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Application of ultrafiltration and stable isotopic amendments to field studies of mercury partitioning to filterable carbon in lake water and overland runoff[☆]

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Abstract

Results from pilot studies on colloidal phase transport of newly deposited mercury in lake water and overland runoff demonstrate that the combination of ultrafiltration, and stable isotope amendment techniques is a viable tool for the study of mercury partitioning to filterable carbon. Ultrafiltration mass balance calculations were generally excellent, averaging 97.3, 96.1 and 99.8% for dissolved organic carbon (DOC), total mercury (Hg_T), and methylmercury (MeHg), respectively. Sub nanogram per liter quantities of isotope were measurable, and the observed phase distribution from replicate ultrafiltration separations on lake water agreed within 20%. We believe the data presented here are the first published colloidal phase mercury data on lake water and overland runoff from uncontaminated sites. Initial results from pilot-scale lake amendment experiments indicate that the choice of matrix used to dissolve the isotope did not affect the initial phase distribution of the added mercury in the lake. In addition there was anecdotal evidence that native MeHg was either recently produced in the system, or at a minimum, that this 'old' MeHg partitions to the same subset of DOC that binds the amended mercury. Initial results from pilot-scale overland runoff experiments indicate that less than 20% of newly deposited mercury was transported in the filterable fraction ($<0.7 \mu m$). There is some indication of colloidal phase enrichment of mercury in runoff compared to the phase distribution of organic carbon, but the mechanism of this enrichment is unclear. The phase distribution of newly deposited mercury can differ from that of organic carbon and native mercury, suggesting that the quality of the carbon (available ligands), not the quantity of carbon, regulates partitioning. Further characterization of DOC is needed to clarify the underlying mechanisms.

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1. Introduction

In response to considerable evidence that atmospheric transport, deposition, and reemission of mercury are key processes in the movement of this neurotoxin throughout the globe, scientists are studying the fate of newly deposited mercury on a watershed in northwest Ontario, Canada (Hintelmann et al., 2002; Harris et al., 2001; Renner, 2001; Rouhi, 2001). In the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS), scientists will be able to differentiate between the newly deposited mercury and standing pool of mercury using stable isotope amendments. These isotopic techniques will provide the first direct evidence of a watershed response to changing atmospheric inputs of mercury and will inform pending controls on mercury emissions that may exceed several billion dollars to implement (USEPA, 1998).

One of the major goals of the METAALICUS project is to determine the mobility of this 'new' mercury through the watershed, and assess the recovery time for an ecosystem should new industrial emissions of Hg be ceased. One of the key transport vectors for mercury in overland runoff, and within lakes, may be the colloidal phase (roughly 0.7 μm –10 kilo Daltons (kDa)). Recent studies have shown that the colloidal phase can be a large component of the <0.4 μm filtered phase mercury concentration, and that organic carbon plays an important role in mercury phase partitioning in freshwaters (Cai et al., 1999; Babiarz et al., 2001). Combining stable isotopic amendments with ultrafiltration presents new analytical challenges. Before full-scale implementation of the larger experiment, it is important to verify the integrity of data produced by novel techniques so that experimental hypotheses developed from the data are valid.

In this paper we present the first data on colloidal phase partitioning of both native mercury and newly deposited stable isotopes of mercury in lake water and overland runoff. In particular we assess the colloidal phase partitioning of native mercury in lake water and runoff, and we compare the phase distribution results for isotopic mercury from different amendment application methods.

These pilot-scale experiments demonstrate the effectiveness of combining ultrafiltration with stable isotope techniques to study colloidal phase transport of mercury. In addition, the data presented informs several hypotheses on factors controlling colloidal phase partitioning of newly deposited mercury that can be tested in future work.

2. Methods

The work presented here is part of the whole-ecosystem METAALICUS Project, currently underway within the Experimental Lakes Area of the Canadian Boreal Forest in northwestern Ontario.

To evaluate the effectiveness of tangential-flow ultrafiltration, we applied the technique to subsamples from larger pilot-scale experiments designed to determine the most appropriate method for introducing stable isotopic amendments to various watershed compartments. A full discussion of the numerous factors that influence a full-scale, non-invasive, timely, and executable amendment is beyond the scope of this paper. In general, the project goals were to select variables (target spike concentration, final lake concentrations, delivery mechanism, delivery time, and delivery matrix) such that defensible scientific method and practical field operations could both be maintained (Harris et al., 2001).

Salient details of the two ultrafiltration-specific experiments are outlined below. The first examines the effect of the spike solution matrix on the initial partitioning of the spike in the epilimnion of the lake. The second experiment examines the relative colloidal phase mobility of the spike in overland runoff after wet and dry application of the spike to the watershed.

2.1. Does the delivery solution affect the partitioning of the amendment in surface waters?

The complexation of Hg in natural deposition, or in an ecosystem spike, may affect the ligand reactivity, reduction, evasion, and methylation of Hg. However, for the full-scale application of the amendment to the lake and its watershed, it would be impractical to collect a sufficient quantity of

fresh precipitation to mimic a rain event. Even if it were practical, the number of binding sites on ligands in natural rainwater would likely be saturated by the concentration of mercury (2.5 mg l^{-1}) required for delivery of the amendment in a reasonable quantity of water and time. Further, in order to keep the spike in solution, and resistant to photo reduction during the lengthy delivery process, some quantity of ligand to stabilize the spike was desirable. Logical alternatives to rainwater included equilibrating the spike in large volumes of lake water or an artificial matrix containing a strong mercury-binding ligand similar to that in rain. The specific concern to be tested with ultrafiltration was whether the quantity and chemical quality of the ligands dissolved in the delivery solution would affect the initial partitioning of mercury in the lake.

To test the leading matrix candidates, three 5-l Teflon bottles were filled with unfiltered surface water from Lake 658. Each bottle was spiked to bring the concentration of $^{201}\text{HgCl}_2$ in the bottle to $\sim 1.3 \text{ ng l}^{-1}$ (the concentration expected from a single application of the full-scale spike mixed into a 2 m depth of the lake). One bottle was spiked using a $130 \text{ } \mu\text{g l}^{-1}$ solution of $^{201}\text{HgCl}_2$ in a 6.5 mM solution of thiolglycolate at pH 3.5 (L658-RSH). Two bottles were spiked using a $130 \text{ } \mu\text{g l}^{-1}$ solution of $^{201}\text{HgCl}_2$ dissolved in unfiltered lake water at a pH of 3.3. One of the latter bottles was processed immediately (L658-T0) and the other was kept at near ambient conditions (capped, dark, and refrigerated) for 3 days before processing to assess equilibration effects (L658-T3). Our hypothesis is that the kinetics of re-equilibration of Hg with ligands in lake water depends on the complexation of Hg in the spike (or in natural deposition), and that re-equilibration may be slow enough that the reduction and partitioning of Hg originating from the spike could differ from that originating in natural deposition.

Although the full-scale experiment will not include MeHg as an amendment, the spiking solutions described above also contained enough MeHg to raise the ^{199}Hg concentration to $\sim 0.3 \text{ ng l}^{-1}$. This MeHg amendment was primarily introduced to assess reduction and evasion in

another component of the larger pilot-scale experiment.

2.2. Does the delivery method affect colloidal phase mobility of isotope in overland runoff?

Two application methods were used to deliver $^{201}\text{HgCl}_2$ on separate upland test patches. The upland sites, contained bedrock outcroppings, thin soils, shrub mosses, and low-lying mixed vascular plants. In one application, the isotope was diluted to 4.1 ng l^{-1} in 1400 l of lake water in a large polyethylene tank, equilibrated, and sprayed onto a small (120 m^2) plot through a sprinkler system delivering water at a rate of 14 mm h^{-1} , equivalent to a typical rainstorm in the region. A composite sample of runoff was collected by integrating small subsamples of water over the full time-course of the experiment ($\sim 30 \text{ min}$). The runoff was collected into a 5-l bottle from the outlet of an acid-cleaned acrylic weir. In the second application, $25 \text{ } \mu\text{g m}^{-2}$ of isotope was sprayed in a fine mist that evaporated shortly after contact with the ground. Runoff from a rainstorm that occurred the following day was diverted through a series of acid-cleaned acrylic weirs into a 300-l polyethylene storage tank, and the 5-l subsample used for ultrafiltration was collected from the same tank.

2.3. Field and analytical procedures

Whole-water samples were filtered in-line using pre-ashed quartz fiber filters rated at a $0.7 \text{ } \mu\text{m}$ pore size (Whatman QMA). Conventional filtrates were further processed using a 10 kDa ($\approx 0.0015 \text{ } \mu\text{m}$) ultrafiltration membrane to isolate the colloidal and dissolved phases. All ultrafiltration separations were conducted in a clean room and fully mass balanced as described by Babiarz et al. (2000) and Hoffmann et al. (2000) and Babiarz et al. (2001). Unless otherwise noted ultrafiltration separations were performed within 2 h of sample collection using 0.23 m^2 spiral-wound regenerated cellulose membranes (Millipore model PLGC). All sample containers, tubing and pump heads were composed of Teflon[®]. An exhaustive, multiple step cleaning process was employed to prepare the

cartridges for trace-metal applications (Babiarz et al., 2000; Hoffmann et al., 2000).

During an ultrafiltration separation, the membrane-passing fraction (permeate) was collected at a rate of $\sim 200 \text{ ml min}^{-1}$. The non-passing fraction (retentate) was recirculated at $\sim 1100 \text{ ml min}^{-1}$ until the ratio of the retentate volume to the feed volume (concentration factor) was approximately 3:1. The concentration factor was kept low to avoid changes in equilibrium metal partitioning to organic carbon. A mass balance was conducted with each separation as part of the QA/QC protocol. Mass balance closure was calculated from the following fractions: (1) the feed solution, (2) the pre-conditioning solution (sampled after the pre-conditioning step was completed), (3) the final retentate, (4) several permeate subsamples, (5) a post-separation Milli-Q flush, and (6) a dilute sodium hydroxide rinse (0.1 N).

Mercury mass balance results were generally excellent, averaging 97.3% (S.D.=9.4) for dissolved organic carbon (DOC), 96.1% (S.D.=18.4) for Hg_T , and 99.8% (S.D.=9.2) for MeHg (Table 1). These error terms are comparable to our laboratory analytical protocols that require the reanalysis of individual samples until the relative standard deviation is within 10% and spike recoveries are within 25%.

Total mercury concentrations were determined using the bromine monochloride oxidation technique followed by stannous chloride reduction, nitrogen purging, gold-trap pre-concentration, thermal desorption and cold-vapor atomic fluorescence spectroscopy (CVAFS) detection (Gill and Fitzgerald, 1987; Liang and Bloom, 1993; Babiarz et al., 1998). MeHg was determined by distillation, aqueous phase ethylation, nitrogen purging, Carbotrap[®] pre-concentration, thermal desorption, chromatographic separation, pyrolytic conversion to Hg^0 , and CVAFS detection (Bloom 1989; Liang et al., 1994; Babiarz et al., 1998). Analytical detection limits (three times the S.D. of the blank) average $0.1 \text{ ng l}^{-1} \text{ Hg}_T$ and $0.05 \text{ ng l}^{-1} \text{ MeHg}$.

Isotopic Mercury analysis was determined using a Perkin-Elmer Elan 6100 that was dedicated for mercury-only analysis and was housed in a state-of-the-art mercury analytical facility operated by

Dr. David Krabbenhoft at the USGS in Middleton, Wisconsin. This ICP-MS was fitted with a continuous flow injector analyzer system, and an inline gold amalgamation system that allows for rapid sample throughput and low-level detection. The method, modeled after the pioneering work of Hintelmann et al. (1995) and Hintelmann and Evans (1997), had an absolute detection limit of approximately 1 pg Hg , or approximately 0.05 ng l^{-1} . The minimum detectable amount of MeHg was also 1 pg .

The ICP-MS was calibrated using native Hg stock solutions diluted from a primary standard. A calibration curve was determined for the following isotopes: ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , and ^{202}Hg . For a given sample, native Hg concentrations were determined by averaging the value calculated for each isotope that was not enriched (^{198}Hg , ^{200}Hg , ^{202}Hg). Isotopic (spiked) Hg concentrations were determined as the difference between the value calculated for that isotope (^{199}Hg or ^{201}Hg) and the averaged native concentration, multiplied by the natural abundance of the isotope in question.

DOC samples were collected in pre-ashed glass bottles, and stored dark in a cold room. DOC concentrations were determined on a Shimadzu TOC-5000 using high temperature ($680 \text{ }^\circ\text{C}$) catalytic oxidation. Analytical uncertainty is typically $\pm 0.1 \text{ mg l}^{-1}$.

3. Results and discussion

Results from our pilot-scale experiments using tangential-flow ultrafiltration to probe the affects of differing spike application methods on the partitioning of the added mercury are shown in Table 1. Beyond the immediate demonstration that the techniques are viable, it is too early to draw definitive conclusions regarding the biogeochemistry of newly deposited mercury. However, the data point to several key questions that will guide future research in the METAALICUS project.

3.1. Lake additions

The three L658 spiked waters averaged $2.4 \text{ (S.D.=0.5) ng l}^{-1}$ native Hg_T unfiltered, and $0.6 \text{ (S.D.=0.2) ng l}^{-1}$ isotopic Hg_T unfiltered. A post-

Table 1
Organic carbon, total mercury, and methylmercury as a percentage of the filtered value

	Organic carbon				Total mercury				Methylmercury										
	Filtered <0.7 μm (mg l^{-1})	UF mass Balance (%)	Colloidal		Dissolved		Filtered <0.7 μm (ng l^{-1})	UF mass Balance (%)	Colloidal		Dissolved		Filtered <0.7 μm (ng l^{-1})	UF mass Balance (%)	Colloidal		Dissolved		
			0.7 μm –10 kDa (mg l^{-1})	(%)	<10 kDa (mg l^{-1})	(%)			0.7 μm –10 kDa (ng l^{-1})	(%)	<10 kDa (ng l^{-1})	(%)			0.7 μm –10 kDa (ng l^{-1})	(%)	<10 kDa (ng l^{-1})	(%)	
<i>Cascade</i>																			
Native	8.0	102.2	3.1	38.5	5.1	63.7	7.7	73.2	2.7	35.0	2.9	38.2	0.47	91.3	0.20	43.6	0.22	47.7	
Amended	^b	^b	^b	^b	^b	^b	0.8	79.2	0.5	57.3	0.2	21.9	^a	^a	^a	^a	^a	^a	
<i>UIF</i>																			
Native	7.1	80.7	2.1	30.0	3.6	50.7	21.4	110.1	12.0	56.1	11.6	54.0	0.10	121.4	0.03	32.1	0.09	89.3	
Amended	^b	^b	^b	^b	^b	^b	0.11	74.2	0.0	36.1	0.0	38.1	^a	^a	^a	^a	^a	^a	
<i>L658 T0</i>																			
Native	9.1	100.8	5.8	63.3	3.4	37.5	2.6	126.4	1.7	66.3	1.6	60.0	0.20	96.1	0.12	58.5	0.08	37.6	
Amended	^b	^b	^b	^b	^b	^b	0.75	96.3	0.6	74.5	0.2	21.8	0.51	99.5	0.35	68.6	0.16	30.9	
<i>L658 T3</i>																			
Native	8.7	103.3	4.7	53.8	4.3	49.4	2.0	102.0	1.0	47.6	1.1	54.3	0.12	97.6	0.08	66.9	0.04	30.8	
Amended	^b	^b	^b	^b	^b	^b	0.4	88.6	0.2	62.4	0.1	26.2	0.31	93.7	0.20	64.0	0.09	29.8	
<i>L658 RSH</i>																			
Native	9.0	99.5	5.4	59.7	3.6	39.8	1.8	119.2	1.2	68.3	0.9	50.9	0.10	100.4	0.07	74.6	0.03	25.8	
Amended	^b	^b	^b	^b	^b	^b	0.4	91.6	2.7	71.2	2.9	20.5	0.20	98.4	0.20	71.6	0.22	26.8	
Mean	8.4	97.3	4.2	49.1	4.0	48.2	3.8	96.1	2.3	57.5	2.2	38.6	0.25	99.8	0.16	60.0	0.12	39.8	
S.D.	0.8	9.4	1.6	14.3	0.7	10.4	6.6	18.4	3.6	14.0	3.5	15.4	0.16	9.2	0.10	14.8	0.08	21.2	
Median	8.7	100.8	4.7	53.8	3.6	49.4	1.3	94.0	1.1	59.9	1.0	38.2	0.20	98.0	0.16	65.5	0.09	30.9	
Minimum	7.1	80.7	2.1	30.0	3.4	37.5	0.1	73.2	0.0	35.0	0.0	20.5	0.10	91.3	0.03	32.1	0.03	25.8	
Maximum	9.1	103.3	5.8	63.3	5.1	63.7	21.4	126.4	12.0	74.5	11.6	60.0	0.51	121.4	0.35	74.6	0.22	89.3	

^a Methylmercury isotope was not added to the solution.

^b Not applicable because carbon isotope ratios were not modified.

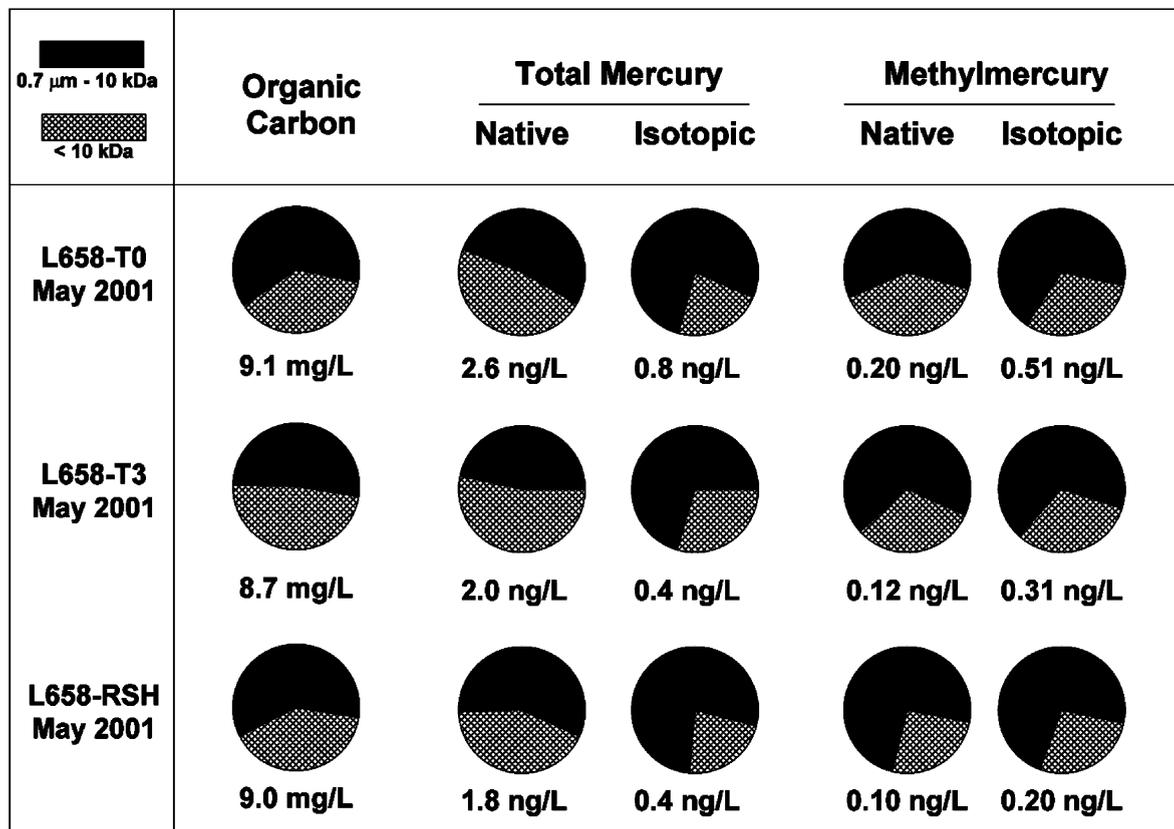


Fig. 1. Results from lake water spike matrix comparison. L658-T0 used a lake water spike matrix and was processed immediately after the spike addition. L658-T3 used a lake water spike matrix and was processed 3 days after the addition. L658-RSH used a thioglycolate matrix and was processed 3 days after the addition.

separation 0.01 N HNO₃ rinse of the process bottle recovered 13 pg of ²⁰¹Hg, indicating a loss to the walls of <1% of the amendment. Of the mercury in solution, 12% of the native Hg_T was in the particulate (>0.7 μm) phase compared to 3% of the isotopic Hg_T. The particulate phase is relatively less important for newly added mercury. A similar result is true for MeHg. The three L658 spiked waters averaged 0.16 (S.D.=0.06) ng l⁻¹ native MeHg unfiltered, and 0.36 (S.D.=0.15) ng l⁻¹ isotopic MeHg unfiltered. The post-separation nitric acid rinse recovered 2 pg of isotopic MeHg, again indicating a loss to the walls of <1% of the spike. Of the MeHg in solution, 10% of the native MeHg was in the particulate (>0.7 μm) phase compared to 5% of the isotopic MeHg. Again, the

particulate phase is relatively less important for newly added mercury.

The filtered phase distribution between the colloidal and <10 kDa fractions offer several practical observations, and raise several hypotheses for future research. First, the ultrafiltration technique was successfully combined with stable isotopic techniques—as validated by the good agreement in the observed phase distribution of carbon and the native mercury species in Fig. 1. As far as we are aware, these are the first reported colloidal phase data from lake waters. Second, the choice of amendment matrix did not affect the initial partitioning of new mercury—as evidenced by the similar phase distributions of the isotope amendments. However, within 3 days of the spike, neither

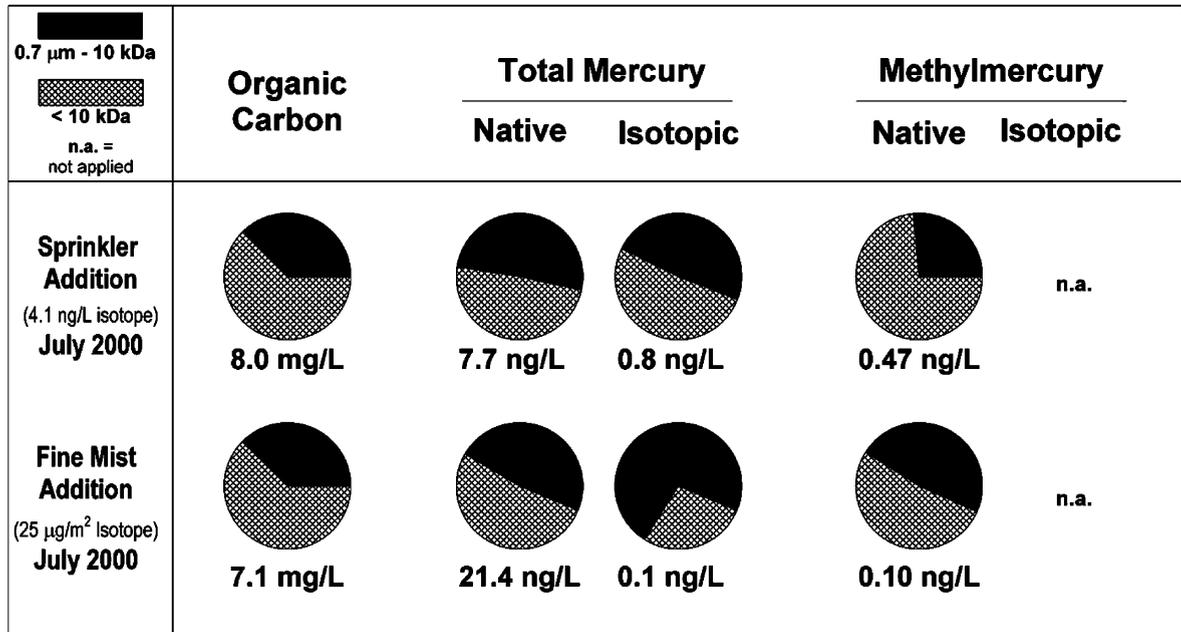


Fig. 2. Results from the upland spike application method comparison.

matrix (HgCl_2 or Hg-thioglycolate) reached the same equilibrium between the dissolved and colloidal phases as that of native Hg in L658. These observations suggest that (a) equilibration times between newly delivered Hg and lake water ligands may be days to weeks (instead minutes to hours as assumed); (b) Hg is transported from uplands and wetlands as non-reactive complexes; or (c) non-reactive Hg complexes form slowly over time in lake water.

Intriguing observations that will guide future work include the apparent predictive capacity of the organic carbon distribution for the native Hg_T phase distribution. Presumably reflecting the long-known association of mercury with organic carbon (Andren and Harriss 1975; Mierle and Ingram 1991), the similar distributions may indicate the long-term equilibrium of ‘old mercury’ in the system. This observation may also reflect a subset of Hg_T that has become recalcitrant and removed from the pool of mercury available for methylation. This supposition is backed, in part, by the observed phase distribution of both inorganic $\text{Hg}(\text{II})$ and MeHg isotopes. Both distributions are quite similar

to each other and to the native MeHg distribution. We hypothesize that on average, native MeHg may be ‘newer’ than native Hg_T , or at minimum, that native MeHg, isotopic $\text{Hg}(\text{II})$, and isotopic MeHg may partition to the same subfraction (ligand quality) of DOC.

3.2. Watershed additions

Two methods were used to apply the isotope to separate watershed test plots. The first was a sprinkler system that delivered the isotope in 1400 l of lake water, thus simultaneously creating the overland runoff that was sampled. The second method was a small-volume fine mist application accomplished using manual sprayers. The latter method relied on a natural rain event to create the overland runoff that was sampled.

Several practical conclusions can be drawn from the results presented in Fig. 2, but additional questions will also direct future research. To our knowledge, these are the first reported colloidal phase mercury data in overland runoff from non contaminated sites.

In general, very little of the added mercury was transported in the filtered phase, regardless of the spike application method (Sprinkler: 4.1 ng l^{-1} applied vs. 0.8 ng l^{-1} observed. Fine Mist: $25\text{-}\mu\text{g m}^{-2}$ applied vs. 0.1 ng l^{-1} observed). The rest of the isotopic mercury must have either stuck to the bedrock, evaded to the atmosphere, or traveled with the particulate phase.

Although the source water was different, the organic carbon phase distributions appear independent of application method. On a concentration basis alone, this observation may indicate that the source of the organic matter is largely from the upland surface itself. However, the color of the two samples of runoff indicates a different ligand composition within the organic carbon in each experiment. The fine mist was applied to an upland plot with deeper soils, and the runoff was darker in color.

The native Hg_T phase distribution appears follow that of organic carbon for both experiments, but there may be evidence of enrichment in the colloidal phase (Fig. 2). This enrichment could be due to several mechanisms including the stripping of native Hg_T from the $<10 \text{ kDa}$ phase as the overland runoff drains the watershed. That is, the depletion of more reactive species (weak complexes and free ions) by photoreduction and evasion, or by adhering to the watershed surface. Alternatively, direct colloidal-phase enrichment of native Hg_T could result from disintegration products if the mercury mainly traveled with the particulate phase. Unfortunately, we do not have particulate phase data from these samples to test this alternate hypothesis.

For the fine mist application, the isotopic Hg_T appears strongly depleted in the $<10 \text{ kDa}$ fraction. This observation is likely due to the contact and drying time between deposition and the rain event that created the runoff, leaving the colloidal phase to emerge as an important vector for transport within the filtered fraction. For the sprinkler application, the striking enrichment of native MeHg in the $<10 \text{ kDa}$ may be a result of flushing from the landscape.

To some extent, these differences in phase distribution for both the isotopic Hg_T and the native MeHg likely reflects differing ligands in the DOC

from each experiment. In addition, the phase distribution of the feed water for the experiments should also be determined to assess questions of source apportionment in each compartment. In general, our results suggest that it is important to further characterize DOC quality.

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