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Origin, Reactivity, and Bioavailability of Mercury in Wildfire Ash

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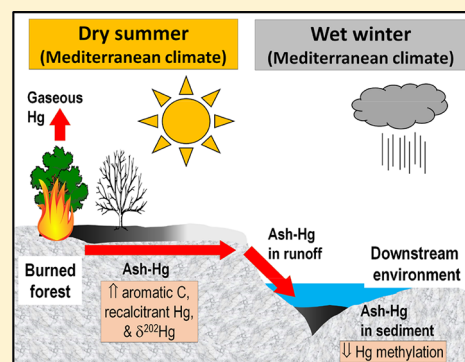
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Supporting Information

ABSTRACT: Wildfires are expected to become more frequent and intensive at the global scale due to climate change. Many studies have focused on the loss of mercury (Hg) from burned forests; however, little is known about the origins, concentration, reactivity, and bioavailability of Hg in residual ash materials in postfire landscapes. We examine Hg levels and reactivity in black ash (BA, low burn intensity) and white ash (WA, high burn intensity) generated from two recent northern California wildfires and document that all ash samples contained measurable, but highly variable, Hg levels ranging from 4 to 125 ng/g dry wt. ($n = 28$). Stable Hg isotopic compositions measured in select ash samples suggest that most Hg in wildfire ash is derived from vegetation. Ash samples had a highly variable fraction of Hg in recalcitrant forms (0–75%), and this recalcitrant Hg pool appears to be associated with the black carbon fraction in ash. Both BA and WA were found to strongly sequester aqueous inorganic Hg but not gaseous elemental Hg under controlled conditions. During anoxic ash incubation with natural surface water, we find that Hg in most ash samples had a minimal release and low methylation potential. Thus, the formation of wildfire ash can sequester Hg into relatively nonbioavailable forms, attenuating the potentially adverse effects of Hg erosion and transport to aquatic environments along with eroded wildfire ash.



INTRODUCTION

Wildfire is an important ecosystem perturbation affecting ~3% of the global vegetated land surface each year.¹ Because of climate change, wildfire is predicted to be more frequent and intense this century in semiarid regions including California, Australia, and the Mediterranean region of Europe.^{2–5} Forest ecosystems not only represent an important sink for atmospheric mercury (Hg), but also are a source of Hg to the environment through biomass burning and runoff.⁶ Wildfire can lead to substantial loss of Hg previously sequestered in vegetation, surficial detritus, and topsoil to the atmosphere, predominantly in the form of gaseous elemental Hg(0).^{7–9}

Despite the prevalence of studies focusing on Hg loss during wildfires, one aspect of wildfire effects on Hg cycling has received very little attention: the concentrations and reactivity of Hg in burned biomass residues (i.e., wildfire ash). To our knowledge, there are only two prior studies reporting Hg levels in wildfire ash. Engle et al.¹⁰ found that ash had 39.2 ng/g of Hg (on a dry mass basis) compared to 91.4 ng/g in unburned forest litter in western Nevada (USA); however, it should be

noted that ash samples were collected almost a year after the wildfire and the results may have been compromised by subsequent rainfall, runoff, and leaching. Campos et al.¹¹ collected wildfire ash 4 weeks after burning from two sites in Portugal that had different burn intensities and found ash with significantly more Hg in areas of moderate burning (112 ng/g) compared to ash in areas with high intensity burning (64 ng/g). In contrast, studies using controlled biomass burning under oxygenated conditions consistently found ash with very low Hg content, ranging from 0.4 to 11.1 ng/g (on a dry mass basis),^{8,12} raising questions regarding the factors controlling the Hg content of wildfire ash.

On the basis of color and percent loss-on-ignition (LOI),^{11,13} wildfire ash can be operationally divided into two major classes: black ash (BA; low intensity fire; 200–500 °C) and white ash (WA; high intensity fire; > 500 °C).¹³ However,

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it should be noted that within each class, ash may consist of a mixture of materials with contrasting mineral and organic matter contents. In essence, BA is generated by incomplete combustion of biomass, while WA is produced by more complete combustion.¹⁴ BA is known to contain appreciable amounts of charcoal or black carbon (BC), while WA generally contains high mineral concentrations that can be dominated by CaCO₃, CaO, or aluminosilicates.^{13,15} As related to Hg cycling, it is essentially unknown how BC in wildfire ash mediates Hg levels, reactivity, and bioavailability. The wildfire ash layer is highly susceptible to runoff-leaching and erosional processes due to the lack of soil cover and the fine powdery nature of the ash materials, thereby resulting in a strong potential for transporting Hg in the wildfire ash to aquatic environments including streams, lakes, and reservoirs.^{16,17} In particular, one area of concern is whether Hg in ash is available for microbial methylation when ash is deposited in anoxic zones, which can serve as biogeochemical hotspots of Hg methylation (e.g., biofilms¹⁸). Methylmercury (MeHg) can form under anoxic conditions¹⁹ and is highly bioaccumulative, thus elevating MeHg levels in downstream biota.²⁰

The overall goal of this study was to provide the first rigorous characterization of Hg in ash by collecting and analyzing ash from two wildfires (Wragg and Rocky Fires) in northern California. Specifically, we examined (i) Hg levels and Hg reactivity using two acid digestion methods as an operationally defined measure of Hg reactivity in ash and compared results with unburned vegetation (i.e., the potential fuel load); (ii) the isotopic composition of Hg in wildfire ash to provide further insights to the origins of Hg in ash; (iii) the capability of wildfire ash to adsorb ambient Hg (both aqueous and gaseous Hg) due to the “higher-than-expected” Hg content in many wildfire ash samples compared to lab-generated ash;^{8,12} and (iv) the bioavailability of Hg released from wildfire ash to methylating microbes to determine whether wildfires might stimulate Hg methylation in downstream aquatic environments.

MATERIALS AND METHODS

Sample Collection. We collected wildfire ash samples 3–5 weeks following two northern California wildfires in the summer of 2015: the Wragg Fire and the Rocky Fire (see site characteristics and specific sampling points in [Supporting Information Table S1](#)). No rainfall occurred between the fire and the sampling, and thus, the ash samples were not eroded or leached by rainfall or runoff.^{10,13} Paired ash samples [i.e., black ash (BA) and white ash (WA) were visually distinguished in the field]²¹ were collected at each site (5 pairs for the Wragg Fire, and 9 pairs for the Rocky Fire). Surface ash samples (generally 0–5 cm) were carefully collected to avoid mixing with underlying soil using a stainless-steel hand shovel and were then placed into a clean polyethylene bag. It should be noted that BA and WA characterization represents the dominant materials visually identified in the field, but they should not be considered pure endmembers as there is significant short-range spatial variability in both the horizontal and vertical dimensions of the ash layer.¹³ At the landscape scale for both sites, we estimated that ~90% of the surface contained BA and ~10% WA, which was a function of local fuel load distribution (e.g., proximity to tree trunks). In general, we expected that the surface materials would be burned at a higher temperature and at more oxygenated conditions than the deeper ash layers leading to inherent

variability within the vertical dimension. Unburned vegetation (twigs and branches) and surface litter were collected as a control from the dominant tree species in unburned areas located adjacent to the fire perimeter (see locations in [Table S1](#)). We present the data for each individual ash sample since there was a large heterogeneity among samples within each ash category (BA or WA; originally considered as replicates).

Ash Characterization and Analyses. All ash samples were dry at the time of collection and therefore did not require further drying in the laboratory. Ash samples were heterogeneous in size, shape, and color of materials (especially BA; see pictures of presieved and 2 mm sieved ash, [Figure S1](#)) and were therefore sieved through a 2 mm acid-cleaned polypropylene mesh and thoroughly homogenized. Unburned litter and dead woody materials were frozen, freeze-dried, and homogenized (<2 mm) using a stainless-steel grinder. All samples were analyzed for color using a Munsell color chart²² (except unburned vegetation materials), and ash color was assigned according to Bodi et al.²³ LOI was determined using a muffle furnace and total calcium (Ca) using an ICP-MS. The chemical composition of organic carbon was characterized using pyrolysis-GC/MS to provide semiquantitative (relative) levels of BC^{24–26} as defined here by the fraction of aromatic hydrocarbon (ArH).¹⁵ It should be noted that the combustion temperature of LOI was set at 500 °C to prevent the loss of dominant inorganic components such as carbonate (e.g., 600–800 °C),²⁷ and thus, we regard LOI as a proxy of organic matter content in the samples. Procedural details of these analyses are found in [SI Text 1](#).

We determined total-Hg concentrations using two digestion methods: Method 1 (reported as [Hg_{method-1}]; targeting organic matter-bound-Hg) used trace-metal grade HNO₃ and H₂O₂ (4:1, v:v) in a 80 °C water bath overnight, and Method 2 (reported as [Hg_{method-2}]; targeting all geochemical pools) used aqua regia (freshly mixed trace-metal grade HNO₃ and HCl, 1:3, v:v). See [SI Text 2](#) for detailed Hg analytical methods. On the basis of previous studies on soils and sediments, digestion methods (e.g., hot HNO₃ and H₂O₂) similar to Method 1 would not result in digestion of charcoal or BC from environmental samples;^{28,29} thus, it may potentially allow us to distinguish Hg bound to organic matter versus Hg bound to BC in ash samples, while Method 2 (aqua regia) is expected to result in digestion of recalcitrant BC from the samples. On the basis of previous sequential extraction studies on Hg, [Hg_{method-1}] includes Hg from all pools except recalcitrant geochemical pools, which include HgS and HgSe, while [Hg_{method-2}] should also include Hg from recalcitrant geochemical pools,^{30,31} but we found no study reporting whether BC-bound Hg belongs to the recalcitrant geochemical pools. On the basis of the above rationale, we operationally defined the “recalcitrant” pool of Hg as

$$\begin{aligned} \text{Recalcitrant Hg (\%)} \\ = [1 - (\text{Hg}_{\text{method-1}}/\text{Hg}_{\text{method-2}})] \times 100 \end{aligned}$$

We compared [Hg_{method-2}] and Hg reactivity in ash samples to unburned biomass samples (collected postburn). To assess the robustness of our approach for estimating Hg reactivity, we included two standard vegetation reference materials (SRMs) and previously characterized litter samples from three reference forests in northern California Coast Range, northern Michigan, and central New Hampshire (see [SI Text 2](#)). We estimated the degree of Hg volatilization from the burned

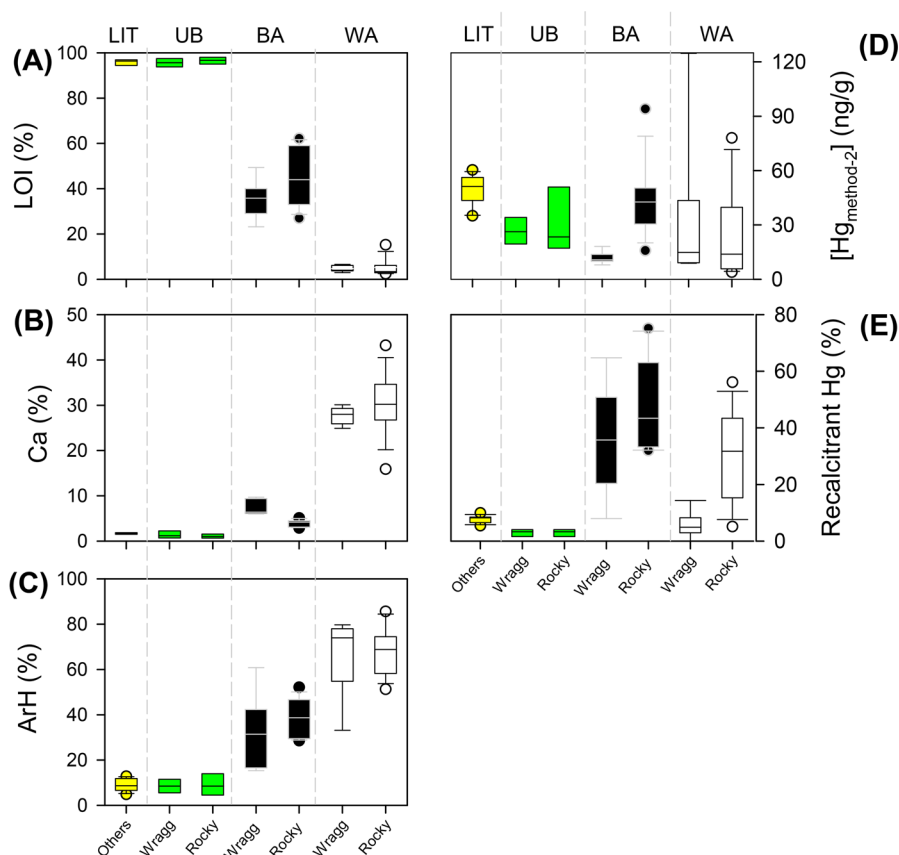


Figure 1. Box plots of (A) loss-on-ignition (LOI), (B) calcium (Ca), (C) pyrolysis products (via Py-GC-MS analysis) as fraction of aromatic hydrocarbon (ArH), (D) Hg concentrations based on digestion method 2, aqua regia ($\text{Hg}_{\text{method-2}}$), and (E) percent recalitrant Hg, in unburned litter (“LIT”) from the three reference forests (“others”) in yellow, litter/wood from the two fire sites (“UB”; in green; $n = 2$ of litter and $n = 2$ of wood per site), black ash (“BA”; in black; $n = 5$ for Wragg, and $n = 9$ for Rocky), and white ash (“WA”; in white; $n = 5$ for Wragg, and $n = 9$ for Rocky).

biomass using a mass balance with LOI and Ca content in the ash (see SI Text 3 for details). Further, we processed 10 ash samples from the Wragg Fire (5 BA and 5 WA) along with litter from the reference forests for stable Hg isotopic composition using a thermal combustion procedure to gain further insights regarding the origins and transformations of Hg in ash (see SI Text 4 for details).

To determine if wildfire ash can adsorb ambient Hg, we used wildfire ash samples from the Wragg Fire to determine the Hg sorption potential of gaseous Hg [as elemental Hg(0)] and aqueous Hg [as inorganic Hg(II)] (see SI Text 5 for details). We also used activated carbon as a reference sorbent for comparison to the ash materials.

To determine the release and potential bioavailability of Hg associated with wildfire ash for microbial methylation, we conducted a sealed incubation experiment similar to Tsui et al.³² by incubating an unburned litter sample from the reference forest in the northern California coast range and BA and WA from both wildfires in natural streamwater for 4 and 12 weeks (see SI Text 6). At the end of the incubation period, aqueous samples were filtered (using prebaked Whatman GF/B filters; 1.0- μm pore size) and analyzed for various physiochemical parameters including the presence or absence of a sulfidic smell (an indicator of anoxic conditions), pH, dissolved organic carbon (DOC), UV absorbance (to calculate $\text{SUVA}_{254\lambda}$, a proxy of DOC aromaticity), total dissolved nitrogen (TDN), dissolved Hg, and dissolved MeHg.

Statistical differences ($p < 0.05$) between two groups were evaluated by student’s t test, and differences between multiple groups were assessed using one-way ANOVA with a posthoc Tukey’s Test. Regression analyses were conducted using SigmaPlot 12.5.

RESULTS AND DISCUSSION

Chemical Properties and Mercury Content of Ash. We found that the LOI value decreased in the order: unburned litter/woody materials ($\sim 95\%$) > BA (23–62%) > WA (3–15%) (Figure 1A) ($p < 0.05$), which was consistent with our expectation of decreasing organic matter content with higher burn intensity.^{11,13} Consistent with other reports,¹⁵ the Ca content in ash was significantly elevated for BA and WA ($p < 0.05$) compared to unburned samples (Figure 1B) and Ca was significantly higher in WA than BA ($p < 0.05$). Black carbon (BC), defined here as the aromatic hydrocarbon (ArH) fraction, decreased in the order: WA > BA > unburned samples ($p < 0.05$; Figure 1C). In general, ArH was negatively and significantly correlated with LOI among ash samples ($p = 0.0013$; Figure S2). These results suggest that increasing burn intensity resulted in ash with a higher proportion of BC, which is consistent with studies that examined water extracts of ash materials.³³

We report Hg concentrations of samples digested with aqua regia (i.e., $[\text{Hg}_{\text{method-2}}]$), as this digestion method releases the most Hg from different geochemical pools.^{30,31,34} Similar to

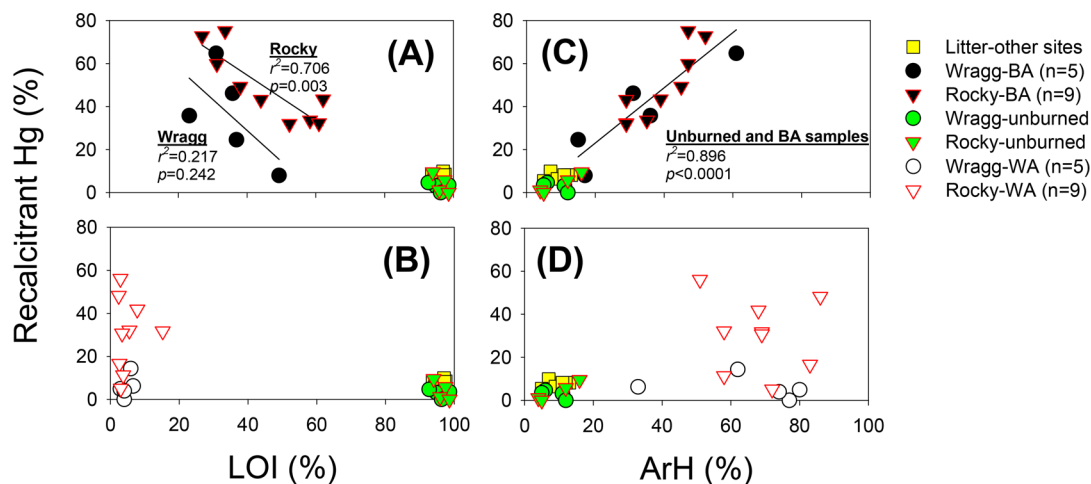


Figure 2. Relationships between loss-on-ignition (LOI) and percent recalcitrant Hg in (A) unburned materials and black ash (BA) and (B) unburned materials and white ash (WA), and relationships between aromatic hydrocarbon (ArH) fraction of pyrolysis products and percent recalcitrant Hg in (C) unburned materials and BA and (D) unburned materials and WA. Unburned samples are litter from three reference forests (as “Others”; in yellow) as well as litter/wood from the two fire sites (in green, different symbols).

vegetation samples across a large geographic gradient in the United States,³⁵ we found only a narrow range of [$\text{Hg}_{\text{method-2}}$] for litter (20.3–40.1 ng/g in study sites; 35.0–57.8 ng/g in reference forests) and dead woody materials (14.6–57.0 ng/g in study sites) (Figure 1D). The [$\text{Hg}_{\text{method-2}}$] among all ashes ranged from 3.9 to 124.6 ng/g ($n = 28$) (Figure 1D), with many samples having [$\text{Hg}_{\text{method-2}}$] higher than ash generated in lab studies.^{8,12} We detected no significant differences in [$\text{Hg}_{\text{method-2}}$] among unburned samples, BA, and WA ($p > 0.05$) (Figure 1D). We found that the pool of “% recalcitrant Hg” averaged 7.6% among all unburned samples tested (Figure 1E; Table S2). In contrast, BA samples had highly variable, but significantly higher, “% recalcitrant Hg” than both unburned and WA samples ($p < 0.05$), while WA samples (Rocky Fire only) had an intermediate-sized pool of “% recalcitrant Hg” (Figure 1E).

The negative relationship (significant for Rocky Fire samples only; $p < 0.05$) between LOI and “% recalcitrant Hg” in BA from both the Wragg and Rocky Fires (Figure 2A) may help explain some variations of Hg reactivity in ash samples. Such relationships between LOI and “% recalcitrant Hg” were absent among WA samples (Figure 2B). For BA samples, we posit that increased burn intensity lowered LOI, and thus, potentially more BC was generated due to limited oxygen availability. It is intriguing that we find a positive linear correlation between ArH and “recalcitrant Hg” among all BA and unburned samples (i.e., $r^2 = 0.896$, $p < 0.001$) (Figure 2C). However, we found no such relationship for WA samples ($p > 0.05$) (Figure 2D).

Apparently wildfire increased the occurrence of benzene-ring containing organic compounds in burned biomass such as the aromatic hydrocarbon (ArH) fraction determined in this study. Aromatic hydrocarbons are known to have a high affinity for trace metals³⁶ as a result of stable pi-complexes between aromatic hydrocarbon ligands and metals.³⁷ Meanwhile, the lack of a relationship between ArH and recalcitrant Hg in WA may be attributed to the fact that the absolute abundance of OC in WA is very low (e.g., assuming half of the LOI is OC). Thus, even WA has a high fraction of ArH (Figure 1C), and the absolute abundance of ArH is still low and has a narrow range of absolute ArH abundance (inferred by small range of

LOI) among WA samples, which may weaken the regression relationship between %ArH and “% recalcitrant Hg” (Figure 2D).

Extent of Hg Volatilization upon Burning. Since Ca was significantly elevated ($p < 0.05$) in BA and WA compared to unburned samples from the Wragg and Rocky Fires, we performed a simple mass balance calculation to estimate Hg volatilization losses from the preburn fuel loads based on LOI and Ca in ash as compared to their unburned counterparts. We assumed a constant LOI of $\sim 95\%$ for the unburned fuels (based on our measured values of unburned materials) and that Ca was conserved during wildfires regardless of temperature and oxygen conditions (see equations in SI Text 3). BA and WA samples from the Wragg Fire (Figure 3 and Table S3)

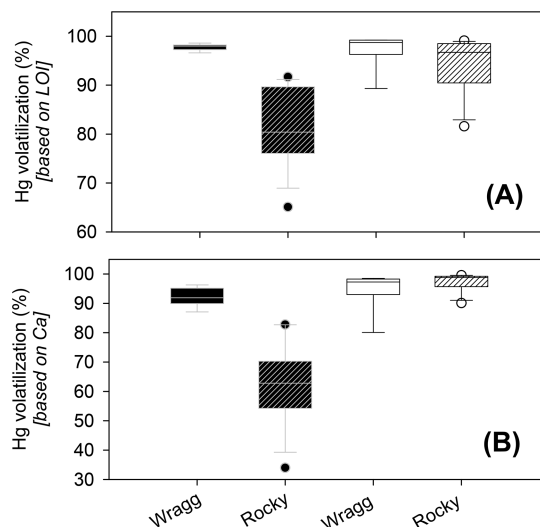


Figure 3. Box plots of estimated mercury (Hg) volatilization from original fuel loads (assumed to be a mixture of litter and dead woody materials) in the Wragg Fire (2015) and the Rocky Fire (2015) based on (A) loss-on-ignition (LOI) and (B) calcium (Ca) content of ash samples. Note: Wragg Fire black ash (in black bars), Wragg Fire white ash (in white bars), Rocky Fire black ash (in hatched black bars), and Rocky Fire white ash (in hatched white bars). See Table S3 for the individual ash data.

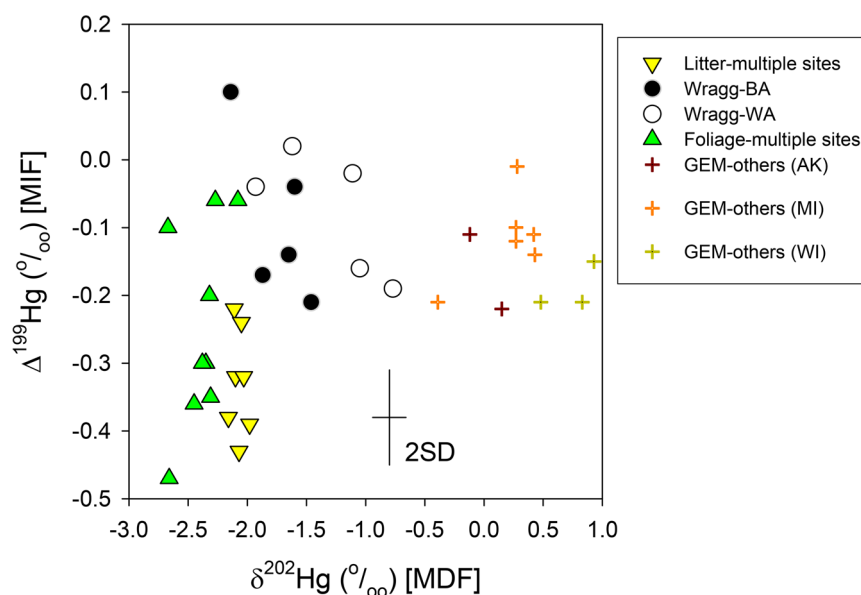


Figure 4. Isotopic composition of mercury (Hg) in unburned forest litter from three reference forests in this study and foliage from Zheng et al.,³⁹ and black ash (BA) and white ash (WA) collected from the Wragg Fire. Data on gaseous elemental mercury (GEM) were obtained from Gratz et al.⁴⁷ for Michigan (MI), Sherman et al.⁴⁸ for Alaska (AK), and Demers et al.⁴⁹ for Wisconsin (WI). Error bars represent the maximum analytical error associated with sample analysis (2SD).

indicated $\geq 80\%$ Hg loss compared to the fuel samples. WA in the Rocky Fire had estimated Hg losses of $\geq 90\%$, but interestingly, BA from the Rocky Fire had a wide range of Hg loss estimates from 34 to 83%. As previously noted, BA samples may contain materials originating from a wide range of fire conditions (temperature and oxygen levels) resulting in a mixture of highly contrasting ash materials in the horizontal and vertical dimensions. These results suggest that fire intensity and burning conditions (i.e., temperature, oxygen availability, and duration) are important in determining Hg volatilization. Although we estimated Hg volatilization in individual samples in the present study, it should be noted that Hg volatilization/emission can be estimated in the field at the landscape level, but this would require the estimation of the total amount of fuel loss.³⁸

Isotopic Composition and Source Analysis of Hg in Ash. Forest litter in the unburned reference forests for this study and foliage from another study³⁹ along a large geographic gradient in North America all show a relatively narrow range of $\delta^{202}\text{Hg}$ (MDF; mass-dependent fractionation) and $\Delta^{199}\text{Hg}$ (MIF; mass-independent fractionation) (Figure 4; Table S4). Since forests receive Hg predominantly from atmospheric deposition, we expect Hg isotopic compositions in the unburned vegetation materials (foliage, litter, and dead wood) to be similar to the MDF and MIF values of our reference sites. Both BA and WA from the Wragg Fire had very different Hg isotopic compositions compared to litter and foliage samples as well as gaseous Hg samples from other studies (Figure 4). Mean $\delta^{202}\text{Hg}$ values (MDF) followed the order: unburned ($-2.25 \pm 0.22 \text{ ‰}$, $n = 16$) < BA ($-1.74 \pm 0.27 \text{ ‰}$, $n = 5$) \approx WA ($-1.30 \pm 0.47 \text{ ‰}$, $n = 5$) (Figure 4). The higher $\delta^{202}\text{Hg}$ values in ash samples are consistent with our expectation that lighter Hg isotopes are preferentially volatilized by fire while the heavier isotopes are concentrated in the residual ash, slightly more so for WA than BA (by an average of 0.44 ‰ , Figure 4). However, it should be noted that there were large variations in $\delta^{202}\text{Hg}$, even within each ash

sample type (WA vs BA), suggesting mixing of partially burned and unburned materials in BA. Importantly, $\delta^{202}\text{Hg}$ was significantly correlated with LOI and ArH content of individual BA and WA samples (Figure S3). Thus, it appears that higher burning intensity leads to higher $\delta^{202}\text{Hg}$ in the residual ash.

There was a narrow range of $\Delta^{199}\text{Hg}$ (MIF) values among litter and foliage samples (-0.47 to -0.06 ‰ ; Figure 4) and the majority of the ash samples had slightly elevated $\Delta^{199}\text{Hg}$ values relative to litter and foliage, with one BA sample even having a slightly positive $\Delta^{199}\text{Hg}$ value ($+0.10 \text{ ‰}$). MIF is not expected to occur as a result of combustion (at least in the dark), and is mainly caused by photochemical reactions.⁴⁰ Given the very small magnitude of differences among ash and the unburned materials, there is no compelling evidence for significant MIF during burning of biomass in wildfires. However, we cannot fully exclude the possibility that a small amount of MIF may have occurred during the postburn period prior to sampling (3–5 weeks) when a surface layer of ash material was exposed to sunlight in the field. We also cannot rule out a small amount of dark microbial reduction in the soils leading to a very small magnitude of MIF through the nuclear volume mechanism.⁴¹

Experimental Investigation of Hg Sorption by Wildfire Ash. To assess if the ash, once released into the environment, may interact with ambient forms of Hg, we conducted a controlled experiment to examine how wildfire ash may adsorb “ambient” Hg. We found that activated carbon ($n = 1$) essentially removed all of the Hg(0) (15 ng per 1.22 g of dry material), consistent with its application to remove Hg(0) from flue gas.^{42,43} In contrast, BA ($n = 4$) and WA ($n = 2$) removed little Hg(0), averaging $2.0 \pm 0.65\%$ and $2.9 \pm 3.6\%$ of Hg(0), respectively (Figure 5 and Table S5). In contrast to the “weak” sorption of gaseous Hg(0) by ash, very strong sorption of aqueous Hg(II) (at 70.3 ng/L in 100 mL solution, per 1 g of materials) was measured using both BA (final Hg(II): $5.3 \pm 3.1 \text{ ng/L}$; removal: $92.5 \pm 4.4\%$; $n = 4$) and WA (final Hg(II): $5.2 \pm 4.9 \text{ ng/L}$; $92.7 \pm 7.0\%$; $n = 4$)

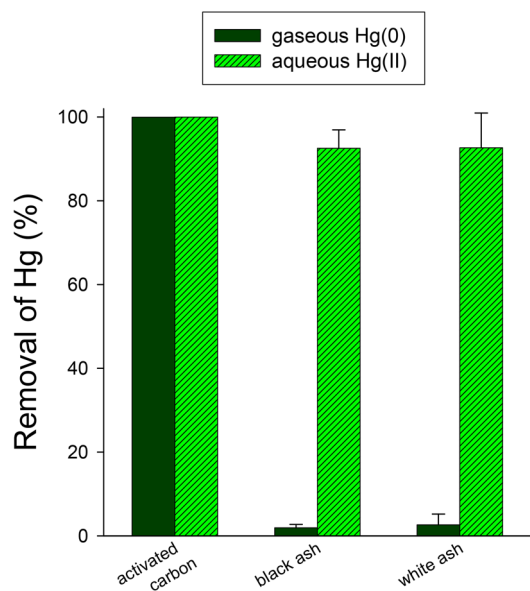


Figure 5. Removal of gaseous Hg(0) (at 15 ng per test, passing through an average of 1.22 g of sorbent) and aqueous Hg(II) (at ~7–7.5 ng per test with 1.0 g of sorbent) by activated carbon ($n = 1$ for both tests), black ash from the Wragg Fire ($n = 4$ for both tests), and white ash from the Wragg Fire ($n = 2$ for gaseous Hg(0) test and $n = 4$ for aqueous Hg(II) test). Error bars represent standard deviation.

(Figure 5), compared to the nearly 100% sorption of Hg(II) by activated carbon (0.01 ng/L; removal: ~100%), which is similar to previous results.⁴⁴

These results suggest that wildfire ash would not be expected to accumulate Hg(0) in the field (e.g., Hg evasion from underlying soil) and this corroborates the isotopic results given

above that indicate Hg in ash is mainly derived from the original vegetation materials. Further, once deposited in aquatic environments, our sorption data suggest that ash can extensively interact with ambient Hg(II) in the water, potentially sequestering ambient Hg(II) into less reactive forms associated with components such as BC. Thus, a higher frequency of wildfire induced by climate change might potentially alter the environmental fate of Hg by producing ash (especially BC) that can sequester Hg(II) in the environment.

Bioavailability of Ash-Associated Hg under Sealed Incubation. We assessed the release and bioavailability of ash-associated Hg for methylation during sealed incubations with freshly collected surface water. This approach of prolonged incubation provides useful information but has some limitations as the resultant water chemistry can change considerably during the course of incubation. For example, the pH of water (beginning pH was 8.0) at the end of the incubations was as follows: litter (5.9 ± 0.64 ; $n = 2$) < BA (7.7 ± 0.36 ; $n = 28$) < WA (10.0 ± 0.91 ; $n = 28$) (Figure S4; Tables S6 and S7). We found that almost all BA or WA samples generated an obvious sulfidic smell, indicating the existence of anaerobic sulfate-reduction across all treatments in addition to the litter-incubated treatment (Tables S6 and S7), which are similar to previous studies.^{32,45}

Compared to litter incubation ($n = 1$ with triplicate incubation), we found much lower dissolved (total-) Hg and MeHg in the majority of BA or WA incubation samples after 4- and 12-weeks of incubation (Figure 6 and Figure S5). After 4 weeks of incubation, the percentage of Hg released from the solid materials (after accounting for all Hg pools from water and solid materials) followed the decreasing order: litter (3.3%; $n = 1$) > BA ($0.83 \pm 0.50\%$; $n = 14$) \approx WA ($0.70 \pm$

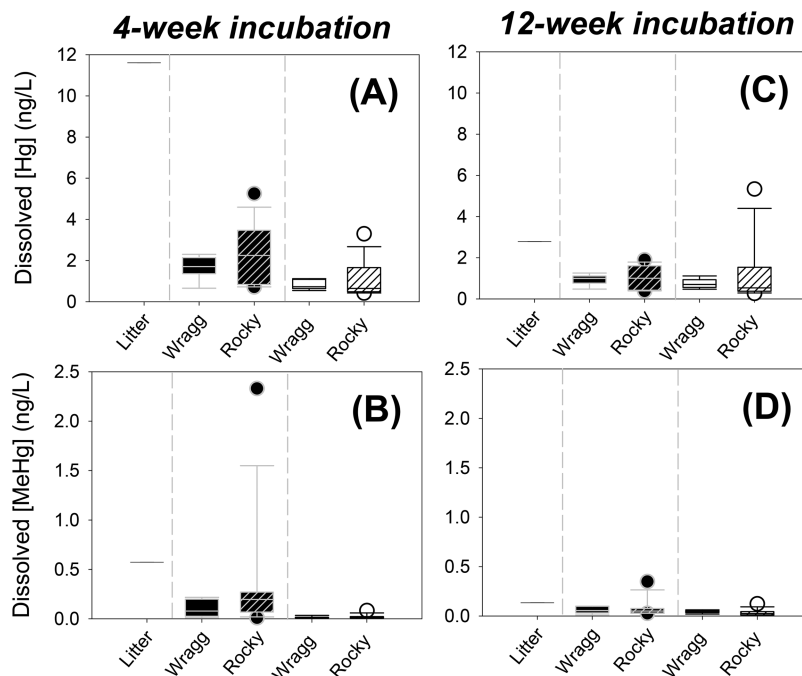


Figure 6. Box plots of (A) dissolved mercury concentrations ([Hg]) after 4 weeks of incubation, (B) dissolved methylmercury concentrations ([MeHg]) after 4 weeks of incubation, (C) dissolved [Hg] after 12 weeks of incubation, and (D) dissolved [MeHg] after 12 weeks of incubation, from an unburned northern California coast range forest litter, Wragg Fire black ash (in black bars), Wragg Fire white ash (in white bars), Rocky Fire black ash (in hatched black bars), and Rocky Fire white ash (in hatched white bars). Individual data points represent triplicate of incubation. See Figure S5 and Tables S6 and S7 for the original data.

0.57%; $n = 14$). Importantly, Hg release appeared to be negatively and significantly correlated with the ArH content of the materials ($p = 0.002$) (Figure S6), implying that “recalcitrant” Hg potentially associated with BC (especially in BA) may limit Hg release into the aqueous phase. However, our interpretation may be confounded by contrasting water quality properties across treatments, such as pH and dissolved organic carbon (DOC) levels (highest in unburned materials, followed by BA, and then WA-incubations; Figure S4), as these parameters may have an influence on Hg release from these solid materials.

After Hg is leached from the solid-phase, microbial MeHg production may take place in the aqueous phase during incubation under anoxic conditions.³² In this study, we found that [MeHg] in filtered leachates was consistently low and close to our analytical detection limit of MeHg (0.02 ng/L) for the majority of BA and WA incubations.

However, the dissolved MeHg concentrations for the WA-incubations (and some BA-incubations) appeared to increase with prolonged incubation from 4- to 12-weeks, and these temporal increases were negatively related to the LOI (Figure S7). These results suggest that Hg associated with ligands in WA results in somewhat higher release of Hg from the solid-phase as compared to Hg released from BA during longer incubations. For most BA samples, dissolved Hg, and to a lesser extent MeHg, decreased from 4 to 12 weeks implying that during prolonged exposure aqueous Hg may be “re-adsorbed” onto the ArH pools in BA, or simply accumulate as a solid-phase Hg-sulfide, which has been shown to extensively bind dissolved Hg.¹⁹ We observed similar patterns for litter-incubated treatments (“Litter”) with temporal decreases in both dissolved Hg and MeHg (Figure S7), which supports the possibility of sulfidic resorption of Hg.

As demonstrated in our aqueous Hg(II) sorption experiment, both BA and WA had the capability to extensively bind Hg(II) (Figure 5), and this may explain the low release of Hg from BA and WA in the 4-week treatment. In contrast, the 12-week incubation data suggest that sorption from the aqueous phase may be “reversed” such that some of the ash-associated Hg was eventually released back to the ambient water.

Implications for Hg Biogeochemical Cycles. This study demonstrates that the Hg content in wildfire ash is different from ash generated from laboratory-controlled burning investigations.^{8,12} We found that the majority of Hg in wildfire ash was derived from Hg that originally resided in vegetation materials (e.g., foliage and litter) based on their Hg isotopic compositions. While the majority (>80%) of the Hg in the litter was volatilized by the fire, considerable concentrations of Hg still existed in the resulting ash. Importantly, pyrolysis appears to generate BC and other constituents that may retain Hg within the residual materials, largely in recalcitrant forms. The recalcitrant forms of Hg in ash appear to sequester additional ambient Hg but inhibit subsequent biogeochemical transformations such as Hg release into solution. Upon deposition into aquatic environments, a small portion of the ash-laden Hg (<1%) is expected to be released based on our incubation data. The extent of Hg release and methylation generally decreased with increasing ArH content, suggesting a possible role of Hg sorption to BC in regulating solubility and bioavailability in the field.

Prolonged exposure to water (especially under reducing conditions) resulted in enhanced Hg release from WA, but a decreased release from BA, highlighting contrasting inter-

actions among ash types generated under different burning conditions on the landscape. Thus, we find that multiple factors (wildfire severity, BC/ArH, length of exposure to water, presence or absence of oxygen, etc.) interact to affect the fate of Hg and determine whether ash serves as a sink or source of Hg for downstream aquatic environments. Our current findings suggest that wildfire ash could play an important role in global Hg cycling and the Hg biogeochemistry of terrestrial and aquatic ecosystems. For example, wildfire ash itself may decrease or have little effect on Hg contamination in downstream ecosystems (e.g., fish Hg accumulation)⁴⁶ due to the less reactive nature of Hg within ash. It should also be recognized that in the burned watersheds other factors such as postburn alteration of food web structures in aquatic ecosystems may lead to subsequent changes in MeHg accumulation in fish.¹⁷ These effects are expected to be more pronounced in the future as climate change results in more frequent and intensive wildfires leading to increasing production of wildfire ash at the global scale.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b03729.

Detailed information on site description, sample collection, pyrogenic carbon and mercury analyses, sorption experiments, incubation experiments, sample processing and mercury isotopic analysis; complete data set on chemical properties, mercury concentrations, mercury isotopic ratios of ash samples, and volatilization estimation, sorption, and incubation study (PDF)

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Notes

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