Assessing the Potential for Re-emission of Mercury Deposited in Precipitation from Arid Soils Using a Stable Isotope

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A solution containing 198Hg in the form of HgCl2 was added to a 4 m² area of desert soils in Nevada, and soil Hg fluxes were measured using three dynamic flux chambers. There was an immediate release of 198Hg after it was applied, and then emissions decreased exponentially. Within the first 6 h after the isotope was added to the soil, ~12 ng m⁻² of 198Hg was emitted to the atmosphere, followed by a relatively steady flux of the isotope at 0.2 ± 0.2 ng m⁻² h⁻¹ for the remainder of the experiment (62 days). Over this time, ~200 ng m⁻² or 2% of the 198Hg isotope was emitted from the soil, and we estimate that ~6% of the isotope would be re-emitted in a year’s time. During the experiment, dry deposition of elemental Hg from the atmosphere was measured with an average deposition rate of 0.2 ± 0.1 ng m⁻² h⁻¹. Emission of ambient Hg from the soil was observed after soil wetting with the isotope solution and after a storm event. However, the added moisture from the storm event did not affect 198Hg flux. Results suggest that in this desert environment, where there is limited precipitation, Hg deposited by wet processes is not readily re-emitted and that dry deposition of elemental Hg may be an important process.

Introduction

Characterizing the mobilization and fate of mercury (Hg) as it interacts with the Earth’s surface is complex. Mercury can be emitted from terrestrial surfaces to the atmosphere and deposited to terrestrial surfaces from the atmosphere by wet and dry processes. After deposition, Hg can be re-emitted back to the atmosphere. One of the large uncertainties in quantifying Hg emissions from terrestrial surfaces is distinguishing between native Hg originally present in the substrate and “newer” Hg deposited from the atmosphere and then re-emitted.

Currently, anthropogenically released Hg is widely distributed and is cycled collectively with native or geological Hg pools. The use of published substrate and flux data to estimate deposition and emission rates is not entirely straightforward because of the difficulty in differentiating between natural, anthropogenic, and recycled Hg. Kim et al. (1) indicated that high deposition rates of atmospheric Hg due to anthropogenic sources could significantly alter our basic picture of natural Hg cycling.

Mercury in the elemental form is capable of long-range transport and following oxidation to the oxidized form may be deposited to soil surfaces with precipitation (2). Once Hg is deposited, it may be re-emitted to the atmosphere, and recent research suggests that elemental Hg may be more rapidly recycled between terrestrial and aquatic surfaces than previously thought (3). Wet deposition estimates based on indirect and direct measurements in North America ranged from 5 to 16 μg m⁻² year⁻¹ (4–6). In addition, 2002–2003 data from the Mercury Deposition Network (MDN) indicates that wet deposition ranges from 3 to 30 μg m⁻² year⁻¹ (http://nadp.sws.uiuc.edu/mdn/); however, this range is based largely on measurements made in the eastern and southeastern U. S. Measurements made in 2003 at the two Nevada MDN sites indicate that annual wet deposition ranged from 3.6 to 4.3 μg m⁻² year⁻¹ because Hg has seven stable isotopes that typically occur in a constant proportions in the natural environment (196Hg 0.15%, 198Hg 9.96%, 199Hg 16.90%, 200Hg 23.08%, 201Hg 13.19%, 202Hg 29.85%, 204Hg 6.87%; ref 7), the use of enriched Hg-isotope spikes is an effective technique for understanding the fate of Hg deposited in the environment. Stable Hg-isotope spikes have been successfully used in several spiking experiments, ranging from bench-scale to whole-watershed-scale studies (e.g., refs 8–11). In addition, Matilainen et al. (12) used radioactive 203Hg to determine the amount of Hg retained in the organic humus layer of soils and concluded that most of the Hg deposited to soils in the last 100 years is present in the active biogeochemical zones of the systems. On the basis of soil lysimeter experiments with radiolabeled Hg(II)-treated podzols, Schlüter (13) estimated that 5.2% of total deposited atmospheric Hg can be expected to evaporate, regardless of variations in atmospheric Hg deposition throughout the year.

This project characterized the potential for re-emission of Hg deposited in precipitation to desert soils. Nonpolar deserts comprise roughly 36% of the earth’s land surface (about 49 million km²) and are characterized by little annual precipitation and intense solar radiation (14). Because solar radiation may enhance Hg emission from soils (15), this is a particularly interesting system for studying Hg re-emission. To investigate the behavior of Hg newly deposited onto arid ecosystems, an enriched stable isotope of Hg (198HgCl2) was sprayed onto the soil surface, allowing the fate of this form to be contrasted with the ambient Hg already existing in the system.

Materials and Methods

Site Description. The study site was located in Hungry Valley (39°45′55.0″ N, 119°44′34.29″ W) approximately 30 km north of Reno, Nevada. The soils had Hg concentrations of 0.010 ± 0.005 mg/kg (n = 27) and are considered background soils (<0.1 mg/kg total Hg concentration; refs 16, 17). The soil texture was sandy loam (78% sand, 12% silt, 10% clay) with pH 7.1 and a cation exchange capacity 4.2 mequiv per 100 g (A&L Laboratories, CA). Organic matter content was determined to be 1.2% (Oklahoma State University Soils Laboratory, soil analyzed with LECO furnace after leaching with sulfuric acid to remove carbonates). Grasses and forbs are the principle vegetation at the site with thinly dispersed

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sagebrush at higher elevations. Annual precipitation ranges from as little as 150 mm to over 300 mm. Most precipitation occurs in the winter and early spring (November–April), and precipitation can significantly vary between years (18).

**Sample Collection.** Mercury fluxes were measured simultaneously using 3 to 4 dynamic flux chambers (FCs), which consisted of transparent cylindrical polycarbonate vessels, with radii of 10 cm, heights of 3.5 cm, volumes of 1 L, bottom surface areas of 0.03 m², and 16 holes (1 cm in diameter) around the circumference to allow unrestricted air movement (Figure 1; refs 19–21). For each flux measurement, the chambers were positioned on the same respective location of bare soil surface with as little soil disturbance as possible. Vacuum pumps connected to a generator produced the flushing flow rate of 1.5 L min⁻¹ (turnover every 0.67 min). In-line flow meters (Dwyer Instruments, Inc.) with stopcocks allowed for control and constant monitoring of flows, and a digital mass flow meter (Sierra Instruments, Inc.) was used to check flow settings every 15 min (Figure 1a). For all measurements except those immediately following the isotope application, chambers were allowed to flush for 40 min before gold-coated glass-bead (Brooks Rand LLC) traps were placed on the outlet and inlet airstreams (~9 m from tubing opening) to collect gaseous Hg. Presumably what was captured on the traps represents slightly less (<5%) than total gaseous Hg. This is because reactive gaseous Hg could stick to the filters and tubing walls, and concentrations of this form are known to be less than ~5% of total atmospheric Hg (22, 23). Because the gaseous Hg that was collected on the gold traps was principally Hg⁰, we refer to the soil Hg fluxes as Hg⁰ fluxes in the text. The inlet line was positioned on the upwind side of chamber just above an inlet air pore (2 cm above the surface). Teflon filters (0.2 μm pore size) were placed 4–10 cm at the beginning of the intake of each line. Traps were blanked by heating to 300 °C the day prior to sampling.

After Hg in the air was collected onto the gold traps, the traps were plugged with Teflon stoppers, wrapped with Teflon tape, double-bagged, and sent to the United States Geological Survey Wisconsin District Mercury Laboratory (WDML) where the Hg was thermally desorbed in a stream of argon into plasma and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (8, 24). Traps were analyzed following U. S. EPA Method 1631, revision E (25), utilizing a Perkin-Elmer Elan 6100 ICP-MS as the detection/quantification method in lieu of the cold vapor atomic fluorescence spectrometer (CVAFS) specified in the method. A natural abundance Hg standard solution with a concentration of 10 ng L⁻¹ was used to generate the response factor of the ICP-MS. The daily detection limit for ambient Hg was <0.006 ng, and measured ¹⁹⁸Hg concentrations were significantly greater than instrument variability. For this study, the experimental tracer was enriched ¹⁹⁸Hg (90.5% assay), and ²⁰²Hg was used to determine the ambient Hg contribution to the total Hg pool (ambient plus tracer). A mathematical algorithm was used to assess and (1) for the contribution of the enriched isotope addition (as well as the ~10% of the applied Hg that was other than the ¹⁹⁸Hg isotope) from the concentration of ambient Hg.

Inlet and outlet atmospheric Hg samples were collected using gold traps for 1–4 h intervals, and Hg fluxes were determined using the following equation: \( F = Q^* (C_0 - C_i)/A \), where \( F \) is the Hg flux of the soil in ng m⁻² h⁻¹, \( C_0 \) and \( C_i \) are the gaseous elemental Hg (Hg⁰) concentration of the outlet and inlet air streams in ng m⁻³, \( A \) is the surface area enclosed by the FC in m², and \( Q \) is the flow of ambient air through the flux chamber in m³ h⁻¹. Positive flux values indicate Hg⁰ emission from the soil into the air, whereas negative flux values represent Hg⁰ deposition. A fourth FC connected to a Tekran mercury analyzer (model 2537A) with an automated dual sampling unit measured 20 min fluxes twice during the experiment: (1) during a (preisotope spike) watering experiment and (2) for 3 days following the application of the isotope. While the Tekran analyzer could not distinguish between Hg⁰ isotopes, it provided a check that the amount of Hg collected on the traps was sufficient for analytical purposes.

The soil temperatures inside and outside one chamber (Omega Thermocouples), air temperature and relative humidity (Vaisala CS105), and incident light (LiCOR LI200X) measurements were collected simultaneously with soil Hg flux measurements and averaged for 5 min intervals using a data logger (Campbell Scientific CR23X; see Table 1).

**Preisotope Spike Study.** Soil Hg fluxes were measured at the beginning of August 2004, and nine soil samples were randomly collected from the study area to a depth of 1–2 cm using a stainless steel shovel and stored double-bagged in the freezer. Significant increases in soil Hg flux have been observed from desert soils with precipitation events (26, 27). For this reason, prior to application of the Hg isotopic spike,
soil Hg flux was monitored for approximately 2 h before and several hours after the application of water (same volume and pH and as that which would later be used in application of the isotope). This was performed twice to characterize the effect of soil wetting on Hg fluxes.

**Application of Isotope 198Hg to Soil.** A 0.10 ± 0.01 mg L⁻¹ solution of 198Hg (stock solution obtained from Oak Ridge National Laboratory, TN) in the form of HgCl₂ was added to a 4 m² plot of soil in a simulated light rain event during the beginning of September 2004. The 4 m² area was divided into two 2 m² sections by a 0.5 m walking path, which allowed easy access to the experimental area (Figure 1b). During the night (04:15), 8.2 ± 3.6 µg 198Hg (±1 standard deviation) was applied in a solution volume of 100 mL (dilution made with ultrapure water and pH-adjusted to 5.0 with optima HCl) to each m² of soil using a small spray bottle. This is slightly higher than the annual amount Hg that would be deposited each m² of soil using a small spray bottle. This is slightly higher than the annual amount Hg that would be deposited each m² of soil using a small spray bottle. The spray volume was reduced and purged onto gold-coated tweezers within 10 min after the isotope was applied, refrigerated sample (same location. In the laboratory, Hg(II) in the isotope solution and glasses had been located to prevent later resampling of same location. In the laboratory, Hg(II) in the isotope solution and the watch glass rinses were reduced and purged onto gold-coated glass-bead traps and analyzed by ICP-MS to verify homogeneity and quantify the amount of isotope that was applied to the soil. Twelve hours prior to the isotope application, four FCs were placed on the soil with pumps drawing air through the chambers (Figure 1). Just before the isotope was applied to each quadrant, the respective FC was lifted from the ground and gold traps were placed in inlet and outlet airstreams. The isotope was then applied, and the chamber immediately replaced over the soil to measure flux before the isotope was similarly applied to the next m² quadrant section of area. Soil Hg flux measurements were made starting at 0, 1, 4, 8, 12, and 17 h, and 1, 2, 3, 6, 14, 21, 35, and 62 days after isotope application (Table 2).

Five samples of surface soil (area 64 cm², ~1–2 cm depth) were randomly collected (in the study area around the chamber locations) each day that soil Hg flux measurements were made. A glass Petri dish was pressed into the soil to designate the area, and a plastic spoon was used to scoop soil into a sandwich bag. These locations were also marked with rocks. One soil sample was weighed before and after drying in an oven at 102 °C for 24 h to determine gravimetric percent moisture. Three soil samples from each collection time were selected and homogenized. A 5 g aliquot of each homogenized sample was digested with 45 mL of concentrated aqua regia solution at 100 °C for 2 h. Then 5 mL of 1% BrCl solution was added, and samples were further digested at 150 °C overnight. After BrCl reduction, a 100–200 µL aliquot of the digestate was purged onto gold traps for isotopic Hg analysis with an ICP-MS.

Prior to isotope application, in an attempt to assess the potential loss of isotope from soil surfaces due to wind erosion, 23 acid-washed Petri dishes were placed in lines along the cardinal compass directions in 3 m increments out to 15 m from the plot (Figure 1b). At the end of the experiment (day 62), Petri dishes were collected, composited into equidistant groups (e.g., all four dishes 15 m out were combined), digested, and analyzed for excess 198Hg isotope.

**Quality Control.** Chambers and tubing underwent rigorous cleaning with a chelating detergent (Microsoap 90, International Products) followed by soaking in nitric acid solution (5–10% v/v), rinsing with ultrapure water, and drying with charcoal-scrubbed air. Before and after collecting soil flux measurements, chamber blanks were routinely determined by placing the FC on a flat polycarbonate surface (original container lid) and measuring flux. Chamber blanks averaged −0.08 ± 0.28 ng m⁻² h⁻¹ (minimum −0.67, maximum 0.33, n = 18). In no case was excess 198Hg detected; indicating chambers were not contaminated with the enriched isotope. Chamber blanks with detectable amounts of ambient Hg were not significantly different from zero and were not subtracted when calculating soil Hg flux values. Mercury concentrations on trip blank traps were found to be significantly less than those on the sample traps (no excess 198Hg detected, and ambient Hg less than 2–4% of that measured in samples). All traps were tested for efficiency by loading 1 ng of Hg on them and measuring recovery with CVAFS (28, 29). Only traps demonstrating less than 5% error were used in the study.
TABLE 2. Summary of Soil Hg Flux Data for Ambient Hg and 198Hg for Three Flux Chambers (FC-A, FC-B, and FC-C)

<table>
<thead>
<tr>
<th>sample date</th>
<th>start time</th>
<th>end time</th>
<th>soil moisture (%)</th>
<th>ambient Hg flux (ng m⁻² h⁻¹)</th>
<th>198Hg flux (ng m⁻² h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>FC-A</td>
<td>FC-B</td>
<td>FC-C</td>
</tr>
<tr>
<td>8/5/2004</td>
<td>09:45</td>
<td>11:15</td>
<td>0.8</td>
<td>0.2 -0.4</td>
<td>-0.2 ± 0.3</td>
</tr>
<tr>
<td>8/5/2004</td>
<td>11:20</td>
<td>13:20</td>
<td>0.8</td>
<td>-0.7 -0.3</td>
<td>-0.6 ± 0.2</td>
</tr>
<tr>
<td>8/5/2004</td>
<td>13:20</td>
<td>14:40</td>
<td>0.8</td>
<td>-0.8 -0.5</td>
<td>-0.7 ± 0.2</td>
</tr>
<tr>
<td>9/1/2004</td>
<td>04:15</td>
<td>05:15</td>
<td>0.8</td>
<td>1.0 0.7</td>
<td>0.6 ± 0.5</td>
</tr>
<tr>
<td>9/2/2004</td>
<td>05:20</td>
<td>06:40</td>
<td>0.8</td>
<td>0.8 -1.5</td>
<td>-0.1 ± 1.2</td>
</tr>
<tr>
<td>9/1/2004</td>
<td>07:00</td>
<td>10:00</td>
<td>0.8</td>
<td>0.3 -2.1</td>
<td>1.1 ± 1.3</td>
</tr>
<tr>
<td>9/1/2004</td>
<td>10:05</td>
<td>14:45</td>
<td>0.8</td>
<td>-1.1 0.4</td>
<td>-0.6 ± 0.9</td>
</tr>
<tr>
<td>9/1/2004</td>
<td>14:50</td>
<td>19:50</td>
<td>0.8</td>
<td>0.1 1.2</td>
<td>0.1 ± 1.3</td>
</tr>
<tr>
<td>9/1/2004</td>
<td>19:55</td>
<td>23:55</td>
<td>0.8</td>
<td>-0.2 -0.3</td>
<td>-0.2 ± 0.1</td>
</tr>
<tr>
<td>9/2/2004</td>
<td>03:55</td>
<td>07:55</td>
<td>0.6</td>
<td>0.5 -0.2</td>
<td>0.1 ± 0.4</td>
</tr>
<tr>
<td>9/2/2004</td>
<td>11:00</td>
<td>15:00</td>
<td>0.6</td>
<td>-0.4 0.5</td>
<td>0.3 ± 1.4</td>
</tr>
<tr>
<td>9/2/2004</td>
<td>18:00</td>
<td>22:00</td>
<td>0.6</td>
<td>0.2 -0.3</td>
<td>-0.1 ± 0.3</td>
</tr>
<tr>
<td>9/3/2004</td>
<td>11:00</td>
<td>14:00</td>
<td>0.7</td>
<td>ND 0.1 -0.3</td>
<td>ND 0.1 ± 0.3</td>
</tr>
<tr>
<td>9/5/2004</td>
<td>11:00</td>
<td>14:00</td>
<td>0.6</td>
<td>-0.2 -0.2</td>
<td>0.0 ± 0.3</td>
</tr>
<tr>
<td>9/7/2004</td>
<td>11:00</td>
<td>14:00</td>
<td>0.5</td>
<td>-0.6 -0.7</td>
<td>-0.5 ± 0.2</td>
</tr>
<tr>
<td>9/14/2004</td>
<td>11:30</td>
<td>14:30</td>
<td>0.6</td>
<td>-0.1 -0.2</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>9/21/2004</td>
<td>11:30</td>
<td>14:30</td>
<td>0.7</td>
<td>-0.1 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>10/5/2004</td>
<td>11:30</td>
<td>14:30</td>
<td>0.5</td>
<td>-0.2 -0.2</td>
<td>-0.3 ± 0.1</td>
</tr>
<tr>
<td>11/2/2004</td>
<td>11:30</td>
<td>14:30</td>
<td>4.0</td>
<td>2.3 1.8</td>
<td>1.9 ± 0.4</td>
</tr>
</tbody>
</table>

* Isotope 198Hg was amended to soils on 9/1/04 at 04:15. Percent soil moisture (by weight) is listed for each sampling date. On 9/3/04, a sample was lost and no data (ND) is reported. The average and standard deviation of the three flux chamber measurements are given.

As normal practice during ICP-MS analysis, a quality control standard comparable to the mass of Hg found on the sample traps was analyzed every 10 samples to verify the system calibration. Control standards were within 10% of the expected values. The Hg standard solutions (National Institute of Standards and Technology (NIST) traceable) used during calibration were routinely compared with standard reference Hg solutions (NIST #3133), and San Joaquin soil (NIST #2709) that was digested with soil samples had 77% recovery. The WDM, where the isotope analysis was performed, participated in an interlaboratory comparison experiment with eight other laboratories as part of the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) study and demonstrated excellent accuracy and precision (30).

Because 202Hg occurs at such a low relative abundance (0.15%) and 204Hg has potential interference problems from 208Pb, these isotopes were not analyzed in this study. Assuming that relative abundances of 198Hg and 204Hg were 0.15% and 6.87%, respectively, the natural isotopic Hg abundance measured at the site in air and soil were 9.86% ± 0.001%, 198Hg, 16.895 ± 0.001%, 204Hg, 23.081 ± 0.002%, 202Hg, 13.189 ± 0.001%, 201Hg, and 29.853 ± 0.002%, 203Hg (n = 25). These values agree quite well with other published values (7, 31, 32).

Results and Discussion

Two experiments were conducted 1 month prior to the application of the isotope to the soil. On August 5, 2004, we calculated an average ambient soil Hg flux of -0.5 ± 0.4 ng m⁻² h⁻¹ based on 12 flux measurements obtained using three FCs and with gold traps. Table 1 presents a summary of meteorological and soil parameters that were measured concurrently with soil Hg fluxes. Figure 2 shows data from a watering experiment (8/4/05) using a FC connected to the Tekran. The same amount of ultrapure water (pH 5.0) was applied at 10:55 and 13:00 to the soil as was later used during the isotope application. There was an immediate response to watering, with soil Hg flux increasing 4 to 7-fold. The amount of water added (100 mL m⁻²) was so small that after 30 min all water had visibly evaporated from the soil and soil fluxes had returned to prewatering values. It should be noted that the watering experiment was performed in light conditions, while the isotope application was done during the early morning (04:15) in dark conditions.

There was a discrepancy between soil Hg fluxes measured on the day of the preisotope spike study (8/5/05) with those measured on the day of the watering experiment (8/4/05). During the watering experiment, the dry soil fluxes ranged from -0.4 to 1.2 ng m⁻² h⁻¹ with an average positive flux of 0.5 ± 0.5 ng m⁻² h⁻¹ (n = 13). Because the watering experiment was performed in position FC-D using a Tekran mercury analyzer and all other measurements throughout the experiment were made in positions FC-A, FC-B, and FC-C using gold traps (Figure 1b), the soil Hg flux of -0.5 ± 0.4 ng m⁻² h⁻¹ collected during the preisotope spike study is more comparable with data collected later.

After application, there was an immediate release of the isotope, after which emissions decreased exponentially (Figure 3). This is similar to what researchers observed following isotope application in the METAALICUS study (10).

The isotope flux did not appear to be affected by light (Tables 1 and 2) with the highest 198Hg fluxes (4.5 ng m⁻² h⁻¹) observed in the 2.5 h immediately following the spike in dark conditions (solar irradiance ranged from 0 to 7 W m⁻²). The average flux after the sun had come up (32–650 W m⁻²) was approximately a third less than the averaged fluxes in the dark, although not significantly less (p = 0.11). On the basis of the fluxes from the first 6 h after the isotope application, approximately 12
ng m$^{-2}$ or 0.1% of the $^{198}$Hg was emitted to the atmosphere. After that, a relatively steady flux of the isotope (0.2 ± 0.2 ng m$^{-2}$ h$^{-1}$) was measured for the remainder of the experiment (62 days).

We fit a power regression curve to the 62 days of averaged data ($R^2 = 0.72$), and integrated the area under the curve to estimate the total emission of the isotope over time (Figure 3). Two slightly negative fluxes (~0.02 and ~0.11 ng m$^{-2}$ h$^{-1}$ collected from 10:00–14:00 and 20:00–24:00 on 9/1/04, respectively) were removed from the data set to allow a power regression to be computed. Negative fluxes of $^{198}$Hg were only observed on the first day following isotope application, presumably when the system was settling and becoming equilibrated. Negative fluxes could result if the isotope volatilized and then promptly redeposited on the soil surfaces inside the chamber or if the isotope volatilized to a greater extent from soils below the inlet line (Figure 1a). Integrating the power regression curve indicated that 180 ng m$^{-2}$ or 2.2% of the $^{198}$Hg isotope was emitted from the soil over the course of the 62 days after the isotope was applied. With all data points (including the negative fluxes) and manual integration between sampling periods with the trapezoid method, indicated that 230 ng m$^{-2}$ of the $^{198}$Hg isotope was emitted during the course of the experiment. Excluding negative fluxes yielded 240 ng m$^{-2}$ of $^{198}$Hg. We feel confident that the 62 day emission of the $^{198}$Hg ranged from 180 to 230 ng m$^{-2}$. This represents only 2–3% of the Hg applied. Assuming that soil $^{198}$Hg flux had stabilized by the end of the experiment (Figure 3), we used flux values obtained during sampling on day 35 and 62 to estimate continued soil emissions of $^{198}$Hg for 1 year. We determined that approximately 500 ng m$^{-2}$ or 6% of the $^{198}$Hg would be re-emitted to the atmosphere annually.

Dry deposition of ambient elemental Hg from the atmosphere to the soil was measured during most of the days after the isotope application with an average deposition rate of 0.2 ± 0.1 ng m$^{-2}$ h$^{-1}$ ($n = 41$, excluding fluxes measured immediately after application of isotope and at the end of the experiment). Emissions of ambient Hg from the soil were clearly observed when the soil was wetted with the application of the isotope solution (9/1/04) and at the end of the experiment (11/2/04) when several rain events increased soil moisture from <1 to 4% (Figure 4). During the latter, temperatures and solar irradiance were the lowest, yet ambient fluxes were the highest (Table 1). These results reveal information about the dynamics of the system and indicate that the ambient Hg is more readily emitted to the air in wet conditions than in dry conditions. The significant influence of soil moisture on Hg emissions has recently received attention (33–35). These studies demonstrated that as soil moisture increases, soil Hg flux continues to increase until the soils become saturated beyond field capacity and the soil Hg flux is suppressed.

Figure 5 illustrates how concentrations of the isotope measured in surface soil samples (~1–2 cm) agreed well with measurements of that applied based on the watch glasses and isotope solution concentrations and support the low flux of $^{198}$Hg measured throughout the experiment. The mean concentration of $^{198}$Hg in the surface soils for days 0–35 was 8.7 ± 4.3 μg m$^{-2}$ ($n = 18$), and the estimated concentration of $^{198}$Hg applied based on measurements made with watch glasses was 8.2 ± 3.6 μg m$^{-2}$ ($n = 8$). On the basis of the volume applied and solution concentration of $^{198}$Hg, 11.0 ± 1.3 μg m$^{-2}$ would have been applied. While there is good agreement between these values, because the isotope was applied in a fine mist, it is likely that some of the solution volatilized into the air and did not reach the ground. For this reason, we believe the watch glasses are more representative of what was actually applied and the viability of that application.

With a two-sample Wilcoxon rank-sum (Mann–Whitney) test, the isotope concentrations in the surface soils at the end of the experiment were found to be significantly lower ($p = 0.02$) than concentrations measured for days 0–35. For the week prior to the day 62 sampling trip, it rained several times, and isotope concentrations in surface soils were approximately half those measured throughout the experiment. It is possible that $^{198}$Hg was leached from the surface to sites deeper in the soil profile. Other studies have observed mobility of HgCl$_2$ through soil columns in leachate waters.
Because the soils in our study were predominantly sand and contained less organic matter than soils used in the column studies, it seems likely that the decrease of nearly half of the $^{198}$Hg(II) in the surface soils could be attributed to the rain leaching the $^{198}$Hg into the soil column. Because the concentration of the isotope was not measured throughout the soil column and no auxiliary experiments were performed, the idea that the isotope traveled down through the soil column after a rain event is speculative.

An alternate scenario is that the isotope was redistributed by wind. A very small excess of $^{198}$Hg (barely detectable) was found in one set of composit Petri dishes that were positioned 9 m from the experiment (Figure 1b). This would suggest that a small amount of the $^{198}$Hg might have been removed from the plots by wind erosion. The influence of wind in this study is uncertain. The Petri dish test was qualitative and not practical for quantification. It is possible that the wind could have redistributed the isotope over such a large area that its presence was below detection.

Despite the reduction in surface $^{198}$Hg and increased soil moisture, soil fluxes of $^{198}$Hg remained relatively constant at day 62 (Table 2). Assuming that the pool of ambient Hg available for emission to the atmosphere was located in the top 1 cm of surface soil and calculating a flux/pool ratio, we determined that if the isotope behaved similarly to the ambient Hg, then there would be a flux of $\sim$10–20 ng m$^{-2}$ of $^{198}$Hg on day 62; however, a average flux of $<1$ ng m$^{-2}$ was measured. This further supports our assertion that the newly applied isotope behaved differently than ambient Hg.

An important question is what happens to atmospheric Hg that is deposited to desert soils in precipitation? Is it sequestered or is it quickly lost? On the basis of the $^{198}$Hg fluxes measured at the site, we suggest that $>90\%$ of the Hg(II) annually deposited with precipitation does not appear to be re-emitted into the atmosphere but remains in the soil. Figure 6 presents a mass balance illustration for this experiment with fluxes normalized to 1 year based on annual climate records for this particular site. It shows how the newly deposited $^{198}$Hg(II) is sequestered in the soil with little re-emitted and some potentially transported deeper in the soil profile with rain. Ambient Hg behaves differently with deposition being the dominant flux for dry soils and emission occurring in wet soils. On the basis of the magnitude of ambient Hg fluxes measured at this one location, it appears that on an annual basis at this specific study area dry deposition of elemental Hg and emissions from wet soils might cancel each other out and produce no net exchange overall. Additional studies need to be done to quantify dry deposition and the degree to which air–surface recycling occurs. In desert environments where there is limited precipitation, dry deposition of elemental Hg may be an important process. An understanding of all processes (both wet and dry) will have strong implications for the effectiveness of actions to minimize both point and nonpoint sources of Hg to the atmosphere.

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