Interaction of gaseous elemental mercury with snow surfaces: laboratory investigation

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Abstract

The interaction of elemental mercury with ice surfaces based on the migration behaviour at sub-ppt concentrations in a packed bed flow tube is discussed. Analysis shows that elemental mercury interacts only weakly with ice surfaces and suggests an adsorption enthalpy of $-28 \pm 2$ kJ mol$^{-1}$. The experiments further reveal an adsorption equilibrium constant, which quantifies the partitioning of elemental mercury between the surface and the gas phase, with a value of 12 cm at 140 K. Extrapolation to environmental conditions gives a range for the equilibrium constant of $3 \times 10^{-4}$ to $4 \times 10^{-3}$ cm at 230 K.

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1. Introduction

Mercury has been found to accumulate in the Arctic environment, and in some biota (see Steffen et al and references therein [1]). This is of concern, as subtle health effects linked to mercury exposure in traditional marine food have been observed among some inhabitants in the Arctic.

The pathways by which mercury accumulates in this ecosystem and its wildlife are not fully understood. This limits the reliability of mass balances and of flux models of Arctic mercury. It is clear that the fate of mercury in the environment and its bioavailability is drastically determined by its oxidation state: for example, during atmospheric mercury depletion events (AMDE), where atmospheric elemental mercury, hereafter referred to as Hg, is oxidized, rapidly removed from the boundary layer gas phase and deposited in the surface snow.

A key question in polar research is what fraction of the mercury deposited in snow—both during AMDEs and continuously—is irreversibly trapped in this medium, delivered to the aquatic system during snow melt and subsequently available for bioaccumulation. It is now well established that re-emission of mercury from the surface snow may occur via reduction of oxidized mercury involving sunlight [2–4]. Furthermore, a night time increase of gaseous Hg in the interstitial air has been observed and is explained by fast reduction reactions [5]. Whatever the underlying process of Hg chemistry in the condensed phase is, the final step would necessarily be the release of Hg from the snow phase into the interstitial air. Yet, laboratory data on the uptake and release of Hg from snow surfaces are lacking.

The goal of this study is to quantify the partitioning equilibrium of Hg between snow surfaces and the gas phase. Better understanding of this interaction would assist in interpretation of correlations between temperature and Hg concentrations observed with depth in the snow pack [6] or with time [7].
1.1. Theoretical background

The retention of a trace gas in a packed bed flow tube can be related to the partitioning equilibrium, as stated in equation (1), where \(z\) is the migration distance of a species in a certain time \((t)\), \(u\) is the linear velocity of the carrier gas and \(k_i\) is the partitioning coefficient \((k_i = n_{\text{ads}}/n_{\text{gas}}}):

\[
\frac{dz}{dt} = \frac{u}{1 + k_i}.
\] (1)

The analysis of this work to quantify the partitioning, i.e. \(k_i\), at a given temperature, has been described in great detail earlier [8, 9]. Briefly, the standard adsorption enthalpy \((\Delta H_{\text{ads}})\) is derived based on the experimentally determined migration distance of Hg and for a given standard adsorption entropy \((\Delta S_{\text{ads}}^0)\). The partitioning constant can then be extrapolated over a temperature range of interest based on these findings.

Equation (2) states the relation of \(\Delta H_{\text{ads}}, \Delta S_{\text{ads}}^0\) and \(k_i\), where \(a\) denotes the surface area of the ice packing, \(v\) free volume in packed bed flow tube, \(V\) molar volume, \(A\) molar surface area and \(R\) the gas constant:

\[
k_i = \frac{aV}{vA} \exp \left( \frac{\Delta H_{\text{ads}}^0}{RT} \right) \left( \frac{\Delta S_{\text{ads}}^0}{R} \right).
\] (2)

\(A\) and \(V\) refer to the standard states in this work. As the standard state for a molecule in the gas phase the pressure \(p^0 = 1\) atm and the temperature \(T^0 = 273\) K are chosen, expressed as a molar volume \((V)\) of \(2.24 \times 10^4\) cm\(^3\). An equivalent standard state, the molar area \((A)\) of \(3.7 \times 10^{11}\) cm\(^2\) can be derived for the adsorbate as suggested by Kemball [10] and as used in other adsorption studies [11–13]. The choice of standard pressure has been shown not to affect the resulting \(\Delta H_{\text{ads}}^0\) [9, 14, 15].

Based on equations (1) and (2), the final relation used to analyse the data is obtained with \(t_e\) (the experimental time), \(T_0\) (standard temperature), \(g\) (temperature gradient), \(u_0\) (linear gas velocity), \(T_A\) (temperature at the peak of the measured radioactivity) and \(T_3\) (warmest temperature of linear temperature gradient):

\[
\left( T_e + \frac{T_0}{g u_0} \ln \frac{T_A}{T_3} \right) \frac{v g u_0 A}{a T_0 V \exp \left( \frac{\Delta S_{\text{ads}}^0}{R} \right)} = \exp \left( -\frac{\Delta H_{\text{ads}}^0}{RT} \right).
\] (3)

Statistical thermodynamics allows us to calculate \(\Delta S_{\text{ads}}^0\) as the difference of the absolute entropy of an ideal particle in the gas phase and in the adsorbed state. The absolute standard entropy of Hg in the gas phase is given by its free motion in three dimensions (Sackur Tetrode equation). In the adsorbed state, the motion perpendicular to the surface \((z)\) axis is considered to be hindered [16]. Mathematically, the motion along the adsorbent’s surface is treated as two translational degrees of freedom, while the motion perpendicular to the adsorbent is treated as a vibrational degree of freedom.

Equation (4) states the relation used in this work, with the molar surface area and volume \((A\) and \(V\)) discussed earlier, the gas constant \((R)\), Avogadro’s number \((N_A)\), Planck’s constant \((h)\), the atomic mass of Hg \((m)\), the Boltzmann constant \((k_B)\), the temperature where the maximum intensity of radioactivity was observed in the packed bed flow tube \((T_A)\) and the vibration frequency of mercury on the ice surface \((v)\). For this analysis the ground state phonon frequency of ice is used as the vibration frequency of the adsorbed molecule. Girardet et al give an approximate value of \(2 \times 10^{13}\) Hz for this vibration frequency of the ice surface lattice [17]:

\[
\Delta S_{\text{ads}}^0 = R \ln \left( \frac{A}{V} \sqrt{\frac{h^2}{2\pi m k_B T_A}} \right) - \frac{1}{2} R + \left( -hu/v + k_B T_A \varphi(hu/v, k_B T_A) \right). 
\] (4)

1.2. Chromatographic process

To confirm that the migration of Hg is purely based on the reversible adsorption equilibrium, which is one prerequisite for using equation (1), a simulation of the migration kinetics in each experiment was performed (for details see supporting information available at stacks.iop.org/ERL/3/045009). In short, we calculated a numerical solution of the partial differential equations, which govern the migration through the packed bed. By choosing proper boundary conditions, we accounted for four processes: (1) advection through the ice bed, (2) adsorption, (3) desorption and (4) the radioactive decay of the trace gas. For a numerical solution of this problem, we modelled the packed ice bed as a one-dimensional slab of 435 regions of equal size with constant concentration in both the gas phase and on the ice surface. This system of equations was solved numerically using a BDF formula for stiff differential equations, as implemented in the IMSL mathematical library in pv-wave software (Visual Numerics, Inc., version 7.0). The simulation differs from the derivation of equation (3) in explicitly numerically modelling the adsorption process in terms of adsorption and desorption rates. Hence, it does not assume thermodynamic adsorption equilibrium on the ice surface.

Figure 1 displays a typical result. The observed peak position could be simulated for all experiments, when the model was fed with the individual experimental settings and with values of \(\Delta H_{\text{ads}}^0\) and of an equilibrium surface concentration given by \(k_i\) as derived from the analysis explained above.

2. Experimental section

Experiments were performed with a packed bed flow tube set-up, to which a steep temperature gradient is applied as described earlier [8, 9]. One end, from which the carrier gas flow exits the apparatus, was cooled with liquid nitrogen. The other end was only moderately cooled with pure ethanol (95%) to 240 or 260 K in some experiments. The temperature inside the column was measured in 1 cm steps with a K-type temperature sensor. Depending on the warmest temperature and on the gas flow, gradients of 6.6, 7.3 or 8.5 K per cm have been determined.
Figure 1. Distribution of Hg isotopes in the packed bed flow tube at the end of the experiment. For a typical run, the temperature of the snow (crosses, right axis) and the measured radioactivity along the column (black squares) is plotted. The black lines are Gaussian fits to the experimental data used to determine the migration distance. Also shown are the results of the simulations of the packed bed flow tube experiments with the kinetic model (dotted red line).

2.1. Packed bed flow tube

PFA tubes of 6 mm inner diameter were densely packed over a length of 40 cm with small ice spheres to serve as the stationary phase. Handling and storing of the tube was done in a cold room at 253 K. The ice spheres were produced by rapidly freezing deionized water (Milli-Q quality) with a resistivity of <0.054 μS cm⁻¹ and by crystallizing them at 253 K for several days. The ice spheres were sieved with calibrated sieves (Retsch, Germany) with a grain size of 400 μm and 500 μm, or 500 μm and 630 μm, to allow calculation of the geometric surface area (using a density of 0.9 g cm⁻³ [18]). The columns were sealed at both ends and stored for at least 12 h. We have shown in another study that this procedure leads to smooth ice spheres, the geometric surface area of which is identical to the BET surface area [9]. For the nine experiments discussed in this work a surface-to-volume ratio of the packing (a/v) between 82 and 275 cm⁻³ has been deduced.

2.2. Production of Hg isotopes

Radioactive mercury isotopes were produced by irradiation of 4 g lead (Fluka, purum p.a.) with neutrons with a maximum energy of up to 590 MeV from the SINQ spallation neutron source of the Paul Scherrer Institute [19, 20].

Typically, irradiation times of 45 min with nearly identical neutron fluxes (s.d. ±1%) were applied. After a waiting time of 2 h the Hg was isolated from the sample by heating the lead to 823 K in a stream of helium carrier gas of 73 ml min⁻¹ (all flows are given at standard temperature and pressure) followed by capturing the volatilized Hg downstream on a gold foil at room temperature. We used γ-spectroscopy to determine the amount of Hg atoms trapped on the gold foil and to verify the absence of other radioactive isotopes potentially interfering with our measurement. The gold foil was then inserted into a quartz tube and connected to the flow system just facing the packed bed flow tube.

2.3. Experimental procedure

Once temperature equilibrium within the ice bed was established, the gold foil was heated to 723 K, allowing the Hg to be rapidly and completely released into the carrier gas flow and to enter into the packed ice bed from the warmer side. After either 1 or 20 min a carrier gas flow of typically 73 cm³ min⁻¹ was stopped, and the migration position of Hg in the ice column was profiled with a γ-counter. The γ-counter consisted of one bismuth-germanate-detector (BGO), 3 cm in diameter and surrounded by lead shielding. This BGO scintillator could automatically be moved along the column to scan the distribution of γ-decays and was connected to a discriminator, preamplifier and a counter. During this measurement the sealed column was placed in liquid nitrogen to stop any further migration within the column. For some experiments the gas flow was set to 1, 7 or 715 cm³ min⁻¹.

2.4. Assessment of Hg concentration

A quantitative analysis of a γ-spectrum allowed us to deduce the total number of Hg atoms on the gold foil of \(3 \times 10^5\), which results in a mixing ratio of approximately 0.2 ppt Hg in the carrier gas entering the packed bed flow tube (supporting information available at stacks.iop.org/ERL/3/045009). For this estimate, a typical gas flow of 73 ml min⁻¹, an observed emission time from the gold foil of 1 min and the known half-lives of the radioactive isotopes [21], which range from 51 min to 24 h, were used. γ-spectroscopy was performed using an EG&G Ortec Gem-13180 coaxial detector equipped with a Canberra multi-channel analyzer. Recording and analysis of the data was done with the Canberra Genie 2000 software using the automated peak detection and integration algorithm.

A typical surface coverage of Hg on the ice at the position of maximum radioactivity was estimated to about \(2 \times 10^7\) atoms cm⁻². For this calculation an average ice surface area of 19 cm² per cm of column length was used, and it was assumed that the Hg deposits within 1 cm of the ice column where the peak was observed. For comparison, Hg concentrations in interstitial air have been reported between 0.04 and 25 ng m⁻³ [6, 22]; the total amount of radioactive Hg used in our experiments corresponds to 1 ng m⁻³ at 273 K.

3. Results and discussion

3.1. Direct observations

Figure 1 shows the distribution of Hg isotopes in the packed bed flow tubes after the experiments. A common feature of all the experiments is a maximum intensity of the measured radioactivity in the temperature range of 169–125 K. This migration of Hg to a position in the column where temperatures are below 169 K already shows that the retention of Hg on ice is negligible at higher temperatures, i.e. up to 260 K. As the experiments were conducted using a surface-to-volume ratio for the ice sample which is comparable to natural snow (a mean of 162 cm⁻¹ versus a typical value of 80 cm⁻¹), the retention behaviour supports previous findings that adsorption onto snow surfaces is not a strong sink for atmospheric
Hg at environmental temperatures and that Hg might be readily released from the snow surface after (photochemical) production [4, 6, 23].

3.2. Enthalpy of adsorption

These observed low temperatures, $T_A$ in equation (1), allow us to derive a $\Delta H^0_{ads}$ of $-28 \pm 2$ kJ mol$^{-1}$, where the uncertainty is the standard deviation of the nine experiments conducted. This result supports the recent findings of Ferrari et al [6] who had argued that an apparent activation energy of $-61$ kJ mol$^{-1}$ from an observed temperature dependence of Hg concentration in interstitial air was determined by fast chemical reactions rather than the adsorption equilibrium. Indeed such a strong adsorption enthalpy, similar to strong acids such as HNO$_3$ [24], seems unreasonable for a molecule that cannot form hydrogen bonds.

An excellent agreement with results from two molecular dynamics simulations indicates that adsorbed Hg interacts with only one water molecule on the ice surface. Interaction energies of $-27$ kJ mol$^{-1}$ [25] and $-29$ kJ mol$^{-1}$ [26] for one water molecule with elemental mercury have been found. The interaction energy is, following the suggestions of these MD simulations, a direct equivalent of $\Delta H^0_{ads}$ as defined in this study.

3.3. Adsorption equilibrium

Figure 2 shows the temperature dependence of the partitioning of Hg between air and ice extrapolated to environmentally relevant temperatures. Following the IUPAC recommendations the partitioning is expressed in terms of the adsorption equilibrium constant, $K_{LinC}$ (equation (5)) [24]. For this extrapolation the mean values of $\Delta H^0_{ads}$ and $\Delta S^0_{ads}$ were used: $-28$ kJ mol$^{-1}$ and $-38$ J K$^{-1}$ mol$^{-1}$.

$$K_{LinC} = k_i \frac{v}{a} = \frac{V}{A} \exp \left( \frac{\Delta H^0_{ads}}{-RT} \right) \exp \left( \frac{\Delta S^0_{ads}}{R} \right) \text{(cm)} .$$

When comparing with other atmospherically relevant species a mean value of 12 cm for $K_{LinC}$ of Hg at the experimental temperature of 140 K and of $1.1 \times 10^{-3}$ cm extrapolated to 230 K again underline that the interaction with ice is extremely weak. For inorganic acids, such as HNO$_3$, or volatile ketones, such as acetone, $K_{LinC}$ of $10^3$ cm and 1 cm, respectively, are currently recommended at 230 K [24]. The negligible partitioning to snow or ice is supported by earlier laboratory studies, which looked qualitatively at this equilibrium. Dommergue et al [4] found no fluxes of Hg from a snowpack when the temperature was raised from $-12$ to $-4$°C.

3.4. Analysis of uncertainties

To assess the accuracy of the extrapolated values of the equilibrium constant, which depends both on uncertainties of $\Delta H^0_{ads}$ and $\Delta S^0_{ads}$, the effect of variation of the input parameters to equation (3) was investigated. The variation reflected the accuracy of measured values, such as gas flow (73 ± 0.7 cm$^3$ min$^{-1}$), temperature gradient (8.5 ± 0.1 K), migration distance (24 ± 0.1 cm) and the temperature at migration distance (139 ± 5 K), or was based on estimates of uncertainty for the weight of ice packing (5.5 ± 0.6 g), diameter of the ice spheres (550 ± 50 μm), the retention time (20 ± 2 min), temperature of gas flow (298 ± 2 K) and of the warmest temperature of the gradient (243 ± 2 K). This analysis confirms earlier results [9], showing that the accuracy in the temperature determination is the most critical factor in the uncertainty of $\Delta H^0_{ads}$. Combined—based on Gauss error propagation rules—a total uncertainty range for $\Delta H^0_{ads}$ of $-25.9$ to $-28.9$ kJ mol$^{-1}$ is obtained, in good agreement with the standard deviation of the nine experiments performed of 1.8 kJ mol$^{-1}$.

For the overall uncertainty estimate the effect of a variation of the calculated $\Delta S^0_{ads}$ by 20% was also treated in addition to the random error to reflect a possible systematic error. Based on these intervals of $\Delta H^0_{ads}$ and $\Delta S^0_{ads}$, ranges for $K_{LinC}$ of 3–56 cm at 140 K and 4 × 10$^{-3}$ to 3 × 10$^{-4}$ cm at 230 K are obtained (figure 2). This range of uncertainty is large, but not unusual for $K_{LinC}$: IUPAC recommendations give a range of 0.7–2 cm for acetone at 230 K and—similar to our estimate—a range of 2 × 10$^5$ to 7 × 10$^5$ for HNO$_3$.

4. Summary of atmospheric implications

A key result, from both the observed low temperatures to which Hg migrates in the packed bed flow tube and from the low value of $\Delta H^0_{ads}$ of $-28 \pm 2$ kJ mol$^{-1}$, is that the adsorption of Hg to ice surfaces at temperatures relevant to the polar environment is negligible. This behaviour is reflected by the equilibrium constant for which a range of $4 \times 10^{-3}$ to $4 \times 10^{-4}$ cm at 230 K can be extrapolated.

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