

Atmospheric depletion of mercury over Antarctica during glacial periods

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Mercury is a globally dispersed toxic metal that affects even remote polar areas. During seasonal atmospheric mercury depletion events in polar areas, mercury is removed from the atmosphere^{1,2} and subsequently deposited in the surface snows³. However, it is unknown whether these events, which have been documented for the past two decades, have occurred in the past. Here we show that over the past 670,000 years, atmospheric mercury deposition in surface snows was greater during the coldest climatic stages, coincident with the highest atmospheric dust loads. A probable explanation for this increased scavenging is that the oxidation of gaseous mercury by sea-salt-derived halogens occurred in the cold atmosphere. The oxidized mercury compounds were then transferred to the abundant mineral dust particles and deposited on the snowpack, leading to the depletion of gaseous mercury in the Antarctic atmosphere. We conclude that polar regions acted as a mercury sink during the coldest climatic stages, and that substantial polar deposition of atmospheric mercury is therefore not an exclusively recent phenomenon.

Elemental mercury (Hg^0) is the predominant atmospheric Hg species, with a residence time of ~ 1 year. Nevertheless, the discovery of 'atmospheric mercury depletion events' (AMDEs) suggests that a much shorter residence time occurs in polar areas¹.

Deep ice cores represent an archive of the past behaviour of atmospheric Hg (refs 4, 5). Seventy ice-core sections were analysed for total Hg concentration (Hg_T) in the Antarctic EPICA (European Project for Ice Coring in Antarctica) ice core⁶ drilled at Dome C (East Antarctica, $75^\circ 06' \text{S}$; $123^\circ 21' \text{E}$; 3,233 m above sea level). The depths of the samples ranged from 86.9 to 3,062.4 m, spanning a period from ~ 2 kyr BP back to the Marine Isotopic Stage (MIS) 16.3, 672 kyr BP (Fig. 1). The time interval encompassed by each sample is ~ 10 years during the Holocene epoch, ~ 20 years during the last glacial stage (LGS) and 40–60 years in the deepest ice. Methylmercury (MeHg^+) and inorganic mercury (Hg^{2+}) were also determined in the upper 36 sections, down to a depth of 2,138.4 m and dated back to MIS 6 (209 kyr BP) (Fig. 2).

Concentrations of Hg species varied considerably during the past climatic cycles. Hg_T and Hg^{2+} were at the picogram per gram level ($1 \text{ pg g}^{-1} = 10^{-12} \text{ g g}^{-1}$), whereas MeHg^+ was about one order of magnitude lower (Fig. 2 and Supplementary Table S1). The maximum Hg_T and Hg^{2+} levels are higher by nearly an order of magnitude than those previously obtained in Dome C ice⁵ (see Supplementary Discussion S1). Hg_T concentrations and fluxes were low during interglacial and warm interstadials, ranging below $\sim 3 \text{ pg g}^{-1}$ and $\sim 6 \text{ pg cm}^{-2} \text{ y}^{-1}$, respectively (see Supplementary Table S2). Conversely, these were higher and more variable during the coldest periods with high levels during MIS 2, 4, 6, 8, 12.2, 14.2 and 16.3, up to values of $\sim 14 \text{ pg g}^{-1}$ and $\sim 29 \text{ pg cm}^{-2} \text{ y}^{-1}$, respectively (Fig. 1).

Hg_T is significantly ($p = 0.01$) correlated with Mn ($r = 0.65$), our proxy for insoluble dust⁷ and matches rather well the insoluble dust concentration profile⁸ (Figs 1 and 2). The crustal enrichment factor (EF_c) (see the Methods section) ranges from ~ 30 up to $\sim 5,000$ (median = 222) and even during periods with the highest dust levels, EF_c is ~ 100 . This is evidence of an insignificant contribution from mineral dust to the determined Hg_T . However, the correlation indicates that, although originating from a different source, Hg_T was deposited concomitantly with continental dust during the coldest climatic stages. As this link seems to be independent from the age of the ice, post-depositional migration of Hg within the ice matrix is unlikely to have occurred.

High Hg_T levels cannot be ascribed to an intensified meridional transport of aerosol. The enhanced dust and sea-salt fallouts in glacial times were probably caused by higher aeolian dust production in South America and a larger sea-ice extent around Antarctica during cold periods^{9,10}. Thus, a change in the atmospheric removal process or in Hg sources should be responsible for the higher Hg accumulation recorded.

Volcanic Hg (calculated using $\text{Hg}/\text{S} = 10^{-4}$) accounts for $\sim 10\%$ (median value) of Hg_T with a maximum single contribution of $\sim 33\%$, whereas the marine Hg contribution was found to be negligible (see the Methods section). In summary, the cumulative input of Hg from continental dust, volcanoes and sea salt accounts for $< \sim 15\%$ of Hg_T during glacial periods.

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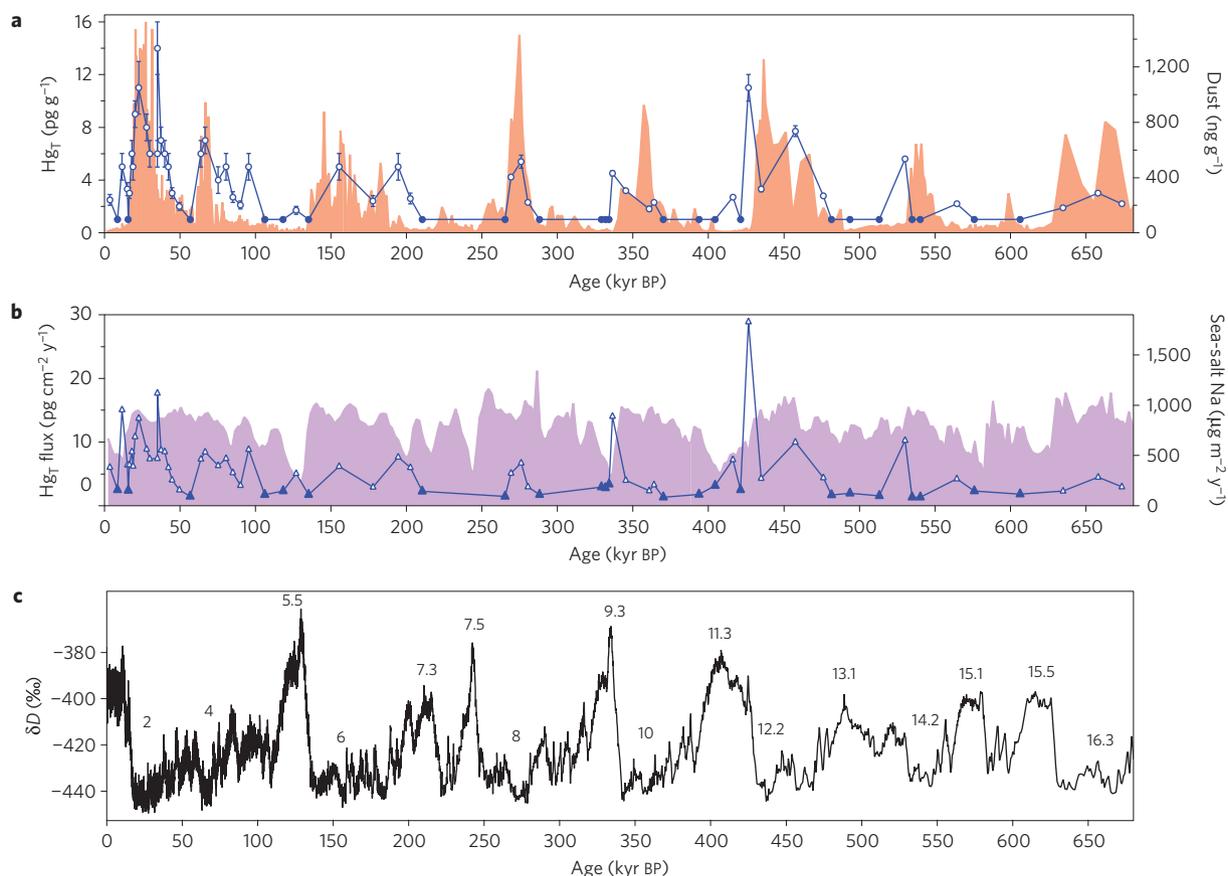


Figure 1 | Concentrations and fluxes of total mercury (Hg_T) to Dome C. **a**, Concentrations of Hg_T (open symbols) compared with the insoluble dust concentration profile⁸ (orange area). **b**, Fluxes of Hg_T (open symbols) compared with fluxes in sea-salt Na^+ (ref. 10) (proxy of marine aerosol, purple area). The filled symbols indicate concentrations below the detection limit in **a** and the upper limits of the fluxes in **b**. **c**, Climatic changes are indicated by variation in the δD ‰ (black line), taken as a proxy of local temperature. The numbers on the δD ‰ graph indicate the climatic MISs. An outlier of Hg_T concentrations (65 pg g^{-1}) and fluxes ($121 \text{ pg cm}^{-2} \text{ y}^{-1}$) at ~ 386 kyr BP is omitted from the graphs. The error bars of the Hg_T concentrations (in several cases smaller than the open symbols) represent standard deviations.

It has been suggested that the primary source of Hg at Dome C during the LGS was probably the biogenic oceanic emission of Hg^0 (ref. 5). This might explain most of the Hg_T during warm periods, compared with 20–50% during the coldest stages (see the Methods section). Although these oceanic processes are complex, owing to a large uncertainty in this estimate, it is difficult to link the large Hg_T fallout only to an enhanced marine productivity during the coldest climatic stages, because the sulphate of non-sea-salt origin (nss. SO_4) flux in Dome C was constant during glacial and interglacial periods¹⁰. In addition, MeHg^+ concentrations were generally $<0.5 \text{ pg g}^{-1}$. MeHg^+ in Dome C ice is probably a direct indication of the contribution of Hg from the Southern Ocean to Antarctica, as this species and dimethylmercury can be formed in the oceans^{11,12}. Thus, concurrently with nss. SO_4 , the low levels of MeHg^+ do not support an intensified marine production of Hg.

A clue to explaining the high Hg_T concentrations relies on the Hg^{2+} levels. These were generally $\leq 1.5 \text{ pg g}^{-1}$ during the Holocene, the last transition and MIS 5. The highest levels for Hg^{2+} were during MIS 2 ($\sim 15 \text{ pg g}^{-1}$, 36 kyr BP; $\sim 9 \text{ pg g}^{-1}$, 22 kyr BP). As Hg_T and Hg^{2+} are significantly ($p = 0.01$) correlated ($r = 0.65$) and their maximum levels are comparable, this indicates that Hg^{2+} often contributed significantly to the Hg_T budget during the coldest stages.

The established mechanism for oxidizing Hg^0 in the atmosphere is through halogen chemistry¹³. Higher levels of I and Br were probably present in the LGS Antarctic atmosphere, owing to a twofold increase in the fallout of marine aerosol to the continent¹⁰

(Fig. 1). Br_2 and BrCl are emitted from frozen surfaces such as snow¹⁴, frost flowers¹⁵ and ice clouds¹⁶ after oxidation of the sea-salt-derived Br^- ions¹⁷. Subsequently, Br radicals are produced through photolysis and the BrO radical is generated by the reaction with O_3 . IO, produced from the biogenic emission of iodo-carbons and I_2 , may also have a role in the activation of bromine¹⁸. Once bromine is activated and atmospheric temperatures are low enough ($< \sim 260 \text{ K}$) for the HgBr intermediate (formed by Hg^0 and Br) to be sufficiently stable to undergo further oxidation, then reactive gaseous mercury (RGM) will form and be scavenged to the snowpack¹⁹. However, a significant fraction of the snowpack RGM is photochemically reduced back to Hg^0 , and then re-emitted to the atmosphere²⁰.

The seasonal behaviour of BrO and IO at Halley Bay in Antarctica shows that these radicals are present throughout the sunlit part of the year, with average concentrations of $\sim 6 \text{ pmol mol}^{-1}$ (ref. 18). These halogen oxides are also present at levels of $\sim 3 \text{ pmol mol}^{-1}$ in air masses originating from the interior of Antarctica, indicating that these radicals remain active for several days. Thus, we assume average IO and BrO concentrations of 5 pmol mol^{-1} in air transiting from coastal Antarctica to Dome C. During the sunlit period, the corresponding concentrations of Br and I are then ~ 0.6 and $2.4 \text{ pmol mol}^{-1}$ (ref. 18).

The oxidation rates of Hg^0 to Hg^{2+} (that is, HgBr_2 and HgBrI) can then be estimated^{18,19}. On the basis of the Dome C boundary layer temperature ($\sim 206 \text{ K}$; ref. 21) during the Last Glacial Maximum (LGM) compared with the Holocene ($\sim 216 \text{ K}$,

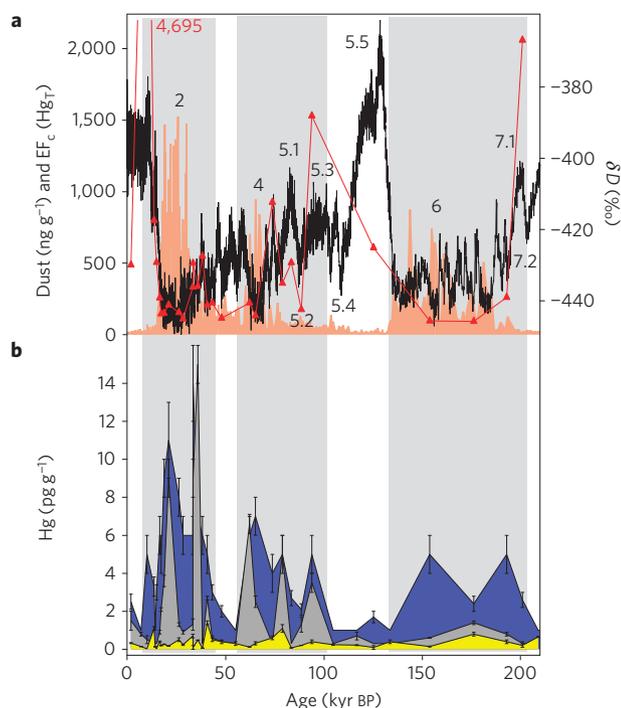


Figure 2 | Concentrations of total mercury, inorganic mercury and methylmercury, in the EPICA Dome C ice core. a, b. Concentrations of Hg species (**b**) compared with the insoluble dust concentration profile⁸ (orange area), with the Hg_T crustal enrichment factor (EF_c, red triangles) and δD‰ (solid black line) (**a**), the last of which is taken as a proxy of local temperature. (Hg_T, blue area; Hg²⁺, grey area; MeHg⁺, yellow area) Concentrations below the MDLs are substituted in the graph with MDLs (1, 0.3 and 0.03 pg g⁻¹ respectively). The error bars are standard deviations. The black numbers in **a** indicate the climatic MISs.

the oxidation rate of Hg⁰ to Hg²⁺ would have varied from 4.8×10^{-5} to $4.3 \times 10^{-5} \text{ s}^{-1}$, that is, an e-folding lifetime of ~6 h, with little change over a climatic cycle. This lifetime is shorter than the transit time from coastal Antarctica to Dome C (>1 day). As halogen levels in the Antarctic atmosphere were probably higher during the coldest periods because of the greater extent of sea ice¹⁰, all of the Hg⁰ in the boundary layer would be oxidized to RGM before reaching Dome C. Thus, the gas-phase oxidation rate of Hg⁰ alone cannot explain the increased Hg²⁺ deposition in Dome C.

A more important factor is the variation of the dust loading in the past Antarctic atmosphere. We have calculated specific surface dust areas during the Holocene and the LGM of 3×10^{-10} and $9 \times 10^{-9} \text{ cm}^2 \text{ cm}^{-3}$, respectively (see Supplementary Discussion S2). As Hg_T correlates well with dust but does not co-vary with the sea-salt input¹⁰ (Fig. 1), this indicates that uptake of RGM on deliquesced sea-salt particles is not an important permanent removal process, probably because the same photochemical reduction of Hg²⁺ occurs on the sea-salt particles²⁰. RGM should predominantly consist of HgBr₂, and at temperatures below ~220 K its vapour pressure is at least ten times below the typical gas-phase concentration of RGM measured during AMDEs (ref. 22). Hence, uptake of RGM on mineral dust is probably efficient, and subsequent deposition of the particulate Hg causes permanent removal of Hg from the atmosphere because the dust particles act as a stabilizing agent in the snow mantle. This is supported by the link of the dust deposition with Hg_T and Hg²⁺ fallout during MIS 2, 4 and 6 (Fig. 2).

To model the role of dust in Hg deposition, we assume: (1) gas-phase halogen levels during the cold periods were similar to or even higher than the present day; (2) uptake of RGM on

dust causes permanent removal into the snowpack; (3) RGM is also deposited directly to the snowpack (deposition velocity 0.2 cm s^{-1} ; boundary layer height 300 m); however, ~60% of this is recycled photochemically to Hg⁰ (ref. 20). If the uptake coefficient for RGM on dust is set to 0.2 (or to 0.05 for the upper limit to the calculated surface areas), then the e-folding lifetime of Hg⁰ against permanent deposition as RGM is ~40 h during the LGM, compared with ~130 h during the Holocene. This is consistent with the approximately fourfold increase in the flux of Hg²⁺ and the doubled flux of Hg_T during the coldest and most dusty period (MIS 2) (on average $\sim 5 \text{ pg cm}^{-2} \text{ y}^{-1}$ of Hg²⁺ and $\sim 11 \text{ pg cm}^{-2} \text{ y}^{-1}$ of Hg_T), compared with the interglacial periods ($\sim 1.2 \text{ pg cm}^{-2} \text{ y}^{-1}$ of Hg²⁺ and $\sim 6 \text{ pg cm}^{-2} \text{ y}^{-1}$ of Hg_T). Importantly, the uptake coefficient required is <1 (the upper limit). Thus, the dust levels in the Antarctic atmosphere during the LGS were sufficient to contribute significantly to the irreversible scavenging of atmospheric Hg.

Our study strongly suggests that Hg⁰ depletion phenomena in the polar atmosphere have taken place over long timescales. There might have been much higher atmospheric Hg fallout during the LGS to Greenland and coastal Antarctica, where the ice was found to contain higher concentrations of sea salt and dust. Polar regions could then have acted as an important sink for Hg during the LGS, possibly modulating its abundance in the Earth's atmosphere and consequently its biogeochemical cycle.

Methods

Analytical procedures. Decontamination of the ice sections was carried out in a class 10,000 clean laboratory equipped with a class 100 laminar flow clean bench. This procedure was validated by determining Hg in the inner ice core as well in the outer layers, showing that Hg contamination during sample preparation was negligible²³.

Quantification of total Hg (Hg_T) was carried out by inductively coupled plasma sector field mass spectrometry²³. The method detection limit (MDL) for Hg_T determination was $\sim 1 \text{ pg g}^{-1}$, the relative standard deviation (RSD) was ~15% and a spike recovery of ~100% was obtained. Some samples (13) were reanalysed over several days to test the stability of Hg_T in Dome C ice and the RSD obtained was $\leq 20\%$. The spectral interferences were checked by monitoring tungsten oxides and were found to be negligible. An instrumental blank of 2.6 pg g^{-1} (RSD = 1.5%) was subtracted from Hg_T. Although this might have hampered the accurate determination of the lowest interglacial Hg_T levels, this should not have significantly affected the determination of the higher glacial Hg_T concentrations.

Determination of MeHg⁺ and Hg²⁺ was carried out by multicapillary gas chromatography hyphenated to inductively coupled plasma time-of-flight mass spectrometry²⁴. To cope with the ultra-trace levels determination, Hg²⁺ and MeHg⁺ were converted into volatile ethylated derivatives and preconcentrated *in situ* using solid-phase micro-extraction. MDLs were 0.03 pg g^{-1} for MeHg⁺ and 0.3 pg g^{-1} for Hg²⁺; RSD was <4% for both species and the spike recoveries were ~100% for MeHg⁺ and ~104% for Hg²⁺.

Mercury sources assessment. We estimated the Hg contribution from aeolian dust by means of the crustal enrichment factor defined as:

$$EF_c = \frac{\frac{[\text{Hg}_T]_{\text{ice}}}{[\text{Mn}]_{\text{ice}}}}{\frac{[\text{Hg}_T]_{\text{crust}}}{[\text{Mn}]_{\text{crust}}}}$$

where $[\text{Hg}_T]_{\text{crust}}/[\text{Mn}]_{\text{crust}}$ is the concentration ratio in the upper continental crust²⁵ and $[\text{Mn}]_{\text{ice}}$ is the Mn concentration in Dome C ice⁷, used as a dust proxy.

The volcanic Hg contribution was calculated using a Hg/S mass ratio in volcanic emissions of $\sim 10^{-4}$ – 10^{-6} (taken from a recent review, ref. 26), and the assumption that ~10% of the nss.SO₄ in ice ($\text{nss.SO}_4 = [\text{SO}_4]_{\text{ice}} - ([\text{SO}_4]_{\text{marine}}/[\text{Na}]_{\text{marine}}) \times [\text{Na}]_{\text{ice}}$) is contributed by volcanoes⁵ ($[\text{SO}_4]_{\text{ice}}$ and $[\text{Na}]_{\text{ice}}$ were taken from ref. 10).

The marine Hg contribution was calculated on the basis of the ratio $[\text{Hg}/\text{Na}]_{\text{sea salt}}$ of $\sim 10^{-12}$ (ref. 27) and assuming that $[\text{Na}]_{\text{ice}}$ (corrected for the crustal contribution) originates exclusively from sea salt.

The biogenic marine contribution of Hg was calculated assuming that ~80% of nss.SO₄ results from the oxidation of dimethylsulphide of oceanic biogenic origin²⁸, and on the basis of an estimated ratio Hg/S of 4.4×10^{-5} (refs 29, 30).

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Author contributions

C.F.B., C.B., C.P.F., P.C. and F.C.A. planned the project; P.G., A.M., P.-A.G. and S.H. carried out sample preparation; P.G., A.M. and F.A.M.P. determined total mercury; P.J. carried out mercury speciation; P.G., J.M.C.P., C.B. and P.J. carried out the data interpretation and wrote the paper.

Additional information

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