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Environ. Sci. Technol., **2009**, 43 (6), 1776-1782• DOI: 10.1021/es802634y • Publication Date (Web): 18 February 2009

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Environ. Sci. Technol. **2009,** *43,* 1776–1782

Forest Fire Effects on Mercury Deposition in the Boreal Forest

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Received September 17, 2008. Revised manuscript received January 9, 2009. Accepted January 19, 2009.

Particulate Hg (pHg) is a component of smoke from biomass burning and has the potential for local redeposition. Throughfall (precipitation collected beneath a conifer or deciduous canopy) and open precipitation samples were collected pre- and postfire in 2005 and 2006 using passive precipitation collectors across the Superior National Forest, located in northern Minnesota, USA. Samples were collected approximately every two weeks and analyzed for total Hg (THg) and methyl Hg (MeHg). THg concentrations increased significantly postfire in conifer throughfall (>4× increase), open precipitation (2.5×), and when all canopy types were considered (2.9×). MeHg concentrations also increased after fire regardless of the cover type (conifer throughfall: 10× increase; open precipitation: 3.5× increase; deciduous throughfall: 1.7× increase; all canopy types analyzed together: 8× increase). Total Hg deposition increased significantly under conifer cover (3.8×). Methyl Hg deposition increased significantly after fire when all canopy types were analyzed together (4.6×) and in conifer throughfall (5.9×). Canopy type influenced the magnitude of postfire THg and MeHg increase and the duration of elevated MeHg levels. Particulate Hg present in forest fire smoke represents a short-term source of increased Hg in the atmosphere that is available for local redeposition during and following fire.

Introduction

Forest fires have been shown as an important mechanism of liberating previously stored Hg to the atmosphere (*1*, *2*). Estimates of the amount of Hg that could be released by fire from boreal forest uplands range from 22.5 Mg Hg yr^{-1} to 53.3 Mg Hg yr^{-1} (*2*, *3*). The redistribution of this previously stored Hg has the potential to impact Hg concentrations in lake water and fish to areas receiving increased atmospheric deposition of Hg as a result of fire.

Burning results in a loss of Hg from vegetation and soils as gaseous elemental Hg (Hg (0)) and particulate Hg (pHg). Particulate Hg released in smoke during burning has the potential for local redeposition, whereas gaseous Hg (0) becomes part of the global Hg cycle (*1*). Experimental vegetation burns have shown nearly complete losses (85−100%) of THg upon combustion (*1*, *4*). Losses were also measured in the litter and soil Hg pools after fire (*5*, *6*). Experimental burns performed on soils showed a 79% decrease in THg content after burning (*4*). MeHg losses were similar to THg losses for vegetation (94% MeHg decrease) and soil (82% MeHg decrease) during an experimental burn (*4*). Hg losses from mineral soil resulting from fire depend on fire severity, with higher severity fires releasing more Hg from the soil. Fires have been shown to affect the upper part of soils, releasing Hg from the top 6 to 8 cm (*7*).

Hg that was stored in vegetation and soils and released by fire is present either in ash or smoke from the fires (*1*). Hg in forest fire smoke is mostly in the form of Hg (0), with a fraction of pHg that is dependent on fuel type (*1*). Hg (0) released as a result of forest fire is transported long distances and may remain in the atmosphere for long periods of time (*1*, *2*, *8*). Particulate Hg released during fire is likely to be deposited locally (*1*) and is removed from the atmosphere more efficiently (*9*). Transport of pHg depends on particle size and mass, and fire associated pHg has been measured up to 250 km from wildfire (*9*, *10*).

Prescribed burning has become a tool for resource managers, and is commonly used in overstocked stands, windblown and insect infested forest systems where fuels build and the potential for wildfire exists. Determining the fate and potential consequences of this redistribution of Hg during fire may be important when making fire-related management decisions. The U.S. Forest Service Superior National Forest experienced heavy fuel loads that resulted from a large scale, straight-line windstorm that occurred in northern Minnesota in 1999. As a result, the Superior National Forest has implemented an intensive prescribed burn program in the blowdown area to minimize the potential of wildfires that start in the wilderness from expanding and affecting private property. In 2005 and 2006, two wildfires occurred that were contained within the wilderness.

The objective of this study was to determine how forest fire effects Hg deposition to nearby landscapes impacted by smoke plumes. Hg concentrations and deposition were hypothesized to increase in throughfall and open precipitation after fire, and canopy type was hypothesized to influence the magnitude of the increase. Conifer canopies, which are better able to scavenge Hg from the atmosphere than deciduous canopies, were hypothesized to have greater changes in throughfall THg and MeHg concentrations.

Materials and Methods

Throughfall collectors and their open precipitation counterparts were positioned in five groups in the U.S. Forest Service Superior National Forest (SNF) in northeastern Minnesota (Figure 1). Each group had a combination of conifer and deciduous throughfall collectors. Three groups also had open precipitation collectors (Figure 1). Forest types and tree species were similar among the groups. Quaking aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*) were the dominant deciduous species in deciduous canopies, while white spruce (*Picea glauca*) and balsam fir (*Abies balsamea*) composed most of the conifer canopies.

Temperatures range from −43°C to 38 °C, with an average annual temperature of 3 °C. The area receives an average of 71 cm annual precipitation, with nearly 75% occurring between May and October. In the two study years, annual precipitation was 85 cm in 2005 and 72 cm in 2006. Prevailing winds are from the west and southwest (*11*).

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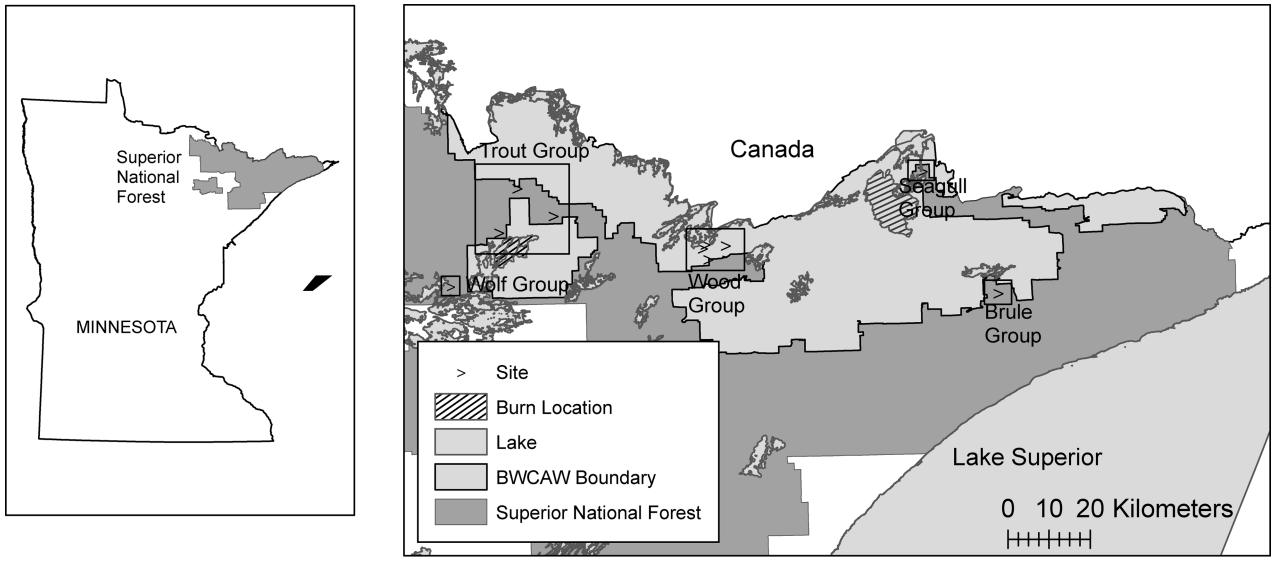
10.1021/es802634y CCC: $40.75 © 2009 American Chemical Society

Published on Web 02/18/2009



Group	Longitude	Latitude	Smoke Impacted?	Number of Sites	Total Number of Collectors	Conifer Collectors	Deciduous Collectors	Open Collectors
Wolf Group	74°25'57" W	47°55'57" N	No	1	9 (1 duplicate)	4	4	0
Trout Group	74°12'15" W	48°6'51" N	Yes	3	9	3	3	3
Wood Group	73°35'9" W	48°0'23" N	No	4	9 (1 duplicate)	4	4	0
Brule Group	72°39'2" W	48°10'12" N	Yes	1	3	1	1	1
Seagull Group	72°53'17" W	47°53'38" N	Yes	1	5 (1 duplicate)	2	1	1
Total				10	35	14	13	5

FIGURE 1. Location of Superior National Forest and sampling group locations with collector and fire information.

Each collector consisted of a one meter tall PVC shell, which housed a Teflon funnel (7.63 cm diameter) attached to a 1 L PFA Teflon bottle by PFA Teflon tubing. An inverted PFA Teflon disk was placed in the base of each funnel to minimize the introduction of particles and other debris into the sampling train. All PFA Teflon components were soaked overnight in an acid bath heated to 70 °C. Prior to deployment, 2 mL of low Hg concentrated HCl was added to each bottle as a preservative.

Samples were collected every two to three weeks during the summer and fall of 2005 and 2006 using PVC gloves and the "clean hands−dirty hands" method (*12*). After collection, samples were transported to the laboratory, where samples from the 1 L bottles were transferred to 125 mL PFA Teflon bottles for THg analysis and 125 mL PETG bottles for MeHg analysis. Subsamples were refrigerated until analysis. In 2005, only THg analysis was performed; in 2006 both THg and MeHg were analyzed.

THg was analyzed using double amalgamation cold vapor atomic fluorescence spectroscopy (CVAFS) (*13, 14*). Analysis was performed using a Brooks-Rand AFS Model III CVAFS equipped with Mercury Guru Software. THg samples received BrCl for digestion in BrCl:sample ratios of 1:100 to 1:20, based on the amount of organic material present in the sample. Samples were then digested overnight in a 70 °C oven. Hg was purged using N_2 gas following reduction by $SnCl_2$. Standard curves were run prior to each day's analysis. Standard reference materials (NIST #2976 mussel tissue and NIST #1515 apple leaves) averaged 92% ± 2% (SE) of the standard concentration while duplicate samples averaged 100% ± 6%. The sample volume used in THg analysis ranged from 10 to 50 mL. The method limit of detection (LOD) for THg was 0.1 ng L^{-1}.

MeHg analysis was performed with a Tekran Model 2500 CVAFS Mercury Detector and gas chromatograph separation (*15*). Prior to analysis, samples were distilled using an aluminum heating block and ultraclean nitrogen purge gas. Samples were ethylated with sodium tetraethyl borate, purged with nitrogen gas, and collected onto a Carbotrap. Mercury species were then released from the Carbotrap by heating in an argon purge stream, converted to elemental Hg by pyrolysis, and analyzed by CVAFS. Sample volumes used for analysis ranged from 20 to 50 mL. The mean MeHg concentration in analytical blanks was 0.008 ng L^{-1} + 0.009 ng L^{-1} (LOD for MeHg was 0.07 ng L^{-1}. MeHg measured in analytical blanks was subtracted from concentrations measured during the sample analysis.

Duplicate collectors in the Wolf, Wood, and Seagull groups and weekly field blanks were included as part of the QA protocol. THg and MeHg concentrations did not significantly differ between the duplicate and colocated collector (p = 0.88, n = 10 for THg; p = 0.46, n = 7 for MeHg). Field blanks consisted of ultraclean water poured through the sampling apparatus and were collected at least once per week and analyzed for THg and MeHg. THg and MeHg concentrations measured in the field blanks were subtracted from the sample concentrations collected during the same week.

Smoke plumes from three fires occurring in SNF during 2005 and 2006 impacted collector groups. Two fires, the Alpine Lake wildfire (2005) and Cavity Lake wildfire (2006), were lightning ignited and impacted the Seagull collector group. In addition to the Seagull group, the Brule group was also impacted by smoke plumes from the Cavity Lake wildfire. The third fire was a prescribed burn (Trout Prescribed Burn) performed by the U.S. Forest Service in 2005, and impacted the Trout Collectors. Cumulative area burned in all three fires was approximately 17 640 ha.

Several methods were used to track smoke plumes from fires that occurred in the SNF during 2005 and 2006. NOAA satellite imagery and GIS-based analysis of smoke plumes

TABLE 1. Summary of Collection Number and Number of Days Post-Burn.[a]

collection number	average number of days postburn at collection time	range of number of days postburn at collection time
1	14	3−47
2	25	13−98
3	39	26−70
4	63	33−98

[a] Sample collection timing depended on precipitation events and sample volumes. Collectors beneath heavy conifer canopies were unable to collect adequate sample volumes for analysis during small precipitation events, and generally had higher days elapsed since fire than deciduous collectors or collectors in the open.

were used for all three fires. Additionally, Remote Automated Weather Station (RAWS) data was used to monitor wind directions and speeds during the fires (*16*). U.S. Forest Service air monitoring data provided additional information.

Preburn THg and MeHg concentrations and deposition were compiled and included all samples from the Seagull, Brule, and Trout collectors that were collected prior to fire activity, as well as samples from the Wood and Wolf collectors that were not impacted by smoke from fires. Deposition refers to the mass of Hg per unit area (ug m^{-2}). Outliers were identified as values exceeding 1.5× the interquartile range. Samples from the Trout collectors taken in 2006 were also included as preburn samples since carry-over of Hg in the canopy from 2005 was unlikely.

Postburn samples were grouped based on the number of collections since the beginning of fire activity. The number of days elapsed since fire for each collection number varied for each fire and collector grouping (Table 1). Sample collection timing depended on precipitation events and sample volumes. Collectors beneath heavy conifer canopies were unable to collect adequate sample volumes for analysis during small precipitation events, and generally had higher days elapsed since fire than deciduous collectors or collectors in the open. Deciduous throughfall samples were collected prior to the onset of litterfall (October 1) (*17*).

Statistical analysis was performed using the Minitab software package, version 14.20. A one-way ANOVA was used to determine if statistically significant differences resulted in THg concentrations, THg deposition, MeHg concentrations, MeHg deposition, or THg:MeHg ratios after the fires. If differences were measured, then Mann−Whitney comparisons were used for pairwise comparisons. This statistical approach was chosen based on the assumption that postburn collections from spatially and temporally distinct fires would be similar in their Hg response and therefore used for intercomparison. The amount of Hg available for capture using the throughfall and open deposition method is likely a result of smoke plume size and density, duration of plume cover, and the length and intensity of precipitation events that occur while the plume is affecting the collector catch. On the basis of our results, it appears that these smoke plume and precipitation event characteristics were similar enough that grouping post fire results for all three fires was warranted.

Results

Preburn THg and MeHg concentrations were similar to those reported in other studies. Conifer throughfall THg concentrations were within the range of 17.5 to 48.4 ng L^{-1} found in other conifer throughfall studies (*18, 19*). MeHg measured in conifer throughfall in this study was within the range reported from Sweden (0.38 ng L^{-1}) and Canada (0.22 ng L^{-1}) (*20, 21*). Deciduous throughfall preburn THg concentrations measured in this study were similar to studies from Vermont (12 ng L^{-1}) and Maine (14.2 ng L^{-1}) (*22, 23*) and MeHg was similar to deciduous throughfall measured in Germany (0.13 ng L^{-1}) (*24*). Both THg and MeHg in open precipitation measured in this study were similar to THg (2.4−24.0 ng L^{-1}) and MeHg ranges (0.01−0.85 ng L^{-1}) measured in the Great Lakes region (*25*).

Significant increases in THg and MeHg concentrations were measured between preburn samples and the first postburn collection when all canopy types were considered (THg: $p = 0.03$, $n = 193$, MeHg: $p \leq 0.001$, $n = 135$) (Figure 2). Mean THg concentrations measured in the first postburn collection were nearly 3× higher than the preburn mean while MeHg concentrations were 8.75X higher than the preburn mean. For THg concentrations, no significant increases were identified after the first postburn collection when compared to preburn levels. For MeHg concentrations, the first ($p \leq 0.001$, $n = 135$) and second ($p = 0.03$, $n = 135$) sample collections were higher than the preburn mean. Total Hg deposition did not significantly increase between the preburn and first postburn collection ($p = 0.114$, $n = 136$), however MeHg deposition was significantly (4.6×) higher in the first samples collected postburn when compared to the preburn mean ($p = 0.004$, $n = 138$) (data not shown).

Significant increases in mean THg and MeHg concentrations in conifer throughfall were identified postfire (THg: $p \leq 0.001$, $n = 83$; MeHg: $p \leq 0.001$, $n = 61$) (Figure 3). Mean conifer throughfall THg concentrations from samples taken in the first sample collection postfire were 4× higher than mean preburn samples ($p = 0.01$, $n = 64$) while mean MeHg concentrations were more than 10× higher than mean preburn concentrations ($p = 0.003$, $n = 51$). After the first postburn sample, THg concentrations in conifer throughfall returned to preburn levels. Methyl Hg concentrations were marginally higher than preburn concentrations in the second sample collection after the fire ($p = 0.07$, $n = 50$), and returned to preburn levels at the third sample collection. Significant increases in THg and MeHg in conifer throughfall deposition were also measured, although the magnitude of the increase was less than that observed for concentrations (3× increase for THg deposition ($p = 0.03$, $n = 46$); 6× increase for MeHg deposition ($p = 0.03$, $n = 52$)) (data not shown).

Significant increases were not measured in deciduous throughfall for either THg or MeHg concentration due to fire (THg: $p = 0.24$, $n = 87$; MeHg: $p = 0.15$, $n = 55$) (Figure 4). The third and fourth postburn samples were combined for THg statistical analysis due to small sample numbers. Similarly, the first and second postburn and third and fourth postburn samples were combined for MeHg statistical analysis due to small sample numbers. No significant increases were measured in either THg or MeHg deposition between preburn and postburn in deciduous throughfall (THg: $p = 0.18$, $n = 60$; MeHg: $p = 0.28$, $n = 55$) (data not shown).

Open precipitation THg concentrations increased 2.5× in the first postburn samples compared to preburn samples ($p = 0.01$, $n = 37$), and returned to preburn levels by the second collection (Figure 5). Although not statistically significant ($p = 0.28$, $n = 28$), MeHg concentrations were nearly 5× the preburn average in the first two combined postburn samples, and returned to preburn levels by the combined third and fourth collection. No significant increases were measured in open precipitation deposition for either THg or MeHg postburn (THg: $p = 0.74$, $n = 40$; MeHg: $p = 0.65$, $n = 30$) (data not shown).

The THg:MeHg ratio did not significantly change as a result of fire for any canopy type. Analysis of variance comparing preburn samples to postburn samples grouped by event number found no significant difference when all canopies were considered together ($p = 0.78$, $n = 114$), in

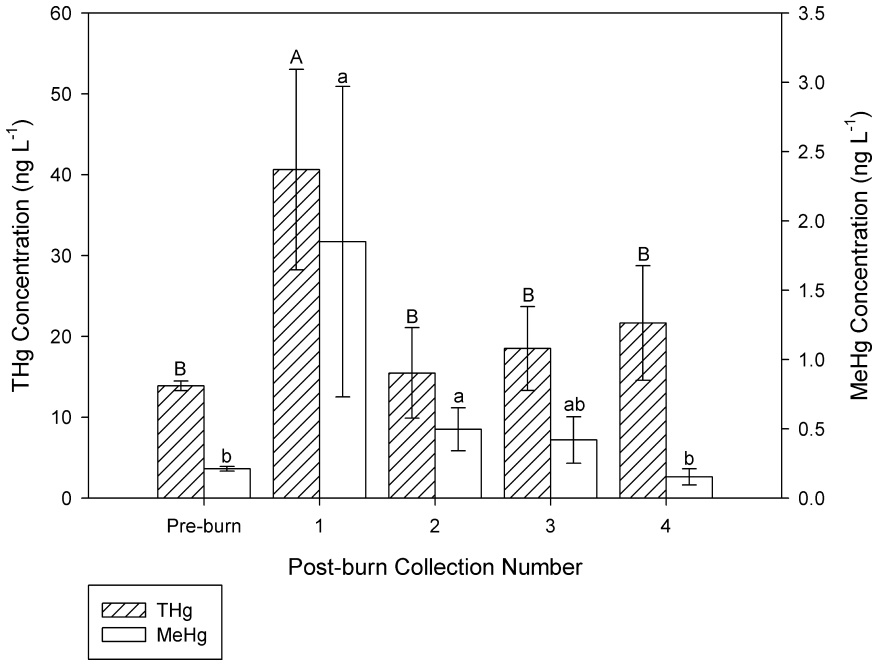


FIGURE 2. Mean THg and MeHg concentrations for preburn and postburn collections for all sample types. See Table 1 for additional information regarding collection numbers. Significant increases were measured in both THg and MeHg concentrations in the first sample following fire; significant increases persisted in MeHg concentrations until after the second postburn collection. Capital letters indicate differences in THg concentration at $p = 0.05$; lowercase letters indicate differences in MeHg concentration at $p = 0.05$. Bars represent standard error.

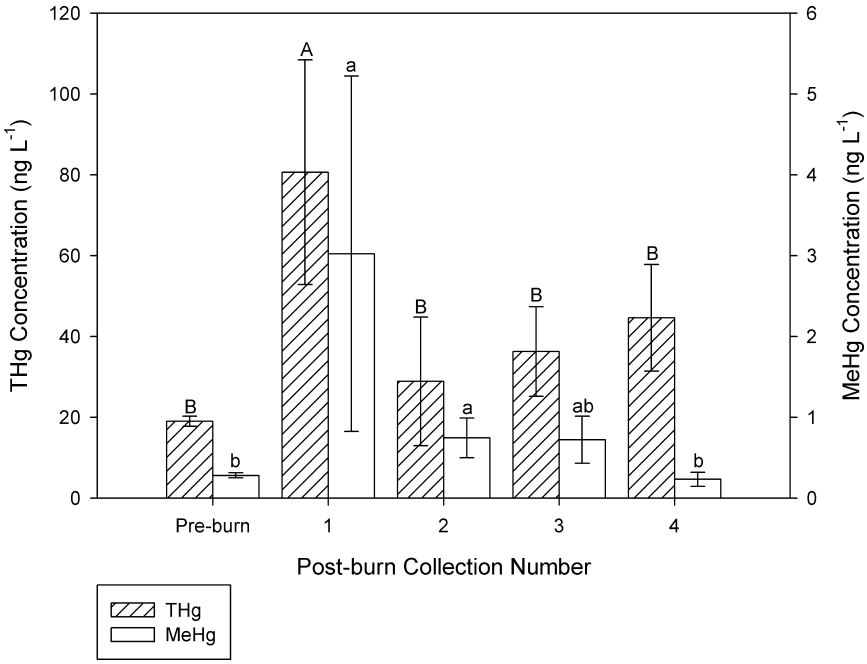


FIGURE 3. Mean THg and MeHg concentrations in conifer throughfall measured pre and postburn. See Table 1 for additional information regarding collection numbers. Significant increases were measured in the first postburn samples for THg and MeHg. MeHg increases persisted until the third collection postburn. Capital letters indicate differences in THg concentration at $p = 0.05$; lowercase letters indicate differences in MeHg concentration at $p = 0.05$. Bars represent standard error.

conifer throughfall ($p = 0.34$, $n = 41$), in deciduous throughfall ($p = 0.65$, $n = 54$), or in open precipitation ($p = 0.54$, $n = 19$).

Discussion

The significant increases of THg concentrations in conifer throughfall and open precipitation and MeHg concentrations in conifer throughfall after fire events strongly suggests that some fraction of Hg liberated by biomass burning is redeposited on areas near forest fires. Our data also indicate that canopy type influences the magnitude of the response of local landscapes to changes in Hg deposition as a result of fire. The influence of canopy type on the fire response is likely due to the greater surface area and density of conifer canopies compared to deciduous canopies or open precipitation. Smoke plume characteristics (size, density, and duration) and precipitation events that occurred while the collectors were impacted, as well as variability due to short-

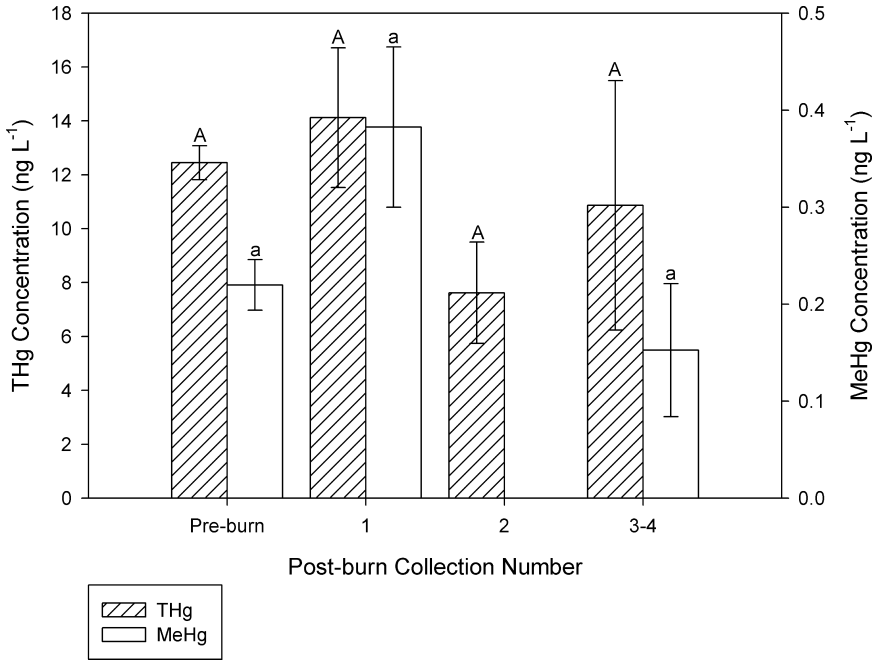


FIGURE 4. Deciduous throughfall THg and MeHg concentrations measured before and after fire. See Table 1 for additional information regarding collection numbers. No significant increase was measured in either THg or MeHg concentration. Methyl Hg sample collections and the final two THg sample collections were combined due to low sample numbers. Bars represent standard error.

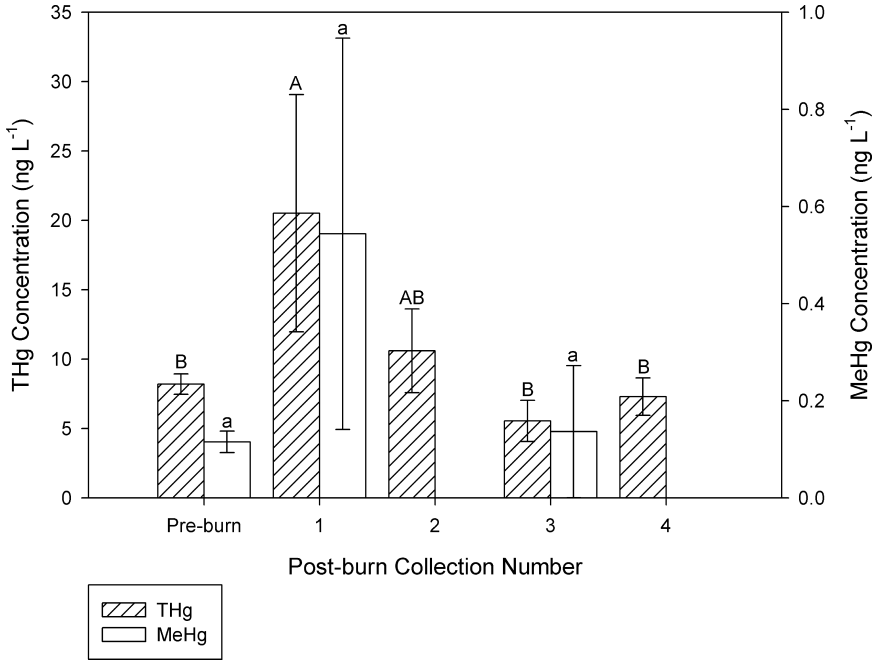


FIGURE 5. Open precipitation THg and MeHg concentrations measured pre- and postburn. See Table 1 for additional information regarding collection numbers. Total Hg concentrations increased significantly from preburn levels in the first samples collected after fire. Methyl Hg sample collections were combined due to low sample numbers; no significant increase was measured in MeHg concentration. Capital letters indicate differences in THg concentration at $p = 0.05$; lowercase letters indicate differences in MeHg concentration at $= 0.05$. Bars represent standard error.

term sampling influenced the Hg measured using the throughfall and open deposition approach.

Analysis of Hg in smoke plumes and laboratory studies have determined that Hg in smoke from biomass burning is primarily present as Hg (0) (*1*). Hg (0) has a long atmospheric residence time (*9*) (approximately one year), and likely does not contribute to local redeposition (*1*). Therefore, the increased THg concentrations measured in this study are likely the result of pHg deposition, since pHg is more easily removed from the atmosphere and available for local deposition (*1, 9*).

Significant increases were seen in THg concentrations in conifer throughfall and open precipitation, but not in deciduous throughfall. Previous studies have determined that conifer canopies, with higher canopy surface areas, are better able to scavenge Hg from the atmosphere (*19, 26*). Therefore, it is not surprising that concentrations and deposition increases beneath conifer canopies were sig-

nificantly higher after a large input of pHg into the atmosphere from fire.

Although deciduous throughfall THg concentrations did not increase significantly following fire, surprisingly concentrations in open precipitation did increase in the first sample collection postfire. We would have expected that deciduous canopies, even if senescing, would have comparable or even higher THg concentrations. After assessing the data, the lone open collector at the Seagull group measured 62.90 ng L^{-1} THg three days postfire, but the comparable lone deciduous collector only measured 6.82 ng L^{-1} during the same collection. Potentially, just the spatial variability in the smoke plume combined with the spatial variability in the precipitation event led to the elevated concentration in the open collector when compared to the deciduous collector. Although we have no reason to disregard the open collector measurement at Seagull, if we were to eliminate that measurement we see no significant increase in THg concentration postfire ($p = 0.112$, $n = 54$), indicating that the one open collector measurement is driving the difference. Similar variability was measured in postfire deciduous collections at Trout group, with one postfire THg concentration measuring 2.5 times THg measured in the other collectors in the area.

MeHg measured in 2006 showed increases in MeHg samples from conifer throughfall, with the magnitude of change from preburn levels more than 10× the preburn concentrations in postburn samples. While measurements of MeHg in smoke plumes have not been performed, analyses of burned plants and soils show losses of MeHg after burning (*4, 27*). Previous Hg analyses of smoke plumes have identified reactive gaseous Hg (RGM) in plumes, and RGM has been linked to the formation of MeHg in precipitation (*28*). We measured no changes in the percent of MeHg as THg between pre and postburn samples, independent of canopy type. Potential sources of MeHg in throughfall include formation of MeHg in soot or on leaf surfaces, atmospheric formation, or in-plume transformation. These data suggest that MeHg is not being removed or added in amounts that are measurable using throughfall and open precipitation as indicators.

Hg that is stored in forest vegetation and soils is liberated by forest fires, and some portion of the newly liberated Hg is redeposited on landscapes near the fire areas. Hg that is locally deposited is likely a result of increased pHg in smoke from biomass and forest floor burning. Increases in THg concentrations were measured postfire in conifer throughfall and open precipitation while increases in MeHg concentrations were measured postfire in conifer and deciduous throughfall. Concentrations generally returned to preburn levels in the second or third sampling event, an average of 14 to 39 days after fire. No change was measured in the fraction of THg present as MeHg, indicating that MeHg is not being removed or added in quantities measurable using throughfall and open deposition methods.

These results indicate that Hg released by forest fires is an input to surrounding areas that is unaccounted for in many Hg budgets. The redistribution of Hg that was stored in forest vegetation and soils after fire has the potential to impact Hg concentrations in lakes, streams, and wetlands in areas surrounding burned areas. Altered fish consumption advisories may be needed for lakes impacted by forest fire smoke from either wildfires or prescribed burns due to the potential for increased Hg loadings in those lakes. Finally, increased dry deposition to land surfaces surrounding burned areas may increase the amount of Hg stored in the system that is available for release by future fires or other disturbances.

Acknowledgments

The authors thank Jessica Wittwer, Chris Allen, and Mark Gabriel for their help. Funding was provided by the Joint Fire Sciences Program.

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ES802634Y