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Isotope effect of mercury diffusion in air

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Abstract

Identifying and reducing impacts from mercury sources in the environment remains a considerable challenge and requires process based models to quantify mercury stocks and flows. The stable isotope composition of mercury in environmental samples can help address this challenge by serving as a tracer of specific sources and processes. Mercury isotope variations are small and result only from isotope fractionation during transport, equilibrium, and transformation processes. Because these processes occur in both industrial and environmental settings, knowledge of their associated isotope effects is required to interpret mercury isotope data. To improve the mechanistic modeling of mercury isotope effects during gas phase diffusion, an experimental program tested the applicability of kinetic gas theory. Gas-phase elemental mercury diffusion through small bore needles from finite sources demonstrated mass dependent diffusivities leading to isotope fractionation described by a Rayleigh distillation model. The measured relative atomic diffusivities among mercury isotopes in air are large and in agreement with kinetic gas theory. Mercury diffusion in air offers a reasonable explanation of recent field results reported in the literature.

Introduction

Mercury in the environment continues to be a concern due to its impacts to human and ecological well being. The recent ability to measure mercury isotope variations in environmental samples has introduced a useful method for assessing mercury pollution and mercury's complex biogeochemical cycle.¹ For example, variability in mercury isotope composition of San Francisco Bay sediments has been attributed to multiple mercury sources including historic mercury and gold mines.² One challenge is that variations in mercury isotope composition are small and result solely from isotope fractionation. Isotope fractionation describes the separation of a reservoir with one isotope composition into "fractions" with different isotope compositions due to small isotopic differences in equilibrium partitioning, rates of mass transfer, or rates of transformation. Quantitative knowledge of these isotope effects enables predictive models of isotope fractionation that

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Supporting Information

The Supporting Information includes a further description of the method used to correct for instrumental mass bias, the manner in which delta values were determined, and the standards used for QA/QC. The Supporting Information also includes data tables of literature values for the isotope composition of the UM-Almaden standard, mercury (mass and isotope ratios) from the diffusion experiments, literature values for bulk-phase gaseous mercury diffusion coefficients in air, and experimental fractionation factors for ¹⁹⁸Hg/¹⁹⁹Hg, ¹⁹⁸Hg/²⁰⁰Hg, and ¹⁹⁸Hg/²⁰¹Hg isotope pairs. There are also figures showing the experimental setup and isotope fractionation during the experiments for isotope pairs ¹⁹⁸Hg/¹⁹⁹Hg, ¹⁹⁸Hg/²⁰⁰Hg, and ¹⁹⁸Hg/²⁰¹Hg. These are available free of charge via the Internet at <http://pubs.acs.org>.

are essential for interpreting isotope data and anticipating cases where isotope data could be helpful. This paper quantifies the isotope effect of elemental mercury (Hg^0) diffusion in air.

There is great interest in applying isotopes to help understand sources and sinks of atmospheric mercury as well as processes affecting its fate.³ Field observations have shown variations in the mercury isotope composition of atmospheric gases and precipitation, but the specific sources and processes that led to these variations are unclear.^{4,5} Most laboratory studies have examined mercury isotope effects related to the gas phase by studying gas/liquid equilibrium,^{6,7} volatilization of mercury to the gas phase,⁸ or isotope effects associated with mercury reduction to Hg^0 and inferring impacts on the gas phase.^{9–12}

Predictions of diffusion isotope effects can be made using the kinetic theory of gases. Under environmental conditions, molecular collisions among gases occur frequently and control the magnitude of isotope effects. Kinetic gas theory, then, holds that:

$$\frac{D_x}{D_y} = \left(\frac{\Gamma_y + \Gamma_g}{\Gamma_x + \Gamma_g} \right)^2 \sqrt{\frac{m_y(m_g + m_x)}{m_x(m_g + m_y)}}, \quad 1$$

where D is the molecular diffusivity, Γ is the collision diameter, m is the mass of molecules, and subscripts indicate molecules of the interest x , y , and the background gas, g .^{13,14} The collision diameters of x and y are often assumed to be nearly identical such that the first term on the right hand side of equation 1 has negligible effect.

The importance of gas-phase diffusion in evaluating isotope effects associated with water evaporation has prompted many experimental investigations that tested the appropriateness of equation 1. Some studies of water vapor diffusion have supported the assumption of identical collision diameters,¹⁴ while others suggest that models of isotope behavior must incorporate differences among collision diameters.¹⁵ Recent work by Luz et al.¹⁶ suggests that differences among collision diameters alone cannot account for discrepancies observed between data and equation 1. In practice, the diffusion isotope effect for water in air used most frequently is based on the empirical work of Merlivat¹⁵ rather than on kinetic theory.¹³ The appropriateness of using equation 1 for estimating diffusive isotope effects, and the simplifying assumption of identical collision diameters, has also been investigated for gases other than water. Bouchard et al.¹⁷ demonstrated that diffusion-controlled fractionation of carbon isotopes is in agreement with models assuming identical collision diameters during hydrocarbon transport through porous columns. Well and Flessa,¹⁸ however, observed isotope fractionation inconsistent with the assumption of identical collision diameters during the diffusion of N_2O gas. The uncertainty associated with using equation 1 to estimate diffusive isotope effects indicates the need for an experimental determination for mercury as described here.

Numerous situations exist where gas phase diffusion of elemental mercury may limit mass transfer processes and control mercury isotopic composition; including the evaporation of metallic mercury, the transport of mercury through arid soils,¹⁹ and removal of mercury by sorbents in combustion flue gases.^{20–22} Isotope fractionation associated with Hg^0 vapor diffusion could help improve process level understanding in these cases, but uncertainties remain in modeling this isotope fractionation. Our work expands on previous laboratory efforts by quantifying the isotope effect of Hg^0 diffusion in air based on first principles, and shows that equation 1 along with the simplifying assumption of identical collision diameters is appropriate.

Materials and Methods

Gas-phase molecular diffusivities and related isotope effects for mercury were determined using reactors containing elemental mercury gas, $\text{Hg}^0_{(\text{g})}$, that were depleted by diffusion through sets of hypodermic needles. A diagram of a reactor is provided in the Supporting Information (Figure SI–S4). The small quantities of Hg^0 used were generated inside the reactors by reacting a $\text{Hg}(\text{II})$ solution with a SnCl_2 reductant solution. A small PTFE coated stir bar, 20.2 mL of 0.5M high purity diluted HCl , 75 μL of SnCl_2 stock solution (20% w/w in 1.2M HCl), and 150 μL of 10 mg/L mercury (dilute NIST 3133) solution were added to clean 70 mL serum bottles. After the addition of mercury, the serum bottles were immediately sealed with PTFE septa and capped. This procedure produced 1500 ng of Hg^0 within the reactors, an amount chosen to avoid the formation of a separate liquid Hg^0 phase.

The experiments were started by inserting five hypodermic needles through the septa of each reactor to connect the bottles with the laboratory atmosphere. After different periods of time, during which Hg^0 diffused from the reactors, individual reactors were stopped to allow for the determination of mass remaining and associated isotope changes. This was accomplished by injecting 800 μL of a KMnO_4 solution (2% w/w in 0.8 M HNO_3) through a needle and immediately removing all needles to prevent further losses. The KMnO_4 solution oxidized Hg^0 to $\text{Hg}(\text{II})$ as well as $\text{Sn}(\text{II})$ remaining in the reactors over several hours before analysis.

The mass of mercury remaining in the reactors was measured by cold vapor atomic fluorescence spectroscopy. Oxidized sample solutions containing $\text{Hg}^{2+}_{(\text{aq})}$ were reduced with sufficient quantities of a $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution (30% w/w $\text{NH}_2\text{OH}\cdot\text{HCl}$ in high purity water) to dissolve all Mn precipitates prior to analysis. $\text{Hg}^{2+}_{(\text{aq})}$ in known volumes of a calibration standard solution or reduced sample solutions was reduced to Hg^0 by SnCl_2 , transferred to gold traps using a bubbler, and analyzed using dual-stage gold amalgamation and cold vapor atomic fluorescence spectroscopy (CVAFS).²³ The relative error of calibration standards was observed to be less than 5%, calculated as two times the standard deviation of errors. Sample errors were estimated from either reproducibility (the error of replicates) or calibration uncertainty (the error of the calibration standards), whichever was greater.

Samples were prepared for isotope analysis by reducing known masses of $\text{Hg}^{2+}_{(\text{aq})}$ to Hg^0 with SnCl_2 in a 150 mL bubbler, purging with $\text{N}_{2(\text{g})}$ at 50 mL/min, and oxidizing the Hg^0 back to $\text{Hg}^{2+}_{(\text{aq})}$ in a HOCl solution. To reduce the introduction of salts to the mass spectrometer, experiment 1 sample preparations used dilute HOCl solutions ($5 \times 10^{-4}\text{M}$ NaOCl adjusted to pH 6.5 with dilute HNO_3), which resulted in incomplete recoveries. Experiment 1 sample preparation recoveries were 36% to 63% and are listed in Table SI–S2 of the Supporting Information. These incomplete recoveries led to fractionation and recovered materials with different isotope compositions than the original samples. This was corrected by measuring the fractionation of known NIST 3133 standards prepared at the same time using the same method. NIST 3133 standards prepared together with experiment 1 samples yielded similar recoveries to that of samples, averaging 48%, and showed consistent isotope fractionation of $1.07 \pm 0.24\text{‰}$ (2SD, $n=3$) in $\delta^{202}\text{Hg}$ (defined in equation 2 below) relative to the initial standard. Experiments 2 and 3 sample preparations used more concentrated HOCl solutions ($2 \times 10^{-3}\text{M}$ NaOCl adjusted to pH 5 with dilute HNO_3), and the sample and standard recoveries were 87% to 103%. NIST 3133 standards prepared together with experiments 2 and 3 showed consistent $\delta^{202}\text{Hg}$ values averaging $-0.12 \pm 0.14\text{‰}$ (2SD, $n=3$) relative to the initial standard. Because samples and standards were exposed to the same processes affecting isotope fractionation during sample preparation, sample isotope values are reported relative to NIST 3133 standards prepared at the same time. Because the observed variability among replicate processed standards was smaller than the in-run

analytical uncertainty of unprocessed NIST 3133 standards, the analytical uncertainty was taken as the uncertainty of prepared samples.

After sample preparations, the isotope composition of mercury remaining in reactors was measured by MC-ICP-MS (IsoProbe, originally Micromass). Nine Faraday collectors simultaneously measured signals corresponding to singly charged atomic ions with masses 195, 197, 198, 199, 200, 201, 202, 203, and 205. Mass 195 was used to correct for potential isobaric interferences resulting from platinum contamination; mass 197 was used to monitor gold ions generated from gold hexapole rods within the IsoProbe system; masses 203 and 205 were used to measure thallium isotopes; and the remaining five masses measured mercury isotopes.

Mercury concentrations were matched within 15% among standards and samples at approximately 18.5 µg/L. Thallium was added to all samples and standards at a final concentration of 15 µg/L for instrumental mass bias correction through an empirical approach outlined by Marechal et al.,²⁴ and described for the mercury system by Meija et al.²⁵ Briefly, Hg and Tl isotopes were measured simultaneously for Hg standards to estimate the instrumental mass bias, which was then used to correct the mass bias for samples. This approach is further described in the Supporting Information. Because the instrument bias for mercury was empirically estimated using thallium, standard-sample bracketing did not significantly affect results and was not used. Mercury memory effects in the ICP-MS were controlled by adding L-cysteine to standards, samples, and washout solutions throughout this work at a final concentration of 200 mg/L. Thiol containing compounds, like L-cysteine, are known to help control mercury memory effects during introduction to ICP-MS instruments and have been used for mercury isotope measurements.^{26–28} Signals of blanks were 100 to 300 times smaller than standards and samples they bracketed and were used for on-peak zero corrections. The concentration of L-cysteine used was chosen to improve washout and lower memory effects while introducing lower salt loads to the mass spectrometer. Even so, it appeared that L-cysteine solutions may have affected the performance of the nebulizer and/or cones of the mass spectrometer as signals measured during an analytical run became smaller with time. An Aridus desolvating nebulizer (Cetac, Omaha, NE, USA) introduced mercury/thallium solutions to the ICP-MS. Between 5 and 7 ng of mercury were used for each isotope measurement.

There are seven stable isotopes of mercury: ¹⁹⁶Hg, ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, ²⁰²Hg, and ²⁰⁴Hg. Variations are reported relative to a standard measured at the same time using delta(δ) notation on a per mil (‰) basis:

$$\delta^x Hg(\text{‰}) = 1000 * \left[\frac{\left(\frac{{}^x Hg}{{}^{198}Hg} \right)_{\text{Sample}}}{\left(\frac{{}^x Hg}{{}^{198}Hg} \right)_{\text{NIST3133}}} - 1 \right], \quad 2$$

where the ¹⁹⁸Hg isotope is used in the ratios, by convention, because it is the lightest isotope with reasonable abundance. This δ notation uses the NIST 3133 mercury standard as the common reference standard as suggested by Blum and Bergquist.²⁹ δ²⁰²Hg is the value most frequently used to examine mass dependent fractionation of mercury isotopes as ²⁰²Hg is the heaviest mercury isotope without significant isobaric interferences.

Using the methods described here, long-term measurements of a mercury standard produced from the Almaden Mine in Spain, UM-Almaden (kindly provided by Professor Joel Blum of the University of Michigan) estimated a δ²⁰²Hg value of −0.69±0.27‰ (2SD, n=11), which is more negative but not significantly different than other reported values (Table SI-S1). Errors in δ values are taken as the greatest of: i) the long-term reproducibility of the UM-

Almaden standard, ii) the in-run analytical uncertainty estimated as two times the standard deviation (2SD) of NIST 3133 measured during the analytical run, or iii) two times the estimated standard error (2SE) of sample replicates during the analytical run. One reason for the larger errors in this work than other recent mercury isotope studies is the small amount of mercury measured, which increased the effect of uncertainties associated with blank corrections. The differences in isotope composition measured here are significantly larger than the estimated errors.

Results and Discussion

Molecular diffusivity of bulk mercury in air

Diffusion coefficients for mercury were calculated using the time series data of mercury remaining in the reservoirs after some simplifying assumptions. Linear $\text{Hg}^0_{(\text{g})}$ concentration profiles were assumed within needles, which is reasonable since the characteristic time for mercury diffusion along the length of the needle is on the order of one minute, much less than the hundreds of minutes required for mercury loss from the reactors. Further, equilibrium partitioning between well-mixed aqueous and gas phases within the reactors was assumed such that gaseous concentrations of $\text{Hg}^0_{(\text{g})}$ in the reactors, C_a (expressed as mass per volume), related to total Hg mass in the reactor, M , as:

$$C_a(t) = \frac{M(t)}{\left(V_a + \frac{V_l}{H}\right)}, \quad 3$$

where V_a was the volume of air in the reactor, V_l was the volume of liquid in the reactor, and H was a unitless Henry's constant defined as the ratio of air to water concentrations. Given the experimental temperature of 23 °C, Henry's constant was 0.303.³⁰ Using equation 3, initial $\text{Hg}^0_{(\text{g})}$ concentrations in the gas phase were approximately 13 mg/m³, which accounts for 42% of the total Hg^0 mass in the reactors and is several orders of magnitude greater than concentrations in the laboratory atmosphere. Some sorption of Hg^0 to surfaces within the reactors likely occurred, but this was assumed to represent a small fraction of the total Hg^0 within the reactors such that aqueous and gas phases were dominant.

Incorporating Fick's Law with a mass balance across the reactor and expression 3, the rate of mercury change in the reactors is:

$$\frac{dM}{dt} = -\frac{N A_n D_a}{\left(V_a + \frac{V_l}{H}\right) L_n} M, \quad 4$$

where N is the number of needles, A_n is the cross-sectional area of each needle, D_a is the molecular diffusivity of mercury in air, and L_n is the length of each needle. The solution to equation 4 indicates that the mass of mercury remaining in reactors decays exponentially:

$$\frac{M(t)}{M_i} = F(t) = e^{-kt}, \quad 5$$

where M_i is the initial Hg^0 mass in the reactor at time $t=0$, $F(t)$ is the fraction of Hg^0 remaining, and k is a first order rate constant defined as:

$$k = \frac{N A_n D_a}{\left(V_a + \frac{V_l}{H}\right) L_n}. \quad 6$$

As suggested by equation 5, a plot of measured $\ln(F)$ vs. t in Figure 1 is linear and yields a slope equal to $-k$ giving estimates of diffusion coefficients for the three experiments. Error-weighted linear regressions were performed using Isoplot software.³¹ Table 1 summarizes the rate constants, k , as determined by the linear regressions, and 95% confidence intervals. The observed rates are inversely proportional to needle length, as indicated in equation 6, suggesting that diffusion is very likely the rate limiting process. The weighted average bulk-phase molecular diffusion coefficient of the experiments, calculated using Isoplot,³¹ was determined to be $0.131 \pm 0.010 \text{ cm}^2/\text{s}$. This value compares very well with literature values for bulk gas-phase Hg^0 diffusion in air and N_2 , as shown in the Table SI–S3 of the Supporting Information. This provides further evidence that diffusion controlled the rate of mercury loss from the reactors; and that the assumption of Hg^0 equilibrium within the reactors with partitioning between gas and aqueous phases, with insignificant effect of sorption to surfaces, was reasonable throughout the experiment. As such, measured isotope effects should reflect differences in diffusion among mercury isotopes.

Isotope effect of Hg^0 diffusion in air

$\delta^{202}\text{Hg}$ values of mercury remaining in the sacrificed reactors are presented in Figure 2, and show an expected increase in $\delta^{202}\text{Hg}$ values as heavier isotopes remain in the reactors longer relative to lighter isotopes, which diffuse from the reactor faster. Individual plots similar to Figure 2 for other isotope pairs ($\delta^{201}\text{Hg}$, $\delta^{200}\text{Hg}$, and $\delta^{199}\text{Hg}$) are provided as Figure SI–S5 in the Supporting Information. Figure 3 shows the relationship between measured $\delta^x\text{Hg}$ values and $\delta^{202}\text{Hg}$ in the reactors. The lines in this figure illustrate expectations for mass dependent kinetic isotope fractionation behavior based on the initial isotopic composition.²⁹ An outlier in the data, identified with an asterisk, may have resulted from incomplete oxidation with KMnO_4 (oxidation time was shortened towards the end of that experiment), or perhaps an unexplained source of laboratory contamination. Calculations and linear regressions in this paper do not incorporate this outlier.

Isotope effects during the experiment were calculated using measured $\delta^x\text{Hg}$ values. Equation 5 can be used to examine ratios of individual mercury isotopes:

$$\frac{n_x(t)}{n_{198}(t)} = \frac{n_{x,i}e^{-k_x t}}{n_{198,i}e^{-k_{198} t}}, \quad 7$$

where n is used to express the moles of the different isotopes remaining in the reactor indicated by the subscripts x and 198 . After replacing n_x/n_{198} with the ratio R_x and rearranging, one finds:

$$\frac{R_x(t)}{R_{x,i}} = e^{-k_x t} \left(1 - \frac{k_{198}}{k_x} \right). \quad 8$$

Another set of substitutions yields:

$$\frac{R_x(F_x)}{R_{x,i}} = F_x^{(1-\alpha_x)}, \quad 9$$

where F_x is the fraction of initial mercury mass remaining in the reactor, as shown in equation 5, and α_x is an isotope fractionation factor defined by the ratio of isotope rates in this system

$$\alpha_x = \frac{k_{198}}{k_x}. \quad 10$$

With the exception of cases of very small F_x , and very large isotope fractionation, $F_x \approx F$. Equation 9 is a Rayleigh equation with a constant isotope fractionation factor, which effectively normalizes for many different factors in the system, including time and absolute diffusion rates.

Given the relationship between $\delta^x\text{Hg}$ values and isotope ratios, R_x , equation 9 is linearized to give:

$$\ln \left(1 + \frac{\delta^x \text{Hg}}{1000} \right) = (1 - \alpha_x) \ln F + \ln \left(1 + \frac{\delta_i^x \text{Hg}}{1000} \right), \quad 11$$

such that a plot of $\ln(1 + \delta^x \text{Hg}/1000)$ vs. $\ln F$ yields a slope equal to $(1 - \alpha_x)$. Figure 4 is a log-log plot as indicated by equation 11. Again, error-weighted linear regressions accounting for uncertainties in both $\delta^x\text{Hg}$ and F were performed using Isoplot.³¹ The Rayleigh relationship that leads to the linearized form in equation 11 describes the data well, and all three experiments show very similar slopes. Table 2 summarizes the experimental fractionation factors a_{202} derived from the results and the weighted average a_{202} of the experiments, calculated using Isoplot,³¹ was 1.00128 ± 0.00011 . Values for other isotope pairs are provided in Table SI-S4 of the Supporting Information

D_y/D_x was estimated using the experimental fractionation factors and estimates for the relative effects of Henry's constant, H_y/H_x , among the isotopes. Combining equations 6 and 10, the relationship between α_x , D , and H is:

$$\alpha_x = \frac{k_{198}}{k_x} = \left(\frac{D_{198}}{D_x} \right) \left(\frac{H_{198}}{H_x} \right) \left(\frac{H_x V_a + V_l}{H_{198} V_a + V_l} \right). \quad 12$$

The effect of Henry's constant and the air and liquid volumes can be simplified if we assume that $\alpha_x \approx 1$ and $H_{198}/H_x \approx 1$. With this assumption:

$$\alpha_x \approx \frac{k_{198}}{k_x} \approx \left(\frac{D_{198}}{D_x} \right) \left(\frac{H_{198}}{H_x} \right)^{\frac{V_l}{H V_a + V_l}}, \quad 13$$

where $H \approx H_x \approx H_{198}$. Examining equation 13, one concludes that an approximation of H_{198}/H_x is necessary to estimate D_{198}/D_x with our experimental data.

The ratios of Henry's constants for the isotopes of mercury are likely to be very near unity. Very limited data are available in the literature regarding the isotope effect of equilibrium partitioning between air and aqueous phases, and these data are for much lighter gases such as He, Ne, N₂, O₂, and Ar.^{32–35} Omitting helium, Figure 5 shows these equilibrium isotope effects from the literature as a function of a factor $\Delta m/m^2$ that has been suggested to be an effective scaling term for mass-dependent behavior of isotopes at equilibrium.³⁶ In this case, Δm is the difference in masses of molecules, and m is the average mass of the molecules. Helium was omitted because it was unlikely to scale well as a result of more complex quantum mechanical behavior. Because data shown in Figure 5 scale well with $\Delta m/m^2$, this was used to estimate H_y/H_x for Hg⁰. With this method, the ratio H_{198}/H_{202} was estimated to be 1.000045, which is quite small as expected.

With the experimentally determined α_x and estimates for H_{198}/H_x , relative diffusion rates among mercury isotopes in air were estimated. Table 2 includes the estimated values of D_{198}/D_{202} in the experiments, and Figure 6 shows D_{198}/D_{199} , D_{198}/D_{200} , D_{198}/D_{201} , and D_{198}/D_{202} compared to kinetic theory, with the assumption of identical collision diameters and an average air molecular mass of 29.0 g/mol. The experimentally determined values for relative diffusion rates match kinetic theory very well. The use of kinetic theory, together with the assumption of identical collision diameters, for modeling isotope effects is debated, but in the case of $\text{Hg}^0_{(g)}$, such simplification appears quite appropriate.

Environmental Relevance

The diffusive isotope effect for Hg^0 in air should be considered while interpreting environmental mercury isotope data. Two examples of recently published mercury isotope research illustrate this – one related to plant uptake of mercury, and the other focused on mercury isotope fractionation at coal-fired power plants.^{37,38}

Yin et al.³⁷ measured mercury isotopes in rice plants, as well as associated soils and the immediate atmosphere, and concluded that rice leaves likely absorbed mercury from atmospheric mercury based on the lack of mass-independent fractionation (MIF) between the two. While we do not discuss MIF in this paper, we note mass dependent fractionation $>1.0\%$ in $\delta^{202}\text{Hg}$ was observed between the atmosphere and leaves, with the leaves being more negative. If the uptake of mercury was diffusion controlled during transport through stomata (as CO_2 uptake by leaves can be), our results show that mass dependent fractionation would be 1.3‰ in $\delta^{202}\text{Hg}$, which is very similar to observed values. While such diffusion limitation is not the only possible mechanism leading to the observed data, it is a simple and compelling explanation.

Coal-fired utility boilers (CFUBs) are the largest contributors of anthropogenic mercury to the global environment and there is substantial interest in the effect of sorbents and fly ash on mercury removal from combustion gases. Sun et al.³⁸ measured mercury isotope compositions among coal, ash, and gypsum at two CFUBs, suggesting that mercury isotopes could help identify power plant sources. Because some limitations in mercury removal by fly ash or other sorbents have been attributed to diffusive mass transfer,^{20–22} we explore the data of Sun et al. in such a context. Figure 7 shows average $\delta^{202}\text{Hg}$ values relative to the initial Hg in coal for bottom ash, fly ash, and gypsum from flue gas desulfurization processes plotted against the average of the fractions of $\text{Hg}^0_{(g)}$ remaining in the combustion gases. Because the $\delta^{202}\text{Hg}$ values reflect a collection of all fly ashes for each CFUB, it is likely the fly ashes described by Sun et al. represent cumulative removal rather than instantaneous removal of Hg^0 from the gas stream. Figure 7 also shows the results of a Rayleigh fractionation model describing $\delta^{202}\text{Hg}$ as $\text{Hg}^0_{(g)}$ is removed under ideal diffusive mass transfer limited conditions from combustion gases using the fractionation factor described in this paper. The data and model agree well for large fractions of Hg^0 remaining ($0.8 < F < 1$), providing evidence that initial sorption onto ashes could be diffusion mass transfer limited. Differences between data and the model at lower fractions of Hg^0 remaining suggest that Hg^0 removal from the gas phase is no longer solely diffusion mass transfer limited, and may reflect other kinetic or equilibrium isotope effects. A diffusion limited signal, such as the isotope fractionation behavior described in this paper, could be quite useful while investigating the performance of mercury sorbents used for mercury removal from combustion gases. Efficient sorbents that lead to near ideal diffusive mass transfer could have large $\delta^{202}\text{Hg}$ values at low fractions of $\text{Hg}^0_{(g)}$ remaining, as predicted in Figure 7. Similarly, $\text{Hg}^0_{(l)}$ recovery efforts using retorts and condensers at historic or artisanal mercury and gold mining operations could lead to large $\delta^{202}\text{Hg}$ values in gaseous emissions due to gaseous diffusion limitations. Large $\delta^{202}\text{Hg}$ values resulting from Rayleigh

fractionation and diffusive processes could prove useful for tracking atmospheric mercury sources. In contrast to these expectations of large $\delta^{202}\text{Hg}$ values, however, a study by Sherman et al.⁵ showed precipitation influenced by a nearby CFUB with negative $\delta^{202}\text{Hg}$ values as low as -4.4% , suggesting to us that most isotope fractionation leading to the mercury in this precipitation was from processes other than diffusion limitations within the CFUB.

In this paper, we have shown that the isotope effect associated with Hg^0 diffusion in air is large and can be modeled with simple kinetic theory. These results can assist in interpreting isotope signals in environmental and industrial settings with predictive models for mercury biogeochemical cycling and the identification of mercury sources.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Natural logarithm of the mercury fraction of mercury remaining in the reactors with time. Experiments 1 and 2 used 2.54 cm needles while experiment 3 used 3.81 cm needles.

Figure 2. $\delta^{202}\text{Hg}$ of mercury remaining in the diffusion reactors. The asterisk (*) identifies an outlier not used during analysis. Experiments 1 and 2 used 2.54 cm needles while experiment 3 used 3.81 cm needles.

Figure 3.

Multi-isotope plot of mercury remaining in the diffusion reactors. Lines indicate expected values if only mass-dependent fractionation occurs. The asterisks (*) identify an outlier sample that does not exhibit only mass-dependent fractionation.

Figure 4. Linearized isotope fractionation of $\delta^{202}\text{Hg}$. The asterisk (*) identifies an outlier not used in analysis.

Figure 5.

Isotope effects associated with Henry's partitioning. The linear regression was forced through $H_y/H_x=1$ at $\Delta m/m^2=0$, and was used to estimate H_{198}/H_{202} for Hg^0 . Data are from Benson and Krause,³² Beyerle et al.,³³ and Klotz and Benson.³⁴

Figure 6. Comparison of experimental results of D_{198}/D_x and kinetic theory for Hg^0 diffusion in air.

Figure 7.

Solid lines indicate modeled $\delta^{202}\text{Hg}$ values for $\text{Hg}^0_{(\text{g})}$ and Hg^0 sorbed to particulates under ideal diffusive mass transfer limitations from gas to solid, with $\delta^{202}\text{Hg} = 0$ for $\text{Hg}^0_{(\text{g})}$ at $F=1$. $\delta^{202}\text{Hg}$ values for ash and gypsum at coal-fired utility boilers as measured by Sun et al.³⁸ have been modified so that the feed coals are assigned to $\delta^{202}\text{Hg} = 0$.

Table 1

Results of air diffusion experiments and calculated diffusion coefficients

Experiment	Needle Length (cm)	Needle inner diameter (cm)	Number of needles	Rate at 23 °C (min ⁻¹) × 10 ³	Estimated D at 23 °C (cm ² /s)
1	2.54	0.119	5	1.49±0.07	0.132±0.007
2	2.54	0.119	5	1.45±0.04	0.128±0.004
3	3.81	0.119	5	1.02±0.05	0.136±0.006
Weighted Average					0.131±0.010

Table 2

Observed isotope fractionation factors in the air diffusion experiments and associated relative diffusion rates for ^{198}Hg and ^{202}Hg

Experiment	α_{202}	$\text{H}_{198}/\text{H}_{202}$	$\text{D}_{198}/\text{D}_{202}$
1	1.00125 ± 0.00019	1.000045	1.00122 ± 0.00019
2	1.00126 ± 0.00016	1.000045	1.00123 ± 0.00016
3	1.00137 ± 0.00027	1.000045	1.00134 ± 0.00027
Weighted Average	1.00128 ± 0.00011	1.000045	1.00125 ± 0.00011