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Reactivity and Mobility of New and Old Mercury Deposition in a Boreal Forest Ecosystem during the First Year of the METAALICUS Study

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The METAALICUS (Mercury Experiment To Assess Atmospheric Loading In Canada and the US) project is a whole ecosystem experiment designed to study the activity, mobility, and availability of atmospherically deposited mercury. To investigate the dynamics of mercury newly deposited onto a terrestrial ecosystem, an enriched stable isotope of mercury (^{202}Hg) was sprayed onto a Boreal forest subcatchment in an experiment that allowed us, for the first time, to monitor the fate of "new" mercury in deposition and to distinguish it from native mercury historically stored in the ecosystem. Newly deposited mercury was more reactive than the native mercury with respect to volatilization and methylation pathways. Mobility through runoff was very low and strongly decreased with time because of a rapid equilibration with the large native pool of "bound" mercury. Over one season, only ∼8% of the added ^{202}Hg volatilized to the atmosphere and less than 1% appeared in runoff. Within a few months, approximately 66% of the applied ^{202}Hg remained associated with above ground vegetation, with the rest being incorporated into soils. The fraction of ^{202}Hg bound to vegetation was much higher than seen for native Hg (<5% vegetation), suggesting that atmospherically derived mercury enters the soil pool with a time delay, after plants senesce and decompose. The initial mobility of mercury received through small rain events or dry deposition decreased markedly in a relatively short time period, suggesting that mercury levels in terrestrial runoff may respond slowly to changes in mercury deposition rates.

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Introduction

The general consensus among mercury researchers is that the primary cause of high fish monomethylmercury (MeHg) concentrations in remote lakes is elevated atmospheric inputs of mercury to lakes and their watersheds (*1*). Mercury in atmospheric deposition is predominantly inorganic mercury (*2*), but the mercury in fish muscle is almost entirely organic MeHg. The transformation of inorganic mercury to MeHg is carried out by bacteria active in lake sediments, peatlands, and saturated upland soils (*3*). Mercury methylation occurring in the water column and by abiotic processes has been reported as well (*4*, *5*). "New" mercury enters lakes each year by direct deposition to their surface and in watershed runoff, but the relative importance of these continuous mercury sources, as compared to the larger pools of mercury already stored in soils and lake sediments for in-lake methylation, is unknown. Previous studies have shown that uplands soils are sinks for MeHg (*3*). In contrast, the same studies identified wetlands as being significant sources of MeHg to downstream water bodies. An understanding of the relative importance of current mercury deposition to terrestrial runoff into lakes and subsequently to fish, mercury accumulation is needed to establish a critical load of atmospheric mercury for aquatic ecosystems.

Scientists are uncertain about the effect of changing mercury emissions on fish mercury concentrations because we lack kinetic data that explains mercury movement from the atmosphere, through watershed and lake ecosystems, and into fish. Such information regarding mercury dynamics has been difficult to obtain because we have previously been unable to distinguish newly deposited mercury from "old" mercury stored in ecosystems over decades to centuries. The amount of stored mercury in watershed soils and sediments is far greater than new mercury delivered annually by atmospheric deposition (*6*, *7*). If the small amount of mercury deposited each year is much more mobile or bioavailable for methylation than the larger pool of stored mercury, then there may be a rapid decline in rates of MeHg bioaccumulation in fish if deposition of mercury is reduced (<10 yr). However, if all the mercury is equally mobile and eventually available for methylation, changes in current deposition rates will take a long time to have an effect on mercury levels in fish. Differentiation of new and old mercury available for methylation is crucial in predicting how quickly and how much fish mercury levels can be expected to respond to changing mercury deposition.

Previous studies typically determined the mass of mercury exported from a terrestrial watershed as compared to the mass that was deposited as wet and/or dry deposition (*8*−*13*). However, this type of data on its own does not reveal the dynamics of the system (i.e., no conclusions about the mobility of mercury from a current deposition event or annual time periods are possible). Often uplands were identified as sinks, but usually the fate of the deposited mercury could

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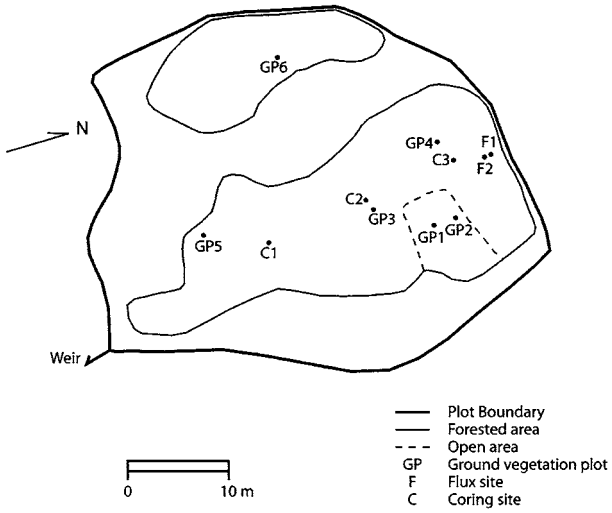

FIGURE 1. Map of the U1F microcatchment with sampling locations (provided by Jenny Graydon, University of Alberta, modified after ref *8*). See text for details.

not be monitored, and relative amounts of mercury that are annually stored and/or volatilized are still unknown.

To obtain more detailed information, isotopes of mercury have been used in two earlier ecosystematic experiments. One study **(*14*)** applied stable ^{199}Hg to a small forest area of 1 m^2. While they observed an initial fixation followed by a slow movement of the applied isotope into the soil, neither evasion nor runoff measurements were conducted. In another study, radioactive ^{203}Hg was added to a Canadian shield lake to study the partitioning of added metals (*15*). Because of the short half-life of ^{203}Hg (44 days) and the low specific activity of the commercial radiotracer, no long-term detailed investigation was possible. The experiment mainly revealed a fast partitioning of the added mercury to particles followed by sedimentation. Uptake of ^{203}Hg into fish was reported, but no evasion or methylation rate measurements were done. The study concentrated on the fate of the added tracers and did not attempt any comparison with the behavior of native mercury.

The METAALICUS study (*16*) was designed principally to investigate the relationship between changes in atmospheric mercury deposition and resulting mercury levels in fish. The experiment described in this paper examined the relative importance of newly deposited mercury by experimentally increasing the inorganic mercury loading to a well-characterized forested upland microcatchment at the Experimental Lakes Area, Ontario (*8*). Mercury was added as an enriched stable isotope, which allowed us to follow this new mercury over time and distinguish it from native mercury already in the ecosystem.

Experimental Section

Site Description and Application to the ^{202}Hg Isotope. The U1F microcatchment, shown in Figure 1, is a 680-m^2 plot in the uplands of the Lake 302 watershed at the Experimental Lakes Area (ELA), Ontario, Canada (*8*). It gently slopes in a north−south direction with little dams defining its boundary and channeling the surface runoff toward a small weir. Approximately 642 m^2 of the plot is densely forested with 50-year-old jack pine (*Pinus banksiana*) and black spruce (*Picea mariana*) trees. The forested area is split into two islands of 165 and 515 m^2. The remaining area is open, of which 7.7, 5.78, and 24.71 m^2 is covered primarily by lichen, moss, and a mixture of blueberry, moss, and lichen, respectively. The average soil depth is 10 cm (*8*). Inorganic mercury loading to this area was initially increased experimentally in the summer of 1999. On July 13, 1999, 7.7 mg of inorganic divalent ^{202}Hg (99.2% enriched) was applied evenly onto the ground vegetation of the microcatchment. In addition to the vegetated area, a small 33-m^2 strip of lichen/moss-covered bedrock connecting the two forested areas was sprayed as well. Prior to the application, 185 L of throughfall was collected under trees in another nearby microcatchment and stored in 10 carboys, containing 18.5 L each. The isotope stock solution was made up by dissolving 20 mg of mercury (as HgO) in 500 mL of dilute HCl. A total of 21 mL of this stock was added to each carboy, and the pH was adjusted to 5.0 by adding 40 mL of 0.675 M NaOH. The isotope solution was allowed to equilibrate with the throughfall water for at least 4 h prior to spraying. The area of the U1F subcatchment covered by vegetation was equally divided into to 45 subplots of approximately 15 m^2, which received exactly 4.1 L of the spike solution using 8-L garden sprayers. To account for potential losses of the mercury isotope to container surface during the application procedure, the ^{202}Hg levels were measured in the carboy and the spray container (39.8 ± 0.9 μg/L). This solution was sprayed directly onto the ground vegetation in the late afternoon to minimize exposure to direct sunlight, which may enhance volatilization of mercury. This application technique simulated a small rain event (0.27 mm precipitation) or dry deposition rather than a large precipitation event since the spraying itself did not create runoff from the catchment. The single application elevated the annual wet deposition of 7 μg of Hg m^{-2} in the open (*7*) by 10.9 μg of Hg m^{-2}. The dry deposition rate of mercury at the ELA is estimated to be between 1 and 10 μg m^{-2} yr^{-1} based on net throughfall (throughfall flux minus wet deposition), litterfall, and recent measurements of reactive gaseous mercury (RGM), which were very low (*7*). The total mercury load of U1F in 1999 was similar to mercury deposition normally received in many areas of the United States, including the Florida Everglades and some urban areas (*17*)**.** For the remainder of the year (until freeze-up), we monitored concentrations of the applied stable isotope and of native mercury in the atmosphere above the plot, in vegetation, in soil, and in surface runoff.

Sample Collection and Mercury Analysis. Native and isotopic elemental mercury concentrations and fluxes over soil and vegetation surfaces were measured using the ORNL polycarbonate dynamic flux chamber (FC) system (transparent, volume = 11 L, bottom surface area = 0.674 m^2) with an outlet on its top and inlets around its lower side (*18*). Elemental mercury concentrations were determined by sampling the FC inlet and outlet airstreams using gold-coated sand traps, which were then transported back to the laboratory for analysis by ICP/MS (*19*−*22*). The flushing flow rate used for the flux chamber in this study was 0.5−1 L min^{-1} provided by portable DC-powered pumps; all flushing and sampling flow rates were determined by portable mass-flow meters. The mercury emission fluxes were computed using the equation $F = (C_o - C_i)Q/A$, where F is the emission flux (ng m^{-2} h^{-1}); C_o and C_i are the 1-h of average mercury concentrations from the outlet and inlet, respectively (ng m^{-3}); Q is the overall rate of the flow that flushes the chamber (m^3 h^{-1}); and A is the soil surface area covered by the chamber (m^2) (*23*, *24*). The blanks of the flux chamber, tubing, and other devices used were found to be insignificant relative to all measured fluxes. Hence, the flux measurement results reported are not corrected for blanks. However, at some of the highest fluxes measured in this study (e.g., the isotope re-emission rates immediately after spike applications), the limited chamber flushing rates used require that these rates be considered as lower bounds to actual fluxes as described in ref *25*.

Surface runoff from the U1F subcatchment was directed to a weir built at the lowest point of the catchment, where

individual point samples were taken over time. The runoff was then directed to and collected in two large 1800-L polyethylene barrels, which were used to collect integrated runoff samples and to measure runoff volume. At the weir, water was sampled directly into 250-mL Teflon bottles. Every time the barrels filled to capacity or after each rain event creating runoff (whichever came first), the barrels were emptied by opening a valve at the bottom, and a 250-mL subsample was collected directly from the spout. Short residence times of the water in the barrels and high flushing rates prevented the potential sedimentation of particles. After draining the barrel, no sedimented particles were visible at the bottom of the barrel. All sampling was done using the clean hand/dirty hand protocol (*26*).

Soil cores were collected using a 4-cm (i.d.) acrylic plastic corer, sectioned every 3 cm in the laboratory and frozen for further analysis. In July, the top vegetation layer was not removed and therefore was analyzed as a composite sample together with the top 3 cm soil section. In October, the vegetation was carefully removed from the top soil layer, and the two compartments were analyzed individually.

In September, ground vegetation was sampled at six sites in both open and forested areas of the U1F microcatchment. Open areas vegetated with either lichen or a mixture of feather mosses (*Pleurozium* sp.), lichen, and blueberry (*Vaccinium* sp.) shrubs covered 7.4 and 30.5 m^2 of the microcatchment's ground area, respectively. The remaining ground area (642 m^2) was equally divided between the four major understory vegetation types (161 m^2 represented by each of plots with feather mosses only, feather mosses and blueberry shrubs, primarily blueberry shrubs, and primarily blueberry shrubs with some feather mosses). Ground vegetation in each of the six sites was collected within 625-cm^2 plots by carefully removing the upper layer of living plant material from the underlying soil layer using gloved hands. The aboveground portions of shrubs were collected using clean stainless steel hand-pruners. Lichens and mosses were peeled off the soil/rock. Material from plots was stored frozen in Ziploc bags until it was freeze-dried. The total dry weight of each plot was measured. Concentrations of mercury at each site were multiplied by areal biomass (g m^{-2}) to estimate the areal mass (μg m^{-2}) of mercury in the aboveground vegetation. To obtain a total mass of mercury on ground vegetation in the U1F microcatchment, the areal mass measured in the plots was multiplied by the estimated total area of the community in U1F.

Soil and vegetation samples were digested at 80 °C using a 7:3 (vol/vol) mixture of concentrated nitric and sulfuric acid. Total mercury content in the digests was determined by flow injection cold vapor ICP/MS using sodium borohydride as the reductant (*19*, *20*).

Total mercury in unfiltered water was measured after oxidation with BrCl. Subsequently, ionic mercury was reduced to elemental mercury by stannous chloride addition and purged with mercury free nitrogen onto gold traps, which were processed as described elsewhere (*19*−*22*).

Methylmercury in water, soils, and vegetation was isolated from the sample matrix by atmospheric pressure water vapor distillation. MeHg in the distillates was derivatized using sodium tetraethylborate and preconcentrated onto Tenax traps. Quantification was achieved after thermodesorption, isothermic GC separation, and detection by ICP/MS (*20*).

Limits of detection (LOD) for the ^{202}Hg isotope in the various samples are dependent on the concentration of native mercury in the respective sample. To detect the applied isotope, it must be present at a concentration ≥0.5−1% of the native mercury. The exact LOD varied with the precision of the isotope ratio measurement that was achieved during each run. Typical LODs for ^{202}Hg (total) were 0.05 ng/L in water, 0.01 ng/m^3 in air, and 0.2−1 ng/g in vegetation and soils, and for Me^{202}Hg they were 1 pg/L in water and 1−10 pg/g in soils.

TABLE 1. Concentrations of Native and ^{202}Hg in Air and Fluxes to the Atmosphere over Different Ground Vegetation Covers in the U1F Catchment[a]

			fluxes of mercury to atmosphere (ng m^{-2} h^{-1})			
	mercury in air (ng/m^3)		over feather mosses		over blueberry bushes and feather mosses	
date, time	native Hg	^{202}Hg	native Hg	^{202}Hg	native Hg	^{202}Hg
7/13, 18:15	2.0	5.2	2.6	3.5	5.1	6.9
7/13, 18:45	1.7	1.4	1.6	2.2	2.5	2.8
9/11, 12:00	1.4	0.10	0.25	0.27	2.1	1.1
10/6, 14:30	1.4	0.09	0.14	0.12	0.58	<0.10
10/6, 15:00	1.3	0.01	<0.10	<0.10	0.80	<0.10

[a] 10.9 μg/m^2 of ^{202}Hg were added at 17:45 on July 13, 1999.

Results and Discussion

Inputs of Isotopic and Native Mercury during the Study Period. To avoid confusion regarding naming of various mercury pools, this paper refers to the added spike as new mercury or ^{202}Hg. The old mercury is termed native mercury, which can be either of geogenic and anthropogenic origin. This paper did not attempt to distinguish between these two sources of old mercury. A total of 7.7 mg of mercury (99.2% enriched with ^{202}Hg) was manually sprayed onto the ground vegetation and soils in the U1F subcatchment. The application procedure resulted in a small wet precipitation event resembling a light drizzle, which is typical for the majority of precipitation events at the ELA (*27*). This compares to approximately 3.2 mg of mercury that was naturally deposited onto the 642-m^2 forested area of the catchment in throughfall and 2.1 mg of mercury that fell onto the 458 m^2 of open area in open precipitation during the study period (totaling 5.3 mg of mercury). The native mercury deposition load was estimated from volume-weighted concentrations of total mercury measured in five throughfall (28.4 ± 11.8 ng L^{-1}) and open precipitation (14.5 ± 5.0 ng L^{-1}) samples collected at the ELA meteorological station between June 23 and September 26, 1999 (*5*). During the study period, 317.5 mm of precipitation was measured at the meteorological station, of which only 55.4 ± 2.4% was shown to make it through the canopy as throughfall (*7*). We estimate that dry deposition contributed an additional 0.3−3 mg of Hg during this time, most of which probably remained in the canopy until litterfall. Both the amount of mercury in the isotope application and the native mercury in deposition were orders of magnitude smaller than the amount of mercury already present in the soils of the catchment (see below for details of these measurements).

Mercury Flux to the Atmosphere. Fluxes of mercury to the atmosphere were measured immediately after the application on July 13 and again in September and October. Measurements took place at shaded areas below black spruce stands over feather mosses and over blueberry shrubs/feather mosses. Mean air temperatures during these measurements decreased from 23.1 to 10.6 to 4.2 °C (July, September, October) over the summer.

While concentrations of native mercury in air decreased by about 35% from July to October, the isotopic mercury concentrations decreased to a much greater degree, by a factor of least 100 during the same period (Table 1). The highest fluxes of both isotopic and native mercury occurred in mid-summer immediately after isotope application. The

emission of ^{202}Hg was as high as 7 ng m^{-2} h^{-1} over blueberry bushes and 4 ng m^{-2} h^{-1} over moss-covered soils and over the summer averaged 3.6 ± 3.0 and 2.0 ± 1.6 ng m^{-2} h^{-1}, respectively. Native mercury fluxes averaged 3.2 ± 1.6 and 1.5 ± 1.2 ng m^{-2} h^{-1} for these same surfaces over the summer and decreased from July to October, as expected on the basis of typical seasonal flux behavior (*28*). Isotopic ^{202}Hg emission rates decreased 40−60% within 30 min after application, and by September, soil fluxes of ^{202}Hg had declined further with fluxes over shrubs decreasing less than those over moss. In October, ^{202}Hg levels in air (≤0.1 ng m^{-3}) and daytime emission fluxes of ^{202}Hg (≤0.1 ng m^{-2} h^{-1}) were near the detection limit, as was the background flux of native mercury. A year after the initial spike (in June 2000), the isotope fluxes remained below detection. In comparison to other regions, the mean daytime native mercury fluxes over these surfaces were near the very low rates (1−3 ng m^{-2} h^{-1}) reported for other northern ecosystems and lower than those in warmer climates (*24*). Generally, both mean ^{202}Hg and native mercury fluxes over low plants were greater than fluxes from moss-covered soil (Table 1).

Total seasonal fluxes to the atmosphere were estimated by integrating under the best-fit regression curves of the time-series emission rate data collected over the growing season (using the mean daytime flux for each measurement period). The best-fit regression equations were as follows for ^{202}Hg and native mercury, respectively: $Y = 4e - 0.04$ ($r^2 = 0.94$) and $Y = -0.03x + 8$ ($r^2 = 0.97$). We estimate the uncertainty level in these integrations to be on the order of ±50% on the basis of replicate runs and regression statistics.

Since all data were collected around midday, scaling the integrated fluxes to estimate the seasonal emission required an adjustment for diel flux cycles typically observed at other locations where background fluxes approach zero at night (*29*, *30*). We estimate that 8% of the ^{202}Hg addition was lost to the atmosphere during the summer by volatilization (0.7 mg). In comparison, 1.1 mg of native mercury was emitted during the same time period. The corresponding fraction of volatilized native mercury strongly depends on the pool that is assumed available for evasion. The observed diel flux pattern suggests that sunlight-exposed mercury is the relevant pool. For the U1F catchment, this would mostly include mercury bound to vegetation, and the amount volatilized was approximately 1.5% of the size of this pool. However, if one considers the native mercury present in the upper 1 cm of soils as also being available for evasion processes, only 0.4% of the relevant mercury was emitted (based on an average native mercury concentration of 144 ± 30 ng g^{-1} and an average soil density of 0.14 g cm^{-3}). The choice of soil depths that contributes to the emission of native mercury is highly arbitrary. We chose to select the uppermost centimeters, since re-emission is believed to occur primarily from this pool (*19*). If one assumes that all of the old mercury is potentially available for mobilization, then the volatilized fraction would be minute (<0.1%).

Over the summer, we estimate that the isotope represented 40% of the total mercury emitted to the atmosphere from this subcatchment, not surprising given the magnitude of the spike. However, the time course of isotope volatilization, as compared to native mercury volatilized, suggests strongly that newly deposited ^{202}Hg was generally more available for reduction and volatilization than the old native mercury stored on vegetation or in the upper soil pool if the mercury in this pool is available for reduction/evasion. This reactivity rapidly decreased as the deposited ^{202}Hg became bound to soil and plant organic matter over the course of time.

Mercury in Soils and Vegetation. The amount of mercury stored in soils is estimated to be 1140 ± 210 mg. This native mercury pool size was calculated from mercury levels measured in soil cores. Figure 2 illustrates the variation of native mercury concentration typically observed in replicate cores at three sites in the U1F plot. The three locations shown represent a north−south gradient across the long axis of the larger forest area within the subcatchment (Figure 1). Mean mercury concentrations in different layers (typically 3-cm segments) were multiplied with the plot area and the average density of the soil (0.14 g cm^{-3}; *8*).

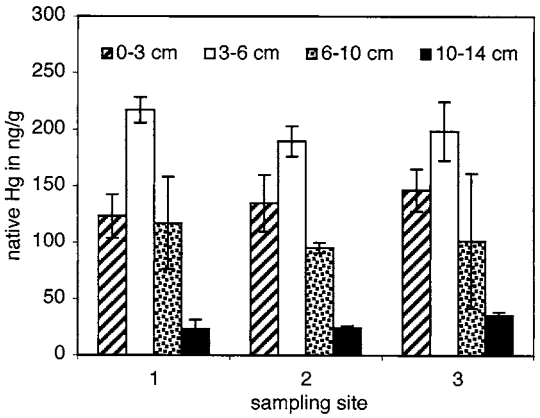

FIGURE 2. Average concentrations of native mercury in U1F soils measured 24 h after application of ^{202}Hg (July 14, 1999). Results from duplicate cores in a north−south transect are shown with error bars representing the range of concentrations measured at each site.

The amount of ^{202}Hg in the top soil and vegetation layer was measured 24 and 48 h after the isotope application and again at the end of the study period. By 48 h after application, the added isotope was easily detectable in the surface layer (0−3 cm; soil including the top vegetation layer), showing an average concentration of 5.5 ± 3.8 ng/g (dw, $n = 8$).

The vegetation was not sampled separately at first to minimize disturbance of the plot, which might have affected runoff from the catchment. In mid-September, 2 months after the initial loadings, aboveground vegetation (excluding trees) collected and analyzed from six 625-cm^2 plots distributed throughout open and understory areas of the microcatchment suggests that approximately 4.4 mg of ^{202}Hg was still stored in this vegetation layer (Table 2). The largest quantities of ^{202}Hg were found on feather mosses under the forest canopy but also on lichens in the open (Table 2). Lichens have been shown to scavenge and retain atmospheric mercury (*31*). In October, the concentration of applied isotope in the top 3 cm (soil only, excluding any vegetation) was 0.69 ± 0.10 ng/g (dw, $n = 3$) representing 2.0 ± 0.3 mg of ^{202}Hg, and the isotope spike had migrated as deep as 10 cm into the soil. However, individual concentrations of ^{202}Hg (0.2−1.4 ng/g) measured at depths between 3 and 14 cm were close to the limit of detection, and it was not possible to accurately quantify the amount of ^{202}Hg that moved into deeper soil layers. Since more than 50% of the added ^{202}Hg remained on the vegetation, this compartment was an important factor in the mass balance of newly deposited mercury (Table 3), whereas the soil pool dominated the mass balance for old mercury (>90%).

The methylation of the newly added mercury was expected to be highest immediately after application before the isotope became bound to soil and plant matrixes. However, unsaturated forest soils typically have a low potential for mercury methylation because they lack anaerobic sites suitable for sulfate reduction. No $Me^{202}Hg$ was detected in soils during the initial 48 h after application, probably because methylation activity was very low in the dry soils. However, three cores taken at the end of the season in October had $Me^{202}Hg$ (0.01−0.03 ng g^{-1}) uniformly distributed throughout them.

TABLE 2. ^{202}Hg and Native Mercury on Ground Vegetation (Excluding Trees) in the U1F Catchment on September 12, 1999[a]

plot community	area (m^2)	biomass (kg)	^{202}Hg (ng/g)	^{202}Hg ($\mu g/m^2$)	^{202}Hg (mg)	ambient Hg (ng/g)	ambient Hg (mg)
Plots in Open							
lichen	7.4	14	3.90	7.2	0.05	46.7	0.6
mixture of feather mosses, lichen, and blueberry shrubs	30.5	51	1.73	2.9	0.09	61.8	3.1
Plots in Understory							
feather mosses	161	167	7.60	7.9	1.3	79.7	13
feather mosses with some blueberry shrubs	161	181	8.60	9.7	1.6	106.8	19
primarily feather mosses	161	188	3.00	3.5	0.56	63.1	12
primarily blueberry shrubs with some feather mosses	161	291	3.01	5.6	0.90	85.4	24
totals	680	890			4.4		73

[a] Approximately 10.9 μg/m^2 was loaded onto the vegetation on July 13, 1999.

TABLE 3. Mass Balance of Native Mercury and Added ^{202}Hg for 1999 in the U1F Catchment[a]

	native mercury (% of Hg in U1F)	^{202}Hg isotope (% of applied)
stored in vegetation	5−9	48−80
stored in soils	91−95	7−48[b]
evasion	0.1−0.2	4−13
runoff	0.1−0.2	0.1−0.5

[a] Input/output data are cumulative from July 13 to October 26. The % pools of ^{202}Hg are based on the 7.7 mg of ^{202}Hg isotope added on July 13. [b] ^{202}Hg soil pools are calculated by difference: total ^{202}Hg experimentally applied minus measured pools and fluxes.

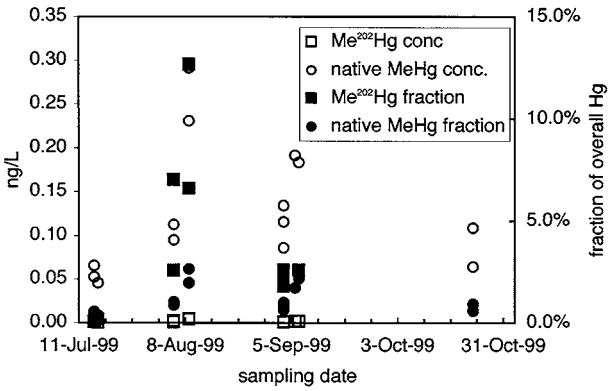

FIGURE 3. Seasonal variation of methylmercury concentrations and fractions of mercury that is in methylated form in runoff.

This indicates that methylation of ^{202}Hg had taken place during the season, probably during periods of soil saturation. However, these limited data did not allow us to identify the location of methylation or the time at which methylation took place.

One of the most important questions of this experiment is whether the newly deposited mercury would be more available for methylation than the older stored mercury. In the top 3 cm of the forest soil, the newly added mercury appeared to be better available for methylation than was native mercury, as only about 0.4 ± 0.2% of the total native mercury in soils was methylated, whereas 1.5 ± 0.3% of the applied ^{202}Hg was present as methylmercury. Methylmercury concentrations in runoff are shown in Figure 3. Me^{202}Hg was sporadically observed in catchment runoff during August (1.3−4.5 pg L^{-1}) only. Native MeHg levels did also peak during

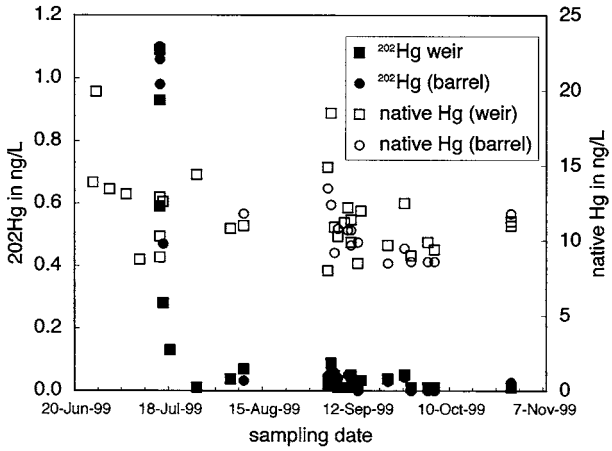

FIGURE 4. Concentrations of native mercury and ^{202}Hg in unfiltered runoff from the U1F catchment, which was channeled through and collected at an ungauged weir and in large polyethylene barrels.

August and September. The fraction of ^{202}Hg present as Me^{202}Hg in August was significantly greater than the fraction of the native mercury present as native MeHg. These observations could suggest that the new ^{202}Hg is more available for methylation reactions than the native mercury during peak times of MeHg production in uplands. However, because of limited data for Me^{202}Hg in soil and runoff, this preliminary hypothesis needs further testing. Additionally, the relationship between net methylation and resulting levels of MeHg in runoff and soil is currently unknown and complicates the interpretation of the MeHg data.

Mercury in Runoff. A major precipitation event started 2 days after isotope application. Levels of ^{202}Hg in initial surface runoff were as high as 1.42 ng L^{-1} (Figure 4) and represented >10% of the total mercury concentration at this time. This finding alone may not be too surprising considering that the upland plot was dosed with a large quantity of ^{202}Hg during a short period of time. However, levels of ^{202}Hg in runoff decreased exponentially during the initial rainstorm and remained at constant low concentrattions of approximately 0.05 ng L^{-1} for the remainder of the season (Figure 4). This demonstrates a drastic change in the mobility of the applied mercury, which was not mirrored by the mobility of native mercury. Concentrations of native mercury (volume-weighted average: 10.44 ng L^{-1}) did not vary significantly from July to October and were not different from prespike concentrations in runoff. Initially, concentrations

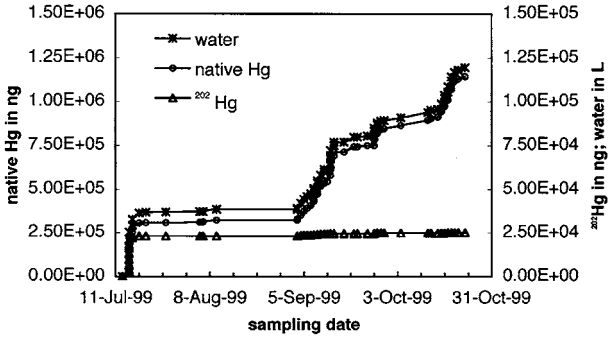

FIGURE 5. Water discharge and cumulative export of native and ^{202}Hg from July to October. Mass export of mercury from the catchment was calculated by multiplying runoff volume with concentrations over time.

of native mercury in the barrels were elevated as compared to the concentrations measured at the weir (19.5 ± 5.9 and 11.2 ± 1.9 ng L^{-1}, respectively). However, because of the rigorous flushing associated with the initial runoff, the native mercury concentrations in the barrels were indistinguishable from the weir levels 3 days later as shown in Figure 4. At the end of the season, the last composite water sample in the barrel (360 L) was acidified with 300 mL of concentrated hydrochloric acid, lowering the pH from the original pH of 4.5 to pH 2 after acidification. This procedure leached small amounts of additional ^{202}Hg and native mercury, which were insignificant for the overall mass balance. Upon acidification, the mercury concentrations in the barrel increased by 0.061 ± 0.013 ng L^{-1} of ^{202}Hg and 2.3 ± 0.76 ng L^{-1} of native mercury. This additional 22.0 ± 4.7 ng of ^{202}Hg and 830 ± 270 ng of native mercury constituted less than 0.1% of the overall seasonal export for both pools.

Runoff was also analyzed for bioavailable mercury using the *mer−lux* bioreporter *Vibrio anguillarum* pRB28 (*32*−*34*) as the fraction of divalent inorganic mercury that is able to enter bacterial cells. The bioreporter response to available mercury in post-addition U1F runoff was not significantly different from values obtained from other nonexperimental catchments at the ELA (*32*). Thus, the increased mercury load onto the catchment did not result in an elevated concentration of bioavailable mercury, which was not surprising since the total mercury concentration in runoff leaving the catchment was only increased at most by about 10% just following the application and insignificantly later. Although the bioreporter cannot distinguish between native mercury and added isotopes, the results suggest that the newly deposited mercury did not immediately increase the exported amounts of bioavailable mercury to downstream lakes.

The observation of initially higher mobility of recently deposited mercury in runoff suggested a higher degree of mobility of atmospheric mercury immediately following a small rain event or dry deposition, but only briefly. The pattern of cumulative native mercury export mirrored the pattern of cumulative water discharge (Figure 5). During the study period, 1.2 mg of native mercury was exported from U1F via runoff, representing only 0.1% of the native mercury stored in the catchment. The cumulative export of ^{202}Hg, however, paralleled the water discharge only during the first rain event after application and then declined substantially. Only a very small fraction of the deposited new mercury (0.25%) was initially exported via runoff. This small mobile fraction probably constitutes mercury bound to dissolved organic matter or particles that are easily flushed out during rain events. The overwhelming fraction of the applied mercury was immobile and remained in plant and, to a lesser extent, soil pools within the catchment. Over the whole season, the total export of ^{202}Hg (0.03 mg) in runoff represented only 0.3% of that applied (Table 3). The added tracer quickly equilibrated with the native mercury in the soil, indicated by the fraction of mercury that was present in the form of ^{202}Hg in soil and runoff. In the top 3 cm, ^{202}Hg constituted 0.5 ± 0.1% of the total mercury present (average ratio of measured concentrations for the ^{202}Hg tracer and total native mercury, measured in October). However, this fraction could be as small as 0.2%, on the basis of the estimated amount of ^{202}Hg that is stored in U1F soils and assuming that the added isotope is homogeneously distributed with depth. This range is similar to the fraction of ^{202}Hg measured in the runoff, which was on average 0.5% from August to October (ranging from <0.2% to 0.8%).

Mass Balance for ^{202}Hg and Native Hg in the U1F Catchment. A comparison of the fluxes of native mercury and ^{202}Hg are presented in Figure 6. The most accurately

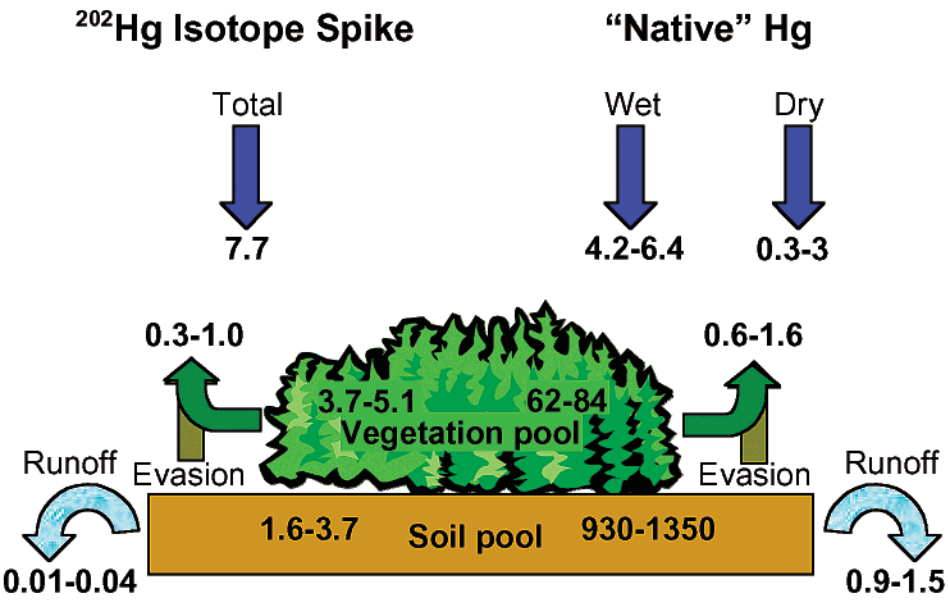

FIGURE 6. Schematic diagram of the estimated mass fluxes and pools for native (old) and ^{202}Hg (new) mercury in the experimental U1F catchment at ELA (area = 680 m^{-2}). All values are in mg; fluxes represent values scaled to the 15-week period from July 13 to October 26, 1999. Ranges are intended to represent levels of uncertainty (see text for description of the vegetation and soil pools).

known numbers in the mass balance budget of ^{202}Hg were the amount added (measured directly) and the amount in runoff (measured directly and continuously). Evasion, vegetation, and soil measurements were less frequent and are more uncertain. However, the picture that emerges is that a small but significant fraction volatilized, while most of the new mercury attached tightly to vegetation and a lesser amount to underlying soils. This suggests that a large fraction of newly deposited mercury is not immediately mobile.

The native mercury in bulk deposition during the summer and fall of 1999 was very small as compared to the amount of native mercury stored in U1F vegetation and soils (Figure 6). However, the amount of native mercury in evasion and runoff together equaled approximately two-thirds of the deposition input (Figure 6) and, in the absence of other information, might be assumed to have been derived from the deposition. Taken together with the isotope data, however, it is more likely that these processes derive in part from current deposition (especially evasion) but benefit to a greater degree from mercury stored in soils.

Some of our interpretations strongly depend on the definition of new and old mercury and the time involved, after which new mercury changes into old mercury. There is reason to determine the time scale after which the applied mercury becomes indistinguishable from the mercury already present in the ecosystem based on the observed physicochemical behavior. The results of this study suggest that mercury deposited onto forest vegetation via dry deposition or small precipitation events that created no immediate runoff attaches to plant and soil surfaces and equilibrates fairly quickly with the pools of native mercury already present in the system. The newly applied mercury is indifferent from old mercury within days or weeks rather than months or years, suggesting that upland runoff may respond very slowly to changes in deposition. In fact, mercury bound to vegetation may only become incorporated into the larger soil pool of mercury when the vegetation dies and decomposes (*6*, *7*).

This conclusion is so far limited to terrestrial upland systems such as U1F. Further METAALCUS studies are underway investigating similar processes in wetlands and aquatic (lake) systems, keeping in mind that lakes receive mercury via direct atmospheric deposition as well as runoff. It is also possible that, under conditions of heavy rain events, mercury may show a higher degree of mobility and appear in runoff before the deposited mercury is bound to soils and vegetation, while less loss may occur via volatilization from soil and ground (and canopy) vegetation once the deposited mercury penetrates the surface layer and moves through the system. Thus, the overall contributions of old versus new mercury to mercury in runoff and the overall response time of watersheds to changes in atmospheric mercury deposition will most likely depend on the balance of wet and dry deposition as well as the fraction of rain events that are large enough to cause significant immediate runoff of newly deposited mercury.

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