

Release of mercury from Rocky Mountain forest fires

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Received 16 January 2006; revised 17 August 2006; accepted 1 September 2006; published 9 January 2007.

[1] Concentrations of mercury (Hg) in soil profiles and vegetation were examined in unburned areas and in areas recently burned by wildfires of low, medium, and high fire severities in western Wyoming. Paired unburned and burned sampling sites with similar tree species composition, forest stand age, climate, and geological substrate were studied. Results indicate that Hg release from forest fires is dependent on the tree species composition of the forest, which affects prefire Hg accumulation, as well as the forest fire severity. On the basis of an average of 2.7×10^6 ha of forest and shrubland burned annually in the United States we estimate that wildfires and prescribed burns in the United States release 19 to 64×10^6 g of Hg annually. This represents between 13 and 42% of the estimated United States anthropogenic Hg flux of 150×10^6 g.

Citation: Biswas, A., J. D. Blum, B. Klaue, and G. J. Keeler (2007), Release of mercury from Rocky Mountain forest fires, *Global Biogeochem. Cycles*, 21, GB1002, doi:10.1029/2006GB002696.

1. Introduction

[2] Mercury is a toxic trace metal with the potential to bioaccumulate in terrestrial and aquatic animals [Hightower, 2004; Mahaffey, 1999]. The dominant atmospheric species, elemental mercury (Hg^0), generally has a long atmospheric residence time (~ 6 months to 1 year), and thus Hg emissions are globally distributed. Oxidation of Hg^0 occurs in the atmosphere forming reactive mercury (Hg^{2+}), which has a short residence time of days to weeks [Lin and Pehkonen, 1999]. Upon deposition into terrestrial and aquatic ecosystems, inorganic Hg can be methylated by microorganisms to methylmercury, a potent neurotoxin [Mahaffey, 1999] that can bioaccumulate up the food web [Morel et al., 1998]. Methylmercury concentrations are especially elevated in piscivorous fish [Boening, 2000] and this has prompted environmental guidelines regarding fish consumption [Mahaffey, 1999]. Thus there is great interest in understanding Hg cycling and in determining the potential for pools of Hg to enter ecosystems. Anthropogenic sources of Hg to the atmosphere have been fairly well quantified [Environmental Protection Agency, 1997]. However, natural sources of Hg to the atmosphere are not as well known, in part owing to their nonpoint nature. Herein we investigate one of these natural sources by examining Hg pools in conifer forests before and after wildfires to estimate both Hg accumulation in forests and wildfire-induced emissions of Hg to the atmosphere.

[3] Recent studies indicate that wildfires may provide a significant flux of Hg from terrestrial ecosystems to the

atmosphere [Brunke et al., 2001; Engle et al., 2006; Friedli et al., 2001, 2003a, 2003b; Harden et al., 2004; Sigler et al., 2003]. Forest fires release Hg^0 to the atmosphere from soils as well as from living and dead vegetation [Artaxo et al., 2000]. The Hg release associated with fires has been estimated for North American coniferous forests [Engle et al., 2006; Friedli et al., 2001, 2003a, 2003b; Harden et al., 2004; Sigler et al., 2003], African fynbos [Brunke et al., 2001], and Amazonian forests [Artaxo et al., 2000; Veiga et al., 1994]. Mercury release from soils burned during both prescribed fires [Woodruff et al., 2001; Harden et al., 2004] and wildfires [Biswas et al., 2003; Cannon and Woodruff, 2003] has been documented.

[4] Mercury enters forest ecosystems by wet and dry atmospheric deposition, and to a lesser extent by assimilation via stomatal uptake [Rea et al., 2002]. Leaf area index, defined as the amount of leaf or needle area per unit ground area [Bond-Lamberty et al., 2002], has been found to influence gas and aerosol deposition to tree canopies [Stachurski and Zimka, 2000] and is thus an important control on the amount of atmospheric Hg that is captured and accumulated onto vegetation from the atmosphere [Rea et al., 2002]. Foliar Hg concentrations are species specific and age-related [Munthe et al., 1998; Rea et al., 2000]. Mercury adsorbed to foliar surfaces eventually enters soil either by leaching from foliage by precipitation, or during litterfall and subsequent litter decomposition [Ericksen et al., 2003; Munthe et al., 1998]. Previous work has demonstrated that $\sim 90\%$ of the Hg in forests is stored in the soil rather than associated with living vegetation [Grigal, 2003]. During forest maturation, forest soils accumulate Hg that is predominantly complexed with soil organic matter (SOM) [Biester et al., 2002; Grigal, 2003; Scherbatskoy et al., 1998; Schwesig and Matzner, 2000; Skjellberg et al., 2000]. Prior to fires, total soil Hg can vary depending on landscape position and stand age, species composition, the amount of SOM, and burn frequency [Munthe et al., 1998].

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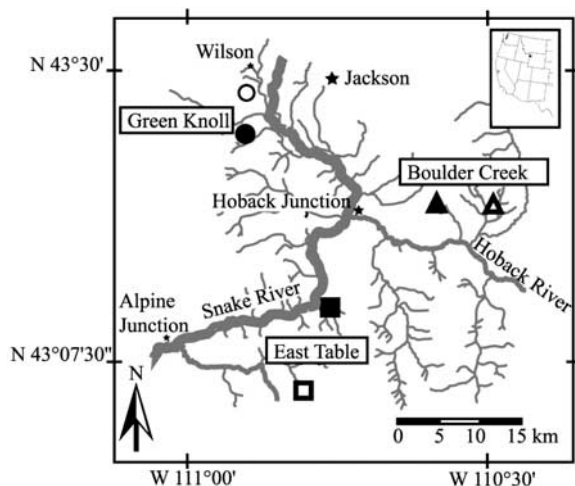


Figure 1. Map of sample sites in northwestern Wyoming (circle, Green Knoll; triangle, Boulder Creek; square, East Table; open symbols represent unburned sites and solid symbols represent burned sites).

[5] The amount of Hg released during a wildfire is limited by Hg accumulation prior to burning. The severity of a fire, which is dependent on the temperature and duration of heating through the soil column [DeBano *et al.*, 1998], is the most important control on SOM volatilization during a fire. Fire severity is influenced by variations in fuel availability, soil moisture, topography, weather, and fire dynamics [Flannigan and Wotton, 2001; Pyne *et al.*, 1996]. Laboratory combustion of vegetation indicates that Hg is almost completely mobilized from organic matter by fire, predominantly in the gaseous elemental form (Hg^0), with less than 5% estimated to be associated with particulate matter [Friedli *et al.*, 2001].

[6] During the period following wildfires, forest ecosystems may continue to lose Hg to the surrounding environment. Burned areas have lower rates of Hg accumulation and a reduced ability to retain previously accumulated Hg [Grigal, 2003]. Increased solar exposure may also cause elevated soil temperatures and increased rates of Hg evasion [Zhang *et al.*, 2001]. In addition, Hg that is stored in ash and burned soil can be mobilized by wind or water erosion, in some instances resulting in elevated Hg concentrations in lake sediments [Caldwell *et al.*, 2000]. It is important to determine the amount of Hg released during wildfires to assess the relative contribution of wildfires to the atmospheric Hg pool and investigate the potential for pulses of Hg to enter aquatic ecosystems following fires. Two approaches have been employed to study Hg release during forest fires (1) atmospheric sampling of Hg in smoke during fires [Brunke *et al.*, 2001; Friedli *et al.*, 2001, 2003a, 2003b; Sigler *et al.*, 2003], and (2) soil sampling of unburned and burned sites to quantify Hg release by difference [Engle *et al.*, 2006; Harden *et al.*, 2004]. This study utilizes the latter method to investigate wildfires of different severity in conifer, aspen, and meadow soils to

gain insight into the importance of vegetation type and fire severity on Hg release from soils.

2. Field and Laboratory Methods

2.1. Fire Events and Experimental Design

[7] Three recently burned sites and adjacent unburned control sites of similar stand age, climate, geological substrate, and tree species composition were sampled in northwestern Wyoming. Ambient atmospheric Hg concentrations in the vicinity of the study sites are similar to other remote areas in the United States, with average concentrations of vapor phase Hg less than 5 ng/m^3 and particulate phase Hg in the range of $1\text{--}15 \text{ pg/m}^3$ [Biswas *et al.*, 2003]. Modeling of natural and anthropogenic Hg deposition [Seigneur *et al.*, 2004] and local Hg concentrations in snow (Teton Range, WY [Abbott *et al.*, 2002]) suggest that this region experiences long-term accumulation of globally distributed background-level inputs of Hg. The nearest major anthropogenic Hg sources are located in Salt Lake City, Utah, and Spokane, Washington, both of which are >250 miles away, thus it is unlikely that the study area is subject to significantly enhanced Hg inputs from point sources. This region is thought to be representative of other boreal and montane forests with similarly low background-level Hg inputs.

[8] During July and August 2003 six sites were sampled in burned (B) and nearby unburned (U) areas associated with the Boulder Creek (BC) Fire (August 2000), the Green Knoll (GK) Fire (July–August 2001), and the East Table (ET) Fire (July 2003). The six sites: BC-U, BC-B, GK-U, GK-B, ET-U, and ET-B are within 50 km of each other (Figure 1). The dominant tree species include lodgepole pine (*Pinus contorta*), Douglas-fir (*Pseudotsuga menziesii*), subalpine fir (*Abies lasiocarpa*), and Englemann spruce (*Picea engelmannii*) with generally $<10\%$ of the total site area covered by quaking aspen (*Populus tremuloides*), shrubs and grasses. Within each of the six sites, we established study plots of conifer, aspen, and meadow vegetation type where possible (aspen and meadow stands were not observed at ET). Conifer study plots at BC-U, BC-B, GK-U, and GK-B sites have stand ages of ~ 130 years and conifer study plots at ET-U and ET-B sites are estimated to average 120–160 years (L. Jones, U.S. Forest Service, personal communication, 2004). Aspen study plots at BC-U and BC-B have stand ages of ~ 75 years and at GK-U and GK-B the stand age is ~ 130 years.

[9] An additional selection criterion for our study sites was based on forest fire severity, which we hypothesized might influence the amount of Hg loss during burning. Using criteria established by the USDA Forest Service [Parsons, 2003], we selected conifer and aspen plots that could be unequivocally categorized as low, moderate, or high fire severity based on tree trunk burn height, the depth of ash on the soil surface, and the proportion of burned canopy. Low fire severity areas were distinguished by 5–30% burned canopy cover, tree trunk burn heights of <1 m, and only slightly charred soil surfaces with discontinuous ash. Moderate fire severity areas were distinguished by 40–60% burned canopy cover, tree trunk burn heights of 1 to 3 m, and a continuous ash layer on the soil surface. High

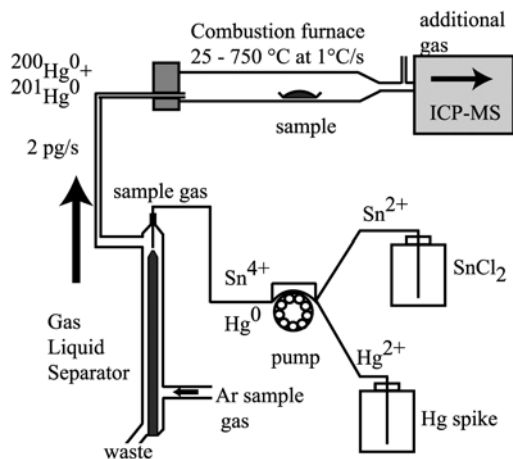


Figure 2. Schematic of the analytical method used to analyze mercury concentrations in soil samples by thermal analysis cold-vapor isotope dilution ICP-MS. The Hg spike, used for isotope dilution, is enriched in ^{200}Hg and ^{201}Hg .

fire severity areas were characterized by 80–100% burned canopy, downed and burned logs, tree trunk burn heights that extended up to the height of the tree and the soil surface appeared to be sintered, ashy, and hardened owing to burning. Conifer plots burned at high fire severity were identified at the GK-B and BC-B, and conifer plots burned at low and moderate severity were identified at ET-B. Aspen plots burned at low and moderate fire severity were identified at GK-B and BC-B, respectively. Meadow plots lacked most indicators of fire severity (tree trunk burn height and canopy conditions) and therefore could not be categorized by fire severity.

2.2. Sample Collection and Preparation

2.2.1. Foliage

[10] Conifer and aspen foliage was collected in triplicate at BC-U at a height of 8–10 m from the forest floor, triple sealed in plastic bags and stored at 4°C. Petioles were removed from the base of aspen foliage to prevent dilution of the sample [Rasmussen *et al.*, 1991]. The moisture content of foliage samples was determined by weight loss

from freeze-drying, and percent organic matter was determined by loss on ignition (LOI) at 550°C for ≥ 6 hours [Heiri *et al.*, 2001]. Samples were homogenized by grinding prior to Hg analysis.

2.2.2. Soil

[11] Triplicate soil core samples were collected when possible in study plots of each vegetation type in a 15 m \times 15 m area at each of the six sites (only 1 core was collected at GK-U aspen; 2 cores were collected at BC-B conifer and aspen and at GK-B meadow). Each core was collected in a split PVC (polyvinyl chloride) tube that was pounded into the soil, capped, and stored at 4°C until analysis. In the laboratory, soil tubes were opened and the core was cut into 1 cm slices from 0–8 cm depth. The moisture content of soil samples was determined by weight loss from freeze-drying and % SOM was determined for each sample by LOI at 550°C for ≥ 6 hours. A representative subsample was homogenized with a boron-carbide mortar and pestle prior to Hg analysis. Soil samples from measured depths of 0 to 1, 1 to 2, 3 to 4, 5 to 6, and 7 to 8 cm were analyzed for Hg content.

2.3. Hg Concentration Analysis

[12] Mercury concentrations of vegetation and soil samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). Approximately 50 mg of each sample was weighed, placed in a quartz boat, and heated from 25 to 750°C at a constant rate of $\sim 1^\circ\text{C}/\text{s}$ in an argon atmosphere [Lauretta *et al.*, 2001]. Samples were thermally decomposed and Hg vapor was mixed with an isotope dilution spike and introduced into a Finnigan Element 2 magnetic sector ICP-MS (Figure 2). Online quantification of the Hg released from each sample was achieved by adding a constant flow of enriched ^{200}Hg and ^{201}Hg spikes, produced by a cold-vapor generation system, through the furnace. The amount of natural Hg released from each sample was evaluated by isotope dilution [e.g., Gelaude *et al.*, 2002] for every 3-s interval during heating (Figure 3). Isotope dilution was used to eliminate matrix effects frequently associated with the combustion of soil samples. The detection limit for this method was ~ 1 pg over the duration of sample analysis and sample replicates agreed to within $\pm 5\%$. Replicate analyses of quality control standards (IRMM olive leaf and NIST 1633b Hg in coal fly ash) agreed with certified values to within $\pm 5\%$.

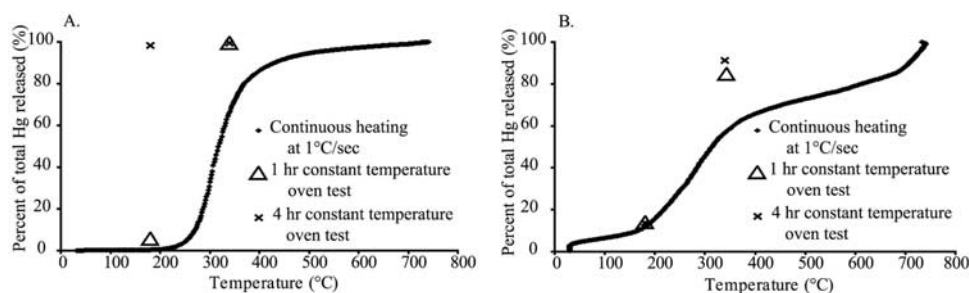


Figure 3. The effects of variable duration (1 and 4 hours) and temperature (180°C and 340°C) of heating on total mercury release from (a) unburned and (b) burned soil.

Table 1. Hg Concentrations and Percent Soil Organic Matter (SOM) for Each Vegetation Type and Site

Site Meas. Depth, cm	Unburned		Adj. Depth, cm	Burned	
	[Hg] ppb (± 1 s.d.)	%SOM		[Hg], ppb	%SOM
<i>Conifer, Boulder Creek, High Fire Severity, 4.1 cm Burned</i>					
s.s. ^a	unburned	unburned	0–4.1	soil loss	soil loss
0–1	72.27 (30.1)	72.8 (24.5)	4.1–5.1	15.5 (16.2)	4.0 (0.3)
1–2		66.0 (19.3)	5.1–6.1	18.3 (18.7)	4.2 (1.0)
3–4	123.3 (84.0)	41.8 (19.6)	7.1–8.1	19.7 (19.8)	4.8 (1.1)
5–6	30.9 (21.8)	17.6 (20.4)	9.1–10.1	30.2 (8.4)	5.4 (1.3)
7–8	31.6 (27.1)	13.2 (16.6)	11.1–12.1	29.8 (6.7)	5.0 (1.2)
<i>Conifer, Green Knoll, High Fire Severity, 3.9 cm Burned</i>					
s.s. ^a	unburned	unburned	0–3.9	soil loss	soil loss
0–1	73.0 (3.5)	63.3 (41.1)	3.9–4.9	18.6 (1.2)	6.9 (1.7)
1–2	111.4 (72.9)	59.8 (30.0)	4.9–5.9	14.0 (9.5)	7.5 (2.3)
3–4	208 (263)	29.9 (36.0)	6.9–7–9	11.8 (6.9)	5.9 (0.4)
5–6	34.7 (7.1)	10.9 (6.3)	8.9–9.9	12.4 (5.4)	4.6 (0.8)
7–8	32.6 (10.3)	12.9 (4.5)	10.9–11.9	13.5 (5.5)	4.7 (0.9)
<i>Conifer, East Table, Moderate Fire Severity, 3.0 cm Burned</i>					
s.s. ^a	unburned	unburned	0–3.0	soil loss	soil loss
0–1	101.0 (58.8)	63.8 (27.6)	3.0–4.0	40.6 (1.4)	49.3 (45.2)
1–2	99.9 (57.7)	54.8 (31.5)	4.0–5.0	37.1 (8.0)	11.4 (3.3)
3–4	124.4 (59.1)	47.1 (33.0)	6.0–7.0	27.4 (5.2)	10.7 (1.8)
5–6	68.1 (66.4)	25.8 (21.5)	8.0–9.0	29.9 (12.4)	9.9 (0.1)
7–8	45.4 (34.2)	14.4 (5.9)	10.0–11.0	43.8 (24.3)	11.7 (2.6)
<i>Conifer, East Table, Low Fire Severity, 2.4 cm Burned</i>					
s.s. ^a	unburned	unburned	0–2.4	soil loss	soil loss
0–1	101.0 (58.8)	63.8 (27.6)	2.4–3.4	56.2 (3.5)	34.2 (13.8)
1–2	99.9 (57.7)	54.8 (31.5)	3.4–4.4	72.8 (49.6)	42.8 (25.1)
3–4	124.4 (59.1)	47.1 (33.0)	5.4–6.4	54.9 (26.2)	55.3 (34.1)
5–6	68.1 (66.4)	25.8 (21.5)	7.4–8.4	62.7 (11.7)	23.3 (9.3)
7–8	45.4 (34.2)	14.4 (5.9)	9.4–10.4	46.3 (9.6)	16.2 (6.5)
<i>Aspen, Boulder Creek, Moderate^b Fire Severity, 1.6 cm Burned</i>					
s.s. ^a	unburned	unburned	0–1.6	soil loss	soil loss
0–1	22.7 (3.5)	13.0 (3.6)	1.6–2.6	7.0	5.8
1–2	21.8 (3.3)	11.0 (1.8)	2.6–3.6	8.2	5.9
3–4	26.1 (5.7)	12.4 (2.6)	4.6–5.6	6.9	7.6
5–6	26.5 (2.7)	12.0 (2.2)	6.6–7.6	16.3	10.4
7–8	19.5 (5.0)	9.1 (1.2)	8.6–9.6	23.4	19.4
<i>Aspen, Green Knoll, Low Fire Severity, 1.4 cm Burned</i>					
s.s. ^a	unburned	unburned	0–1.4	soil loss	soil loss
0–1	37.5 (11.5)	34.5 (15.3)	1.4–2.4	40.7 (4.0)	25.0 (7.4)
1–2	33.3 (10.5)	25.3 (10.9)	2.4–3.4	39.5 (0.8)	24.4 (1.9)
3–4	39.2 (12.4)	23.6 (9.2)	4.4–5.4	33.7 (4.0)	19.3 (6.0)
5–6	35.4 (10.0)	22.1 (8.8)	6.4–7.4	33.6 (3.5)	15.5 (4.2)
7–8	37.7 (12.7)	23.3 (9.2)	8.4–9.4	23.8 (1.7)	12.3 (3.0)
<i>Meadow, Boulder Creek, 1.1 cm Burned</i>					
s.s. ^a	unburned	unburned	0–1.1	soil loss	soil loss
0–1	34.2 (13.8)	19.2 (10.4)	1.1–2.1	21.6 (13.6)	8.1 (3.8)
1–2	35.0 (12.1)	17.0 (7.8)	2.1–3.1	23.2 (13.6)	4.5 (3.4)
3–4	36.4 (11.9)	16.3 (8.2)	4.1–5.1	20.9 (10.4)	5.6 (1.2)
5–6	38.3 (12.2)	15.6 (8.3)	6.1–7.1	17.2 (9.9)	6.1 (1.3)
7–8	38.6 (12.2)	14.9 (7.6)	8.1–9.1	18.6 (3.8)	6.4 (0.6)
<i>Meadow, Green Knoll, 1.3 cm Burned</i>					
s.s. ^a	unburned	unburned	0–1.3	soil loss	soil loss
0–1	25.2 (5.4)	18.6 (6.7)	1.3–2.3	26.1 (5.9)	14.8 (5.9)
1–2	25.2 (3.7)	14.4 (1.4)	2.3–3.3	22.5 (2.1)	12.3 (3.7)
3–4	24.2 (1.0)	13.3 (1.5)	4.3–5.3	21.6 (3.0)	10.9 (1.9)
5–6	23.6 (1.2)	13.1 (2.8)	6.3–7.3	15.6 (2.0)	10.0 (1.0)
7–8	23.7 (1.1)	13.9 (4.3)	8.3–9.3	16.8 (6.0)	9.1 (0.4)

^aHere s.s. denotes soil surface.^bOnly one core collected.

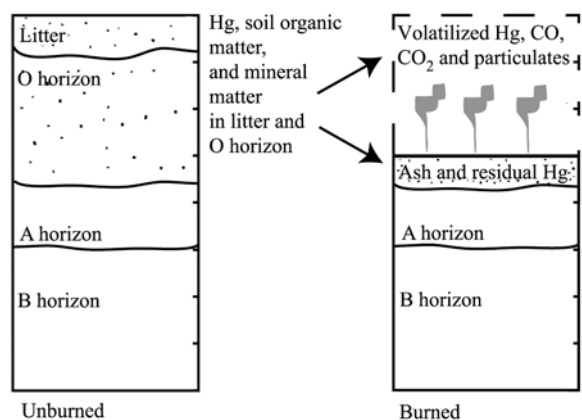


Figure 4. Schematic of mercury and soil organic matter volatilization from soil profile during fires. During combustion, Hg in the litter and O horizon is partitioned between elemental and particulate Hg in the atmosphere and the residual ash and char on the burned soil surface. Mineral matter in ash is a combination of mineral matter in the unburned litter and O horizon.

[13] The pyrolysis method used for Hg analysis is similar to the mercury-thermo-desorption (MTD) technique of *Biester et al.* [2002] and *Biester and Nehrke* [1997] who demonstrated that organic-bound Hg and mineral-bound Hg are thermally desorbed at different temperatures during heating. In our study, the unburned and burned soils consistently released a single peak of Hg during heating that was similar to the MTD profile of organic-bound Hg from *Biester et al.* [2002]. In both unburned and burned soils, the onset of Hg release was typically $\sim 180^{\circ}\text{C}$ and the peak of Hg release was $\sim 320^{\circ}\text{C}$ (Figure 3). This finding applies to $>99\%$ of our samples and indicates that the Hg released from these unburned and burned soils is predominantly in an organic-bound form.

[14] Having established that pyrolysis (heating soils to 750°C) resulted in complete Hg release from soils, we conducted heating experiments to more precisely establish the time-temperature regime necessary to accomplish complete release of Hg from soils during combustion. Heating soils for 1 hr at 180°C released $<10\%$ of the Hg, while heating the samples at 320°C for 4 hrs released $>95\%$ of the Hg (leaving $<1\text{ ng Hg g}^{-1}$ in the ash). Intermediate heating of the samples at 180°C for 4 hrs and 320°C for 1 hour released 56% and 91%, respectively, of the Hg stored in the soil (Figure 3). Thus the 750°C heating procedure employed for Hg analysis during this study was demonstrated to completely release the Hg stored in soil samples.

2.4. Calculation of Soil Volatilization During Burning

[15] The amount of soil volatilized during burning was quantified following the method of *Turetsky and Wieder* [2001] (Table 1). For each vegetation plot at each site, we quantified the average mass of mineral matter on the burned soil surface by multiplying the mass of the 0 to 1 cm depth soil increment by the percent mineral content. The ash on the burned soil surface represents an accumulation of the

mineral matter stored in the overlying soil organic horizons prior to burning. At the corresponding unburned vegetation plot at each site, we quantified the average mass of mineral matter in each 1 cm soil increment from the unburned soil surface. On the basis of the amount of mineral matter on the burned soil surface we determined the thickness of the organic horizons that would have had to burn in order to produce the amount of mineral matter observed on the burned soil surface (Figure 4).

2.5. Statistical Analyses and Calculation of Mercury Loss From Soil

[16] We quantified the total soil Hg (Hg_T) over a 0–8 cm soil depth in conifer, aspen, and meadow study plots at each unburned and burned site in units of g Hg ha^{-1} by the equation

$$\text{Hg}_T^{\text{Plot, Site}} = \sum_{0-8} M^{\text{Plot, Site}} * \text{Hg}^{\text{Plot, Site}} * 10^8 \text{ cm}^2 \text{ ha}^{-1}, \quad (1)$$

where M is the density (g cm^{-3}) (provided in auxiliary Table S1¹) and Hg is the concentration (ng Hg g^{-1} dry wt.) for each 1 cm of the soil profile. In soil increments where M and Hg were not measured directly, the values were assumed to follow a linear trend between the bounding depths. We determined Hg_T in study plots at burned sites by the same method as at unburned sites, though with consideration of the depth of soil that was volatilized during burning (as calculated in section 2.4) to ensure that the equivalent prefire Hg pool in the 0–8 cm upper soil layer was compared both before and after burning.

[17] The release of Hg from conifer, aspen, and meadow soils burned during wildfires was quantified for different fire severities. The wildfire-induced Hg release (Hg_R) for each vegetation type, during fires of different severities, was defined as the difference in total soil Hg from 0–8 cm (Hg_T) between a burned study plot (with depth adjusted to include consideration of the soil volatilized during burning) and its corresponding unburned control study plot as

$$\text{Hg}_R^{\text{Plot, Site}} = \text{Hg}_T^{(\text{Unburned})\text{Site, Plot}} - \text{Hg}_T^{(\text{Burned})\text{Site, Plot}}. \quad (2)$$

[18] A two-way analysis of variance (ANOVA) was used to test the effect of vegetation type and burning on the amount of soil Hg_T . In this model, vegetation type and burning were fixed effects, and we used the interaction of these two factors to determine whether burning had a vegetation-type-specific effect on soil Hg_T . This analysis was also used to determine whether vegetation type, burning, and their interaction (vegetation type \times burn) exerted a significant influence on soil Hg concentration at measured depths of 0 to 1, 1 to 2, 3 to 4, 5 to 6 and 7 to 8 cm below the sampled soil surface. Treatment and interaction mean concentrations were compared using a protected Fisher's least significant difference (LSD) test, with significance

¹Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/gb/2006gb002696>. Other auxiliary material files are in the HTML.

Table 2. Mercury Accumulation and Hg Release During Wildfires

Vegetation Plot	Site ^a	Hg _T at Unburned Sites ^b	Observed Fire severity	Hg _T at Burned Sites ^b	Hg _{GR} ^b	%Hg _{GR}
Conifer	BC	30.6	high	7.5	23.1	75.4
Conifer	GK	31.7	high	4.2	27.5	86.7
Conifer	ET	33.2	moderate	12.6	20.6	62
Conifer	ET	33.2	low	25.8	7.4	22.3
Aspen	BC	20.4	moderate	7.5	12.9	63.1
Aspen	GK	20.9	low	17.3	3.6	17.2
Meadow	BC	34.8	unknown	11.8	23.0	66.1
Meadow	GK	13.9	unknown	9.8	4.1	29.3

^aBC, Boulder Creek; GK, Green Knoll; ET, East Table.

^bUnits are g Hg ha⁻¹.

accepted at $\alpha = 0.1$ to account for the heterogeneity in Hg accumulation in forest soils.

3. Results

3.1. Soil and Foliar Mercury Concentrations (in Unburned and Burned Vegetation Plots)

3.1.1. Unburned Study Plots

[19] Foliage samples collected from Douglas fir at the Boulder Creek site had an average Hg concentration of 24.4 ng Hg g⁻¹ with a range of 18.6 to 38.5 ng Hg g⁻¹ ($n = 6$). Mercury concentrations of BC aspen foliage had an average of 17.3 ng Hg g⁻¹ with a range of 14.8 to 18.9 ng Hg g⁻¹ ($n = 4$). Foliage samples were not collected in meadow plots, as the dominant vegetation consisted only of grasses and low-lying shrubs with minimal biomass.

[20] High depth resolution analyses of soil profile samples (1 cm soil increments) indicated that in unburned conifer, aspen, and meadow plots, Hg concentrations increased with depth through the organic (O) horizon (down to ~2–4 cm) and then decreased with depth through the mineral soil (Table 1). Among the three conifer plots Hg concentrations in the O horizon (0–4 cm) had an average concentration of 108 ng Hg g⁻¹ and a range of 58.4 to 208 ng Hg g⁻¹. The highest concentration observed in a single sample was 510 ng Hg g⁻¹. In conifer plots Hg concentrations in soils from 5 to 8 cm averaged 40.5 ng Hg g⁻¹ and had a range of 30.9 to 68.1 ng Hg g⁻¹. In aspen and meadow plots, the average Hg concentration in the O horizon (0–2 cm) was 31.7 ng Hg g⁻¹ with a range of 25.2 to 37.5 ng Hg g⁻¹. Mercury concentrations of deeper soil increments, down to 8 cm, were on average 33.0 ng Hg g⁻¹ and had a range of 19.5 to 39.2 ng Hg g⁻¹.

3.1.2. Burned Study Plots

[21] Mercury concentrations of soil profile increments at burned sites were lower relative to unburned sites for the same vegetation type (Table 1) when comparing the same measured depths. The conifer study plots at burned sites were subjected to low, medium, or high fire severities, which is reflected in the wide ranges of Hg concentrations in conifer soil profiles. Among conifer plots, Hg concentrations of the upper soils (0–4 cm measured depth) at burned sites were on average 53.5 ng Hg g⁻¹, and a ranged from 14.0 to 72.8 ng Hg g⁻¹. In deeper soils, the average Hg concentration was 35.9 ng Hg g⁻¹ with a range of 12.4 to 62.7 ng Hg g⁻¹.

[22] At burned sites, aspen study plots were subjected to low or moderate fire severity, while the fire severity at meadow plots was difficult to determine. Surface soils (0–2 cm depth) at burned aspen and meadow plots had an average Hg concentration of 28.9 ng Hg g⁻¹, with a range of 21.6 to 40.8 ng Hg g⁻¹, which was slightly lower than at unburned sites. In deeper soil increments from 3 to 8 cm measured depth, the average Hg concentration was 22.4 ng Hg g⁻¹ with a range of 15.6 to 33.7, which again was lower than observed at unburned sites. In general, burned aspen and meadow study were characterized by similar Hg concentrations and ranges through the soil profiles (from 0 to 8 cm measured depth).

3.2. Relationship Between Soil Hg and SOM

[23] Among unburned conifer, aspen, and meadow study plots, SOM was significantly higher in conifer plots than in aspen and meadow plots at depths of 0–1, 1–2, and 3–4 cm. In conifer plots, %SOM decreased with depth at unburned sites (Table 1) and was only weakly correlated with Hg concentrations ($R^2 = 0.13$, $p = 0.18$, $n = 55$). At unburned sites, conifer soil increments with >30% SOM had Hg concentrations between 55 and 208 ng Hg g⁻¹, while increments with <30% SOM had Hg concentrations in the range of 30 to 70 ng Hg g⁻¹. In aspen and meadow plots at unburned sites, SOM was observed to decrease with depth and was strongly correlated ($R^2 = 0.46$, $p < 0.05$, $n = 45$) to soil Hg concentrations.

[24] At burned sites, Hg concentrations of soil profile samples generally decreased with measured depth from the soil surface and were lower than Hg concentrations of soil increments from plots of the same vegetation type at unburned sites. In conifer plots at burned sites, %SOM did not appear to decrease with depth and was correlated to Hg concentrations ($R^2 = 0.59$, $p < 0.05$, $n = 50$). At burned sites, conifer soil increments with >30% SOM had Hg concentrations between 40.6 and 72.8 ng Hg g⁻¹, while soil increments with <30% SOM were in the range of 4.0 to 62.7 ng Hg g⁻¹. At measured depths of 0–1, 1–2, and 3–4 cm, the SOM of samples from burned sites was significantly lower than samples from unburned sites. In aspen and meadow plots at burned sites SOM of soil increments was observed to decrease with depth and was well correlated to soil Hg concentration ($R^2 = 0.69$, $p < 0.05$, $n = 40$). Aspen and meadow soil samples from burned sites had consistently lower SOM than soils from unburned sites.

3.3. Total Soil Mercury in Study Plots

3.3.1. Unburned Sites

[25] Total soil Hg (Hg_T) at each study plot, summarized in Table 2, is consistent with soil Hg pools following a trend of conifer > aspen > meadow. Unburned study plots also have Hg stored in the forest canopy that would be susceptible to volatilization during wildfires. We estimated the Hg content of the overlying canopy by multiplying the estimated mass of the foliage by the average Hg concentration for analyzed foliage. The potential contribution from the combustion of wood and xylem sap determined by Bishop *et al.* [1998] and Fleck *et al.* [1999] is minor relative to the forest canopy and soil studied here and thus was not considered significant.

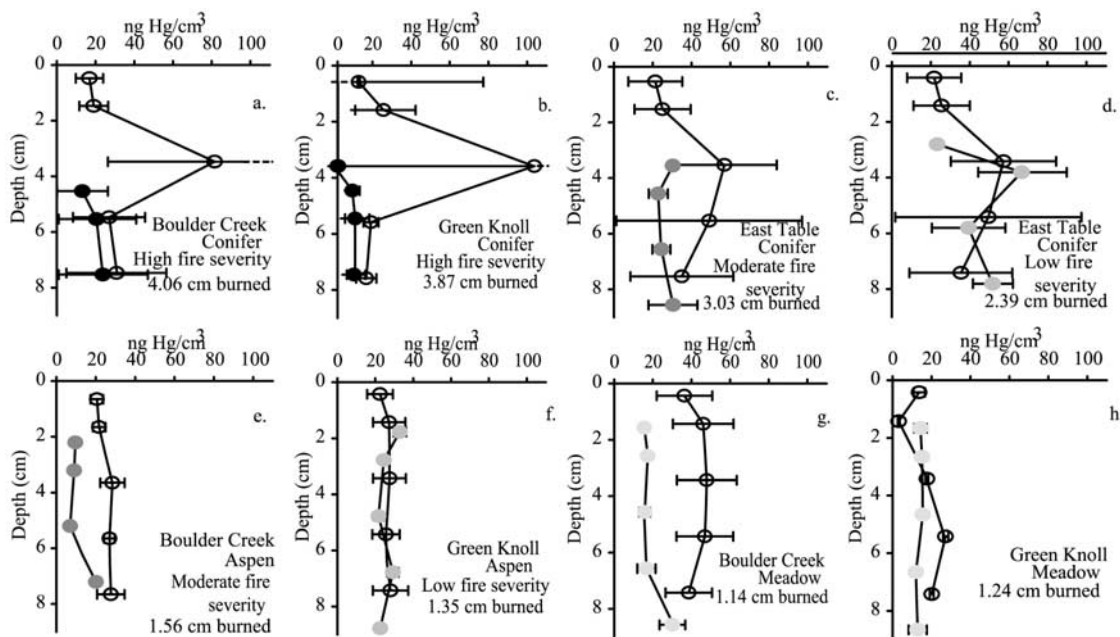


Figure 5. Total soil Hg at unburned and burned sites (open circles, unburned sites; solid symbols, burned sites) calculated as $M^{\text{Plot, Site}} * Hg^{\text{Plot, Site}}$ based on data in Table 1, auxiliary Table S1 ($M^{\text{Plot, Site}}$), and depth adjusted for soil burning.

[26] The conifer plots had dense canopy cover and high stem density at all three sites. The mass of foliage covering a given area was estimated using two approaches: (1) an estimate based on work by *Monserud and Marshall* [1999] for a Douglas fir and Ponderosa pine-dominated forest; and (2) an allometric equation from *Wang et al.* [2000] for subalpine fir foliar mass ($\text{Foliage (g)} = 0.504 * \text{DBH}^{1.779}$, where $\text{DBH} = 300 \text{ mm}$). Using an observed stem density of approximately 600 trees per hectare, these two approaches lead to estimates of $8.1 \times 10^6 \text{ g foliage ha}^{-1}$ and $15.3 \times 10^6 \text{ g foliage ha}^{-1}$ respectively. An average conifer foliage Hg concentration of $24.4 \text{ ng Hg g}^{-1}$ (BC-U, WY) was used to represent the average foliar Hg concentration of conifers in this region. Combining the conifer foliar mass limits and the approximate average foliar Hg concentration we estimated total foliar Hg of 0.2 g Hg ha^{-1} and 0.4 g Hg ha^{-1} which comprises only 1% of the earlier calculation of $\sim 30 \text{ g Hg ha}^{-1}$ for total soil Hg in conifer plots.

[27] In the aspen plots sampled during this study, the canopy cover was very sparse owing to low stem density at both the ~ 75 year old BC stand and the ~ 130 year old GK stand. We estimated aspen foliar mass using an allometric equation based on tree diameter at breast height (DBH) from *Freedman et al.* [1982] and *Wang et al.* [2002] for trembling aspen ($\ln(\text{Foliage (kg)}) = -4.0359 + 1.6093 * \ln(\text{DBH})$, where $\text{DBH} = 15 \text{ cm}$ at BC; $\text{DBH} = 25 \text{ cm}$ at GK). Considering both sites, and based on an observed stem density of approximately 20 stems per 0.1 hectare, we estimate a foliar mass of 0.3 to $0.6 \times 10^6 \text{ g foliage ha}^{-1}$. On the basis of an average aspen foliar Hg concentration of $17.3 \text{ ng Hg g}^{-1}$ (BC-U), aspen foliage

stored 5.2 to $10.4 \text{ mg Hg ha}^{-1}$ which is insignificant compared to the Hg stored in the underlying soil profile.

[28] In meadow plots a canopy contribution was not calculated because the soil profile was the only significant Hg reservoir. During sampling, it was not possible to establish meadow plots far enough from conifers to prevent windblown inputs of vegetation, particularly at the BC site where meadow plots were only a distance of one average tree height away from coniferous stands. The BC meadow plots had elevated values of Hg_T uncharacteristic of Hg accumulation in meadows and thus were excluded from calculated averages for this vegetation type.

3.3.2. Burned Sites

[29] Among burned conifer plots, Hg_T was 7.5 g Hg ha^{-1} at BC, 4.2 g Hg ha^{-1} at GK, and $12.6 \text{ g Hg ha}^{-1}$ at ET. In burned aspen plots, Hg_T was 7.5 g Hg ha^{-1} at BC and $17.3 \text{ g Hg ha}^{-1}$ at GK. In burned meadow plots, Hg_T was $11.8 \text{ g Hg ha}^{-1}$ at BC and 9.8 g Hg ha^{-1} at GK (Table 2). Mercury release (Hg_R) data agrees with the trend in Hg pools of conifer > aspen > meadow indicating that areas which accumulate more Hg also release more Hg during fires.

3.4. Mercury Release During Wildfires and Consideration of the Effects of Fire Severity

[30] We calculated the percent Hg release from study plots at unburned and burned site pairs as

$$\%Hg_R^{\text{Plot, Site}} = Hg_R^{\text{Plot, Site}} / Hg_T^{(\text{Unburned})\text{Plot, Site}} \quad (3)$$

to provide a direct comparison of Hg release relative to Hg accumulation prior to burning.

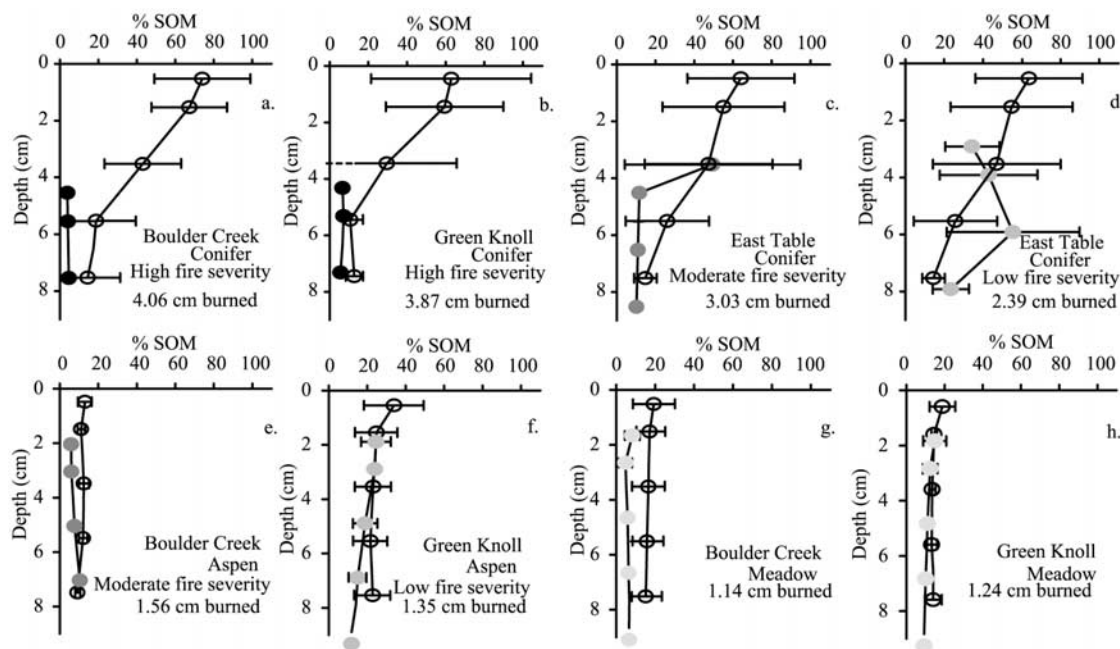


Figure 6. Total % SOM (soil organic matter) at unburned and burned sites (open circles, unburned sites; solid symbols, burned sites) based on data in Table 1 and using depth adjusted for soil burning.

3.4.1. Conifer Vegetation Plots

[31] The calculated %Hg_R values of 75.4 and 86.7% in conifer plots at the BC and GK sites, which correspond to releases of 27.5 and 23.1 g Hg ha⁻¹, are consistent with the high fire severity observed at the respective burned sites. The lower %Hg_R values of 22.3% and 62.0% found at the ET conifer plots, which correspond to releases of 7.4 and 20.6 g Hg ha⁻¹, are consistent with the low and moderate burn severities observed at the sites (Table 2 and Figures 5, 6, and 7).

3.4.2. Aspen and Meadow Study Plots

[32] Aspen vegetation plots examined during this study tended to have lower %Hg_R values than conifer plots. At BC and GK respectively, the calculated %Hg_R values of 63.1% and 17.2%, corresponded to Hg releases of 23.0 and 4.1 g Hg ha⁻¹, and were consistent with the moderate and low fire severities observed. Burned meadow plots likewise tended to have lower %Hg_R values than conifer plots. At BC and GK, the calculated %Hg_R values of 66.1% and 29.3% correspond to Hg releases of 12.9 and 3.6 g Hg ha⁻¹ respectively. The elevated %Hg_R for the BC meadow is attributed to elevated Hg accumulation (associated with conifer inputs) at the unburned site.

3.4.3. Consideration of the Effects of Fire Severity

[33] This study was designed to quantify the effects of fire severity on Hg release. The results clearly demonstrate that the burning of SOM and vegetation releases the majority of organic-bound Hg into the atmosphere. The amount of Hg released varied among the three fires studied and by vegetation type at each fire. Fire severity appeared to play an important role in the amount of stored Hg that was released (Figure 7). In all cases, the Hg release was lower

than the ~100% efficiency estimated from laboratory foliage and litter combustion studies [Friedli *et al.*, 2001] (Table 2).

3.5. Statistical Analysis of Hg_T Data From Burned and Unburned Locations

3.5.1. Hg Concentrations and SOM

[34] Using a two-way ANOVA we determined that vegetation type, burning and their interaction (vegetation type × burn) exerted a significant influence ($p < 0.1$) on soil Hg concentration at depths of 0–1, 1–2, and 3–4 cm. A protected Fisher's LSD test indicated that the high soil Hg concentrations in unburned conifer vegetation type soils drove the significance of our findings. Vegetation type, burning, and their interaction did not have a significant

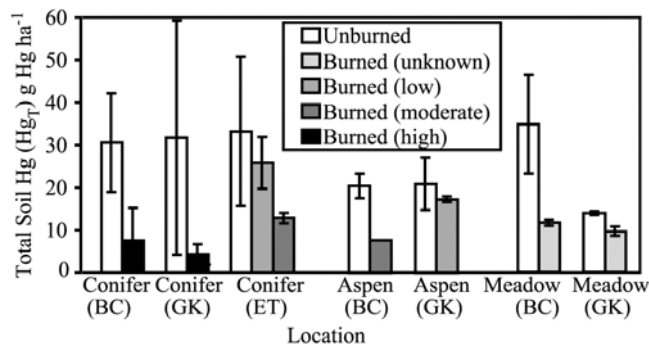


Figure 7. Total soil mercury pool (g Hg ha⁻¹) of paired unburned and burned sites (BC, Boulder Creek; GK, Green Knoll; ET, East Table).

Table 3. Two-Way ANOVA Assessing the Effects of Vegetation Type (Conifer, Aspen, and Meadow), Burn Status (Unburned, Burned), and the Interaction of Vegetation Type Times Burn Status on Hg in Soil Profiles

Hg Concentrations With Depth	Vegetation Type		Burn Status		Vegetation Type Times Burn Status	
	F	Pr > F	F	Pr > F	F	Pr > F
	0–1 cm	3.97	0.06	9.26	0.02	3.64
1–2 cm	9.21	0.01	19.9	0	9.36	0.008
3–4 cm	9.17	0.01	20.8	0	9.53	0.008
5–6 cm	0.86	0.46	4.44	0.07	0.37	0.7
7–8 cm	0.73	0.51	1.94	0.2	0.19	0.83

influence on soil Hg concentrations at depths of 5–6 and 7–8 cm (Table 3).

3.5.2. Total Soil Hg and Hg Release

[35] A two-way ANOVA revealed that burning exerted a significant influence on soil Hg_T across vegetation type ($p < 0.05$). However, owing to our limited sampling size this analysis did not indicate that vegetation type or the interaction between vegetation type and burning had a significant influence on soil Hg_T . We were also unable to statistically distinguish between the different fire severities owing to the small number of sample cores for each fire severity. At BC and ET conifer plots (which were burned at high and moderate severity respectively) and at BC and GK meadow sites (which were burned at low fire severity) the difference between the average soil Hg_T values at unburned vs. burned plots is greater than the sum of the respective standard deviations (Figure 7). Notwithstanding the small sample size of soil cores burned at different fire severities, our data suggest that there is a relationship between fire severity and Hg release during fires.

[36] We observed very strong correlations between observed fire severity and Hg_R and observed fire severity and $\%Hg_R$, both of which supported our premise that increased fire severity resulted in increased Hg release (Figures 8a and 8c). We also examined the correlation between SOM and Hg release. The calculation of SOM release from the ET low severity fire returned a slightly negative value (which we interpret as reflecting heterogeneous carbon accumulation and release), which we treat as zero SOM release. The correlations observed between SOM release and Hg_R ($R^2 = 0.47$, $p = 0.1$) and SOM release and $\%Hg_R$ ($R^2 = 0.45$, $p = 0.1$) were reasonable given that these were natural samples, while the scatter of the data reflect the heterogeneity in Hg and carbon accumulation in forests (Figures 8b and 8d).

4. Discussion

4.1. Hg Accumulation and Release by Fires in the Rocky Mountains

[37] Four previous studies have systematically quantified Hg concentrations in soil profiles. *Engle et al.* [2006], *Amirbahman et al.* [2004], *Munthe et al.* [1998], and *Schwesig and Matzner* [2000] reported values of 1.0–6.6, 12, 120, and 115.8 $g\ Hg\ ha^{-1}$ respectively for the organic horizon of conifer forest soils; and values of 35–84, 183, 280, and 891 $g\ Hg\ ha^{-1}$ respectively for entire soil profiles.

In deciduous forest soils, *Amirbahman et al.* [2004] and *Schwesig and Matzner* [2000] reported values of 5 $g\ Hg\ ha^{-1}$ and 9.7 $g\ Hg\ ha^{-1}$ for the organic horizon and values of 133 and 193 $g\ Hg\ ha^{-1}$ for the entire soil profile. The differences in Hg_T values among these studies are related to variations in the tree species present, the forest age, atmospheric Hg inputs, and the depths of soil over which Hg_T is calculated in each study; in general they are consistent with our finding that coniferous forests accumulate more Hg than deciduous forests.

[38] At unburned sites we observed an increase with depth in soil Hg from the surface to a maximum in the zone of humus accumulation that was consistent with other investigations conducted in similar settings [*Amirbahman et al.*, 2004; *Munthe et al.*, 1998; *Schwesig et al.*, 1999; *Schwesig and Matzner*, 2000]. Similar patterns have been attributed to the formation of complexes between atmospherically deposited Hg and soluble organic species and their migration downward in the soil column [*Biester et al.*, 2002; *Schuster*, 1991; *Shotyky et al.*, 2003]. Decomposition of SOM at depth can lead to the concentration of Hg, similar to the process of lead concentration in forest soils [*Miller and Friedland*, 1994]. The relatively lower soil Hg at the surface may also reflect the recent decline in Hg deposition to this region [*Schuster et al.*, 2002].

[39] Our data indicate that wildfire-associated Hg and SOM release during these fires extended to only ~6–8 cm depth; consistent with previous estimates in the literature [*Oakley et al.*, 2003; *Preisler et al.*, 2000]. This suggests that deeper soil horizons may act as Hg reservoirs on a timescale longer than the fire frequency in this region. However, soil heating can extend much deeper into the soil in instances of longer fire duration. For example, a smoldering fire in duff can impact soil to a depth of 40–50 cm

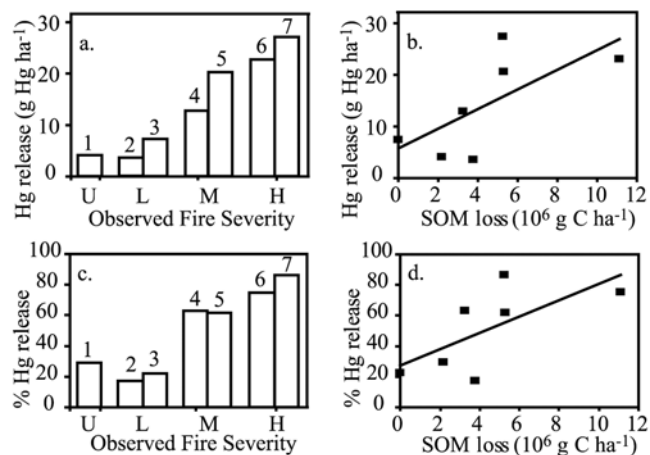


Figure 8. Hg release (Hg_R , $g\ Hg\ ha^{-1}$) during wildfires as a function of (a) observed fire severity (U, unknown; L, low; M, moderate; H, high) and (b) SOM (soil organic matter) loss, and $\%Hg_R$ as a function of (c) observed fire severity and (d) SOM loss. In Figures 8a and 8c, columns are labeled as follows: 1, GK meadow; 2, GK aspen; 3, ET conifer; 4, BC aspen; 5, ET conifer; 6, BC conifer; 7, GK conifer.

Table 4. Summary of Hg Emission Estimates From Fires in the United States

Study Location	Fire Type	Hg Emission Estimate, g Hg ha ⁻¹	Reference
Wyoming conifer forest	wildfire	7.4–25.3	this study
Wyoming deciduous forest	wildfire	3.6–12.9	this study
Wyoming meadow	wildfire	4.1	this study
California conifer forest	prescribed	2.0–5.1	Engle <i>et al.</i> [2006]
Nevada conifer forest	wildfire	2.2–4.9	Engle <i>et al.</i> [2006]
Nevada desert sagebrush	wildfire	0.36 ± 0.13	Engle <i>et al.</i> [2006]
Alaska boreal forest	prescribed	2 ± 2	Harden <i>et al.</i> [2004]
Quebec boreal forest	wildfire	1.5	Sigler <i>et al.</i> [2003]
Washington state conifer forest	wildfire	2.9 ± 1.1	Friedli <i>et al.</i> [2003b]

owing to the combination of heat generated by duff combustion and insulation provided by the overlying ash layer [DeBano *et al.*, 1998]. Because the soil Hg reservoir is greater than the foliar Hg reservoir, surface fires are of greater concern for Hg release than canopy fires. Thus fire intensity, which tends to be elevated during canopy fires, may be less indicative of the degree of Hg release than fire severity, which is elevated when the soil Hg reservoir has been burned.

[40] The results of this study have notable implications for forest management. Forest fuel accumulation in the United States, which has been attributed to fire suppression as well as a shift in climate [Millspaugh *et al.*, 2000; Murray *et al.*, 1998; Pierce *et al.*, 2004], has likely enlarged the soil Hg reservoir and may potentially influence annual Hg release. The abundance of surface fuels and the prevalence of droughts increase the likelihood of soil burning, which can result in increased Hg release. Prescribed fires designed to reduce fuel loads may decrease the occurrence of high severity (high Hg release) fires in the near future.

4.2. Comparison to Other Methods of Estimating Hg Release by Fires

[41] Using a paired unburned-burned sampling site method and considering fire severity, we estimate that conifer wildfires release 7.4 to 25.3 g Hg ha⁻¹ (low to high fire severity); aspen wildfires release 3.6 to 12.7 g Hg ha⁻¹ (low to moderate fire severity); and meadow fires release 4.1 g Hg ha⁻¹ (low fire severity). Harden *et al.* [2004] applied a similar technique and estimated a Hg release of 2 ± 2 g Hg ha⁻¹ for a prescribed burn of a boreal black spruce forest in Alaska. The large uncertainty in their estimate reflects considerable heterogeneity in Hg_T values at the burned and unburned areas they investigated. Engle *et al.* [2006] used total soil Hg to estimate that a desert sagebrush fire released 0.36 (±0.13) g Hg ha⁻¹, a prescribed conifer fire released 2.0 to 5.1 g Hg ha⁻¹ and a conifer wildfire released 2.2 to 4.9 g Hg ha⁻¹ (Table 4). The results from our study area generally agree with previous estimates, but suggest the possibility of greater Hg release during some wildfires.

[42] Another approach employed to estimate Hg emissions from wildfires (referred to here as the Hg:CO method)

uses atmospheric measurements of Hg and CO in smoke to determine an emission factor relating the mass of Hg released to the mass of fuel consumed. Friedli *et al.* [2003b] estimated that the Rex Creek (RC) fire, a low-intensity conifer forest fire in Washington and Oregon, released 2.9 (±1.1) g Hg ha⁻¹ on average, and Sigler *et al.* [2003] estimated boreal forest fires in Quebec, Canada, released 1.5 g Hg ha⁻¹ (Table 4). Both the soil method (this study) and the Hg:CO method provide estimates of the amount of Hg volatilized per unit area from a single burned region. We compared the RC Fire (studied by the Hg-CO method) with the Wyoming fires (studied using our soil-based method), and found that the soil-based estimate for the low-severity Wyoming fires was 2 to 4 times higher than the Hg-CO estimate for the low-intensity RC Fire.

[43] We suggest that the Wyoming forest may have accumulated more Hg prior to burning owing to a longer Hg accumulation period since the last fire, greater atmospheric Hg inputs, or differences in forest species composition. Also, the Wyoming forest fire may have experienced more soil burning than the RC forest fire. An alternate explanation for the differences in Hg release relates to differences in the methodologies employed, namely that (1) the Hg:CO method requires assumptions of combustion efficiency (CE) ($CE = CO_2 / (CO + CO_2)$) and the mass of fuel per unit area, which are known to include significant uncertainties [Friedli *et al.*, 2003b], and (2) the Hg:CO approach samples the fire plumes at altitude using aircraft, and thus this method may not account for Hg that was volatilized as Hg⁰, then adsorbed to fire-derived coarse particles [Ward, 2001] and deposited locally [Mason *et al.*, 1994; Schroeder and Munthe, 1998] (which might result in a measurement of percent particulate Hg (%pHg) measured at altitude that does not accurately represent the %pHg of the total Hg being released from the fire).

[44] Estimates of Hg release from both approaches yield important information. The Hg:CO method has the advantage that the atmospheric sampling spatially averages Hg and CO release from a wildfire during the sampling period and averages the heterogeneity in Hg released from the entire burned area. In contrast, the soil method produces results that reflect the amount and spatial variability of Hg in the different vegetation plots [Harden *et al.*, 2004], Hg concentrations with depth through the soil column, and the degree of volatilization due to fire severity. Differences between estimates of Hg release using these two methodologies suggest the need for intercomparisons between these methods to improve regional and global extrapolations of forest fire Hg release.

4.3. Estimates for Hg Release From Forest Fires and Biomass Burning

[45] The results of this study can be generalized to estimate the Hg release from forest fires over large regions. However, we have shown that one must consider the total burned area and the areal distribution of fire severity, which are quite variable and can be difficult to estimate over broad areas. In the case of fires where the vegetation and fire severity have been documented or estimated, we can factor fire severity into our estimate of Hg release. We used the

Despain *et al.* [1989] fire severity distribution (7% low (meadow areas), 17% low (conifer areas), 35% moderate, and 41% high) for the Yellowstone National Park (YNP) fires of 1988, which occurred 50–150 miles north of the study area, to estimate that the YNP fire released $\sim 6.1 \times 10^6$ g Hg. To extrapolate further and make estimates of areas where fire severity has not been mapped we take a conservative approach and calculate lower and upper limits for Hg release based on our estimates for low and high fire severity. To make an estimate for the entire continental USA, where wildfires annually burn $\sim 2.1 \times 10^6$ ha (average 1995–2004, NIFC), which includes 0.2×10^6 ha of California shrubland [Lavoue *et al.*, 2000], and prescribed fires burn an additional 0.6×10^6 hectares (average 1995–2000, NIFC), we make the assumption that our results of Hg release for conifers (7.4 to 25.3 g Hg ha⁻¹) and meadows (4.1 g Hg ha⁻¹) are reasonable estimates for forests and shrublands. We estimate that wildfires in the USA together release 19 to 64×10^6 g Hg/year which represents between 13 and 42% of the estimated U.S. anthropogenic Hg flux of 150×10^6 g [Environmental Protection Agency, 1997]. On a broader scale, Northern Hemisphere fires annually burn 6.8×10^6 ha of boreal and temperate forests and 2.9×10^6 ha of shrublands and grasslands. This equates to a Hg release of 62 to 184×10^6 g Hg/year which is 2 to 7% of the estimated global natural Hg atmospheric input of 2500×10^6 g Hg/year [Nriagu, 1989]. Other natural sources include volcanoes, biogenic particulates, volatiles of marine and continental origin, soil particles, and sea spray.

[46] Southern Hemisphere biomass burning may also provide a significant source of Hg to the atmosphere, but the area of tropical forests and savannas burned has not been well quantified. Global estimates suggest that fires started by lightning and humans burn 1300×10^6 ha/year and the practice of slash and burn agriculture burns an additional $20\text{--}60 \times 10^6$ ha/year [Crutzen and Andreae, 1990]. Estimates of Hg release are not available for biomass burning in these expansive areas. However, depending on the amount of Hg stored in these regions and the fire severity that occurs, the annual Hg release from total biomass burning may be quite significant compared to the total natural Hg release estimate of 2500×10^6 g Hg/year [Nriagu, 1989].

5. Conclusion

[47] Analyses of total soil Hg in unburned temperate forests dominated by mixed conifer vegetation indicate that total soil Hg pools increase from meadow to aspen to conifer sites. Sites recently burned by wildfires are characterized by significantly lower total soil Hg. Our results indicate that greater fire severity is associated with a greater percentage of soil Hg being released, from 22.3% (low severity) to 81.2% (high severity).

[48] Calculations of total soil Hg at paired unburned and burned sites can be used to estimate that Hg release during fires is 4.1 g Hg ha⁻¹ in meadow areas and 7.4 to 25.3 g Hg ha⁻¹ in conifer areas. Extrapolating to the average area of forest and shrublands burned by wildfires and prescribed burns in the United States, we estimate that 19 to 64×10^6 g of Hg are released annually, which represents 13 and 42%

of the estimated US anthropogenic Hg flux of 150×10^6 g [Environmental Protection Agency, 1997]. On a broader scale, Northern Hemisphere fires burn 9.7×10^6 ha annually, which release an estimated 62 to 184×10^6 g Hg/year and amount to 2 to 7% of the estimated global natural Hg release of 2500×10^6 g Hg/year [Nriagu, 1989].

[49] Fire suppression practices in the USA have caused a buildup of flammable materials, which combined with the legacy of pollution in the 20th century suggests that contemporary fire regimes may result in greater Hg release than historic fire regimes. This study reinforces the importance of wildfires to the global Hg cycle and indicates that forests in the Rocky Mountain region may contain large reservoirs of Hg that can be released during fires, adding to the global Hg budget. Future research should investigate Hg loss from a wider variety of forest (and shrubland) types and climates regimes, and should further evaluate the possibility that estimates of Hg release during fires using the Hg:CO method may underestimate total Hg loss from burned areas. Further comparisons of the soil-based and Hg:CO based methods of estimating Hg loss from forest fires will elucidate the amount of Hg released from forest fires that is deposited regionally versus globally.

[50] **Acknowledgments.** The authors would like to thank T. Jasiak, N. Bielaczyc, P. Ong, B. O'Donnell, P. Knoop, and C. Malvica for their assistance in the field. D. Zak provided invaluable statistical counsel. Two anonymous reviewers helped improve the manuscript. Partial funding was provided by a Turner grant from the University of Michigan to A. B. and by NIEHS grant ES-07373 to J. D. B.

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