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Baseline atmospheric mercury studies at Ross Island, Antarctica

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Abstract: The first extended baseline studies of total gaseous mercury (TGM) and dimethylmercury (DMM) in Antarctica are reported. Mean TGM concentrations of 0.52, 0.60 and 0.52 ng m^{-3} were obtained for three consecutive years at the southern tip of Ross Island (77°S). The levels of DMM in Antarctica are less than 10% of the TGM, and frequently fall below the limit of detection. These results represent the lowest TGM concentrations recorded globally and extend into polar regions the observation of a decrease in atmospheric mercury concentration with increasing latitude.

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Introduction

Antarctica is a pristine environment and represents one of the best sites available for conducting baseline studies of atmospheric constituents. Such investigations complement ice core analyses and allow both the fundamental geochemical cycle of several elements to be determined and any anthropogenic perturbations to be assessed. Environmental concentrations of mercury have been greatly influenced by Man's activity, to the extent that present flux strengths from natural and anthropogenic sources are considered to be equal (Lindquist & Henning 1985). Knowledge of the global distribution of atmospheric mercury is incomplete and, in particular, data for the southern hemisphere are sparse. Moreover, relatively few speciation studies have been made and temporal variations are essentially unknown.

Metals in the atmosphere are generally present in association with particulate phases and so have relatively short residence times typical of aerosols. However, in marked contrast, mercury is a volatile element with an atmospheric residence time of about one year (Lindquist & Henning1985, Mason *et al.* 1992, Slemr *et al.* 1985). Only a small fraction of the atmospheric burden exists as particulate mercury (Schroeder *et al.* 1991). Although elemental mercury dominates the gaseous speciation, dimethylmercury (DMM) of biogenic origin can influence concentrations in the marine atmosphere (Fitzgerald 1986, Kim & Fitzgerald 1986, Slemr *et al.* 1985). Atmospheric mercury concentrations exhibit a marked latitudinal variation. Background concentrations of total gaseous mercury (TGM) in the range of 2–3 ng m^{-3} are found in the mid-latitudes of the northern hemisphere (Lindquist & Henning 1985, Slemr *et al.* 1985, Slemr *et al.* 1981) and decrease southwards becoming < 1 ng m^{-3} in New Zealand (Bibby *et al.* 1988, de Mora *et al.* 1991, Fitzgerald 1986). No reliable data are available for TGM levels in southern polar regions. This paper presents the first baseline data for the concentration and speciation of atmospheric mercury in Antarctica.

Methods

Speciation analysis of atmospheric mercury was achieved by drawing air through a pair of stacked collectors containing silvered and gilded sand, respectively (Braman & Johnson 1974, de Mora *et al.* 1991, Kim & Fitzgerald 1986). The silver removed all forms of mercury other than dimethylmercury (DMM) which was subsequently accumulated on the second collector. These two categories of material are generally referred to as "inorganic" and "organic" mercury, respectively. The inorganic fraction is likely to be dominated by elemental mercury, but the actual species composition is unknown.

Air was pumped through the collection tubes at *c.* 1 l min^{-1} for 24 or 48 h. As particulate mercury concentrations are extremely low and the aerosol concentration was itself low, the air was not pre-filtered during sample collection. Previous studies using double gold or silver accumulators have verified the integrity of the sampling system (Bibby *et al.* 1988, de Mora *et al.* 1991). The quartz tubes were sealed with Parafilm and analysed within a few days of collection. This procedure results in neither mercury contamination nor desorptive losses (checked using samplers loaded with known amounts of mercury and stored for a few days).

Mercury was determined by photoacoustic spectroscopy (de Mora *et al.* 1987, Patterson 1984). The silica tube containing either silvered or gilded sand was mounted in a gas line. The trapped mercury was volatilized by heating to *c.* 600°C and flushed out using mercury-purified air or nitrogen initially onto a gold collector and then subsequently into a silica tube. The mercury was then quantified by measuring the sound produced from fluorescence quenching when the sample vapour was irradiated with a modulated mercury vapour lamp. The instrument was calibrated by injecting aliquots of mercury-saturated air from a constant reservoir with a 2 ml glass syringe. The absolute detection limit for the photoacoustic spectrometer was 0.05 ng. Blanks were determined by repeated firing of a collector. Procedural

blanks were obtained by analysing unused collectors that had been sealed with Parafilm and stored for some time. Based on 81 blanks, the mean absolute value was 0.14 ng Hg with a standard deviation (σ_{Blank}) of 0.30 ng Hg. The detection limit (blank mean + 3 $\times\sigma_{Blank}$) was therefore 1.04 ng Hg, which for a typical 20 m^3 sample was equivalent to 0.05 ng m^{-3}.

Results and discussion

Atmospheric mercury was determined at three sites in Victoria Land. A preliminary sampling programme was carried out on the frozen surface of Lake Vanda (77°33'S, 161°37'E) in the Wright Valley during December 1985. This comprised an ideal sampling location, about 1 km upwind from the small station at Lake Vanda and experiencing pristine winds directly from the Antarctic Plateau. The two sets of samples obtained showed very low TGM levels, namely 0.21 and 0.23 ng m^{-3}. While obviously limited, the data were extremely interesting suggesting that TGM concentrations in Antarctica were substantially lower than those observed elsewhere. TGM concentrations at Baring Head (41°S), New Zealand, are about 0.8 ng m^{-3} (Bibby *et al.* 1988, de Mora *et al.* 1991) which are already low on a global scale. Accordingly, further studies were conducted throughout 1987 and 1988 at Scott Base and during 1989 at Arrival Heights on Ross Island. (Table I). As sampling was conducted throughout the year, these results should indeed be representative of the annual means.

Table I. Speciation and total gaseous mercury (TGM) concentrations (ng m^{-3}) in the atmosphere at Ross Island during 1987 to 1989.

	1987*	1988*	1989#	1987–89
Number of samples	68	78	50	196
Inorganic mercury				
mean	0.50	0.54	0.48	0.51
standard deviation	0.14	0.39	0.16	0.27
standard error	0.02	0.04	0.02	0.02
maximum	0.81	1.78	0.74	1.78
minimum	0.06	0.01	0.09	0.01
Dimethylmercury				
mean	0.02	0.06	0.04	0.04
standard deviation	0.06	0.10	0.06	0.08
standard error	0.01	0.01	0.01	0.01
maximum	0.31	0.63	0.35	0.63
minimum	0.00	0.00	0.00	0.00
Total gaseous mercury				
mean	0.52	0.60	0.52	0.55
standard deviation	0.14	0.40	0.16	0.28
standard error	0.02	0.04	0.02	0.02
maximum	0.83	1.85	0.78	1.85
minimum	0.16	0.02	0.11	0.02

* Scott Base; # Arrival Heights.

Duplicate samples were collected during the period February 1987 to December 1988 at a site within 100 m of Scott Base. Sampling was not controlled for a preferred wind sector. Gaps in the data record occurred at the end of each year as new base staff were being trained to operate this and a wide range of other experiments. Some problems were experienced in sampling for both these years. During 1987 the flow measurements were in error and had to be corrected by 5% following re-calibration. In 1988 the teflon lines between the sample tubes and the pump fatigued in the severe polar winds and one channel became unreliable. Notwithstanding the difficulties encountered, a valuable data set for atmospheric mercury concentrations was obtained in each year. The mean TGM for 1987 with 68 measurements was 0.52 ± 0.14 ng m^{-3} whereas the corresponding 1988 value was 0.60 ± 0.40 ng m^{-3}, based on 78 samples.

At the beginning of 1989 a new, single channel sampling arrangement was adopted. The sampling train incorporated a set of quartz sample tubes, thick-wall 1/8 inch (3.5 mm) teflon tubing, a pump and an integrating flow meter. No flow controllers were used, but rather the teflon tubing directly restricted the flow to 1 l min^{-1}. This flow rate was consistent throughout the sampling period except for a few days during the coldest part of the winter when erratic results were associated with icing up of the lines. The sampling location for 1989 was transferred from Scott Base to Arrival Heights (77°11'S, 166°40'), 2.7 km north of McMurdo Station, to be further removed from base activities. Although the sample collection was not controlled for a preferred wind sector, the site experiences prevalent northeasterly winds, the result of pristine air masses of southern origin being deflected by topographic features (Sinclair 1988).

A total of 50 atmospheric samples was collected and analysed for both inorganic mercury and organomercury during 1989. The data depicted in Figs 1 & 2 constitute one of the longest time series for atmospheric mercury measurements at a single baseline site. Considering firstly the TGM (Fig. 1), the concentrations ranged from 0.11–0.78 ng m^{-3}, with a mean value of 0.52 ± 0.16 ng m^{-3}. The true variation was exaggerated by episodic marked departures from a "normal" background level due to the apparent influx of air containing very low levels of mercury, and comparable to those observed at Lake Vanda. The source of such mercury depleted air is currently under investigation. The average TGM concentration was substantially lower than values obtained elsewhere and confirmed the world-wide latitudinal variation of this element in the atmosphere. TGM levels of 2–3 ng m^{-3} have been reported in the marine troposphere of the mid-northern latitudes (Lindquist & Henning 1985, Slemr *et al.* 1985, Slemr *et al.* 1981), and in the range 1–1.5 ng m^{-3} near the equator. They are about 1 ng m^{-3} in the low latitudes of the southern hemisphere (Fitzgerald 1986, Kim & Fitzgerald 1986) and an average TGM value of 0.73 ng m^{-3}, observed near Wellington, New Zealand, (41°S) represents the minimum average

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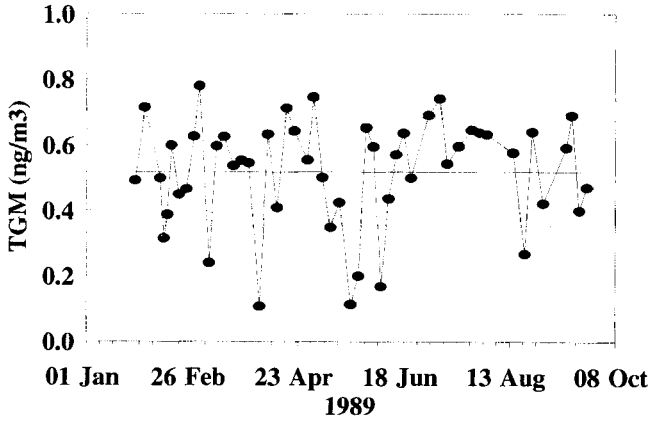

Fig. 1. Total gaseous mercury (TGM) concentrations (ng m^{-3}) measured at Arrival Heights, during 1989. The horizontal lines signify the mean concentration ±1 s.d. Time axis ticks denote one week intervals.

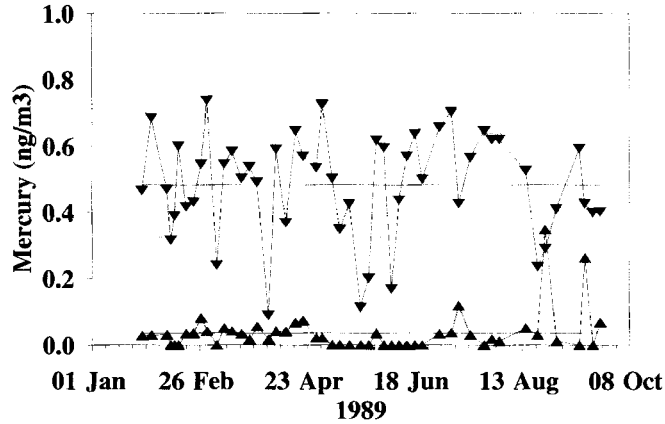

Fig. 2. Atmospheric concentrations (ng m^{-3}) of inorganic mercury (▼) and dimethylmercury (▲) measured at Arrival Heights, during 1989. The horizontal lines signify the mean concentration of each fraction ± 1 s.d. Time axis ticks denote one week intervals.

concentration previously reported (Bibby *et al.* 1988).

Despite the low concentration of atmospheric mercury observed in Antarctica, it is worth noting that the latitudinal variation is not as pronounced as for other metals, such as lead. There are two main reasons for such behaviour. Firstly, atmospheric mercury is predominantly gaseous rather that particulate. Hence, Hg will have a longer residence time and thus be transported more readily to polar latitudes. Secondly, the atmospheric burden of many metals, especially exemplified by lead, is predominantly anthropogenic in origin, with only a limited source strength south of 60°S. In contrast, Hg has important natural sources, both volcanic and oceanic, in the polar region. Mercury evasion from the Southern Ocean is expected to be an important source. This is especially true for the Ross Sea, a region of relatively high biological productivity (Smith & Nelson 1985). In terms of the Antarctic continent, Mount Erebus on Ross Island no doubt acts as a significant source of mercury. However, the importance locally is more difficult to ascertain given the rather poor vertical mixing that has been observed in atmospheric tracer studies (Mroz *et al.* 1989).

Schroeder *et al.* (1991) have remarked that the wide variation in mercury vapour pressure with temperature (2.78×10^{-3} Torr at 30°C and 4.78×10^{-6} Torr at -30°C) should promote gas to particle transfer at low temperature. TGM has been shown to vary directly with temperature in the range 2.5–15°C (Dumarey & Dams 1985). Given the variation in ambient temperature on the Ross Island, it was surprising that the TGM data show no seasonal trend.

In terms of speciation (Fig.2), the mean concentration of inorganic mercury and organomercury was 0.48 ± 0.16 ng m^{-3} and 0.04 ± 0.06 ng m^{-3}, respectively. Thus, the atmospheric mercury burden in Antarctica was dominated by inorganic forms and organomercury constituted less than 10% of the TGM. Both this low percentage and the frequency of samples in which no DMM was detected (ie 18 out 50 samples) is in good agreement with other clean air studies. Slemr *et al.* (1985) found DMM concentrations in the range 0.02–0.12 ng m^{-3} in marine air over the Atlantic Ocean, although it was detected in only 34% of the samples. Elemental mercury comprised 80–96% of the TGM in marine troposphere in the equatorial Pacific Ocean (Kim & Fitzgerald 1986). Anthropogenic influences can create higher DMM levels (de Mora *et al.* 1991, Slemr *et al.* 1985). At Arrival Heights there were two instances of relatively high levels of DMM (0.26 and 0.35 ng m^{-3}). This DMM cannot have been of local marine origin because of the extensive sea ice coverage during the winter. As the first of these sampling dates coincided with resupply flights by Hercules aircraft at the end of August (Winfly operations), the elevated DMM could be interpreted to be of local anthropogenic origin and indicative of the late winter increase in base activities, particularly those related to the ozone measurement programme at Arrival Heights.

Owing to the non-specific nature of the sampling programme, local contamination due to fossil fuel combustion and waste incineration cannot be completely eliminated as a contributing factor to the observed TGM levels. Thus, the low values reported here constitute an upper limit for atmospheric mercury in Antarctica. There are very few mercury-in-air data from Antarctica for comparison. McMurty *et al.* (1979) cited concentrations in the range 0.74–4.0 μg m^{-3} for ten samples from the McMurdo vicinity. They also reported TGM concentrations at Don Juan Pond, in the vicinity of Lake Vanda, of 12.1 ± 4.4 μg m^{-3} (eight samples). These data are about three orders of magnitude higher than levels observed in clean air investigations conducted elsewhere (de Mora *et al.* 1991, Kim & Fitzgerald 1986, Lindquist &

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Henning 1985) and so must be regarded as suspect. Furthermore, mercury concentrations in the soils and biota of Ross Island and the Wright Valley are known to be very low (Matsumoto *et al.* 1983, Siegel *et al.* 1980, Siegel *et al.* 1981). Surface snow in the region contains exceptionally small amounts of mercury. Concentrations are 2.7 pg g^{-1} on the Ross Ice Shelf immediately south of Ross Island (Dick *et al.* 1990) and < 1 pg g^{-1} on the Antarctic Plateau near the head of the Wright Valley (Sheppard *et al.* 1991). Given these considerations, these results from 1987 to 1989 comprise the most reliable mercury-in-air record yet obtained in Antarctica. Moreover, the overall mean TGM concentration of 0.55 ng m^{-3} represents the lowest value yet recorded globally.

Conclusions

The baseline concentration and speciation of atmospheric mercury was measured over a three year time period at Ross Island (77°S). The speciation was dominated by inorganic mercury. Based on 196 measurements, the mean total gaseous mercury concentration observed was 0.55 ng m^{-3}, the lowest average value yet reported for atmospheric mercury.

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References

Bibby, D.M., Patterson, J.E. & O'Neill, S. 1988. Levels of atmospheric mercury at two sites in the Wellington area, New Zealand. *Environmental Technology Letters*, **9**, 71-74.

Braman, R. & Johnson, D. 1974. Selective absorption tubes and emission technique for determination of ambient forms of mercury in air. *Environmental Science and Technology*, **8**, 996-1003.

de Mora, S.J., Bibby, D.M. & Patterson, J.E. 1991. Baseline concentration and speciation of atmospheric mercury at Baring Head (41°S), New Zealand. *Environmental Technology*, **12**, 943-946.

de Mora, S.J., J.E., P. & Bibby, D.M. 1987. Atmospheric mercury inside Scott Base. *New Zealand Antarctic Record*, **8**, 5-8.

Dick, A.I., Sheppard, D.S. & Patterson, J.E. 1990. Mercury content of Antarctic snow: initial results. *Atmospheric Environment*, **24A**, 973-978.

Dumarey, R. & Dams, R. 1985. The influence of meteorological parameters on atmospheric volatile and particulate mercury distribution. *Environmental Pollution*, **B10**, 277-285.

Fitzgerald, W.F. 1986. Cycling of mercury between the atmosphere and oceans. *In* Buat-Ménard, P.*ed. The Role of Air-Sea Exchange in Geochemical Cycling*. Dordrecht: D. Reidel Publishing Co., 363-408.

Kim, J.P. & Fitzgerald, W.F. 1986. Sea-air partitioning of mercury in the equatorial Pacific Ocean. *Science*, **231**, 1131-1133.

Lindquist, O. & Henning, R. 1985. Atmospheric chemistry - a review. *Tellus*, **37B**, 136-159.

Mason, R.P., Fitzgerald, W.F. & Vandal, G.M. 1992. The source and composition of mercury in Pacific Ocean rain. *Journal of Atmospheric Chemistry*, **14**, 489-500.

Matsumoto, G., Chikazawa, K., Murayama, H., Torii, T., Fukushima, H. & Hanya, T. 1983. Distribution and correlation of total organic carbon and mercury in Antarctic dry valley soils, sediments and organisms. *Geochemical Journal*, **17**, 247-255.

McMurty, G., Brill, R. & Siegel, B.Z. 1979. Antarctic mercury distribution in comparison with Hawaii and Iceland. *Antarctic Journal of the United States*, **14**, 206-209.

Mroz, E.J., Alei, M., Cappis, J.H., Guthals, P.R., Mason, A.S. & Rokop, D.J. 1989. Antarctic atmospheric tracer experiments. *Journal of Geophysical Research*, **D94**, 8577-8583.

Patterson, J.E. 1984. A differential photoacoustic mercury detector. *Analytica Chimica Acta*, **164**, 119-126.

Schroeder, W.H., Yarwood, G. & Niki, H. 1991. Transformation processes involving mercury species in the atmosphere - results from a literature survey. *Water, Air, and Soil Pollution*, **56**, 653-666.

Sheppard, D.S., Patterson, J.E. & McAdam, M.K. 1991. Mercury content of Antarctic ice and snow: Further results. *Atmospheric Environment*, **25A**, 1657-1660.

Siegel, S.M., Siegel, B.Z. & McMurty, G. 1980. Atmospheric-soil mercury distribution: the biotic factor. *Water, Air, and Soil Pollution*, **13**, 109-112.

Siegel, S.M., Siegel, B.Z. & McMurty, G. 1981. Antarctic iron-mercury abundance ratios: evidence for mercury depletion in an active volcanic zone. *Water, Air, and Soil Pollution*, **15**, 465-469.

Sinclair, M.R. 1988. Local topographic influence on low-level wind at Scott Base, Antarctica. *New Zealand Journal of Geology and Geophysics*, **31**, 237-245.

Slemr, F., Schuster, G. & Seiler, W. 1985. Distribution, speciation, and budget of atmospheric mercury. *Journal of Atmospheric Chemistry*, **3**, 407-434.

Slemr, F., Seiler, W. & Schuster, G. 1981. Latitudinal distribution of mercury over the Atlantic Ocean. *Journal of Geophysical Research*, **86C**, 1159–1166.

Smith, W.O. & Nelson, D.M. 1985. Phytoplankton bloom produced by a receding ice edge in the Ross Sea: spatial coherence with the density field. *Science*, **227**, 163-166.