near Montréal, where levels fell by -13%. This is in good agreement with the overall trend in total mercury concentrations in precipitation observed within the comparable NADP-MDN

Table 9.4 Summary of the trend statistics of total mercury concentrations in precipitation within the MDN network compared with the TGM changes within CAMNet

MDN Site	Total Change*(%)*	Annual Change*(%)*	Years		CAMNet site *(TGM)*	Total Change*(%)*	Annual Change*(%)*	Years
NB02	-13.4	-1.9	7	→	St. Andrews	-7.4	-0.83	9
NS01	-17.7	-2.0	9	→	Kejimkujik	3.3	0.37	9
ON07	n.s.		5	→	Egbert	-2.2	-0.04	9
PA30	n.s.							
ME02	-14.7	-1.8	8	→	St. Anicet	-13.1	-1.46	9
ME96	-13.9	-1.7	8					
PQ04	-12.1	-1.5	8					
ME09	n.s.							
ME98	n.s.							
NY20	-14.7	-2.5	6		Point Petre	-16.6	-1.81	9.5
PA90	-12.3	-1.4	9					
ON07	n.s.							
PA30	n.s.							
ON07	n.s.		5	→	Burnt Island	-5.1	-0.67	8
upwind	n.s.							
WA18	-9.7	-1.1	9	→	Reifel Island	-10	-2.03	6
	n.c.				Fort Chipewyan			
	n.c.				Bratt's Lake			
	n.c.				Esther			

notes: n.s. = not significant; n.c. = no comparison possible

Table 9.5 Half lives for decrease in Hg concentration and deposition in precipitation

	t½ (years)	
Sites	Hg concentration in precipitation	Hg deposition due to precipitation
St. Anicet (98-03)	15	9.9
St. Andrews (96-03)	14	7.0
Kejimkujik Park (96-03)	22	13

sites, indicating that these changes are most likely driven by local or regional changes in mercury emissions.

At other sites in rural eastern Canada decreases in TGM concentration up to -7% were seen, with one site, at Kejimkujik National Park in Nova Scotia, recording an increase of 3%. The data record for western Canada is shorter than others and, at times, incomplete. Therefore, a trend with time could not be determined with the same statistical significance as for the other locations. Most sites show higher TGM concentrations in winter and spring, and lower concentrations in summer and fall. It is suggested that the meteorological seasonal variability is the most important factor in the establishment of the observed seasonal cycles of the TGM concentrations. This is consistent with the latest modeling results. Nevertheless further investigations on photochemistry and correlation with meteorological parameters could provide further evidence.

9.2.1.5 Mercury Speciation Analysis

More recently, some sites within CAMNet have been measuring atmospheric Hg-species concentrations in addition to TGM. Reactive gaseous mercury (RGM) includes inorganic Hg compounds such as $HgCl_2$, $HgBr_2$, HgClBr and Hg^0. Current measurements in ambient air cannot distinguish one of these RGM species from another. Concentrations of organic forms of Hg, such as methylmercury or dimethylmercury, are very low in the atmosphere and are not measured in the gas phase, though some measurements have been made in precipitation. In Atlantic Canada, levels of methylmercury have been found to represent 1 to 2% of total Hg in precipitation (Tordon Unpub. Data 2005). Total gaseous mercury (TGM) is the Hg that is detected in particle-free air which has not been deliberately scrubbed of RGM. In most cases, RGM is lost by adsorption to the walls of the inlet system used for the measurement, but some RGM may be detected along with the Hg^0 and this total detected is the TGM.

The current method used consists of a denuder to collect RGM followed by a filter to collect the PM. An impactor which removes particles of aerodynamic diameter greater than 2.5 μm is used at the inlet of the denuder to remove particles in the size range which can be collected by the denuder. Keeler et al. (1995) have shown that the majority of PM is attached to fine particles. A detailed description of this technique is given in Landis et al. (2002). Briefly, a known volume of ambient air is drawn at a set flow rate of 10 L min^{-1} through the following series of collectors: an impactor inlet which removes particles >2.5 μm aerodynamic diameter, a KCl-coated annular denuder of quartz which collects RGM, and a quartz filter housed in a quartz tube which collects p-Hg of aerodynamic diameter <2.5 μm. The typical sample integration period is 2 hours. Analysis for Hg content is carried out by first releasing the Hg species from the collection medium (quartz filter or KCl coating of the denuder) with the medium still contained in the filter housing or denuder. The filter and denuder are heated at separate times (filter before denuder for an automatic integrated system) with a stream of Hg-free air flowing across the collection surface. The filter is heated to 800°C to release the Hg species that are on the filter and to decompose them to Hg^0; the denuder is heated to 500°C, releasing the Hg species from the KCl. The Hg^0 released by this process is collected and analyzed by the method described for Hg^0 above. The fully automated system is produced by Tekran™, Inc. (Model 1130/1135), which in addition to the process above, heats the particle filter to 800°C during the analysis for PM and RGM for complete decomposition of any Hg species eluted from the filter or denuder. There has been one intercomparison study to verify measurement techniques for RGM and PM. Preliminary results indicate significant variability and point to the need for more research (Aspmo et al., 2005).

Continuous measurements of RGM and PM have been made in Quebec, Nova Scotia and Ontario. Poissant et al. (2005) reported values of RGM: 3 ± 11 pg m^{-3} and PM: 26 ± 54 pg m^{-3} at St-Anicet. These values are similar to those found at Point Petre RGM: 5 ± 5 pg m^{-3} and PM: 6 ± 7 pg m^{-3} and at Sterling on the south shore of Lake Ontario, RGM: 6 ± 11 pg m^{-3} (Han, Holsen et al., 2004). Even though RGM and PM constitute a relatively small portion of total Hg in air (0.2 to 1.4%), an evaluation of their role in the atmosphere is essential to understanding the cycle of

Hg. Poissant et al. (2005) reported diurnal and seasonal cycles for both RGM and PM. Additional continuous measurements of RGM and PM are needed to fully assess the seasonality of these species. It should be noted that the values reported for RGM and PM are very often near the detection limit of the measurement method.

Cloud droplets scavenge particles from the air in the nucleation process, and cloud droplets and rain scavenge soluble gases such as RGM. Cloud water concentrations of total Hg were determined in a limited number of samples collected during the summer of 1995 in eastern Canada (Banic et al., 2003).

At the observed cloud liquid water contents in the clouds studied, the median value for the amount of Hg scavenged from the air by the cloud water was 0.02 ng m^{-3}. In south-eastern Canada, concentrations of RGM and p-Hg are near 5 pg m^{-3} and 10 pg m^{-3}, respectively, as given above, suggesting that much of the Hg seen in cloud water can be explained by in-cloud scavenging of these species. Atmospheric mercury speciation measurements consisting of Hg^0, RGM and PM began in January of 2006 in Halifax, Nova Scotia Canada (Figures 9.2–9.4). A summary of the ambient atmospheric mercury species concentrations is given in Table 9.6. The median concentration for Hg^0, RGM and PM were 1.67 ng m^{-3} (0.716 to 46.5 ng m^{-3}), 2.42 pg m^{-3} (detection limit (dl) to 140 pg m^{-3}), and 1.73 pg m^{-3} (dl to 30.8 pg m^{-3}), respectively. The median levels of RGM and PM were a small percentage of the TGM, 0.2% for RGM and 0.1% for PM.

9.2.1.6 Mercury Measurements (incl. air craft) Related to Emissions, and Source Attribution

In the mid- to late-1990s, measurements of Hg^0 were made in three locations in Canada at altitudes up to 7 km (Banic et al., 2003). The data show that, on average, Hg^0 shows a relatively constant distribution with altitude. In the summer in south-eastern

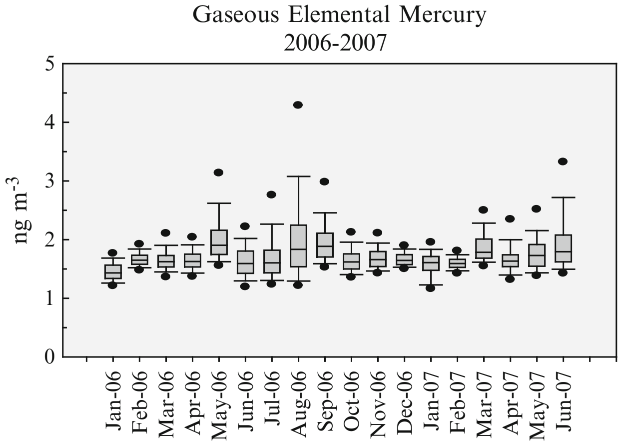


Figure 9.2 Monthly Box-whisker plot trends of Gaseous Elemental Mercury from 2006 and 2007 at Halifax (Nova Scotia, Canada)

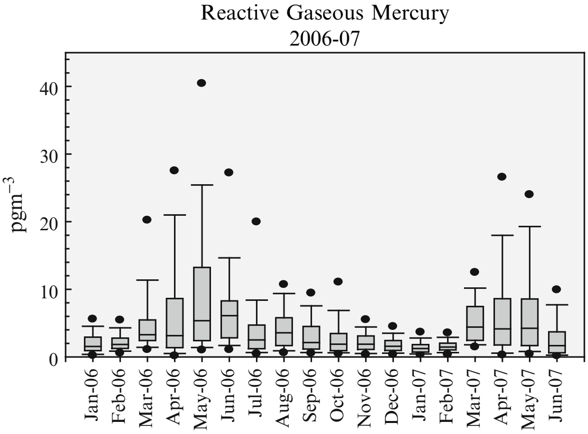


Figure 9.3 Monthly Box-whisker plot trends of Reactive Gaseous Mercury from 2006 and 2007 at Halifax (Nova Scotia, Canada)

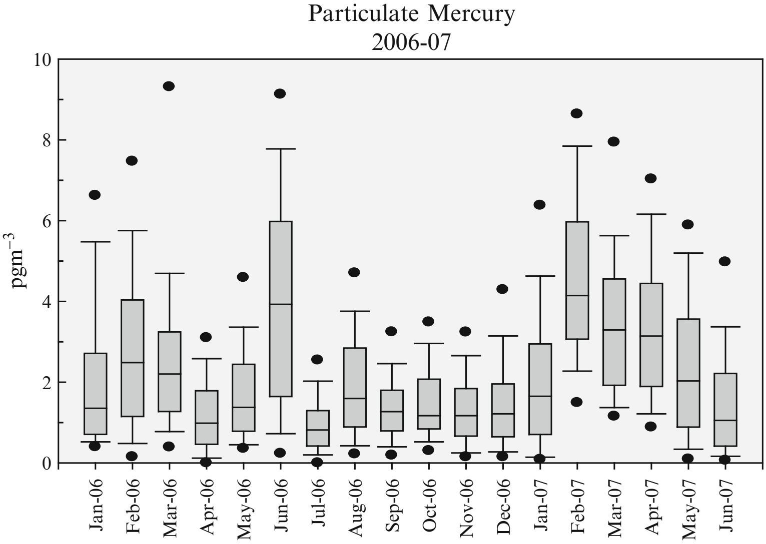


Figure 9.4 Monthly Box-whisker plot trends of Particulate Mercury from 2006 and 2007 at Halifax (Nova Scotia, Canada)

Canada, north-westerly winds bring air with a constant mixing ratio of Hg^0 at altitudes up to 7 km with a concentration near 1.5 ng m^{-3}. In the winter in southern and central Ontario and in spring over the Beaufort Sea and Arctic Ocean, the mixing ratio is still approximately constant at altitudes above 1 km but the concentration is 1.7 ng m^{-3}. Thus, despite differences in the proximity to sources and meteorology,

Table 9.6 Statistical summary of mercury speciation measurements from January 2006 to June 2007 in Halifax (Nova Scotia, Canada)

	Hg^0 (3 hr avg.) *(ng m^{-3})*	RGM *(pg m^{-3})*	PM *(pg m^{-3})*	Hg^0 (5 min.) *(ng m^{-3})*
Mean	1.79	4.62	2.37	1.77
Median	1.69	2.42	1.73	1.67
SD	0.45	7.61	2.30	0.61
Sample #	2835	2835	2835	106283

the observation that there is little difference in Hg^0 aloft over these distance and time scales indicates that there is mixing and uniformity in the Hg^0 concentrations aloft over continental scales. This atmospheric Hg aloft can be drawn down to the Earth's surface by atmospheric mixing processes even in remote regions of the world. The long average atmospheric residence time for Hg^0 is sufficient for this species to become relatively well mixed throughout the troposphere in the northern and southern hemispheres. Thus, since most of the Hg in the gas phase is in the elemental form, TGM concentrations should be of similar magnitude at a wide variety of background sites. Table 9.7 shows differences in Hg^0 below 1 km in the Ontario winter and Arctic spring. The measurements made at altitudes less than 1 km in Ontario demonstrate input of Hg^0 due to anthropogenic sources and over the sea ice in the Arctic demonstrate depletion of Hg^0.

Summary of Measurement Locations

Table 9.8 presents an overview of the measurement efforts that have occurred in the contiguous USA since high-precision measurements have been made (since early 1990s). Generally, a mean and standard deviation is presented, or a range of means from difference subsets of the data.

9.2.2 Measurements of Air Concentrations in the United States

Measurements of airborne species of mercury (Hg) [total gaseous (TGM), elemental (Hg^0), reactive gaseous (RGM), and particulate (PM)], as well as dissolved mercury in precipitation have been measured in many geographical areas of the USA including the northeast (New York, Connecticut, Vermont, Maine), north-central (Michigan, Wisconsin, Ohio, Indiana, Illinois), south-eastern (Georgia, Alabama, Tennessee, Florida), eastern seaboard (Maryland and the Atlantic Ocean), the mountain west (Nevada), coastal California, west coast free troposphere (Mt. Bachelor, Oregon), and west coast marine boundary layer (Cheeka Peak, Washington). These locations are shown on a map of the contiguous USA in Figure 9.5. Regions of the USA where there is a lack of published mercury measurements include the middle of the country from the northern plains south to Texas, most of the west (with the exception of Nevada), and the Southwest including southern California. In addition to great

Table 9.7 Elemental mercury for different altitude ranges over Canada. The units are *ng* m^{-3}, with the cubic metre referenced to 0°C and 1 atm in all cases (from Banic et al., 2003)

	< 1 km		1 – 3 km		> 3 km	
Time, Location of Measurement	Mean	Median	Mean	Median	Mean	Median
Summer 1995 Nova Scotia	1.4	1.3	1.5	1.4	1.4	1.4
Summer 1997 Eastern Ontario	1.5	1.5	1.5	1.5	1.5	1.5
Winter 97-98 Southern Ontario	1.7	1.6	1.6	1.6	1.5	1.5
Spring 1998 Arctic Ocean and Beaufort Sea	1.2	1.4	1.7	1.7	1.7	1.7

geographic and climate diversity in the USA, the spatial distribution of mercury emissions are not uniform; the vast majority of point sources lie in the eastern half of the country and are dominated by coal-fired power plants, waste incinerators, and manufacturing facilities. There are some large mercury sources in the West, dominated by mining and metal processing facilities and a few coal-fired power plants, but these emitters are spread out across wide regions and nowhere in the West are there the density of point sources as is found in the East. Thus, the majority of research to date has taken place at locations in the eastern half of the USA, and these studies are largely focused on determining the influences of local (< ~50 km) and regional (< ~500 km) mercury sources on air concentrations of mercury species and mercury concentration in precipitation and its subsequent depositional loadings to the environment. Additionally, some research in the West has determined that mercury emissions from distant locations such as industrial regions in East Asia and boreal fires in Alaska and Siberia contribute to enhanced air concentrations of Hg in the western USA, and that in pristine locations at certain times of the year, this transport may play a dominant role in the overall mercury burden in the environment.

9.2.2.1 Remote Locations

Because most studies in the USA have focused on the impact of regional or local emissions on air concentrations and deposition, there have been few measurements at locations that are truly remote. Figure 9.5 gives an overview on locations in the United States from which there are published measurements of gaseous and particle mercury species.

Perhaps the most pristine location in the USA is Cheeka Peak on the Washington State coast at an elevation of 500 m. At this location when the wind direction is between 160°-315°, the air can be generally classified as “marine“ with no influence from continental sources at least 7 days prior to arrival to the site (Weiss-Penzias et al., 2003).

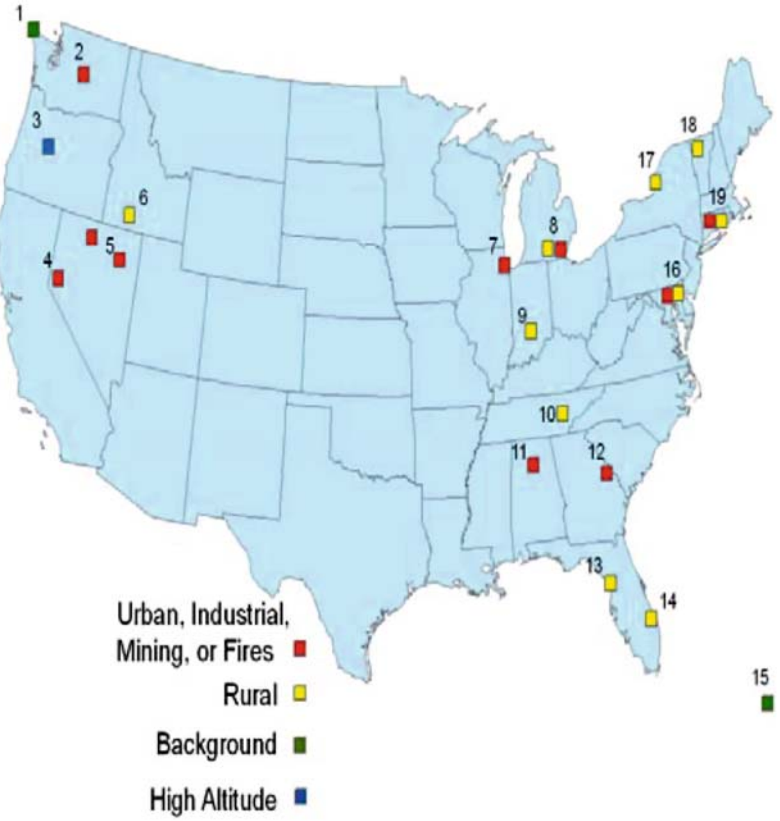
Table 9.8 Summary of Hg^0, RGM and Hg(p) measurements made at remote, rural and urban locations in the United States. NR means "not reported"

Location	Site details	Duration of study	Hg^0 mean (*$ng\ m^{-3}$*)	RGM mean (*$pg\ m^{-3}$*)	Hg(p) mean (*$pg\ m^{-3}$*)	Reference
Remote Sites						
Mount Bachelor, Oregon	2.8 km elevation, mountain top site	1.5 yr, 4 mth	1.4-1.8	39-60	4.4	Weiss-Penzias et al., 2007; Swartzendruber et al., 2006
Cheeka Peak, Washington	500 m elevation, marine boundary layer	1 yr	1.45-1.55	0-2.7	0-2.9	Weiss-Penzias et al., 2003
Ship, between Bermuda and Barbados	Subtropics, marine boundary layer	2 mth	1.63 ± 0.08	5.9	NR	Laurier and Mason, 2007
Rural Sites						
Chesapeake Bay Laboratory, Maryland	70 km south of Baltimore	7 mth	1.7-1.8	6-13	NR	Laurier and Mason, 2007
Look Rock, Tennessee	Smokey Mountains. at 813 m asl	2 mth	1.65	5	7	Valente et al., 2007
Salmon Creek Falls Reservoir, Idaho	SW Idaho (1510 m asl) 100-300 km from large gold mines and industrial plants	1.25 yr	1.3-1.6	1-10	NR	Abbott et al., 2007
Great Mountain Forest, Connecticut	Relatively remote area of NW Connecticut	5 yr	1.4-1.6	NR	NR	Sigler and Lee, 2006
Cove Mountain, Tennessee	Smokey Mountains at 1243 m asl	40 days	3.2	16.4	9.7	Gabriel et al., 2005
Dexter, Michigan	80 km west of Detroit	4 mth, 6 mth	1.49-1.51	2-3	12 ± 5.2	Lynam and Keeler, 2005a; Gildemeister et al., 2005
Potsdam, Stockton, and Sterling, New York	Western New York State	3 yr	1.84-2.59	NR	NR	Han et al., 2004
Pompano Beach, Florida	50 km northeast of Miami	1 mth	1.6-2.0	1.6-4.9	3.5 ± 2.8	Malcom et al., 2003
Stillpond, Maryland	42 km east of Baltimore	1 yr	1.7 ± 0.5	21± 22	42 ± 50	Sheu et al., 2002

(continued)

Table 9.8 (continued)

Location	Site details	Duration of study	Hg^0 mean *($ng\ m^{-3}$)*	RGM mean *($pg\ m^{-3}$)*	Hg(p) mean *($pg\ m^{-3}$)*	Reference
Walker Branch Watershed, Tennessee	20 km away from large coal fired power plants	6 studies over 3 yr	2.2	92 ± 60	NR	Lindberg and Stratton, 1998
Urban, Industrial, Mining, or Fire Sites						
North-central Nevada	1300-1800 m asl, close proximity to enriched substrates, and ore processing facilities	1 mth	2.5-3.0	7-13	9-13	Lyman et al., 2008
Detroit, Michigan	Close proximity to coal-fired power plants and metal smelting plants	1 yr	2.2 ± 1.3	17.7 ± 28.9	20.8 ± 30.0	Liu et al., 2007
Detroit, Michigan	Close proximity to coal-fired power plants and metal smelting plants	2 mth	NR	NR	1-39	Lynam and Keeler, 2005b
Desert Research Institute, Reno, Nevada	1340 m asl, close proximity to enriched substrates and urban emissions	3 yr, 3 mth	2.1-2.5	37 ± 28	7 ± 9	Stamenkovic et al., 2005
Chicago, Illinois	Heavy industrial development 10-20 km away from site	15 mth	3.6 ± 2.9	NR	70 ± 67	Landis et al., 2002
Baltimore, Maryland	Roof of Maryland Science Center	2 yr	4.4 ± 2.7	89 ± 150	74 ± 197	Sheu et al., 2002
Athens, Georgia	Within 350 m of a mercury cell chlor-alkali plant	5 days	3.9-8.7	9-129	NR	Landis et al., 2004
Tuscaloosa, Alabama	Small mercury sources are < 5 km from site	1 mth	4.05	16.4	16.4	Gabriel, et al., 2005
Earlham College, Richmond, Indiana	60-120 km away from large coal-fired power plants	6 studies over 3 yr	4.1	104 ± 57	NR	Lindberg and Stratton, 1998



1 Weiss-Penzias et al., 2003
2 Friedli et al., 2003
3 Weiss-Penzias et al., 2006; 2007; Swartzendruber et al., 2006
4 Stamenkovic et al., 2005
5 Lyman and Gustin, 2008
6 Abbott et al., 2007
7 Landis et al., 2002
8 Liu et al., 2007; Lynam and Keeler, 2005a, b; Gildemeister et al., 2005
9 Lindberg and Stratton, 1998
10 Valente et al., 2007; Gabriel et al., 2005; Lindberg and Stratton, 1998
11 Gabriel et al., 2005
12 Landis et al., 2004
13 Pollman et al., 1995; Gill et al., 1995
14 Malcom et al., 2003
15 Laurier and Mason, 2007
16 Laurier and Mason, 2007; Sheu et al., 2002
17 Han et al., 2004
18 Burke et al., 1995
19 Sigler and Lee, 2006; Chen et al., 2004; Nadim et al., 2001

Figure 9.5 Map of locations in the United States from which there are published measurements of gaseous and particle mercury species

Here, TGM averaged 1.45-1.55 ng m^{-3} over an annual cycle in 2001-2002, which is on the low end of the range of commonly accepted northern hemisphere background concentrations (1.5-1.7 ng m^{-3}). Concentrations were slightly (5%) higher in the summer and slightly higher (5%) when the winds were from the direction of the ocean and not the continent. Another set of TGM measurements in a pristine location were made from a ship in the subtropical Atlantic Ocean between Bermuda and Barbados. These data showed that TGM was also within the northern hemispheric background value, averaging 1.63 ± 0.08 ng m^{-3} in the late summer of 2003 (Laurier and Mason, 2007). The lack of temporal variation in these data suggest that there was little influence from local or regional sources.

Other studies at remote and rural sites reveal average Hg^0 concentrations that are within the 1.5-1.7 ng m^{-3} range or slightly above. Hg^0 at Chesapeake Bay Laboratory (CBL), a rural site in the marine boundary layer, was 10% elevated relative to open ocean value (Laurier and Mason, 2007). Short-term spikes in Hg^0 at CBL never exceeded 2.5 ng m^{-3}. Two deployments at CBL revealed average Hg^0 concentrations of 1.8 ng m^{-3} in the fall of 2002 and 1.7 ng m^{-3} in the fall-spring 2003-2004. Speciated mercury measurements were made at Pompano Beach, Florida during June of 2000. The winds alternated from a clean marine sector that produced an Hg^0 concentration of 1.6 ± 0.06 ng m^{-3} and a mixed flow regime that included some continental flow, which produced an Hg^0 concentration of 2.0 ± 0.4 ng m^{-3}.

Gaseous and particle mercury species along with some additional trace gases were measured at Look Rock during two field studies totaling 84 days in the spring and summer of 2004 (Valente et al., 2007). Look Rock is located just west of Smokey Mt. NP at 813 m a.s.l. Hg^0 averaged 1.65 ng m^{-3} over sampling period (spring/summer of 2004). Concentrations were slightly higher in spring. Hg measurements were made at a rural site in Michigan (Dexter, MI) during selected times from 1999 to 2002 (Lynam and Keeler, 2005a). Hg^0 measurements at Dexter (80 km west of Detroit) show an average concentration of 1.51 ng m^{-3} during the winter and 1.49 ng m^{-3} in the spring 2000-2001. Maximum concentration during winter was 4.39 ng m^{-3} and 1.94 ng m^{-3} in spring. TGM was measured at three locations in rural western New York State during the summers of 2000-2001 (Han et al., 2004). The northern (Potsdam) and southern (Stockton) sites revealed equivalent concentrations of 1.84 ng m^{-3}, but the central site was much higher (2.59 ng m^{-3}). The authors suggest that the central site is closer to Hg point sources.

Furthermore, Hg^0 was measured at a rural site about 42 km to the east of Baltimore during 1997-1998 (Sheu et al., 2002). It essentially showed background values (1.7 ± 0.5 n g m^{-3}) albeit with relatively high variability, representative of the regional signal. Not much seasonality was observed. Between 1992 and 1995, TGM was measured at a rural site in eastern Tennessee (Walker Branch Watershed) and produced an average value of 2.2 ng m^{-3} (Lindberg and Stratton, 1998). Two large coal-fired power plants are located approximately 20 km away from the upland forested site, which suggests that there is a higher background signal at this site relative to others in the region. TGM was measured at Underhill Vermont during a complete annual cycle in 1993 (Burke et al., 1995). The average TGM concentration was 2.0 ng m^{-3} with a maximum of 4.2 ng m^{-3}, suggesting that local sources were influencing these measurements.

9.2.2.2 Urban Locations (including mining areas)

Many studies have been carried out in urban and mining locations with the aim of assessing the impact of urban, industrial, and metal processing activities on mercury air concentrations and deposition in the local environment. There have been measurements made in several major USA cites (Chicago, Detroit, Baltimore), some smaller cities (Tuscaloosa, Alabama), sites near industrial facilities (Georgia), and mining areas (central Nevada). One of the major questions is to address the great spatial and temporal heterogeneity that is commonly observed in atmospheric mercury when measured in and around these areas.

The emission of RGM from a mercury cell chlor-alkali plant cell building and the impact on near field (100 km) dry deposition was investigated from sites inside and around the facility over a 5 day study (Landis et al., 2004). Measurements in the cell building roof vent showed that RGM constituted 2.1 ± 0.7% of the concurrently measured Hg^0. The percentage of RGM/Hg^0 at ambient monitoring sites 350 m (1.5%) and 800m (1.3%) away while being impacted by cell building emissions suggests the rapid deposition of RGM species. Previous estimates of the RGM% from the emissions in this sector done by the US EPA in the 1997 Mercury Report to Congress were much higher (30%) compared to the 2% observed in this study. Even so, the authors calculate that the magnitude of dry deposition from this plant at a 10 km radius is around 50% (4.6 mg m^{-2} yr^{-1}) of wet deposition (9.8 mg m^{-2} yr^{-1}). A study confirmed that there can be large changes in the near-field environment on short time scales (Gildemeister et al., 2005). TGM values in Detroit were 3-11 times higher than the rural site in Dexter Michigan (Lynam and Keeler, 2005a). TGM varied greatly and generally depended on meteorology conditions that favoured transport to the site. Another study in the Chicago/Gay urban area was investigated to determine its impact on atmospheric Hg concentrations and wet deposition in the Lake Michigan basin (Landis et al., 2002). Over the 1 ½ year period from 1994-1996, the TGM average concentration was 3.6 ± 2.9 ng m^{-3} and the maximum was 22 ng m^{-3} at the downtown Chicago site. These values are elevated and more variable relative to observations at other sites across the Lake Michigan Basin (rural site TGM = 2.2 ± 0.7 ng m^{-3}). Using meteorological clustering, the authors concluded that proximity to the industrial sources in the Chicago/Gary area were the cause of the elevated values. Elevated TGM concentrations were detected at a sampling site in downtown Baltimore (4.4 ± 2.7 ng m^{-3}) (Sheu et al., 2002). When the air came from the SE, S and SW directions, the urban sampling site tended to be impacted by the local emission sources, with higher THg and PM concentrations detected. TGM measurements were also made in smaller cities, but TGM values at these sites are often as high if not higher than in the largest cities. TGM measurements at Tuscaloosa, Alabama averaged 4.05 ng m^{-3} (maximum of 12 ng m^{-3}) during the summer (Gabriel et al., 2005). As with the other studies, short periods of high concentration for all mercury species were found. TGM measurements in Richmond Indiana between 1992-1994 averaged 4.1 ng m^{-3}. Richmond is a small city on the Ohio border and situated nearby (60-120 km) several major coal-fired power plants (Lindberg and Stratton, 1998).

TGM measurements were made at two arid-land rural sites in north-central Nevada, which is an area of diverse natural and anthropogenic mercury sources that include undisturbed and mining-disturbed enriched substrates, coal-fired power plants, ore processing facilities, and industrial facilities (Lyman et al., 2008). The TGM concentration averaged over all campaigns was 3.1 ± 1.7 ng m^{-3} at NV02 and 2.57 ± 3.1 ng m^{-3} at NV99. The highly variable temporal behaviour of TGM was found to be influenced by both local substrate emission and transport from regional source areas.

In summary, the behaviour of TGM in the urban or near-source environment is quite different from its behaviour in the rural, remote, or pristine environment. At near-source areas the concentrations can be between 2-10 times higher than areas beyond about 40-120 km from the emission source, which can be considered the spatial extent of the term “local”.

9.2.2.3 Temporal Trends at Single Locations

Measurements of TGM and Hg in precipitation over at least two annual cycles can identify the temporal variation on annual and seasonal timescales. Since Hg is of special concern as an air pollutant and there have been efforts to remove Hg from stack emissions from some facilities, it is of great interest to know if emissions reductions cause an annual decrease in TGM concentrations and Hg deposition at sites downwind of the emissions sources. Also, determining the magnitude and the timing of seasonal changes in TGM and Hg in precipitation can constrain the Hg budget and help to identify natural processes that affect sources and sinks.

TGM concentrations were measured at Desert Research Institute in Reno, Nevada from 2002 to 2005 and averaged 2.3 ng m^{-3} (0.9-8.6 ng m^{-3}) (Stamenkovic et al., 2007). The slope of the daily TGM concentrations at this site over the three year period showed a decrease of ~6% per year, although the concentrations are highly variable suggesting near-field emissions sources (Figure 9.6).

Three main causes of short-term TGM enhancements were identified: 1) after rain events the soil and foliar emissions increase, 2) when the site intercepts an urban plume with high concentrations of co-pollutants, and 3) marked change in meteorological conditions (e.g. inversions). Seasonally averaged concentrations were found to be spring = 2.2 ng m^{-3}, summer = 2.2 ng m^{-3}, fall = 2.1 ng m^{-3}, and winter = 2.5 ng m^{-3}. These data agreed with the patterns for CO and NOx, but this does not necessarily mean that the major sources of TGM are from combustion. The likely cause of this pattern is the greater presence of inversions as well as

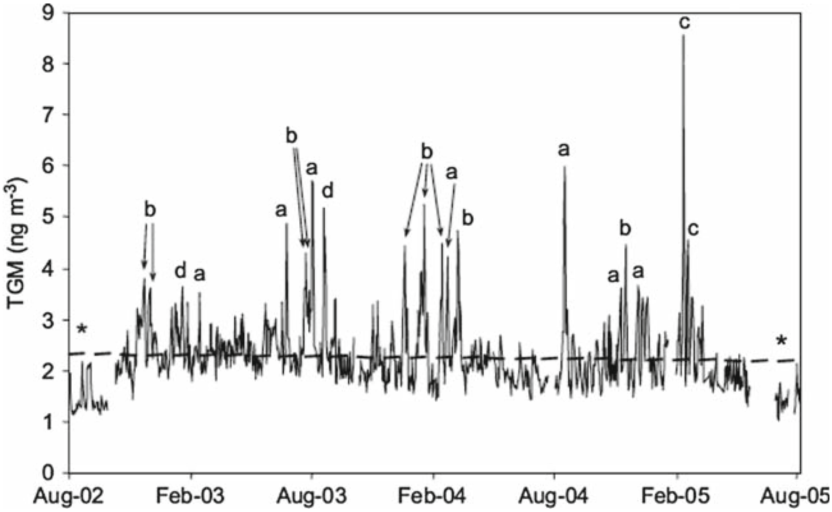


Figure 9.6 Time series plot of average daily concentrations of TGM measured at Desert Research Institute (Reno, Nevada) from 2002 to 2005. Fitted trend equation for all data: y = 2.3–0.00013t (in days). Letters indicate potential sources/causes of elevated TGM (a) following precipitation), atmospheric signature of pollution plumes (b), elevated NOx, CO or PM10 concentrations), marked change in meteorological conditions (c), change in barometric pressure), or no specific indicator (d). Asterisks denote periods of unusually low TGM (Stamenkovic et al., 2005)

weakening atmospheric sinks for all species in winter. There was also significant diurnal variability in TGM (2.1-2.6 ng m^{-3}), with a peak in the morning and gradually decreasing through the afternoon. A decreasing TGM annual average was also observed at a rural site (Chesapeake Bay Laboratory - CBL) near Baltimore/ Washington in the marine boundary layer (Laurier and Mason, 2007). TGM was measured in 2003/2004 and also in 1998/1999. The mean for the earlier time period was 1.9 ng m^{-3} and 1.7 ng m^{-3} for the later time period and no seasonal variation was evident. TGM concentrations never exceeded 2.5 ng m^{-3} at this site, and showed little diurnal pattern. Hg in wet deposition was measured continuously for 11 years (1993-2003) in the Lake Champlain basin at Underhill Vermont (Keeler et al., 2005) (Figure 9.7). There was considerable sample-to-sample and year-to-year variability due amount to variation in precipitation, temperature, and source receptor relationships. As a result of large variability, no increasing or decreasing trend was observed in either annual means of deposition or concentration. This is in contrast to what is observed for the record of sulphate deposition at Underhill, VT, which shows a decreasing trend due to emissions reductions of SO_2 from coal-fired power plants. Hg in wet deposition also displayed a strong seasonal cycle (higher by 4-6 times in May-September), which suggests that atmospheric removal processes play a large part in determining the variability of Hg in wet deposition, as opposed to seasonally varying sources of TGM.

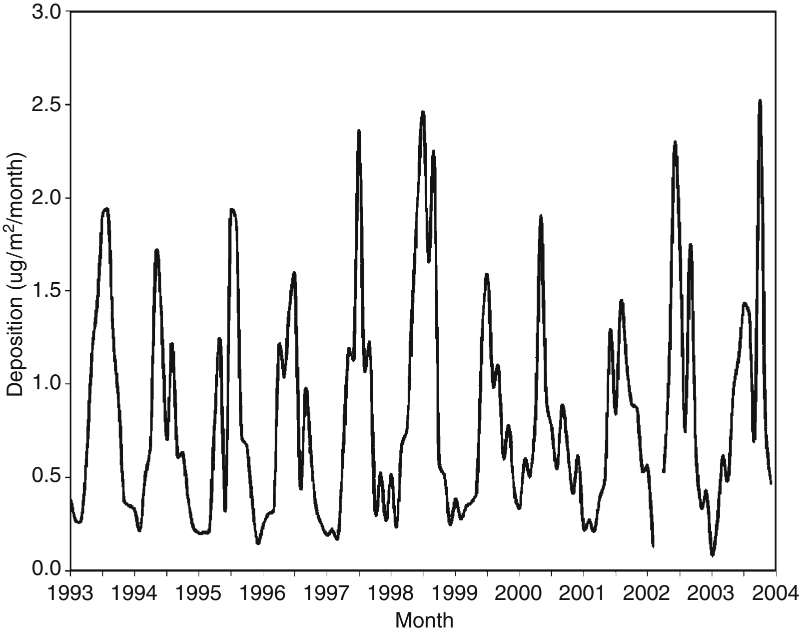


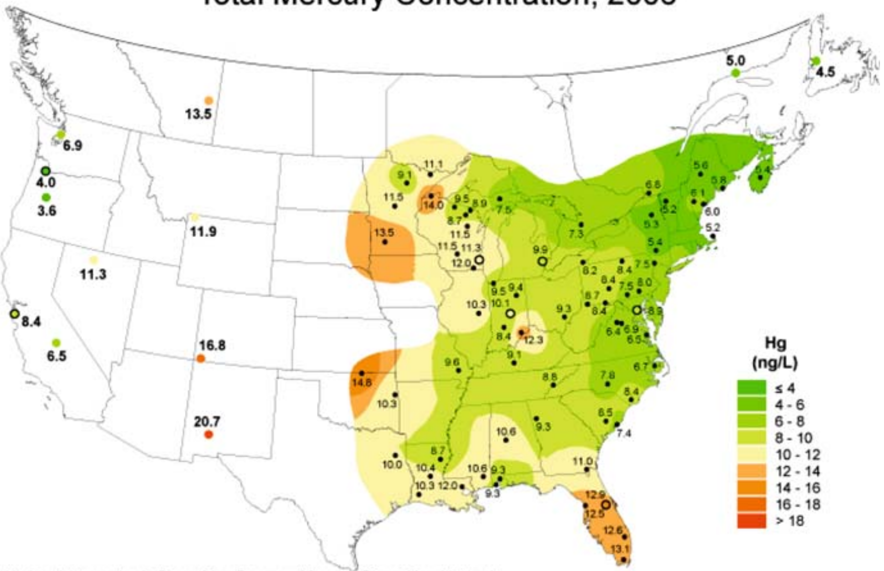
Figure 9.7 Monthly Total Hg wet deposition at Underhill, VT (Keeler et al., 2005)

In summary, there is some evidence that TGM at a rural location on the eastern seaboard downwind of major urban and industrial centers is decreasing and this decrease is likely due to cutbacks in the USA emissions. At more remote sites, there appears to be little change, and Hg is likely controlled by the northern hemispheric pool. However, the temporal dynamics of TGM and Hg in wet deposition are complex, with the magnitude of diurnal and seasonal changes often being larger than annual changes.

9.2.2.4 Monitoring Networks and Trends

Recognizing that TGM and Hg in wet deposition are spatially heterogeneous, several studies have aimed to set up monitoring networks in order to compare trends between sites in the same region, between regions, and to determine the influence of local and regional emissions sources. There is also interest in understanding the processes that contribute to Hg variability on a diurnal, weekly, seasonal, and annual basis. The largest, most ambitious network of sites is the MDN, which has sites across the USA that collect weekly precipitation samples and measure dissolved Hg (Figure 9.8). Some sites are co-located with Nation Trends Network (NTN) sites which measure concentrations of the major ions in precipitation (SO_4^{2-}, NO_3^-, Na^+, Cl^-, etc.) (Figure 9.9).

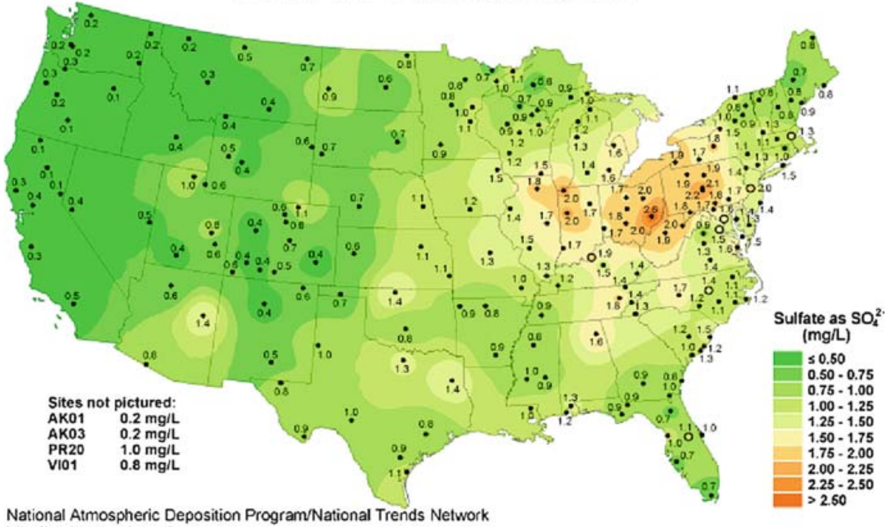
Total Mercury Concentration, 2006



National Atmospheric Deposition Program/Mercury Deposition Network

Figure 9.8 Total mercury concentration from the Mercury Deposition Network in 2006

Sulfate ion concentration, 2006



Sites not pictured:

AK01	0.2 mg/L
AK03	0.2 mg/L
PR20	1.0 mg/L
VI01	0.8 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure 9.9 Sulfate concentration from the National Trends Network in 2006

The spatial pattern of Hg concentrations in wet deposition has some aspects that have been difficult to reconcile based on known sources and removal processes. For example, there are high mercury concentrations in Florida, where there are few mercury sources, and there are relatively low concentrations in Pennsylvania and Ohio, where there are many coal-fired power plants. Clearly the total mercury and sulphate concentration patterns do not agree in these regions, suggesting that sulphate is not a good proxy for Hg and that removal processes (not only proximity to sources) are important in determining Hg deposition patterns.

One study using MDN Hg wet deposition data in which spatial and temporal trends were evaluated, focused on 13 MDN stations in the north eastern USA (1996-2002) and the Underhill Vermont event-based monitoring site (1993-2002) (Vanarsdale et al., 2005). It was found that mercury deposition and concentrations are not uniform across the region, and that distinct depositional sub-regions could be identified. These sub-regions in order of decreasing deposition are: sites to the south and west that are more influenced by large urban/industrial areas, maritime influenced sites, and northern inland sites. Each site was characterized by a large amount of week to week and seasonal variability with the highest concentration and deposition generally occurring in the spring and summer. Because of this high variability, no increasing or decreasing trend in annual mean deposition or concentration was evident at any site. “Enhanced” mercury deposition weeks (> 250 ng m^{-2}), which may occur only a few times during the year, were found to contribute a large portion of the annual mercury loading (20-60%) at most sites (Figure 9.10). Thus, Hg deposition in this region can be thought of as being episodic, although whether these episodes are driven by sink processes (oxidation/scavenging) or the influence of pollution plumes is not well understood.

In the state of Connecticut, USA, a TGM monitoring campaign was conducted from January 1997 to December 1999 (Chen et al., 2004; Nadim et al., 2001). The three-year mean TGM concentration was 2.08 ng m^{-3} across all 8 sites. Most

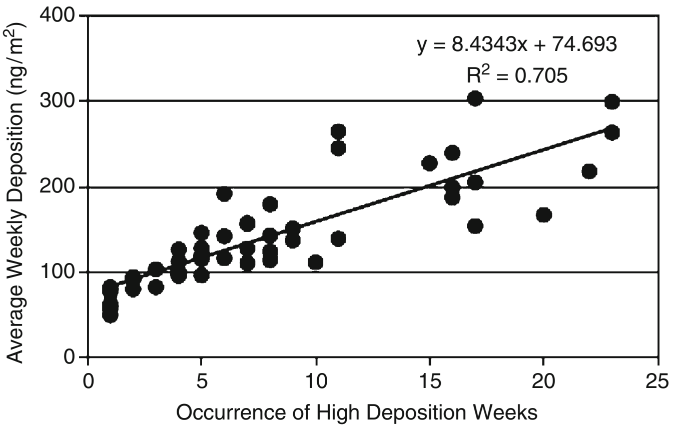


Figure 9.10 The relationship between the annual occurrence (sum) of high mercury deposition weeks (>250 *ng m*$^{-2}$) and the average annual deposition for those weeks for 13 MDN monitoring sites located in northeast North America (Van Arsdale et al., 2005)

sites displayed mean concentrations slightly above 2 ng m^{-3}, but one site (Waterbury) had a mean close to 4 ng m^{-3}. This anomaly is assumed to be caused by the close proximity of industrial Hg sources at Waterbury. At all sites, the annual mean concentration had no significant differences among the three years of measurements. In the state of Connecticut, USA, a TGM monitoring campaign was conducted from January 1997 to December 1999 (Chen et al., 2004; Nadim et al., 2001).

In another study, TGM and Hg in wet deposition were measured at several sites around Lake Michigan in order to determine the influence of emissions in the Chicago area (Landis et al., 2002). The largest difference in Hg concentration in wet deposition was between the downtown Chicago site (IIT) and remote northern Lake Michigan site (SBD).

The IIT mean summer Hg concentration was ~23 ng L^{-1} while the SBD summer mean was ~12 ng L^{-1}. The IIT site was elevated relative to all other sites in all seasons except winter, when inter-site differences were small. SBD (northern Lake Michigan) was much lower than all sites in every season except spring. Particulate Hg was much higher at IIT (70 pg m^{-3}) relative to other sites (12-24 pg m^{-3}). TGM concentrations were 2.0-2.2 for all sites and 3.6 ng m^{-3} at IIT. The impact of anthropogenic emissions from the Chicago/Gary area on wet deposition flux of mercury to Lake Michigan was modelled and is shown in Figure 9.11. Here it can be seen

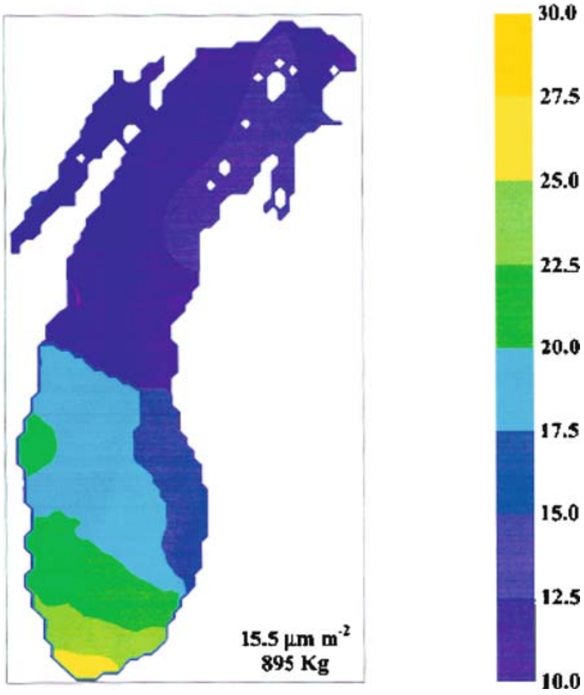


Figure 9.11 Estimated over-water wet deposition flux (July 1, 1994-October 31, 1995) (Landis and Keeler, 2002). The annual mean wet deposition value and total Hg deposited to the lake during the study period is shown at the bottom of the figure

that there is a factor of 3 difference between fluxes near Chicago and at the central/northern end of the lake.

An early study employing sites across Florida and in the Everglades measured TGM and Hg in rainfall between 1992-1994 (Pollman et al., 1995; Gill et al., 1995). The amount of Hg wet deposited shows a strong seasonal pattern with 2-3 times higher concentrations and 4-6 higher deposition in April-September. This pattern along with the lack of a spatial gradient in TGM or rainfall Hg, suggests that deposition is driven by large-scale regional processes as opposed to local emission/deposition processes. Chemical and/or photochemical processes in the atmosphere likely produce the high levels of summer time Hg in rainfall. The pattern of TGM concentrations was consistent with a lack of strong point sources. TGM across all sites had a mean concentration of 1.64 ng m^{-3} (n=191), and no spatial or temporal gradients were observed.

In summary, it seems that not enough attention has been focused on monitoring networks in the USA due to the difficulty and cost in carrying out sensitive measurements at many sites simultaneously. The MDN is essential for understanding the spatial and temporal patterns of Hg in wet deposition, but without at least TGM measurements (and speciated Hg measurements would be the best) in conjunction with precipitation measurements, little can be inferred about the processes responsible for controlling Hg deposition. It is not well understood, for example, which sites would respond most quickly to emissions reduction in various industrial sectors (e.g. coal-fired power plants, incineration, mining, manufacturing, etc.), or if enhanced deposition events are independent of local or regional sources and supplied predominantly by the global Hg pool being caused by natural variations in photochemistry and meteorology. The few studies that have both speciated Hg measurements as well as Hg in wet deposition suggest that Hg in deposition can vary by 2-fold between an urban and a rural site, TGM might vary by 50-75%, and PM may vary 5-10 fold between sites.

9.2.2.5 Mercury Speciation Analysis

In most cases, TGM and Hg in wet deposition measurements provide only part of the story concerning the advection of Hg from point sources and the natural air-surface cycling of Hg. Speciated Hg measurements include the longer lived Hg^0, and the shorter lived RGM, and PM, and these data can provide a wealth of information on the locality of sources and sinks, boundary-layer/free-tropospheric dynamics, and rapid air-sea exchange.

Since the late 1990s it has been possible to make accurate measurements of RGM and PM, and since the early 2000s, automated instruments have been available that can be operated unattended at remote sites.

Some of the important questions that have been investigated are 1) what is the importance of RGM formation in the marine boundary layer as a way of cycling Hg between the air and sea? 2) What is the diurnal pattern of RGM and PM? 3) What are the spatial distributions of these species, especially in close proximity to urban/

mining areas? 4) How do clouds, boundary layer dynamics and exchange with the free troposphere affect the concentration RGM? 5) Are there detectable longer-term changes in RGM or PM that suggest reductions in local emissions?

At two sites in Maryland and on a cruise in the subtropical Atlantic Ocean, the behaviour of RGM and PM in three environments was investigated during 2002-2003: open ocean, coastal, and urban (Laurier and Mason, 2007). RGM showed a distinct diurnal cycle at all sites, especially over the open ocean, where it is believed there is active recycling of Hg between air and water (oxidation by OH and halogens followed by rapid dry deposition of RGM, reduction to Hg^0 and subsequent evasion to replenish the MBL with Hg^0). Open ocean RGM ranged between 0-25 pg m^{-3}, and was generally negatively correlated with O_3, that is, the conditions that destroyed O_3 were responsible for producing RGM (assumed to be the presence of halogens and/or OH). At the rural coastal site (CBL), RGM showed a daytime average of 13 pg m^{-3} and a night time average of 6 pg m^{-3} (maximum value = 113 pg m^{-3}). These values are higher than what was observed over the ocean. The RGM daily peak at CBL generally occurred with the solar maximum under low wind speed conditions, suggesting the importance of in situ production. RGM and Hg^0 were seen to be occasionally elevated simultaneously at CBL, which was never seen over the open ocean. This is likely due to the occasional advection of polluted air to the site. High O_3 days generally produced elevated RGM, although the correlation was weak. No significant peaks of RGM were associated with clean marine air. RGM was very low during precipitation events. RGM variability at the coastal site is largely explained by photochemical production and dry deposition, with other factors such as advection from sources and changes in boundary layer height making minor contributions. Urban RGM concentration averaged 16.9 pg m^{-3} (down from 89 pg m^{-3} in 1997/98), suggesting a long-term reduction in point source emissions. RGM reached concentrations of > 200 pg m^{-3} at the urban site, occurring at night, probably a result of local inputs into a shallow nocturnal boundary layer. Another interesting observation was that RGM was generally depleted to zero during precipitation events at CBL but not at the urban site. This can be explained by the fact that higher concentrations at the urban site are not completely scavenged by precipitation, but that the lower concentrations at CBL are effectively drawn down to near zero.

Semi-continuous measurements of Hg^0, RGM, and PM were made throughout 2003 in Detroit, Michigan, where significant seasonal and diel cycles were observed. Hg^0 and RGM were elevated in the warm months, whereas PM was higher in the winter. RGM displayed a diel cycle that had a daytime maximum and Hg^0 and PM were higher at night, generally being inversely correlated with RGM (Figure 9.12). Multivariate and probability function analysis of Hg spikes with other parameters (ozone, SO_2, meteorology) revealed that both local and regional sources, in addition to boundary layer dynamics, were important in controlling mercury behaviour. The finding that each Hg species had their distinct seasonal and diurnal patterns suggests that the dry and wet deposition of Hg in Detroit and the surrounding area may also vary significantly across different seasons and throughout the day, highlighting the importance of conducting long-term highly time-resolved

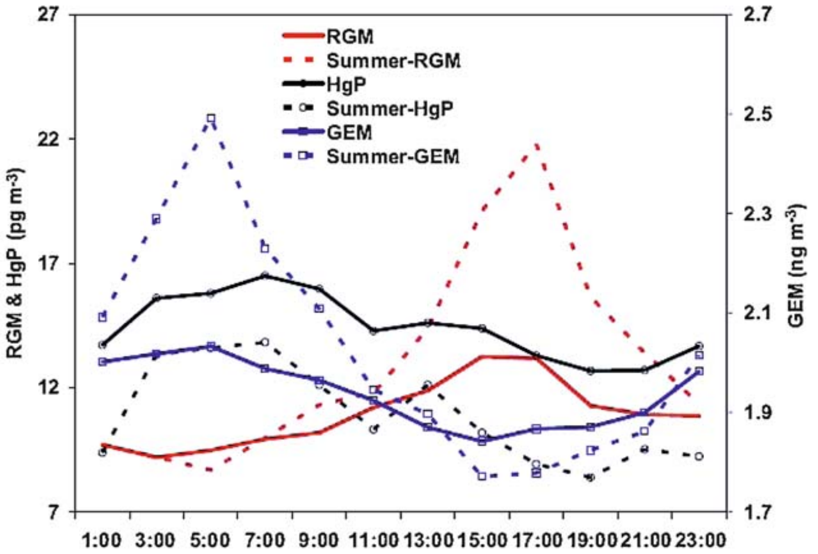


Figure 9.12 Diurnal variation of Hg species (median concentrations) in Detroit (2003) (Liu et al., 2007) Note the inverse relationship between RGM and Hg^0. Hg(p) has the least amount of diel variability

measurements in urban areas that potentially have more Hg source contributions to the surrounding areas.

Earlier efforts by the Keeler group made automated speciated Hg measurements at a rural (Dexter, Michigan) and an urban (Detroit, Michigan) site between 1999 and 2002 (Lynam and Keeler, 2005a). Median RGM at the rural site was 2-3 pg m^{-3} (max = 38.7 pg m^{-3}), was not correlated with Hg^0 in winter and weakly negatively correlated with Hg^0 in the spring. Poor correlations between Hg^0 and RGM at both sites, suggest multiple sources and/or different sinks for these species. Particulate Hg showed a range of 5-60 pg m^{-3} in Detroit. Precipitation and dew caused a decrease in concentration of both species, which was also observed in the Chesapeake Bay-Baltimore studies (Laurier and Mason, 2007). The diurnal cycle in Detroit is much less pronounced than Dexter, with significant amounts of RGM and PM present during the night time hours (presumably due to the trapping of nocturnal emissions and transport).

Higher RGM/PM ratios occurred under drier upper altitude air from the east with fewer point sources and urban areas, whereas lower RGM/PM ratios occurred with wetter low level air from the west, which picked up pollutants from the Chicago area. There was some evidence that high ozone episodes in the Detroit/Dexter region caused enhanced RGM (simultaneous afternoon peak in both species). Additionally, there was a slight negative correlation between Hg^0 and O_3, suggesting photochemical depletion of Hg^0, which produced RGM. However, high ozone conditions (> 80 ppb) also produce a positive sampling bias in the PM measurements on KCl denuded filters versus undenuded filters (Lynam and Keeler, 2005).

The marine boundary layer was determined to not be a source of Hg^0 or RGM at Pompano Beach, Florida, during June of 2000 (Malcom et al., 2003). Higher mercury concentrations were correlated with HNO_3 and SO_2, suggesting urban and industrial sources on land. Hg(p) concentrations were higher than can be explained by sea spray alone suggesting that gaseous Hg is diffusing into the sea salt aerosol. This suggests that deposition of aerosols enriched in Hg via this process may constitute a significant global mercury flux to the oceans.

RGM and PM measurements were made in two contrasting south-eastern USA airsheds (Cove Mountain, Tennessee, and Tuscaloosa, Alabama) during the summers of 2002 and 2003 (Gabriel et al., 2005). A comparison of mercury species concentration shows that the urban site has much higher mean PM concentrations (16.4 vs. 9.73 pg m^{-3}), but mean RGM concentrations between the two sites are roughly equivalent (16.4 pg m^{-3}). There was a stronger dependence between RGM and wind speed at Cove Mtn. suggesting a greater role of boundary layer dynamics and free tropospheric exchange in controlling RGM. The maximum RGM concentration at Tuscaloosa was much higher (162 pg m^{-3}, with higher variability overall) than Cove Mtn. (58.1 pg m^{-3}), suggesting that local point sources of Hg were impacting the urban site. At Cove Mt. there was a small diurnal cycle in RGM with a maximum in the midday, similar to other remote sites. No diurnal cycle was apparent at Tuscaloosa, similar to other urban sites. At another site in the south eastern USA (Look Rock, Tennessee) in the spring and summer of 2004, Valente et al. (2007) observed RGM and Hg(p) means of 5 and 7 pg m^{-3}, respectively. These are lower concentrations than what were seen at other sites in the region (Gabriel et al., 2005; Lindberg and Stratton, 1998). $Hg^{(II)}$ species were found to account for < 1% of TGM.

Urban and rural sites were sampled for RGM and PM along the coast of Chesapeake Bay and in Baltimore (Sheu et al., 2002). One year of data collected at Stillpond (rural) showed that RGM averaged 24 pg m^{-3} in 1997 and 21 pg m^{-3} in 1998. PM at Stillpond for 1997 was 39 pg m^{-3} and for 1998 was 61 pg m^{-3}. There was no seasonal pattern in RGM at Stillpond, but for PM there were higher values in the colder months, suggesting that reactive mercury species favour the condensed phase under colder temperatures. One site in the study (Curtis Creek) displayed the highest mean RGM concentration (385 pg m^{-3}), mean PM concentration (715 pg m^{-3}), and mean Hg^0 (6.1 ng m^{-3}), evidently reflecting near field contamination. RGM + PM as a percentage of TGM varied between 2-19% among sites. Because of the high concentration of RGM, annual dry deposition fluxes at the most polluted site was calculated to be as high as wet depositional fluxes.

Speciated mercury measurements were made in the Pacific Northwest in the marine boundary layer at Cheeka Peak, Washington (Weiss-Penzias et al., 2003), and in the free troposphere at Mount Bachelor, Oregon (Swartzendruber et al., 2006). These locations show very different behaviours of RGM and PM. At Cheeka Peak RGM and Hg(p) were very low (0 - 2.7 and 0 - 2.9 pg m^{-3}, respectively), mostly due to frequent cloudiness and precipitation. Occasional wind-shifts to continental directions (downwind of Seattle and Vancouver) would cause RGM and PM to increase to

10-20 pg m^{-3}, much lower than what is seen downwind of eastern USA cities. At Mount Bachelor, RGM is quite elevated under certain meteorological conditions that bring high-pressure subsidence under high UV conditions (summer). These episodes were clearly marked by dry air at night generally accompanied by higher O_3 and a decrease in Hg^0. There is a nearly quantitative shift in speciation with an increase in RGM and a loss of Hg^0 under subsidence conditions. RGM concentrations as high as 600 pg m^{-3} were observed. Mean RGM concentration at night (n = 203) was 60 pg m^{-3} and the daytime mean (n = 527) was 39 pg m^{-3}, in contrast to other studies that show an RGM maximum at solar noon. PM concentrations for day and night at Mount Bachelor were equivalent (~4.4 pg m^{-3}), indicating that RGM was being formed and unable to condense to particles under these dry air conditions.

In summary, given the available knowledge of speciated mercury, it can be concluded that RGM in situ formation is very important in both the marine boundary layer under cloud-free conditions, and in the free troposphere, where concentrations reach those of the most polluted urban atmosphere. Additionally, because of the diurnal nature of photochemistry and boundary layer/free tropospheric exchange, RGM and to a lesser extent Hg^0 and PM generally have prominent diel cycles. Superimposed on the natural variability is the episodic nature of advection of more or less polluted air masses to a sampling site from urban/industrial/mining sources. With regard to long term changes in RGM or Hg(p) concentrations, the data do not go back far enough or have sufficient spatial coverage to really address this question.

9.2.2.6 Mercury Measurements Related to Emissions and Source Attribution

In an effort to understand the relative importance of anthropogenic and natural emissions of airborne Hg, several studies have attempted to calculate Hg fluxes from source regions. This is primarily done by directly measuring fluxes (usually from enriched surfaces) using flux chambers, or by correlating Hg enhancements in plumes to other tracers whose emissions are known (CO). Source attribution for Hg in precipitation has been done using variations on principal component analysis using other elements as tracers of Hg emission types. Other studies, which are less quantitative, have used back trajectories and meteorological cluster analysis to provide weight-of-evidence for the causes of Hg enhancements in gaseous and precipitation samples.

In two recent studies, total airborne mercury and CO were measured in 22 pollution transport "events" at Mount Bachelor (2800 m a.s.l.) between March 2004 and September 2005 (Weiss-Penzias et al., 2006; 2007) (Figure 9.13). East Asian industrial events yielded a ΔTGM/ΔCO enhancement ratio of ~0.005 ng m^{-3} ppb$_v$, whereas plumes from western USA anthropogenic sources and from biomass burning in the Pacific Northwest and Alaska gave a ratio of ~0.001 ng m^{-3} ppb$_v$. Thus, the ΔTGM/ΔCO ratio is an important distinguishing feature of Asian long-range transport. Scaling these ratios with estimated emissions of CO from China and global biomass burning, an emission of 620 Mg yr^{-1} is calculated for total mercury emissions from Chinese anthropogenic sources and 670 Mg yr^{-1} for global biomass burning.

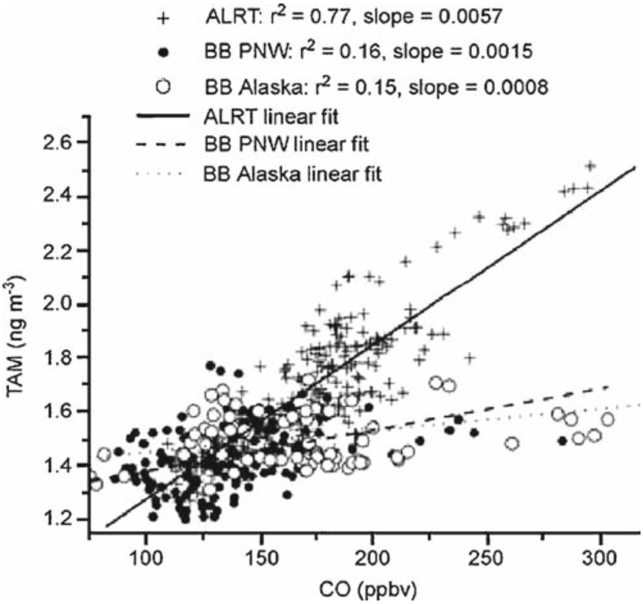


Figure 9.13 Scatter plot of total airborne mercury (TAM) vs. CO measured during 22 pollution events at Mt. Bachelor Observatory, Oregon during 2004-2005. The events are categorized at Asian long-range transport (ALRT), and biomass burning from Alaska or the Pacific Northwest. (Weiss-Penzias et al., 2007)

In a related study, the Hg^0/CO molar enhancement ratio was observed in pollution plumes at Okinawa, Japan and produced a value of 6.2×10^{-7} mol/mol (0.0056 ng m^{-3} ppb_v) (Jaffe et al., 2005). These plumes were identified to have originated in the industrialized region of eastern China, and they produced a similar ratio to those observed at Mt. Bachelor. This implies that there should be the same molar ratio of Hg^0 and CO emissions in China. However, recent Chinese emissions inventories are a factor of two lower than the ratio in the plumes. Likely explanations for this discrepancy are 1) Chinese Hg emissions have been underestimated, 2) there are large natural sources of Hg that are not accounted for and, 3) Hg^0 emissions in China make up larger fraction of the inventory and the shorter lived RGM and PM are less important. Speciated measurements were also made at Okinawa and revealed no correlation between CO (a marker of Asian outflow) and RGM or PM. This suggests that the marine boundary layer and the presence of clouds and precipitation at Okinawa effectively scavenges these reactive Hg species. Thus, the question remains as to the spatial extent of RGM and PM transport from point sources.

Another study also employed the Hg/CO molar enhancement ratio, this time in smoke plumes from large temperate forest wildfires and a wheat stubble fire which burned in August 2001 as sampled by the University of Washington's Convair 580 research aircraft (Friedli et al., 2003). TGM concentrations as high as 7.5 ng m^{-3} were observed in smoke plumes. Hg was in its elemental form (95%) with the remaining fraction in the particulate form. TGM was linearly correlated with CO and using known emission factors (EF) for CO, an EF for TGM was calculated to be 113 μg Hg kg^{-1} of fuel. From these data, an estimate of 3.7 Mg of Hg per year from North American temperate forests was generated based on burn area estimates between 1997-2001. Agricultural waste burning is estimated to contribute 20 Mg yr^{-1} worldwide, but this number is highly uncertain.

Five years of wintertime TGM measurements at a background site in Connecticut were combined with measurements of CO2 as a regional combustion tracer in order to investigate regional Hg emissions (Sigler and Lee, 2006). A 20% decrease in Hg emissions between 1999/2000 and 2001/2002 was found to be not fully explainable by climatological changes in air mass transport, but rather a significant correlation was seen with interannual changes in the emissions from the power sector in the region. The Hg flux from the power sector was calculated to account for 47-75% of the atmospheric flux, yet if 50% or more of the Hg emitted by power sources is RGM and PM and deposits locally, then the power sector can only account for 23-40% of the observed elemental Hg flux to the atmosphere. This suggests that there are other important unaccounted for elemental mercury sources in the region, or that there is significant reduction of $Hg^{(II)}$ in the power plant plumes.

Beginning in the fall of 2002, measurements were made in Steubenville, Ohio as part of a multi-year comprehensive mercury monitoring and source apportionment study to investigate the impact of local and regional coal combustion sources on atmospheric mercury deposition in the Ohio River Valley (Keeler et al., 2006). Using multi-variate component analysis involving numerous trace metals, coal combustion was found to be the source of ~70% of Hg in wet deposition in Steubenville Ohio. The volume-weighted mean Hg concentration over a 2 year period was 13.7 ng L^{-1}, 2-3 times higher than what is observed in Wisconsin and the north-eastern USA.

Source-receptor relationships for Hg and other trace elements wet deposited in south Florida were investigated using daily event precipitation samples collected concurrently at 17 sites from August 6 to September 6, 1995 (Dvonch et al., 2005). A multivariate receptor modeling approach found municipal waste incineration and oil combustion sources to account for 71 ± 8 % of the Hg wet deposited at five Florida Everglades sites. A similar analysis of a year-long record of event samples (June 22, 1995-June 21, 1996) collected at Davie, FL, found 73 ± 6% of the Hg wet deposited to be accounted for by local anthropogenic sources.

In another study, size segregated Hg(p) measurements were made at several urban sites in Detroit, Michigan, in 1996 (Gildemeister et al., 2005). One site (LIV) is located in heavily industrialized section of Detroit near coal-fired power plants, iron and steel smelting, and coke production. This site observed the highest mean concentrations of TGM (2.8 ng m^{-3}) and PM (54 pg m^{-3}) compared to less industrialized sites. PM in the coarse mode made a median daily contribution of 37% of total Hg(p) at the LIV site compared to a median daily contribution of 20% at the rural site. This suggests that industrial sources are impacting the local environment and the impact lessens with a greater distance away from the source. Other studies have been less quantitative but are able to show using back trajectories and cluster analysis that higher concentrations are observed in gaseous or precipitation samples that have been impacted by anthropogenic Hg emissions regions.

Event wet-only precipitation, total particulate, and vapour phase samples were collected for Hg, and trace element determinations from five sites around Lake Michigan from July 1994 through October 1995 as part of the Lake Michigan Mass Balance Study (LMMBS) (Landis et al., 2002). The cluster modelling results indicate that urban and industrial sources in the Chicago area were contributing to enhanced Hg in precipitation and PM concentrations across the entire Lake Michigan basin. Rain water measurements at marine and inland sites in central California show that higher Hg concentrations were associated with back trajectories that stayed the 20-40°N range across the Pacific, suggesting a contribution from Asian sources (Steding and Flegal, 2002).

The Nevada Study and Tests of the Release of Mercury From Soils (STORMS) project focused on the measurement of mercury emissions from a naturally enriched area (Gustin et al., 1999). Hg^0 measurements were as high as 200 ng m^{-3}, indicating large local sources. Fluxes were quite variable due to site heterogeneity, but ranged from 50 to 360 ng m^{-2} hr^{-1}. This represents an increase in the magnitude of natural soil flux by 10-100 times over previously held values.

Finally, to assess the sources, transport and deposition of atmospheric Hg in Michigan, a multi-site network was implemented in which Hg concentrations in event precipitation and ambient samples (vapor and particulate phases) were determined (Hoyer et al., 1995). Elevated Hg concentrations at all rural sites were associated with air mass transport from the west, southwest, south, and southeast. The most northern site (Pellston, MI) had the lowest concentration of vapor phase Hg and precipitation Hg.

9.2.3 Measurements of Air Concentrations in Mexico

Short term field measurements of TGM concentration in ambient air were undertaken at 4 locations in Mexico in 2002 in order to characterize mercury concentration in areas contrasting in mercury sources and exposure. Locations and dates of sampling are provided in Table 9.9. TGM was measured using a Tekran 2537A mercury vapour analyser using a 5 min sampling interval. Mexico City is a large urban/industrial city consisting of a mixture of residential and industrial activities. Zacatecas is a smaller semi-urban centre with a prolonged history of gold and silver mining activities which have traditionally involved mercury amalgamation processes in metal extraction. Mine tailings are a dominant feature in and around Zacatecas and several brick manufacturing facilities are located in the vicinity. Brick manufacturers use the mine tailings as a raw material in the manufacture of bricks.

The other two sites were selected to provide more regionally representative assessments of mercury concentrations in ambient air at locations having little or no known exposure to substantial anthropogenic sources of mercury. Puerto Angel

Table 9.9 Site description and sampling dates for measurements of TGM in air in Mexico

Site	Sampling Date	Lat - Long	Elevation	Description
Zacatecas	Sep 17-20 2002	22° 44'N 102° 28'W	2420 m	mining legacy
Mexico City	Oct 18-21 2002	19° 21'N 99 ° 04'W	2240 m	large urban
Puerto Angel	Oct 16-18 2002	16° 47'N 96 ° 28'W	13 m	rural-remote
Huejutla	Oct 20-23 2002	21° 08'N 98 ° 25'W	172 m	rural-remote

Table 9.10 Location and sampling dates for Puerto Angel and Huejulta MDN sites in Mexico (adapted from NADP-MDN)

Station	Puerto Angel*(OA02)*	Huejutla*(HD01)*
Location	Pochutla County, Oaxaca	Huejutla de Reyes County, Hildago
Dates of Operation	9/28/2004 - 10/11/2005	10/26/2004 - 11/29/2005
Latitude	15.65	21.1583
Longitude	-96.4833	-98.3706
Elevation (m)	110	180

is a very small rural village located on the Pacific coast several hours drive south west of Mexico City. Puerto Angel is a small fishing village and undeveloped beach resort area. Huejutla is located well to the northeast of Mexico City and is a small rural centre. In addition to measurements of TGM, Puerto Angel and Huejulta were also selected as MDN sites to assess regionally representative concentrations of mercury in precipitation. Mexican MDN site descriptions are given in Table 9.10.

9.2.3.1 Remote Locations

TGM concentrations measured at Puerto Angel and Huejutla were consistently at or slightly below the expected hemispheric average concentration (~1.5 ng m^{-3}) and showed very little variability over the brief sampling period of a few days indicating that these two remote sites were not subject to any significant anthropogenic sources of mercury. Slightly lower values may indicate slight TGM depletion through depositional processes since both sites are surrounded by dense forests and subject to frequent moisture through rain and cloud water impaction (Huejulta) and rain and possibly marine advection fog (Puerto Angel). TGM concentrations between Puerto Angel and Huejulta were not statistically different (de la Rosa et al. 2004) (Table 9.11)

Mercury concentration in precipitation at these 2 remote sites had similar annual average precipitation mercury concentrations between 11 and 12 ng L^{-1} (Table 9.12) although concentrations were somewhat more variable between weekly composite samples. These concentrations are well within the range of concentrations observed at other sites in North America.

Table 9.11 Summary of TGM concentrations *(ng m^{-3})* measured at 4 locations in Mexico

Site	Mean	Min	Max	St Dev	n
Zacatecas	72.	0.26	702.	82.	742
Mexico City	9.8	2.8	34.	4.0	1148
Puerto Angel	1.46	0.76	2.45	0.4	546
Huejutla	1.32	1.13	2.93	0.3	701

Table 9.12 Summary of annual mercury concentration (*ng L^{-1}*) in precipitation between Oct 2004 to Oct 2005 at 2 rural-remote locations in Mexico

Site	Mean	Min	Max	St Dev	n
OA02	12.0	9.02	1.33	39.1	10.1
HD01	10.8	8.42	3.21	40.8	7.91

9.2.3.2 Urban Locations (Including Mining Areas)

TGM concentrations measured in Mexico City and Zacatecas stand in direct contrast to those measured at the 2 rural remote sites. Mexico City TGM averaged 9.8 ng m^{-3} with concentrations reaching 34 ng m^{-3}. Higher mean concentrations and variability are clearly related to varying exposures to anthropogenic mercury sources typical of many large, heavily populated urban-industrial centers. However, the largest average and maximum TGM concentrations were observed in Zacatecas which is a much smaller urban area with substantially more limited industrial development compared to Mexico City. There is little doubt that the long history of mining precious metals and the legacy of mercury used in the amalgamation process is reflected in ambient TGM concentrations. Mine tailings are found extensively in the area and the release of mercury into the air may be further exacerbated by the use of the tailings material in the manufacture of bricks which are baked at high temperatures during their manufacture. TGM measurements were not made adjacent to any brick manufacturing facility and would be representative of concentrations found in and around the town. TGM concentrations were significantly different ($p < 0.01$) between sites and significantly different from the two remote sites (de la Rosa et al., 2004).

9.3 Measurements of Air Concentrations in South America

Relatively few observations of atmospheric Hg have been carried out in South America or Mexico. The few observations to date have mostly been carried out near to, or downwind of, major sources. This includes mining, industrial facilities and biomass fires. For nearly all South American observations, measured Hg^0 concentrations were substantially greater than the accepted global background level. Relatively few publications have converted the observed air concentrations into an emission flux. One emission inventory for Hg emissions associated with gold mining has been conducted using estimated gold production and an Hg emission factor. This inventory suggests that gold mining is the largest source of TGM to the atmosphere in South America. At present, there is no information in South America or Mexico that can be used to establish long-term trends.

9.3.1 Urban Locations (including mining areas)

Widescale mining has occurred in the Amazon Basin since at least the 18th century (e.g. Hachiya et al., 1998; Higueras et al., 2005 and references therein). Associated with current and past operations, a number of researchers have examined the TGM air concentrations in mining regions. Hachiya et al. (1998) sampled in urban and rural areas of Brazil near several tributaries of the Amazon river. Samples were collected on gold coated quartz. Hg analysis was carried out in the lab by desorption and UV absorbance. Urban areas sampled included Rio de Janero, Manaus and Brasilia, where concentrations up to 10 ng m^{-3} were found. Adjacent to mining areas concentrations up to 16 ng m^{-3} were found. In some gold workshops, very high levels of TGM were found (max 3.7 ng m^{-3}).

Amouroux et al. (1999) sampled at several sites in two Amazon basins of French Guiana. These sites were also strongly influenced by current and past mining activities. TGM samples were collected on gold coated quartz, with analysis in the lab by desorption and ICP-MS. High TGM concentrations were found and attributed to nearby illegal gold mining. Concentrations were highest at midday and lower at night. The authors attributed this to influence from lake-air exchange. Concentrations were much higher in the Petit Inini River Basin site (mean 15.0 ng m^{-3}), compared to the Petit Saut Lake (2.8 ng m^{-3}), which the authors attributed to mining sources.

De la Rosa et al. (2004) sampled at four sites in Mexico for a few days at each site. The authors measured TGM using a Tekran 2537a instrument and standard calibration methods. High values and high variability were found at the Mexico City and Zacatecas sites, suggesting strong nearby sources. Mean Hg values at Zacatecas were very high at 71.7 ng m^{-3}, whereas the Mexico City site was not as elevated (9.8 ng m^{-3}). At two rural sites, mean TGM values were near accepted global background concentrations (1.46 and 1.32 ng m^{-3}). Brick manufacturing, using mining waste, and mining tailings were attributed by the authors as the most likely source of high Hg at the Zacatecas site.

Higueras et al. (2005) sampled along roads in the Coquimbo region of Northern Chile using a Lumex RA-915+. Their sampling took them past several major ore mining and processing operations for gold and other metals (e.g. Hg, Cu and Mn). Very high concentrations of TGM were found in these current and historical mining regions (some mining back to 16th century). Extreme TGM concentrations, up to nearly 100 µg m^{-3} were observed at some gold recovery operations (milling and amalgamation).

Fostier and Michelazzo (2006) sampled at two sites in Sao Paulo state, Brazil, near the Paulínia industrial area. Hg samples were collected on Au coated quartz sand followed by desorption and CVAFS detection in laboratory. Samples for TPM analysis were also collected on quartz fiber filters. Sampling was conducted for about 5 days at each site during both the rainy and dry seasons. The two sites had an overall mean TGM concentration of 7.0 ng m^{-3}, with no significant difference between the two sites. There was evidence for a diurnal cycle, with higher TGM concentrations during the day. The enhancement in TGM, compared to the global background, was attributed to the wide array of industrial sources in the area. Concentrations of TPM were high, 400 pg m^{-3}. Based on the sampling methodology, this high value likely includes some contribution from RGM sticking to the filters or particulate matter on the filters.

Garcia-Sanchez et al. (2006) measured soil and air concentrations along with some height profiles in the El Callao region of Venezuela using a Lumex RA-915+. The sites included some highly polluted sites due to past mining activities. Extremely high TGM concentrations were observed in some gold processing shops, with several concentrations between 50 and 100 μg m^{-3}. These high values exceed recommended workplace limits (e.g. NIOSH or WHO limits of 50 and 25 μg m^{-3}, respectively).

From the above data, it is clear that past and current gold mining represents a large source of Hg to the atmosphere. Lacerda (1997) estimated global Hg emissions to the environment from gold mining. By this estimate 460 Mg yr^{-1} are released to the environment globally, 300 Mg or 65%, of this is released to the atmosphere. Of this total, nearly 60% is released in South America. The atmospheric emissions of Hg in South America by gold mining (179 Mg yr^{-1}) calculated by Lacerda (1997) is nearly twice the total Hg emissions from all sources in South America estimated by Pacyna et al. (2006). This estimate was updated by Lacerda (2003) to 107-228 Mg yr^{-1}. However it should be noted that the Pacyna et al (2006) inventory does not quantify Hg emissions from South American gold mining nor does it attempt to quantify Hg emissions from illegal gold mining activities. In addition the Pacyna study used a Hg emission factor of 0.5 gram Hg emitted/gram Au mined, whereas Lacerda uses a factor of 1.5. Thus, while emissions of Hg from gold mining in South America are clearly a substantial source to the global atmosphere, there is a significant uncertainty in the actual emissions. Future work on Hg emissions in South America should focus on reducing the large uncertainty in the emissions.

9.3.2 Mercury Measurements (Including Aircraft) Related to Emissions, and Source Attribution

Ebinghaus et al. (2007) observed enhanced CO and TGM on two CARIBIC (*C*ivil *A*ircraft for *R*egular *I*nvestigation of the *A*tmosphere *B*ased on an *I*nstrumented *C*ontainer) flights between São Paolo and Santiago de Chile in 2005. The CARIBIC container is operated monthly onboard a Lufthansa Airbus 340-600 during regular passenger flights. The measured TGM/CO ratio on these two flights, 1.2×10^{-7} and

2.4 × 10^{-7} mole/mole, respectively, were similar to previous reports of biomass burning plumes, despite significant differences in geographic regions. From these ratios the authors estimate global emissions of TGM from biomass burning in the range of 210-750 Mg yr^{-1}.

9.4 Measurements of Air Concentrations in Europe

9.4.1 Remote Locations

TGM concentrations at remote sites are influenced by the regional and global background pool. Due to emission controls in Europe the regional contribution is declining and gradually less important. As a consequence the TGM background concentration of the Northern hemisphere is dominating at remote European locations. Measurements of TGM have been made over a period of one year using a cold vapour atomic fluorescence absorption technique at Harwell, a rural site in central southern England (Lee et al., 1998). The mean concentration was 1.68 ng m^{-3}, with a maximum hourly mean concentration of 20.5 ng m^{-3} and a minimum hourly mean concentration of 0.26 ng m^{-3}. The data from Harwell show greater variability than those from more remote sites.

Lake Balaton to be between 0.4 and 5.9 ng m^{-3} with higher concentrations during day time. Comparing marine background sites in the Southern Baltic Sea (Preila, Hoburg and Kap Arkona) with a more urban-influenced site in the Gulf of Gdansk, Beldowska et al. (2006) have shown that TGM concentrations and temporal variability at the latter site was much more pronounced. Based on principal component analysis, Beldowska et al. (2006) have separated three air masses reflecting marine, terrigenous and anthropogenic sources. Urba et al. (2000) have identified the southern Baltic Sea and in particular the Gulf of Gdansk as a source region during the summer months.

Another study carried out in Poland explicitly showed the influence of residential heating on air concentrations (Zielonka et al., 2005). TGM concentrations have been measured during one summer campaign (19 - 29 August 2003) and one winter campaign (26 January - 3 February 2004) at a rural Polish site. An average TGM value of 1.63 ± 0.35 ng m^{-3} was obtained in the summer campaign, whereas a 2.5 times higher TGM concentration was found during winter. Since 85% of the houses in this rural environment use low capacity domestic heating units and are fuelled with hard coal during the cold season, Zielonka et al. concluded that residential heating is the most likely explanation for enhanced TGM winter levels.

9.4.2 Urban Locations (Including Mining Areas)

The dominance of the main anthropogenic European mercury source categories varies country wise. However, it appears that the contribution of combustion sources in general is about one third, while industrial emissions make the maximum contribution. Atmospheric mercury levels around the world's largest mining and refining complex (Almaden, Spain) were determined during two field campaigns (September 1993 and February 1994) using both point monitors and LIDAR techniques (Ferrara et al., 1998). High mercury concentrations (0.1 - 5 μg m^{-3}) were measured over the village of Almaden in the prevailing wind direction. At the second largest mercury mine in Idrija, Slovenia five centuries of mining have influenced atmospheric mercury concentrations. Kotnik et al. (2005) have reported that TGM concentrations have decreased significantly in the last decade, from more than 20 ng m^{-3} in the early 1970s to values below 100 ng m^{-3} in the 1980s, and finally reached a level of 10 ng m^{-3} or even lower at the summer of the year 2004.

Total gaseous mercury (TGM) has been monitored at Champ sur Drac, a suburban site of Grenoble in southern east France (Dommergue et al., 2002). TGM measurements have been made over 4 periods of approximately 10 days throughout 1999-2000. The mean TGM concentration was 3.4 ng m^{-3} with maximum hourly mean concentration of 37.1 ng m^{-3}. Although mean TGM concentration was not greatly different from those previously measured in the troposphere, the greater TGM variability as well as the occurrence of high TGM concentration linked to particular wind conditions suggested the strong influence of anthropogenic sources.

9.4.3 Temporal Trends at Single Locations

Continuous monitoring data sets exist for the time period 1998 to 2004 for two coastal background sites. At Mace Head, west-Irish Atlantic coast and Zingst peninsula on the southern shore-line of the Baltic Sea, automated TGM measurements have been carried out with the same instrumentation. An intensive evaluation of the two data sets has been published by Kock et al. (2005).

Between 1998 and 2004 the annually averaged TGM concentrations measured at Mace Head (1.74 ng m^{-3}) and Zingst (1.64 ng m^{-3}) remained fairly stable. For both stations higher concentrations were detected during the winter months and lower concentrations during summer, respectively.

Since Mace Head is located at the European inflow boundary and therefore considered to be less influenced by continental emissions an unexpected West to East gradient was observed. Kock et al. found that the overall mean Mace Head TGM concentration was 0.06 ng m^{-3} higher (i.e. between 3 – 4%) than those of Zingst. For the January to June period, the Mace Head TGM values (6-year mean = 1.75 ng m^{-3}) are significantly elevated compared to the Zingst results (6-year mean = 1.64 ng m^{-3}). Since no local anthropogenic mercury sources exist near the Mace Head station, it was concluded that enhanced emission from the sea provide the most probable explanation for the observed differences. During the time period March 1990 to May 1996 total gaseous mercury (TGM) has been monitored at the summit of the Wank mountain (1780 m a.s.l.) in the Bavarian Alps (Slemr and Scheel, 1998, Slemr et al., 1995). This time period covers the probably most drastic changes in the European emission situation, mainly dominated by political and economical changes in East Germany. TGM measurements at Wank showed a linear decrease of 0.169 ± 0.009 ng Hg m^{-3} yr^{-1} i.e. about 7% per year. The frequency of occurrence of extremely high TGM concentrations and the amplitude of the seasonal variation decreased over the observation time. Slemr et al. (1995) concluded that the decrease in TGM concentrations of about 22% in the years between 1990 and 1994 indicate a significant change in the trend of global TGM concentration and that this is most likely the result of reduction in coal consumption and control measures taken in the OECD countries. A decrease in TGM concentrations with time was earlier shown for south-western Scandinavia (Iverfeldt et al., 1995).

Samples for measurements of TGM in air have been collected and evaluated for the time period 1980 to 1992 and show a clear decrease with time. At the Swedish west-coast, yearly average air concentrations and median levels of 3.3 and 3.1 (1980 - 1984), 3.2 and 2.8 (1985 - 1989), and 2.7 and 2.6 ng m^{-3} (1990 - 1992), respectively, were found. Increased average and median winter concentrations were always found, with levels at 3.7 and 3.4, 3.7 and 3.3, and 3.0 and 2.7 ng m^{-3} for the respective time period. Higher winter values were expected due to increased anthropogenic emissions and changes in the mixing height of the atmosphere. As Slemr and Scheel (1998) have substantiated later, a decreased number of episodic events of TGM levels in air, from 1990 and further on is already indicated in the Scandinavian data set (Iverfeldt et al., 1995).

9.4.4 Monitoring Networks and Trends

An extensive evaluation of mercury measurements in air and precipitation at EMEP or OSPAR stations respectively has been carried out by Wangberg et al. (2007). These data were obtained at coastal sites around the North Sea and originate from Ireland, Netherlands, Germany, Norway and Sweden. The observation period is 1995 to 2002 and the two periods 1995 to 1998 and 1999 to 2002 were compared. The reduction in deposition is 10 – 30% when comparing the two periods and the authors relate the decrease to emission controls in Europe. In contrast, no decreasing trend in TGM data could be observed during the same time periods. The authors suggest that a plausible explanation is that TGM concentrations measured in the OSPAR area are to a larger extent dominated by the hemispherical background than before, i.e. European emission reductions may be over-compensated by increasing emissions in other Northern hemispheric regions.

This conclusion is supported by Berg et al. (2006) who found that current mercury levels in surface sediments, surface soils and mosses at background in Norway are substantially affected by long-range atmospheric transport. The project "Mercury species over Europe" (MOE) was aimed at identifying sources, occurrence and atmospheric behaviour of atmospheric mercury species (Pirrone et al., 2001; Munthe et al., 2003). Within MOE simultaneous measurements were carried out on a regional scale as depicted in Figure 9.14.

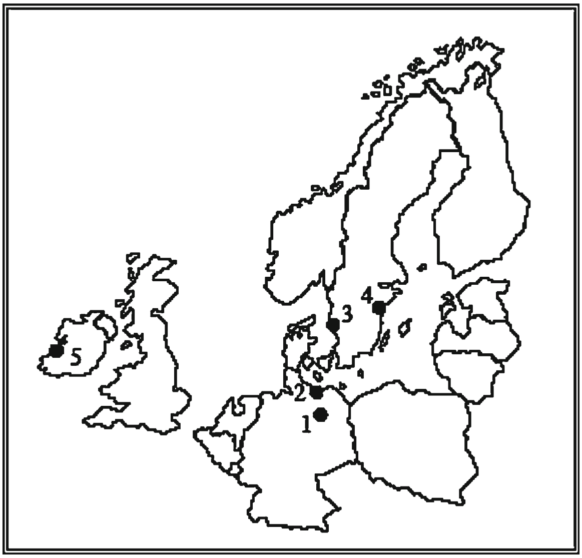


Figure 9.14 MOE measurement sites. (1) Neuglobsow, Germany; (2) Zingst, Germany; (3) Rörvik, Sweden; (4) Aspvreten, Sweden; and (5) Mace Head, Ireland

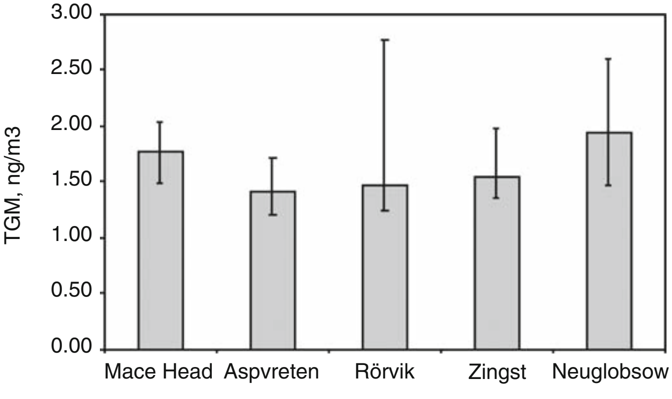


Figure 9.15 Regional differences of TGM concentrations measured during the MOE project Munthe et al., 2003)

As depicted in Figure 9.15 for TGM, the concentration at Mace Head is higher than at the two Swedish stations Rörvik and Aspvreten and more similar to the levels at Zingst on the German Baltic Sea coast. The results from Neuglobsow, Zingst, Rörvik and Aspvreten follow a slightly decreasing trend, which is in line with the location of the main European source areas. There are no local sources of

Hg at Mace Head and the slightly elevated concentrations are most likely caused by re-emissions from the sea surface (Pirrone et al., 2003; Munthe et al., 2003). Wangberg et al. (2001) compared the MOE data with results of a similar project focusing on Southern European sites around the Mediterranean Sea (EU funded project MAMCS) and reported that observed concentrations of TGM (and other species such as TPM and RGM as well) were generally slightly higher in the Mediterranean region compared with Northwest Europe.

Hladíková et al. (2001) reported TGM concentrations from 20 different localities of the Slovak Republic measured in 24-h samples of ambient air in eight times during the period 1996 - 1997. Their results showed that in 34% of the 160 individual cases the WHO guideline value of 5 ng m^{-3} for TGM was exceeded. The range of total mercury concentrations in the ambient air of Slovakia was: 1.13 - 3.98 ng m^{-3} (geom. mean 2.63) in the background area; 2.25-5.27 ng m^{-3} (geom. mean 3.64) in the agricultural areas; 1.73 - 20.53 ng m^{-3} (geom. mean 4.57) in the urban areas; and 1.53 - 39.85 ng m^{-3} (geom. mean 5.28) in the industrial areas. The highest mercury levels occurred in areas with metallurgical industry and coal combustion.

A synoptic view of regionally different background concentrations of TGM in North Central Europe was published by Schmolke et al. (1999). Over a distance of approximately 800 km simultaneous measurements of total gaseous mercury (TGM) were performed at four sampling sites between Stockholm and Berlin. The time resolution of mercury concentration measurements was 5 min. During the sampling period from 26 June to 7 July 1995, in addition to the TGM concentrations, the most common meteorological and air- quality parameters were determined. Comparing the TGM background concentrations at the four sites, a weak but statistically significant south-to-north declining TGM gradient was found. From the most southern sampling site to the northern most site median values of 1.93, 1.78, 1.53 and 1.54 ng m^{-3} TGM were detected.

Compared with the median TGM concentration observed at the two Swedish sites, the regional background concentration near Berlin was elevated by about 25%. Whereas the 0.5 h average TGM varies at the Swedish sampling sites in a very narrow range of only 0.69 ng m^{-3}, a much broader range of 3.28 ng m^{-3} was observed at the southern sites. The short time variability of the TGM concentration measured at the four sites on the south-to-north transect showed regional differences with decreasing variability from the most southern to the most northern site.

In the Mediterranean region recent studies have highlighted the importance of gaseous mercury exchange processes between the atmosphere and surface waters (Sprovieri et al., 2003; Hedgecock and Pirrone, 2004; Horvat et al., 2001; 2003; Gardfeldt et al., 2003; Kotnik et al., 2007; Sprovieri and Pirrone, 2008); the lack of knowledge of the magnitude of these exchange mechanisms is one of the main factors affecting the overall uncertainty associated with the assessment of net fluxes of mercury between the atmospheric and marine environments in the Mediterranean region. Deposition rates of mercury species from the atmosphere to receptors bodies depend on the chemical and physical properties of the species involved and their cycling, from speciated emission, transport, deposition, interaction with biota and possible re-emission to the atmosphere.

In the MBL it has been shown (Pirrone et al., 2000; Hedgecock et al., 2001) that the extremely high chloride ion concentration in sea-salt aerosol is of a great importance in the cycling of RGM species. The sea salt aerosol provides a large excess of complexing ligands for $Hg^{(II)}_{(aq)}$. The sea salt aerosol as well as scavenging Hg^0 produced by the reactions between $Hg^0_{(g)}$ and $OH_{(g)}$, $O_{3(g)}$ and to a lesser extent $H_2O_{2(g)}$ also releases RGM to the gas phase in the form of $HgCl_2$ as a result of the high $Cl^-_{(aq)}$ concentration in the sea-salt aerosol and the fact that the Henry's Law constant for $HgCl_2$ although high is lower than that of HgO (Schroeder and Munthe, 1998). From this point of view, the sea-salt aerosol represents not only a medium by which atmospherically produced $Hg^{(II)}$ could enter the sea, but is also a continuous source of RGM cycling HgO to $HgCl_2$ in the MBL. Photochemical processes in the MBL lead to enhanced oxidation of elemental mercury vapour which would lead to increased concentrations of RGM and TPM via gas-particle interactions. More recently, with the improvement of RGM sampling techniques investigations of the atmospheric chemistry of Hg have been performed across the Mediterranean sea basin (Munthe et al., 2001; Wangberg et al., 2001; 2008; Pirrone et al., 2001).

9.4.5 Mercury Speciation Analysis

For TPM, the North-western European distribution pattern has been measured during the MOE project as well. The results are depicted in Figure 9.16. The data represents median values with error bars indicating the 10% and 90% percentiles. Since this data was collected during 4 – 5 campaigns, they include values from all four seasons. Since no direct emissions of particulate mercury were found, a possible explanation for the clear gradient is that TPM is formed after emissions and the measured fractions are actually secondary TPM, i.e. formed in the air mass during transport. A plausible mechanism is adsorption of RGM on existing particles. Reactive gaseous mercury (RGM) is an operationally defined gaseous Hg fraction present in ambient

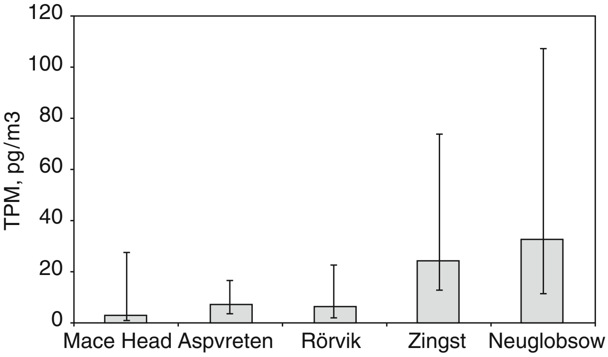


Figure 9.16 Regional differences of TPM concentrations measured during the MOE project (Munthe et al., 2003)

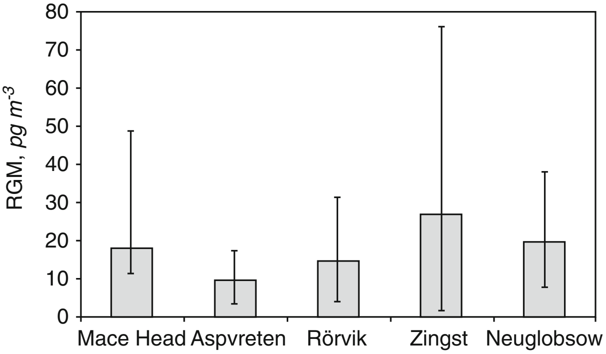


Figure 9.17 Regional differences of RGM concentrations measured during the MOE project (Munthe et al., 2003)

air. However, it is believed that RGM to the most part consist of Hg dichloride ($HgCl_2$), but other divalent Hg species are also possible. MOE results for RGM are given in Figure 9.17.

The results of a number of studies performed first within the MAMCS project (Pirrone et al., 2001; Sprovieri and Pirrone, 2006) and after in MERCYMS project (Hedgecock and Pirrone 2004; Wangberg et al., 2008) highlighted that photochemical processes occur in the MBL of the Mediterranean sea basin, leading to enhanced oxidation of Hg^0 and thus increasing of RGM and PM concentrations via gas-particle interactions.

This suggests that catalytic destruction involving $BrO_{(g)}$ or another Br containing is compound responsible for the sharp increase in the oxidation rate of Hg^0 and the formation of less volatile $Hg^{(II)}$ compounds (Hedgecock and Pirrone, 2001; Hedgecock et al., 2003; 2006). The inclusion of the reactions between halogen molecules and atoms and Hg^0 (Ariya et al., 2002) in a modelling study (Hedgecock and Pirrone, 2004), suggest that the lifetime of Hg^0 may be significantly shorter than 12 months in the MBL. The rate of oxidation of Hg by O_3 could have particular relevance for the Mediterranean MBL because of the consistently high BL concentrations of O_3 throughout the year, and particularly in spring and summer. High $Hg^{(II)}$ concentrations have also been observed in the MBL of the North Atlantic (Bermuda) (Mason et al., 2001) and the Pacific (Laurier et al., 2003) ruling out the possibility of anthropogenic source influences. However in semi-closed sea such as the Mediterranean basin it is possible that they do have an influence.

All methods employed for measurements of TGM, TPM and RGM in the framework of MAMCS project were evaluated in a field intercomparison in Sassetta, Tuscany (Italy) approximately 100 km south of Pisa. The site is situated in a hilly area 25 km from the coastline. All sampling was conducted roughly within a 10m distance. A number of different sampling techniques were employed for different mercury species. A summary of the methodology used is given in Table 9.13. More detailed descriptions of the applied methods are given in Munthe et al., 2001. TGM was measured from the start of the intercomparison exercise using all four methods

Table 9.13 Applied methods for sampling and analysis of atmospheric mercury species

Method	Hg species	Analytical method
Tekran	TGM	CVAFS. semi-continuous
Gardis	TGM	CVAFS. semi-continuous
Manual gold trap	TGM	CVAAS
Charcoal adsorbents-1 NAA	TGM	INAA
Teflon filters	TPM	Acid digestion, $SnCL_2$-CVAFS
Miniature quartz fibre filters	TPM	Thermal desorption, CVAFS
Cellulose acetate filters	TPM	Acid digestion, $SnCL_2$-CVAFS
Glass fibre filters	TPM	Acid digestion, $SnCL_2$-CVAFS
Mist Chamber with 0.1 M HCI	RGM	$SnCL_2$-CVAFS
Tubular KCI-coated denuders	RGM	Thermal desorption, CVAFS
Annular KCL-coated denuders	RGM	Thermal desorption, CVAFS/ Acid rinse-$SnCI_2$-CVAFS

Table 9.14 Average. median and range of observed concentrations of TGM, TPM and RGM in Tuscany, June

	TGM *(ng m^{-3})*	TPM *(ng m^{-3})*	RGM *(ng m^{-3})*
Average	1.98	56	22
Median	1.93	25	22
Maximum	3.38	314	41
Minimum	1.28	13	3

and the results showed that TGM measured with the different techniques are in excellent agreement, provided that careful site selection is made and stringent operational procedures are followed. In Table 9.14, the results of all applied methods for TGM, TPM and RGM are summarised.

The results of RGM and TPM measurements show a larger variability probably due to use of different sampling times but mainly this reflects the analytical difficulties for this operationally defined species. As for TGM, the variability in RGM and TPM results is higher in the beginning of the campaign than in the final three samples.

This indicates that optimisations of the sampling set-up made during the initial phase of the campaign were beneficial for the measurements. Synchronized seasonal field campaigns of 14 days duration were performed during the MAMCS and MOE projects around the Mediterranean and in North Europe from the end of 1998 to 1999; one of the major findings was that TPM and RGM concentrations were generally higher in the Mediterranean area than over northern Europe in spite of the higher density of industrial installations and urban centres in northern compared to southern Europe (Pirrone et al., 2001; Wangberg et al. 2001; Munthe et al. 2001; Pirrone et al. 2001). The most probable interpretation which comes to mind is higher emission rates and/or more active atmospheric transformation processes in the Mediterranean basin. Photochemical processes in the MBL lead to enhanced oxidation of elemental mercury vapour which would lead to increased concentrations of RGM and TPM via gas-particle interactions. The time schedule of each campaign is shown in Table 9.15 and the locations

Table 9.15 MAMCS, MOE multi-sites measurement campaigns

Campaign	Start date	Stop date
MAMCS-1/MOE-1	23-11-1998	06-12-1998
MAMCS-2/MOE-2	15-02-1999	01-03-1999
MAMCS-3/MOE-3	03-05-1999	17-05-1999
MAMCS-4/MOE-4	19-07-1999	02-08-1999
MOE-5	01-11-1999	15-11-1999

Figure 9.18 MAMCS, MOE measurement sites: 1. Mallorca (39°40'30" N, 2°41'36"E); 2. Calabria (39°25'N, 16°00'E); 3. Sicily (36°40'N, 15°10'E); 4. Turkey (36°28'12"N, 30°20'24"E); 5 Israel (32°40'N, 34°56'E); 6. Germany (53°08'34"N, 13°02'00"); 7. Germany (54°26'14"N, 12°43'30"E); 8. Sweden (57°24'48"N, 11°56'06"E); 9 Sweden (58°48'00", 17°22'54"E); 10. Ireland (53°20'N, 9°54'W)

of the measurement sites are shown in Figure 9.18. Three airborne mercury species, TGM, TPM and RGM were simultaneously measured at all sites along with meteorological parameters.

Average TGM, TPM and RGM values from the MOE and MAMCS campaigns at different seasons, are shown in Figures 9.19 – 9.21. The average TGM concentrations varied between 1.6 and 2.4 ng m^{-3} with no significant seasonal variations mainly due to the relatively stable global/hemispheric background concentration and only occasionally shows higher values for the influence of major sources. Except for the first campaign, the data indicates that the TGM is slightly but significantly higher in the Mediterranean area than in North Europe.

These findings are justified by several reasons: (a) natural emissions both from diffuse sources (Hg enriched minerals) and volcanoes (Ferrara et al., 2000; Pirrone et al., 2001) characterizing the Mediterranean area; (b) enhanced re-emission fluxes of mercury from the sea surface which are partly governed by sunlight and temperature and the warmer climate in the Mediterranean basin.

A similar trend has also been observed for the Mediterranean RGM and TPM concentrations probably due to higher emission rates and/or more active atmospheric transformation processes.

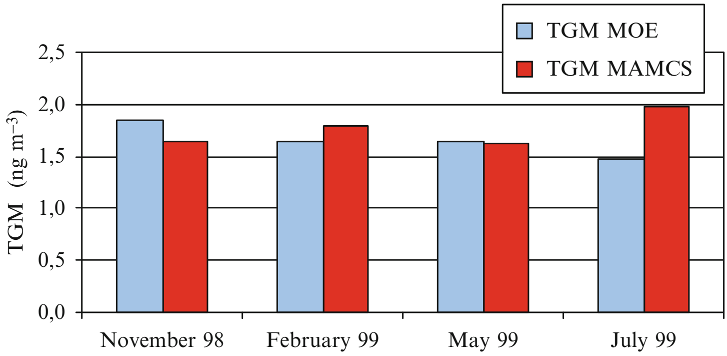


Figure 9.19 Average TGM, values obtained at campaign MOE 1-5 and MAMCS 1-4. The TGM value from the MAMCS campaign 4 should be regarded with some caution since it is based on measurements from two sites only

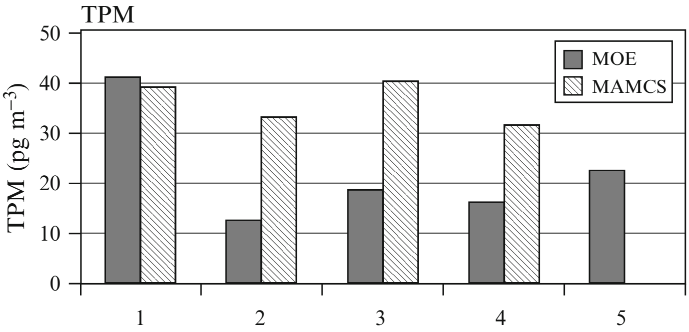


Figure 9.20 Average TPM values obtained at campaign MOE 1-5 and MAMCS 1- 4

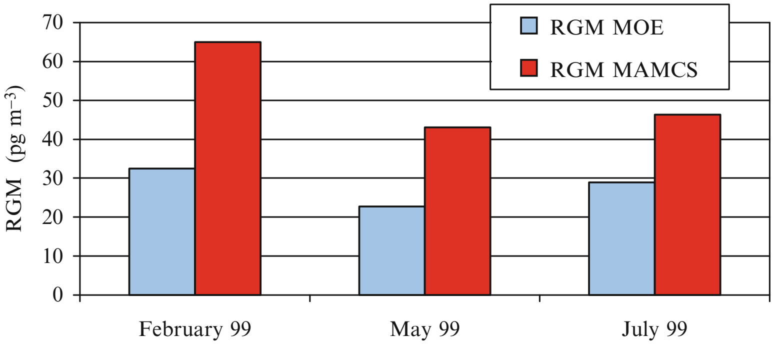


Figure 9.21 Average RGM values obtained at campaign MOE 1- 5 and MAMCS 1- 4

Photochemical processes in the marine boundary layer may lead to enhanced oxidation of elemental mercury vapour which would lead to increased concentrations of RGM and possibly TPM, via gas-particle interactions. Table 9.16 shows the TGM, RGM and TPM average values observed at the five sites in the Mediterranean during the 4 sampling campaigns of the MAMCS project (Pirrone et al., 2001) (http://www.cs.iia.cnr.it/MAMCS/project.htm).

In order to fill the gaps firstly observed during the MAMCS and MOE projects and to assess the relationship between the atmospheric input of mercury and its compounds to the Mediterranean Region and the formation/production of the most toxic forms of mercury (i.e., MeHg, Me_2Hg) in the marine system, five intensive sampling campaigns at five locations around the Mediterranean sea basin have been performed within the MERCYMS project (Pirrone, 2006). The sampling sites are shown in Figure 9.22 (http://www.cs.iia.cnr.it/MERCYMS/project.htm).

The time schedule of measurement campaigns is reported in Table 9.17. The sampling time schedules applied with manual and automatic sampling systems are shown in Table 9.18, whereas the site locations along with mercury species and methods used are shown in Table 9.19. The measurement periods was chosen to

Table 9.16 TGM, RGM and TPM average values observed at the five sites in the Mediterranean during the 4 sampling campaigns of the MAMCS project

Sites	Coordinates	MAMCS-1	MAMCS-2	MAMCS-3	MAMCS-4
TGM Average (*ng m^{-3}*)					
Mallorca, Spain	39°40’ N, 2°41’ E	3.16	3.08	3.85	4.15
Fuscaldo Marina Calabria, Italy	39°25’ N, 16°0.0’ E	1.30	1.86	1.42	1.09
Porto Palo, Sicily, Italy	36°40’ N, 15°10’ E	1.34	2.37	1.89	2.18
Antalya, Turkey	36°28’ N 30°20’ E	1.68	8.71	1.34	---
Neve Yam, Haifa, Israel	32°40’ N, 34°56’ E	1.83	0.90	1.45	---
RGM Average (*pg m^{-3}*)					
Mallorca, Spain	39°40’ N, 2°41’ E	1.88	99.59	76.02	-----
Fuscaldo Marina Calabria, Italy	39°25’ N, 16°0.0’ E	40.18	24.84	46.74	35.47
Porto Palo, Sicily, Italy	36°40’ N, 15°10’ E	90.14	46.39	77.49	29.48
Antalya, Turkey	36°28’ N 30°20’ E	-----	10.44	21	-----
Neve Yam, Haifa, Israel	32°40’ N, 34°56’ E	-----	36.14	34.81	-----
TPM Average (*pg m^{-3}*)					
Mallorca, Spain	39°40’ N, 2°41’ E	34.40	86.12	44.11	33.56
Fuscaldo Marina Calabria, Italy	39°25’ N, 16°0.0’ E	26.32	28.55	22.71	45.50
Porto Palo, Sicily, Italy	36°40’ N, 15°10’ E	5.57	8.46	11.02	9.11
Antalya, Turkey	36°28’ N 30°20’ E	14.66	14.39	25.25	65.25
Neve Yam, Haifa, Israel	32°40’ N, 34°56’ E	115.39	27.3	97.89	4.19

Figure 9.22 MERCYMS coastal measurement sites: 1 Cabo de Creus, 2 Meze, Thau Lagoon, 3 Piran Marine, 4 Fuscaldo, 5 Neve Yam

Table 9.17 Time-schedule of sampling campaigns in the framework of the MERCYMS Project

Coastal campaigns	Start date	Stop date
Autumn 2003	20-10-2003	03-11-2003
Winter 2004	19-01-2004	02-02-2004
Spring 2004	26-04-2004	10-05-2004
Summer 2004	19-07-2004	02-08-2004

Table 9.18 Sampling type and time schedule applied during MERCYMS campaigns

Specie	Manual	Automatic
TGM	Two 12 h average samples per 24 h period. starting 7:30 and 19:30 UTC	Continuous 5 mm average samples yielding 288 samples per 24 h period
RGM	Two 12 h average samples per 24 h period. starting 7:30 and 19:30 LTC	One 2 h sample per every 3 h period, alternatively one 5.25 h sample per every 6 h period
TPM	Two 12 h average samples per 24 h period. starting 7:30 and 19:30 UTC	One 2 h sample per every 3 h period

cover four seasons. Table 9.20 shows the average TGM, RGM and TPM values from coastal stations during four season.

9.4.6 Mercury Measurements (Including Aircraft) Related to Emissions, and Source Attribution

Many emission inventories for mercury have been compiled but rarely constrained using observations of ambient air concentrations with a known quality. Slemr et al.

Table 9.19 Site locations and mercury species and methods used during MERCYMS project

Sites	Coordinates	TGM	RGM	TPM
Cabo de Creus, Spain	42°19.2’ N, 3°18.9’ E	Automatic measurements with 5 min time resolution, Tekran Model 2537A	Manual 12 h samples on KCl annular denuders. Automatic measurements during the spring and summer campaigns	Manual 24 h samples on TPM mini-traps
Mèze,Thau Lagoon, France	43°25’ N, 3°35’ E	Manual Au traps 2h samples	Manual 12 h samples on KCl annular denuders	Manual 12 h samples on TPM mini-traps
Piran Marine, Slovenia	45°32.9’ N, 13°33.0’ E	Manual Au traps 12 h samples (24 h during winter)	Manual 12 h samples on KCl annular denuders (24 h during winter)	Manual 12 h samples on TPM mini-traps (24 h during winter)
Fuscaldo/S. Lucido, Calabria, Italy	39°25’ N, 16°0.0’ E	Automatic measurements with 5 min time resolution, Tekran Model 2537A	Automatic sampling on KCl annular denuders using the Tekran 1130 speciation unit	Automatic sampling of fine particulate mercury, using the Tekran 1130 speciation unit
Neve Yam, Haifa, Israel	32°40’ N, 34°56’ E		Manual 12 h samples on KCl denuders	Manual 12 h samples on TPM mini-traps

Table 9.20 Average TGM, RGM and TPM values from coastal stations during four seasons

	Fall			Winter			Spring			Summer		
Site	TGM	RGM	TPM	TGM	RGM	TPM	TGM	RGM	TPM	TGM	RGM	TPM
Cabo de Creus, Spain	1.6	2.2	9.6	1.5	0.24	9.1	2.0	1.2	9.5	2.1	1.2	11.2
RGM Automatic		–	–		–			1.9			6.9	
Mèze,Thau Lagoon, France	1.6	8.6	3.0	2.9	41.9	82	1.9	10.4	26.7	3.3	191	662
Piran Marine, Slovenia	-	4.5	-	0.8	1.0	18.7	1.8	2.5	7.4	4.0	15.4	9.4
Fuscaldo/S.Lucido, Italy	1.3	1.6	1.0	1.9	4.2	6.1	1.8	2.1	1.7	1.6		
Neve Yam, Israel	Day 1.19 Night 0.78	33	89	Day 0.80 Night 0.50	2.2	3.9	Day 0.86 Night 0.46	10.7	40.1	Day 1.24 Night 1.21	8.3	22.7

(2006) have derived Hg/CO, Hg/halocarbon, and Hg/CH_4 emission ratios from pollution episodes observed during the long-term mercury monitoring at the Mace Head Atmospheric Research Station in Ireland. The authors conclude that mercury emissions calculated from the emission ratios and the European emissions of the above gases are in reasonable agreement with the estimated anthropogenic total mercury emissions of 250 Mg yr^{-1} in 1995. However, the measurements encompass almost exclusively elemental mercury whose anthropogenic emissions are estimated to be only 152 Mg yr^{-1}. Slemr et al. propose several hypotheses to explain this discrepancy, including natural sources, underestimation of the emissions of elementary mercury, and erroneous speciation of anthropogenic emissions.

One of the very few aircraft measurements in Europe have been carried out on 13 June 1996, during a level flight from Munich to Halle at an altitude of 900 m a.s.l. and back at 2500 m a.s.l. Ebinghaus and Slemr (2000) showed that TGM was horizontally evenly distributed over a distance of 400 km. TGM concentration at an altitude of 2500 m a.s.l. (in the free troposphere) was 1.635 ± 0.094 ng m^{-3} (n=22) slightly lower than at 900 m a.s.l. (in the mixing layer) 1.774 ± 0.101 ng m^{-3} (n=17). Higher TGM concentrations of 2.190 ± 0.255 ng m^{-3} (n=2) during the southernmost part of the flight south of Munich and of 2.321 ± 0.133 ng m^{-3} (n=8) at the summit of the mountain Wank was attributed to a different air mass. Substantially higher TGM concentrations were observed in the mixing layer downwind of a former chlor-alkali plant in East Germany. From the downwind/upwind concentration difference and the prevailing wind conditions, a mercury emission of about 0.4 kg d^{-1} was estimated for the plant area.

9.5 Measurements of Air Concentrations in Asia

9.5.1 Remote Locations

Kim et al. (1996) have reported TGM concentrations from 13 remote mountainous sampling stations in Korea, for the time period October 1987 through February 1993. The TGM concentrations determined during these field campaigns were found to be in the range of 1.48 to 8.00 ng m^{-3}, 75% of them spanning between 2 to 5 ng m^{-3}. Kim et al. concluded that the observed Hg levels and the wide spreadness of the observed data suggests that Hg pollution in the Korean atmosphere may result in generally enhanced levels compared to other Northern hemispheric regions. This finding is supported by Sohn et al. (1993) who reported rural concentrations in Korea to be between 1.0 to 7.0 ng m^{-3} (mean 3.8 ng m^{-3}) for the years 1988 – 1989.

Liu et al. (2002) have reported Chinese data for two remote sampling locations for 1998 in the Beijing area to be between 3.1 – 5.3 ng m^{-3} in winter and 4.1 – 7.7 ng m^{-3} in summer. Wang et al. (2007) also found higher concentrations in summer compared to winter for a remote site on the Mount Waliguan, China to be 1.7 ± 1.1 ng m^{-3} in summer and 0.6 ± 0.08 ng m^{-3} in winter. TGM data for a remote site in the Yangtze Delta were higher and expressed a more pronounced variability (5.4 ± 4.1 ng m^{-3}). Different seasonal variation patterns of TGM concentration were found between urban and remote sites. In Beijing (urban) the highest TGM concentration was in winter and the lowest in summer, while in Mt. Waliguan the TGM concentration in summer was higher than that in winter. These indicated that different processes and factors controlled TGM concentration in urban, regional and remote areas.

TGM monitoring data for Korean GAW station (An-Myun Island) have been published by Nguyen et al. (2007). Measurements were routinely recorded on An-Myun Island off the coast of Korea between December 2004 and April 2006. The mean TGM concentration for the measurement period was 4.61 ± 2.21 ng m^{-3} with a range of 0.10 – 25.4 ng m^{-3}. Analysis of the seasonal patterns indicated TGM concentration levels generally peaked in spring, while reaching a minimum in summer. Nguyen et al. (2007) concluded that Hg concentration levels at An-Myun Island can be affected intensively by trans-boundary input processes over certain periods of time. and that its springtime dominance hence suggests combined effects of various local source processes and the meteorological conditions favourable for the massive air mass transport phenomenon (such as Asian Dust storms).

9.5.2 Urban Locations (including mining areas)

For Seoul, Korea Sohn et al. (1993) have reported TGM data for the years 1988 – 1989 to be in the range from 5.0 to 88.8 ng m^{-3} with a mean of 25.1 ng m^{-3}. For September 1997 and May/June 1998 Kim et al. (2001b) have found mean concentrations of TGM in Seoul (1999–2000) for the two study periods were computed as 3.94 and 3.43 ng m^{-3}, respectively. For January 1999 to August 2000 the mean hourly TGM concentration was 5.26 ± 3.27 ng m^{-3} and when divided seasonally, the highest mean of 6.01 ng m^{-3} was observed during winter. Kim et al. (2001a) suggested that this most likely due to anthropogenic sources such as household heating systems.

Urban data for Beijing, China, show a similar distribution between summer and winter. Liu et al (2002) and Wang et al. (2007) give winter concentration ranges between 8 and 25 ng m^{-3}, and lower summer values between 5 and 13 ng m^{-3}, with autumn and spring concentration in between. Feng et al. (2004) have reported TGM concentration data for Guiyang city, in 2001. The mean TGM concentration at this site is 8.40 ng m^{-3} on the basis of one year observation. Feng et al. concluded that TGM concentrations in Guiyang are significantly elevated compared to the continental global background values and that coal combustion from both industrial and domestic uses is probably the primary atmospheric source. Similar data were obtained earlier (Feng et al., 2003) during 4 measurement campaigns in 2000 and 2001 in Guiyang. The seasonal geometric mean of TGM in Guiyang was 7.45 ng m^{-3} for winter, 8.56 ng m^{-3} for spring, 5.20 ng m^{-3} for summer and 8.33 ng m^{-3} for autumn. The overall average TGM covering the sampling periods was 7.39 ng m^{-3}. Data for Guangzhou were reported to be 13.5 ± 7.1 ng m^{-3} (Wang et al., 2007).

9.5.3 Temporal Trends at Single Locations

In 1995, Nakagawa published data for TGM levels in air that have been monitored over a period of 17-years (1978-1994) at three different stations in Japan. Nakagawa concluded that TGM was at minimum levels at the three sampling stations in 1988 and was corresponding to background levels. Afterwards Nakagawa found TGM levels rising steadily up to the present time and claimed that the current atmospheric concentrations of total mercury inferred from measurements of air sampled at the Japanese stations has an increasing tendency every year in the time period 1978-1994 (Nakgawa, 1995).

9.5.4 Mercury Speciation Analysis

Xiu et al. (2005) have published data of size-fractionated particulate mercury (TPM-species) in Shanghai, China, collected from ambient air between March 2002 to September 2003. Speciation data are operationally defined as (i) volatile particle-phase mercury (VPM), (ii) reactive particle-phase mercury (RPM) and (iii) inert particle-phase mercury (IPM). Concentrations for particulate phase mercury as published by Xiu et al. (2005) are:

- volatile particle-phase mercury (VPM) = 0.058 – 0.252 ng m^{-3}
- reactive particle-phase mercury (RPM) = 0.148 – 0.398 ng m^{-3}
- inert particle-phase mercury (IPM) = 0.233 – 0.529 ng m^{-3}

Fang et al. (2001a; 2001b) have measured particulate phase mercury concentration in Changchun, an urban location in China, Changchun between July 1999 to January 2000. During non-heating season they found PM concentration levels in air between 0.022 to the 0.398 ng m^{-3} with an average of 0.145 ng m^{-3}. During the heating season PM concentration in air were reported to be 0.148-1.984 ng m^{-3} with an average of 0.461 ng m^{-3}. Coal burning and wind-blown soil material were identified to be two important sources of Hg(p) for the Changchun area.

For Guiyang, an urban location in southwest China (Shang et al. (2003) have measured average concentrations for TGM to be 7.09 ng m^{-3}, and RGM as 37.5 pg m^{-3} in March 2002. They concluded that TGM concentrations in Guiyang are significantly elevated comparing to the global background values, whereas RGM concentrations are only slightly higher than the reported values in remote areas in Europe and the USA.

9.5.5 Mercury Measurements (Including Aircraft) Related to Emissions, and Source Attribution

In situ mercury emission fluxes from soil in Lanmuchang Hg-Tl mining area, in south-western Guizhou, China, were measured using the dynamic flux chamber method (December 2002 and May 2003). Huge mercury emission fluxes from soil were obtained in the mining area, ranging from 623 to 10,544 ng m^{-2} h^{-1} with the maximal mean Hg flux of 2,283 ± 2,434 ng m^{-2} h^{-1} (Wang et al. 2005).

Tomiyasu et al. (2000) have shown that Hg emissions from localized sources are reflected in ambient air concentrations. For Kagoshima City, Japan, the influence of mercury emitted from Sakurajima has been measured between January 1996 to January 1997. The mercury concentration obtained was in the range 1.2-52.5 ng m^{-3} (mean 10.8 ng m^{-3}, n = 169). Values of 8.1 ± 5.3 ng m^{-3}, 14.8 ± 7.9 ng m^{-3}, 13.9 ± 11.7 ng m^{-3} and 4.4 ± 1.6 ng m^{-3} (mean ± S.D.) were obtained for spring, summer, autumn and winter, respectively. For July 1999 to March 2002 the concentration ranged from 1.24 to 29.4 ng m^{-3} in the daytime and 1.38 to 14.8 ng m^{-3} overnight. The concentration gradient showed a high degree of dependency on solar radiation. These observations suggested that mercury is emitted from the ground with an increase in solar radiation and rise of the temperature in the daytime and deposits with the fall of temperature at nighttime. The influence of rain and volcanic activity on the periodic variation of mercury is also discussed in detail by Tomiyasu et al., (2006).

Kim et al. (2002) have published data from flux measurements over a paddy field in Kang Hwa, Korea, carried out in March 2001. The Hg fluxes over a bare paddy field at Hari, were comparable to those reported in the literature for polluted environments and showed clear diurnal pattern with maximum (< 600 ng m^{-2} h^{-1}) during midday and the minimum (~100 ng m^{-2} h^{-1}) at nighttime. The mean air concentrations of TGM was found to be elevated compared to global background concentrations, i.e. 3.72 ng m^{-3}.

Friedli et al. (2004) reported that during the Aerosol Characterization Experiment (ACE-Asia), research flights the air at all sampled altitudes contained concentrations of atmospheric mercury above the global background. Highest mixing ratios for Hg^0 were found in industrial plumes exiting China (6.3 ng m^{-3}), Korea (3 ng m^{-3}), and Japan (3 ng m^{-3}).

9.6 Measurements of Air Concentrations in Africa

9.6.1 Monitoring Networks and Trends

The monitoring of total gaseous Hg (TGM) was established at the Cape Point Global Atmospheric Watch (GAW) station in September 1995. Baker et al. (2002) presented the first data obtained until June 1999. Atmospheric Hg concentrations were found to be fairly homogeneous fluctuating between 1.2 – 1.4 ng m^{-3}. Whilst no significant diurnal variation is detectable, a slight seasonal variation with a TGM minimum in March-May and maximum in June-August was observed. A minimum annual TGM concentration was detected in 1997. The Cape Point GAW station was found to constitute a suitable site for monitoring TGM concentrations in the Southern Hemisphere (SH).

9.6.2 Mercury Measurements (Including Aircraft) related to Emissions, and Source Attribution

During mid-January 2000 the plume from a fire, which destroyed 9000 ha of mixed vegetation in the southern part of the Cape Peninsula, passed over the Cape Point Global Atmosphere Watch station (34°S, 18°E). Measurements of total gaseous mercury (TGM) made during this episode provided Hg/CO and Hg/CO_2 emission ratios of $(2.10 \pm 0.21) \times 10^{-7}$ and $(1.19 \pm 0.30) \times 10^{-8}$ mol/mol, respectively (Brunke et al. 2001).

9.7 Summary and Conclusion

Mercury concentration measurements in ambient air of documented and accepted quality are available since the mid 1970 and concentration data are available for both hemispheres. A significant impulse on international mercury research was achieved by the implementation of new automated analysers in the early 1990’s. Long-term monitoring of atmospheric mercury with high time resolution has been started at Alert, Canada (January 1995) and Mace Head, Ireland (September 1995), followed by numerous other sites since then. Field intercomparisons have been carried out and included the comparison of new automated analysers with traditional manual methodologies. One major conclusion derived from these studies is that good agreement of TGM concentration data in air determined with different techniques, including techniques dating back to the 1970’s, makes a combination of these data sets with contemporary ones from different regions of the world feasible.

General scientific consensus exists about the current global background concentration of airborne mercury which is taken as ca. 1.5 to 1.7 ng m^{-3} in the Northern Hemisphere and ca. 1.1 to 1.3 ng m^{-3} in the Southern Hemisphere. Seasonal variations of TGM concentrations are observed at almost all sites with sufficient data coverage. Most sites show higher concentrations in winter and spring, and lower in summer and fall. It is suggested that the meteorological seasonal variability is the most important factor in the establishment of the observed seasonal cycles of the TGM concentrations. Temporal dynamics of TGM and also Hg in wet deposition are complex, with the magnitude of diurnal and seasonal changes often being larger than annual changes.

Canadian data show that the seasonality of Hg concentration in precipitation exhibits an opposite pattern to TGM air concentrations with higher concentrations during the summer months. Two possible factors have been suggested for this seasonal behaviour: increased particle scavenging capacity of rain relative to snow and/or increase in the oxidation of Hg, either in cloud or in the gas phase, during summer. However, sites with the highest observed concentrations do not necessarily have the highest Hg deposition per unit and surface area since the deposition is also dependent on the precipitation amount. Regional differences, temporal trends and potential sources and source regions can be identified by monitoring, especially when carried out in networks. In principal, an increase of the global atmospheric pool should also be reflected in the background concentration of mercury in ambient air. Fitzgerald's initiative for the installation of a global AMNET has partly been accomplished on a regional scale within the CAMNet that may be considered as seminal in this respect. CAMNet has revealed a decreasing trend for TGM at a number of rural sites for the time period 1995 to 2005. The largest declines were observed close to urban areas of Toronto and Montreal. This is supported by data from United States giving evidence that TGM concentrations at rural locations on the eastern USA seaboard downwind of major urban and industrial centers are decreasing.

The changes are mostly driven by local or regional changes such as cutbacks in emissions. Many of the TGM changes are comparable with the overall trends of total mercury concentrations in precipitation, again reflecting local or regional emission reductions in decreasing concentration levels. For remote sites in Europe and North America it could be shown that only slight decreases or no statistically significant trend in the TGM concentration exist over the same time period. This is in contrast with emission estimates especially for Europe, where drastic reductions have taken place over the past 10 to 20 years. It has been suggested that TGM concentration in the North-western European atmosphere are to a larger extent dominated by hemispherical background than before, i.e. European emission reductions may be over-compensated by increasing emissions in other Northern hemispheric regions. It should be noted that for the same time period and same set of stations (1995 to 1998 vs. 1999 to 2002) a reduction in deposition of 10 to 30% was found which can possibly be related to emissions controls in Europe.

Deposition networks on a regional scale are essential for understanding the spatial and temporal patterns of Hg in wet deposition, but without at least TGM measurement and additional speciated Hg measurements wherever possible in conjunction with precipitation measurements, little can be inferred about the processes responsible for controlling Hg deposition. It is still not well understood which sites would respond most quickly to emission reductions in certain industrial sectors, or if enhanced deposition events are independent of local or regional sources and supplied predominantly by the global pool being caused by natural variations in photochemistry and meteorology. US studies show that Hg deposition can vary by 2-fold between an urban and a rural site, TGM might vary by 50 – 75%, whereas TPM may vary 5 – 10 fold between sites. Regional differences of individual speciation have also been reported for Europe. Observed concentrations of TGM, TPM and RGM are generally slightly higher in the Mediterranean region than in Northwest Europe.

In general, it may be concluded that RGM in situ formation is very important in both the marine boundary layer under cloud-free conditions, and in the free troposphere, where concentrations reach those of the most polluted urban atmosphere. Additionally, because of the diurnal nature of photochemistry and boundary layer/free tropospheric exchange, RGM, and to a lesser extent Hg^0, and TPM generally have prominent diel cycles. Superimposed on the natural variability is the episodic nature of advection of more or less polluted air masses to a sampling site from urban/industrial/mining sources. With regard to long-term changes in RGM or TPM concentrations, the data do not go back far enough or have sufficient spatial coverage to appropriately address this question.

Asian emissions are considered to be of global importance and are suggested to be rapidly increasing in the past decade. The importance of Asian emissions is obvious from recent emission estimates. Furthermore, experimental data are showing long-range transport across the Pacific and suggest a significant underestimate of Asian mercury emissions. However, potentially increased Asian emissions are neither reflected in the long-term measurement of TGM at Mace Head (1995 – 2007), nor in the precipitation data of the North American MDN. The reason for this is not yet clear however, it was hypothesized that atmospheric mercury cycling is possibly going on a faster rate than previously thought.

In general it can be concluded that monitoring at single locations or in networks is a very useful scientific tool in order to identify regional differences, temporal trends and for source attribution. Monitoring is necessary to evaluate the effectiveness of control measures, as demonstrated on regional scales. In connection with air quality data, mercury monitoring can be used to verify and/or improve emission estimates. Monitoring data can give new insights in the mercury cycling on different temporal and spatial scales, due to “unexpected findings”, such as AMDEs as a prominent example. They help us to improve our understanding of the global mercury cycle in order to evolve purposeful regulations on an international scale. The value of long-term atmospheric mercury monitoring and the need for additional sites is obvious, especially in the remote Southern Hemisphere.

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