Supporting Information (SI)

Origin, reactivity, and bioavailability of mercury in wildfire ash

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SI Text 1 – Physiochemical measurements and Py-GC/MS analysis

Loss-on-ignition (LOI) for all samples was measured after being held in a muffle furnace (Thermo Scientific; Thermolyne™) at 500 °C for 4 hours at the University of North Carolina at Greensboro (UNCG; Greensboro, NC). Total carbon (TC) and total nitrogen (TN) contents were analyzed on a CHN-O elemental analyzer (Thermo Scientific; FLASH 2000) at Baruch Institute of Coastal Ecology, Clemson University (Georgetown, SC). Major cations and trace elements were also analyzed for samples after acid digestion (aqua regia; following Olund et al.)[1] and dilution with Barnstead™ Nanopure™ water (18.2 MΩ/cm) using inductively coupled plasma–mass spectrometry (Perkin Elmer; NeXion 300S) at Institute of Environmental Sustainability, Loyola University Chicago (Chicago, IL).

The organic carbon composition in ash and unburned samples was determined by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) at Baruch Institute of Coastal Ecology, Clemson University, following a method described by Song and Peng[2] and Chen et al.[3] In brief, individual samples (0.1-30 mg depending on organic matter content) were placed in pre-baked quartz tubes with samples held in place by glass wool. The sample-filled quartz tube was introduced into the CDS Analytical Pyroprobe 2000 "Pyrolyzer" and heated from 250 to 700 °C with a temperature ramping rate of 5 °C/millisecond and then held for 10 s on a pyrolysis injector (CDS Analytical Inc., Oxford, PA) connected to a gas chromatography-mass spectrometer (GC-MS; Agilent 7890A). Helium gas at 1 mL/min was used to flush the pyrolytic compounds into the GC column. The GC injector was operated in split-mode (10:1 to 50:1 depending on the organic matter content in sample) with an inlet temperature of 250 °C. Pyrolysis products were identified and quantified according to their GC retention time and mass spectra with reference to the Wiley/NIST library supplied with the MS workstation software 7.0.1.

The identified and quantified pyrolysis products were classified into nine groups according to their chemical similarity: (*i*) saturated hydrocarbon (SaH), (*ii*) unsaturated hydrocarbon (UnSaH), (*iii*) aromatic hydrocarbon (ArH), (*iv*) polyaromatic hydrocarbon (PAH), (*v*) carbohydrate (Carb), (*vi*) phenolic carbohydrate (PhC), (*vii*) lignin phenol carbohydrate (LgPhC), (*viii*) halogen-containing compounds (Hal), and (*ix*) nitrogen-containing compounds (Ntg). Relative abundance of each group was calculated as the sum of the major ion peak areas in each group divided by the sum of all major ion peak areas. An R-script (R Studio Desktop version 1.0.44; Boston, MA) was developed for automated identification and quantification.

SI Text 2 – Sample digestion and Hg analysis

All sample processing and analysis for Hg was performed in a semi-clean analytical laboratory at UNCG. For all samples, we used two acid digestion methods to release Hg in order to assess Hg reactivity based on the differences of Hg concentrations generated by the two digestion methods. In *Method 1* (reported as [$Hg_{method-1}$]), 0.20±0.01 g of dry samples were weighed into acid-cleaned PFA digestion vessels (Savillex, Eden Prairie, MN), and 5 mL of trace-metal grade HNO_3 and H_2O_2 (4:1, v:v, both from Fisher Scientific) were added and allowed to sit at room temperature overnight with the cap loosely tightened (i.e., cold digestion). On the following day, the digestion vessels were tightly closed and placed in a water bath at 80 °C overnight to complete the digestion (i.e., hot digestion). *Method 2* (reported as [$Hg_{method-2}$]) followed the procedure of Olund et al.[1] in which samples were weighed into acid-cleaned 40 mL borosilicate glass vials with PTFE-lined septa (Thermo Scientific), and 8 mL of trace-metal grade HNO_3 and HCl (i.e., aqua regia; 1:3, v:v, both from Fisher Scientific) was added and allowed to sit at room temperature for 24 h (i.e., cold digestion). Then, 22 mL of 5% BrCl was added to the acidic mixtures, and the vials containing sample mixtures were placed in a water bath at 80 °C overnight (i.e., hot digestion). To test the robustness of this approach to assess Hg reactivity in environmental samples, we also analyzed two vegetation standard reference materials (SRMs) (i.e., NIST-1515 Apple Leaves; IAEA-359 Cabbage) and litter samples from three reference forests (Angelo Coast Range Reserve in northern California, University of Michigan Biological Station in northern Michigan, and Hubbard Brook Experimental Forest in New Hampshire).

For both digestion methods, aliquots of digested samples (0.5 to 2 mL, depending on estimated Hg content) were added to 100 mL of Nanopure water (18.2 MΩ/cm) in a glass bubbler with stopper/sparger and 200-600 µL of 30% hydroxylamine (Alfa Aesar) were added to partially reduce the reagent. Gold traps were attached in connection to a soda lime trap to collect gaseous Hg(0) following complete reduction by 200 µL of 20% stannous chloride (Alfa Aesar), and the mixture was purged with Hg-free N_2 gas for 15 minutes. Gold traps loaded with Hg were heat-desorbed at 400-500 °C using the double amalgamation technique, and sample Hg was quantified using a Brooks Rand Model III CVAFS detector.

Throughout sample analyses, random samples were digested in duplicate and run for Hg. A primary calibration standard solution (1 ng/mL) was prepared from SMR-NIST-3133 Hg solution and checked against an in-house secondary calibration standard (1 ng/mL) prepared from SRM-NIST-1641d Hg solution; Hg in the two standards always matched within 3%. For each batch of digestions using both methods, we included reagent blanks and standard reference materials (SRM-NIST-1515 Apple Leaves and SRM-IAEA-

83   359 Cabbage). Hg results were not significantly different ($p>0.05$) based on the two digestion methods for

84   SRM-NIST-1515: [$Hg_{method-1}$] was 42.3$\pm$0.99 ng/g (n=7; mean$\pm$s.d.) and [$Hg_{method-2}$] was 45.1$\pm$2.19 ng/g

85   (n=9) (**Table S3**), while the certified value for SRM-NIST-1515 had a mean of 44.0 ng/g (range = 40.0-48.0

86   ng/g). Similarly, Hg results were not significantly different ($p>0.05$) based on the two digestion methods for

87   SRM-IAEA-359: [$Hg_{method-1}$] was 10.2$\pm$0.88 ng/g (n=3) and [$Hg_{method-2}$] was 10.8$\pm$1.29 ng/g (n=3) (**Table S3**).

88   The certified value for SRM-IAEA-359 has a mean of 13.0 ng/g (range = 11.0-15.0 ng/g). All digested

89   reagent blank had Hg concentrations <1 ng/g (based on the same procedure as in method 2).

90

91   **SI Text 3 – Estimation of Hg volatilization in ash samples**

92   We estimated the Hg volatilization percentage for each ash sample collected in the field. We assumed

93   the wildfire ash was generated from the combustion of the unburned vegetation components (litter and

94   wood) from each site. We used two mass balance methods to calculate Hg volatilization loss based on

95   either LOI or calcium content of ash samples.

96   Using LOI of the ash, we assumed that the mineral components in the ash samples were completely

97   "conserved" during combustion from the original vegetation materials. We found that the average LOI of

98   unburned vegetation was 95.9%, which means that 4.1% of the original vegetation materials was retained

99   in the BA and WA samples after wildfire/combustion. Therefore, we calculated the amount of biomass

100   combusted to form the ash mineral component (total sample weight – loss on ignition) (Mineral content % =

101   100% - LOI%), using the equation <u>%Hg volatilized = 1 – Hg_{ash} / [(1-LOI_{ash}%)/ (1-$LOI_{unburned}$%) $\times$ Hg</u>

102   <u>$_{unburned}$] $\times$ 100%,</u> in which the average $LOI_{unburned}$% was 95.7% for Wragg Fire, and 96.0% for Rocky Fire

103   and the average $Hg_{unburned}$ was 26.8 ng/g for Wragg Fire and 21.2 ng/g for Rocky Fire site (LOI and Hg

104   data are shown in **SI Table S2**)

105   Using Ca content of the ash, we assumed no change in Ca content in the original vegetation of the

106   wildfire conditions (i.e., no loss of Ca). We used this equation: <u>%Hg volatilized = 1 – Hg_{ash} / [(1-Ca_{ash}%)/</u>

107   <u>(1-$Ca_{unburned}$%) $\times$ $Hg_{unburned}$] $\times$ 100%,</u> in which the average Ca content of unburned vegetation was 14.7

108   mg/g for Wragg Fire site and 10.5 mg/g for Rocky Fire site, and the average $Hg_{unburned}$ concentration was

109   26.8 ng/g for Wragg Fire site and 21.2 ng/g for Rocky Fire site (Ca and Hg data are shown in **SI Table S2**).

110

111   **SI Text 4 – Sample processing and stable Hg isotope analysis**

112   We performed thermal combustion for stable Hg isotope analysis on unburned litter from three natural,

113   unburned forests in the U.S. (Angelo Coast Range Reserve in northern California, University of Michigan

114   Biological Station in northern Michigan, and Hubbard Brook Experimental Forest in central New Hampshire)

115   and the Wragg Fire ash samples (n=10; 5 black ash [BA] and 5 white ash [WA]). Prior to thermal

116   combustion, each dry sample was weighed into two clean ceramic sample boats (~0.5-1.0 g per boat), and

117   packed with layers of pre-baked combustion powders (Nippon Instruments Corporation). Samples with low

118   Hg content required multiple rounds of combustion and sample Hg was later combined during the purge-

119   and-trap sample purification step in order to have sufficient Hg (> 10 ng) for high-precision isotopic analysis

120   (*see below*).

121   In brief, samples were thermally combusted in a two-stage furnace (the first furnace ramped from room

122   temperature to 750 °C over 6 hours and the second furnace was held at 1,000 °C for the entire period). The

123   released gaseous Hg(0) was collected into a 24 g trap solution containing 1% $KMnO_4$ (w/w) in 10% trace-

124   metal grade H_2SO_4 (v/v). Following combustion, the trap solution was transferred into an acid-cleaned 40

125   mL borosilicate glass vial with PTFE-lined septum. To analyze Hg content, the trap solution was completely

126   neutralized with 30% hydroxylamine, and an aliquot of solution was taken for quantification of Hg using the

127   CVAFS system (Brooks Rand Model III CVAFS; described in **SI Text 2**).

128   Mercury in the initial trap solution (from combustion) was purged (upon complete reduction by 20%

129   $SnCl_2$) and trapped into a smaller trap solution (6 to 15 g of 1% $KMnO_4$ in 10% H_2SO_4, depending on the

130   total amount of sample Hg) in order to (*i*) separate sample Hg from other combustion products in the initial

131   trap solution, and (*ii*) concentrate Hg in this final solution for Hg isotope analysis. The final trap solution was

132   neutralized and an aliquot of solution was taken for analyzing Hg to determine the recovery of Hg during

133   the purge-and-trap (typically > 95%). Hg levels in the final trap solution were precisely adjusted to a uniform

134   Hg concentration (± 5%) along with a bracketing Hg isotope standard (SRM-NIST-3133) ranging from 2-5

135   ng/g (Blum and Bergquist, 2007).

136   Stable Hg isotope ratios were measured using a Nu Instruments multicollector-inductively coupled

137   plasma-mass spectrometer (MC-ICP-MS) following the methods of Blum and Bergquist[4] in the

138   Biogeochemistry and Environmental Isotope Geochemistry Laboratory at the University of Michigan (Ann

139   Arbor, MI). Mass-dependent fractionation (MDF) of Hg isotopes was reported as $\delta^{202}Hg$ in permil (‰)

140   referenced to SRM-NIST-3133, while mass-independent fractionation (MIF) of Hg isotopes is the difference

141   between the measured $\delta^{202}Hg$ value and the value that would be predicted based on mass

142   dependence. The mass-independent Hg isotope composition is reported in ‰ for both odd-mass isotopes

143   $\Delta^{199}Hg$ and $\Delta^{201}Hg$ and even-mass isotopes $\Delta^{200}Hg$ and $\Delta^{204}Hg$. Isotopic compositions were calculated

144 according to Blum and Bergquist[4] as:

145

146 $\delta^{202}Hg = \{[(^{202}Hg / {}^{198}Hg)_{sample} \div ({}^{202}Hg / {}^{198}Hg)_{NIST\ 3133}] - 1\} \times 1000$ (1)

147 $\Delta^{201}Hg \approx \delta^{201}Hg_{measured} - (\delta^{202}Hg_{measured} \times 0.752)$ (2)

148 $\Delta^{199}Hg \approx \delta^{199}Hg_{measured} - (\delta^{202}Hg_{measured} \times 0.2520)$ (3)

149 $\Delta^{200}Hg \approx \delta^{200}Hg_{measured} - (\delta^{202}Hg_{measured} \times 0.5024)$ (4)

150 $\Delta^{204}Hg \approx \delta^{204}Hg_{measured} - (\delta^{202}Hg_{measured} \times 1.4930)$ (5)

151

152   Analytical uncertainty was determined from replicated analyses of a secondary standard solution (UM-

153 Almadén, mean values: $\delta^{202}Hg$ = -0.56 ‰; $\Delta^{199}Hg$ = -0.02 ‰; n=11), and replicate combustions and

154 analyses of SRM-NIST-1515 (Apple Leaves [UNCG lot], mean values: $\delta^{202}Hg$ = -2.64 ‰; $\Delta^{199}Hg$ = 0.05 ‰;

155 n=6) along with the field samples. These isotopic compositions are similar to previous studies (e.g., Demers

156 et al.)[5]. External analytical reproducibility of $\delta^{202}Hg$ measurements was estimated to be ±0.08‰ for

157 solutions with 5.0 ng/g and ±0.14 ‰ for 1.9 ng/g (2 SD) and for $\Delta^{199}Hg$ it was estimated to be ±0.07 ‰ (2

158 SD), based on the repeated analyses of SRM-NRCC-TORT-2 analyzed at different final Hg concentrations

159 on MC-ICP-MS (1.9-5.0 ng/g).[6,7]

160

161 **SI Text 5 – Testing sorption capability of Hg by wildfire ash**

162   The ability of wildfire ash to adsorb aqueous Hg(II) was assessed in two sorption experiments that

163 involved adding 1.0 g of ash (4 black ash and 4 white ash from the Wragg Fire, and activated carbon [CAS

164 7440-44-0; Alfa Aesar] as a positive control) into 100 mL of 18.2 MΩ/cm water spiked with $HgCl_2$ (Sigma-

165 Aldrich) in 500 mL acid-cleaned borosilicate glass Erlenmeyer flasks. The mean actual Hg concentration in

166 filtered, spiked solution before sorption was 70.3 pg/mL in the first experiment and 74.8 pg/mL in the

167 second experiment. The ash as a solid slurry was shaken for 24 h on a shaker table at room temperature.

168 The slurry was filtered through a pre-baked glass fiber filter (Whatman GF/B, 1.0-μm pore size). Filtered

169 aqueous samples were treated with an acidic mixture of permanganate/persulfate and heated at 80 °C

170 overnight to complete sample digestion.[8] Digested samples were neutralized, and weighed aliquots were

171 analyzed for Hg as previously described.

172   To test the capability of ash at adsorbing gaseous elemental Hg(0), we set up a sorption experiment

173 using the purge-and-trap setup we routinely used for purging large volumes of stream water for Hg isotopic

174 analysis (*see setup and detailed procedures in* Woerndle et al.)[8]. The Hg(0) gas is slowly released by this

175 method as $SnCl_2$ is slowly added to the reservoir of aqueous sample with Hg, as opposed to the situation

176   for Hg analysis described above. In brief, we prepared 500 mL of acidic solution spiked with 15.0 ng of Hg

177   from our SRM-NIST-3133 standard solution. We purged this solution by adding 10% $SnCl_2$ at a rate of ~1

178   mL/min. Reduced Hg(0) was sparged with 0.45-µm filtered Hg-free ambient air (produced by a vacuum

179   pump and passed through a Teflon filter and a gold-coated glass trap), and transferred through a soda lime

180   trap (to remove moisture and neutralize acidic fumes) and a Teflon trap with only glass wool (as a negative

181   control) or filled with an ash sample (Wragg Fire BA and WA) or activated carbon (CAS 7440-44-0; Alfa

182   Aesar) as a positive control. The length of packed material inside the Teflon trap was 4.2 cm with an

183   average mass of materials of 1.22±0.14 g (mean±s.d.). Any Hg(0) not removed by the ash or activated

184   carbon trap was collected by the final, downstream gold trap. The gold trap was dried with Hg-free N_2 gas

185   for 20 minutes, and analyzed for Hg as described above.

186

187   **SI Text 6 – Examining bioavailability of Hg in ash during incubation**

188   We conducted 4- and 12-week incubation experiments of ash and an unburned litter sample from a

189   northern California forest (Angelo Coast Range Reserve, Branscomb, CA) using sealed bottles. Previous

190   studies have demonstrated that sealed bottle incubation with fresh litter and freshly collected stream water

191   quickly turned anoxic (<1 week) and active microbial Hg methylation quickly proceeded with inorganic Hg(II)

192   released from the decomposing litter.[9,10] This study inoculated samples with the microbial community in

193   freshly collected surface water from an urban stream near UNCG (South Buffalo Creek at Greensboro, NC;

194   GPS location: 36.050563, -79.748731). A preliminary experiment using "aged" stream water (>3 months

195   stored at 4 °C) from the catchment burned by the Wragg Fire in California did not result in detectable levels

196   of MeHg even in the litter-incubated treatment (*data not shown*). This suggests that the anaerobic,

197   methylating microbes needed to be derived from water freshly collected from the ambient environment.

198   In brief, the incubation experiments used 250 mL air-tight, sterile PETG bottles (Nalgene), and each

199   bottle received 2.80±0.01 g of 2-mm sieved ash or homogenized litter sample. A 280±1.21 mL of unfiltered

200   stream water (with resultant minimal head space in the container) was added to achieve a solid-to-water

201   ratio of 10 g/L, which was 5 times higher than our previous incubation experiments using similar methods.[10]

202   The bottle was tightly capped and further wrapped with layers of Parafilm to secure the closing. We did not

203   flush the ash slurry with N_2 gas as anoxia was expected to develop quickly over the course of incubation.

204   Each treatment was performed in triplicate. Sealed bottles were placed in the dark at room temperature

205   (20-22 °C) for 4 weeks or 12 weeks. Each bottle was shaken daily to mix the contents.[10,11]

206 At the end of the incubation, bottles were opened and the "rotten egg" odor (i.e., hydrogen sulfide) was

207 noted if it was present or absent to indicate the existence of sulfate-reduction during incubation.[9,10] The

208 aqueous solution was immediately filtered through a pre-baked Whatman GF/B filter (1.0-μm pore size) in

209 an acid- and BrCl-cleaned glass filtration apparatus (Kimble™ Kontes™). Filtered samples were analyzed

210 separately for pH, specific conductivity (12-week samples only), total-dissolved nitrogen (TDN), dissolved

211 organic carbon (DOC), $SUVA_{254}$ (proxy for aromaticity of DOC), Hg and methylmercury (MeHg).
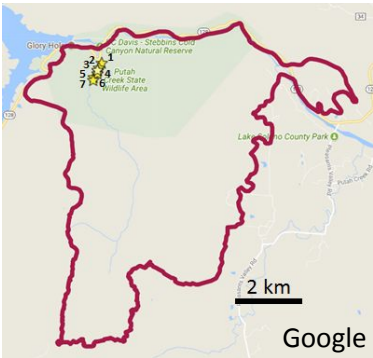
212 Hg in filtered water samples was analyzed after digestion using an acidic mixture of $KMnO_4$ and

213 $K_2S_2O_8$, and heated at 80 °C overnight.[8] Filtered water samples were preserved with 0.4 % HCl[12] and kept

214 in the dark at 4 °C prior to distillation for matrix removal and MeHg analysis (Brooks Rand Model III CVAFS

215 with GC/pyrolysis module). Procedures for MeHg analysis in aqueous samples at the UNCG laboratory are

216 fully described in Woerndle et al.[8] Percent of Hg as MeHg (i.e., %MeHg) in the filtered solution was used to

217 evaluate Hg methylation potential, or conversely, the bioavailability of Hg for microbial methylation.[10,13]

218 Measured physiochemical properties of the filtered solution included pH (Mettler Toledo pH meter),

219 specific conductivity (Fisher Scientific conductivity meter), dissolved organic carbon (DOC) and total-

220 dissolved nitrogen (TDN) (Shimadzu TOC analyzer). The UV-absorbance at 254 nm (UV_{254}) was measured

221 using a diode array spectrophotometer (Hewlett Packard P8452A) and then used to calculate specific UV

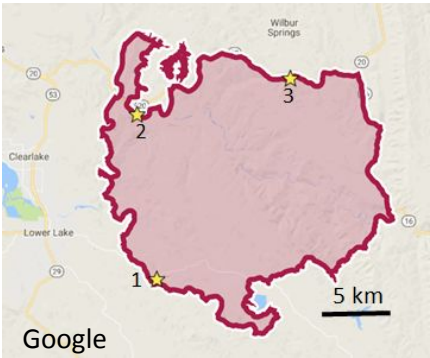222 absorbance at 254 nm ($SUVA_{254}$; in L/mg-C/m) as a proxy for DOC aromaticity.[14]

223   **Table S1** Summary of wildfire site characteristics and sampling information.

	Wragg Fire	**Rocky Fire**
Dates	July 22 to August 5, 2015	July 29 to August 14, 2015
Locations	Lake Berryessa, CA	Clearlake, CA
Coordinates	38°29'12.98"N, 122° 4'30.29"W	38°57'48.29"N, 122°29'10.91"W
Burned area	33 km^2	281 km^2
Soil parent material	Mixed sedimentary: shale, mudstone & sandstone	Mixed sedimentary: shale, mudstone & sandstone
Dominant soils	Lithic Haploxerepts & Typic Dystroxerepts	Typic Dystroxerepts & *Mollic Haploxeralfs*
Dominant vegetation	Blue oak, live oak, scrub oak, chamise, manzanita, ceonothus	Blue oak, live oak, scrub oak, chamise, manzanita, ceonothus
Date of sampling	August 25, 2015	September 19, 2015
Rainfall prior to sampling	No	No
Sampling points	*~ 0.5 km transect / trail*	*~ 10-11 km between sites, along fire perimeter*

WR1: 1xWA, 1xBA
WR2: 1xWA
WR3: 1xWA, 1xBA
WR4: 1xBA
WR5: 1xBA
WR6: 1xWA
WR7: 1XWA, 1xBA

RO1: 3xWA, 3xBA
RO2: 3xWA, 3xBA
RO3: 3xWA, 3xBA

224

Table S2 Different physicochemical properties of standard reference materials (SRMs), litter samples from reference forests, ash and unburned samples from the Wragg Fire (2015), and ash and unburned samples from the Rocky Fire (2015). *Note:* SRM-NIST-1515: apple leaves (*n*=9); SRM-IAEA-359: cabbage (*n*=3); CA-Litter: Angelo Coast Range Reserve (*n*=1); NH-Litter: Hubbard Brook Experimental Forest (*n*=3); MI-Litter: University of Michigan Biological Station (*n*=3). Individual sample data are shown for all ash and unburned samples. ND = not determined.

Category	Sample ID	Munsell color (Hue Value/Chroma)	LOI (%)	TN (%)	Ca (%)	Fe (%)	$Hg_{method-1}$ (ng/g)	$Hg_{method-2}$ (ng/g)	Recalcitrant Hg (%)	Relative abundance of pyrolysis products (%)								
										SaH	UnSaH	ArH	PAH	Carb	PhC	LgPhC	Hal	Ntg
SRMs	NIST-1515	ND	ND	ND	1.7	0.012	42.3	45.1	8.7	ND	ND	ND	ND	ND	ND	ND	ND	ND
	IAEA-359	ND	ND	ND	1.7	0.020	10.2	10.8	6.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Litter (ref. forests)	CA-Litter	ND	93.7	0.69	2.0	0.048	32.2	35.0	8.2	0	2	13	0	20	50	16	0	0
	NH-Litter	ND	96.3	1.73	ND	ND	53.2	57.8	8.2	4	19	8	4	21	23	17	1	6
	MI-Litter	ND	97.1	0.90	ND	ND	41.7	45.0	7.3	4	19	9	4	21	24	16	0	5
Wragg-unburned	Oak Litter	ND	94.8	1.97	1.4	0.80	27.2	28.1	3.1	1	0	11	0	36	13	8	0	30
	Pine Litter	ND	96.3	1.39	1.0	0.14	42.6	40.1	0	1	0	12	1	33	22	10	1	19
	Oak Wood	ND	92.7	0.69	3.1	0.04	25.4	24.3	4.6	1	1	6	0	25	11	15	0	41
	Pine Wood	ND	98.6	0.44	0.4	0.02	14.1	14.6	3.5	0	0	5	0	21	26	16	5	31
Wragg-black ash	WR1-BA	Gley1 3.5/N	31.0	0.64	9.7	2.3	2.8	7.9	64.7	3	4	61	2	7	5	0	2	15
	WR3-BA	Gley 1 3/N	35.8	1.39	6.4	2.7	9.8	18.1	46.1	5	5	31	1	16	20	6	3	12
	WR4-BA	Gley 1 3.5/N	23.2	1.08	6.1	2.8	7.8	12.2	35.7	7	7	36	1	16	13	1	4	15
	WR5-BA	ND	49.3	1.54	9.3	1.4	9.7	10.6	7.9	9	33	17	2	6	26	2	0	6
	WR7-BA	Gley 1 2.75/N	36.9	1.17	6.0	2.9	8.1	10.7	24.5	7	38	15	3	4	14	0	0	20
Wragg-white ash	WR1-WA	Gley1 5.5/N	6.6	0.23	24.9	1.7	8.6	9.2	6.2	7	30	33	3	6	2	0	3	15
	WR2-WA	Gley1 7/N	2.9	0.11	29.0	1.4	15.6	16.4	4.9	0	0	80	5	1	0	0	0	14
	WR3-WA	Gley1 5.5/N	4.0	0.14	26.2	2.1	15.0	14.8	0	0	1	77	5	3	0	0	0	13
	WR6-WA	Gley1 5.5/N	4.0	0.15	30.1	1.6	119.8	124.6	3.9	0	3	74	6	4	0	0	0	14
	WR7-WA	Gley1 5.5/N	5.9	0.17	28.0	1.3	7.5	8.8	14.3	2	12	62	6	1	0	0	0	17
Rocky-unburned	Oak Litter	ND	94.0	1.87	1.3	0.02	18.3	20.3	9.5	1	0	16	0	34	24	6	0	20
	Pine Litter	ND	97.4	0.62	0.7	0.01	28.4	30.1	5.8	0	0	12	2	33	26	8	1	19
	Oak Wood	ND	95.9	0.67	1.8	0.02	16.0	16.2	1.1	1	0	4	0	15	8	24	0	49
	Pine Wood	ND	98.6	0.55	0.6	0.01	73.3	57.0	0.0	0	0	5	0	17	39	15	0	24
Rocky-black ash	RO1-BA1	Gley1 2.5/N	26.9	0.60	5.1	4.8	7.2	26.5	72.7	2	5	52	3	8	18	1	1	9
	RO1-BA2	Gley1 2.5/N	31.2	0.40	2.9	5.2	12.8	31.8	59.8	5	11	47	2	14	13	3	1	4
	RO1-BA3	Gley1 2.75/N	33.6	0.45	4.4	5.2	14.1	56.5	75.1	4	10	47	3	10	12	3	2	9
	RO2-BA1	Gley1 2.5/N	58.3	2.06	4.2	1.8	28.3	42.6	33.6	4	7	35	2	15	19	2	2	13
	RO2-BA2	10YR 2/1	62.1	2.11	3.1	1.2	8.9	15.8	43.4	4	6	39	3	12	16	5	2	14
	RO2-BA3	Gley1 2.5/N	44.0	1.54	3.1	2.6	27.4	48.2	43.2	4	7	29	1	14	21	9	2	12
	RO3-BA1	10YR 2/1	38.0	1.00	4.8	3.4	47.8	94.0	49.2	3	6	45	4	12	18	1	2	11
	RO3-BA2	2.5Y 2.5/1	60.9	1.85	4.2	1.8	29.0	42.9	32.3	4	5	29	1	16	21	11	1	11
	RO3-BA3	5Y 2.5/1	52.3	1.40	3.4	2.3	27.1	39.9	32.0	4	5	29	1	18	21	8	3	12
Rocky-white ash	RO1-WA1	10YR 7.5/1	2.4	0.08	26.5	2.3	40.4	78.0	48.2	0	1	86	4	3	0	0	0	7
	RO1-WA2	10YR 7/1	2.6	0.09	26.8	2.3	11.6	13.9	16.6	0	0	83	5	3	0	0	0	10
	RO1-WA3	2.5Y 7/1	5.5	0.16	27.5	2.1	42.0	61.8	32.1	3	5	58	5	13	1	0	0	16
	RO2-WA1	2.5Y 6.5/1	15.2	0.06	15.9	1.4	4.0	5.9	31.7	6	7	69	4	9	1	0	0	5
	RO2-WA2	Gley1 7.5/N	3.0	0.07	34.0	1.5	30.8	32.4	5.1	2	4	72	7	7	1	0	0	7
	RO2-WA3	WP 8.75/N	2.9	0.00	36.5	1.1	1.7	3.9	56.1	6	16	51	3	22	0	0	0	2
	RO3-WA1	2.5Y 7.5/1	7.8	0.00	33.9	1.0	2.9	5.0	41.8	2	5	68	7	5	0	0	0	14
	RO3-WA2	2.5Y 6/1	3.7	0.07	43.2	0.6	12.4	14.0	11.3	7	10	58	4	12	3	0	2	3
	RO3-WA3	Gley1 7.5/N	3.4	0.05	30.2	1.4	5.8	8.4	30.7	3	5	69	6	7	0	0	0	10

230 **Table S3** Estimated mercury (Hg) volatilization from original fuel loads (assumed to be a mixture of litter
231 and dead woody materials) in the Wragg Fire (2015; WR) and the Rocky Fire (2015l RO). Our estimations
232 are based on two approaches: loss-on-ignition (LOI) and calcium (Ca) content of ash samples.

Sample ID	Hg volatilization (%) *based on LOI*	Hg volatilization (%) *based on Ca content*
WR1-BA	98.6	96.3
WR3-BA	96.6	87.1
WR4-BA	98.1	90.9
WR5-BA	97.5	94.8
WR7-BA	98.0	91.9
WR1-WA	99.2	98.2
WR2-WA	98.6	97.3
WR3-WA	98.7	97.3
WR6-WA	89.3	80.1
WR7-WA	99.2	98.5
RO1-BA1	91.7	82.6
RO1-BA2	89.4	62.8
RO1-BA3	80.4	56.6
RO2-BA1	76.5	66.2
RO2-BA2	90.4	82.8
RO2-BA3	80.2	47.2
RO3-BA1	65.1	34.0
RO3-BA2	74.7	65.4
RO3-BA3	80.7	60.5
RO1-WA1	81.6	90.1
RO1-WA2	96.7	98.3
RO1-WA3	84.9	92.4
RO2-WA1	98.4	98.8
RO2-WA2	92.3	96.8
RO2-WA3	99.1	99.6
RO3-WA1	98.7	99.5
RO3-WA2	96.6	98.9
RO3-WA3	98.0	99.1

233

234 **Table S4** Stable mercury (Hg) isotope compositions of undecomposed litter from reference forests, published data on foliage in other North
235 American forests[15], and black ash (BA) and white ash (WA) samples from Wragg Fire (2015). *Note:* MDF=mass dependent fractionation; MIF=mass
236 independent fractionation.

Sample type and/or sources	Location / Sample ID	δ^{202}Hg (‰) [MDF]	Δ^{204}Hg (‰) [MIF]	Δ^{201}Hg (‰) [MIF]	Δ^{200}Hg (‰) [MIF]	Δ^{199}Hg (‰) [MIF]
Reference forests	Angelo Forest / CA-Litter	-2.07	0.12	-0.37	-0.04	-0.43
	Hubbard Forest / HB-Litter 1	-1.98	0.01	-0.38	0.03	-0.39
	Hubbard Forest / HB-Litter 2	-2.16	0.00	-0.34	-0.01	-0.38
	Hubbard Forest / HB-Litter 3	-2.10	0.02	-0.28	0.01	-0.32
	U-M Biostation / MI-Litter 1	-2.03	-0.01	-0.30	0.00	-0.32
	U-M Biostation / MI-Litter 2	-2.11	0.05	-0.21	-0.04	-0.22
	U-M Biostation / MI-Litter 3	-2.05	0.03	-0.22	0.00	-0.24
Published data in foliage in other North American forests (Zheng et al.)[15]	Truckee, CA	-2.67	-0.01	-0.04	0.01	-0.10
		-2.27	0.01	-0.04	0.04	-0.06
		-2.08	-0.01	0.00	0.02	-0.06
	Niwot Ridge, CO	-2.31	-0.01	-0.31	-0.04	-0.35
		-2.32	0.01	-0.18	0.00	-0.20
	Howland, ME	-2.35	0.08	-0.24	-0.05	-0.30
		-2.38	0.06	-0.27	-0.02	-0.30
	Thompson Forest, WA	-2.66	0.00	-0.47	0.01	-0.47
		-2.45	0.02	-0.35	-0.01	-0.36
Black ash (BA)	WR1-BA	-1.87	-0.01	-0.20	0.08	-0.17
	WR3-BA	-1.65	-0.03	-0.20	0.03	-0.14
	WR4-BA	-1.60	-0.05	-0.13	0.03	-0.04
	WR5-BA	-1.46	0.09	-0.19	0.01	-0.21
	WR7-BA	-2.14	0.00	-0.03	0.01	0.10
White ash (WA)	WR1-WA	-1.93	-0.04	-0.05	0.04	-0.04
	WR2-WA	-1.05	-0.12	-0.24	-0.03	-0.16
	WR3-WA	-1.11	-0.14	0.00	-0.02	-0.02
	WR6-WA	-0.77	0.00	-0.23	0.04	-0.19
	WR7-WA	-1.62	-0.07	0.01	0.00	0.02

238 **Table S5** Summary of results from Hg in sorption experiments examining sorption of ash (from the Wragg
239 Fire only) and activated carbon on aqueous Hg(II) and gaseous Hg(0). ND = not determined.

	Removal of aqueous Hg(II) (~7.0-7.5 ng per test)	Removal of gaseous Hg(0) (15 ng per test)
Activated carbon	99.9%	99.9%
WR1-BA	97.2%	2.9%
WR3-BA	89.2%	1.6%
WR4-BA	95.3%	ND
WR5-BA	ND	1.4%
WR7-BA	88.3%	2.1%
WR1-WA	95.6%	ND
WR2-WA	98.3%	5.4%
WR3-WA	94.4%	0.4%
WR6-WA	ND	ND
WR7-WA	82.4%	ND

240

241 **Table S6** Summary of results of sealed incubation experiments after 4-weeks. Results are means ± S.D.,
242 except for MeHg in which we pooled the majority of samples from replicates for analysis. All dissolved
243 constituents represent <1.0-μm fraction. *Note:* smell is sulfide, "rotten" egg smell present (+) or absent (-);
244 DOC=dissolved organic carbon; SUVA$_{254}$=specific ultraviolet absorbance at 254 nm (proxy of DOC
245 aromaticity); TDN=total dissolved nitrogen; Hg=mercury; MeHg=methylmercury; %MeHg=percent of Hg as
246 MeHg.

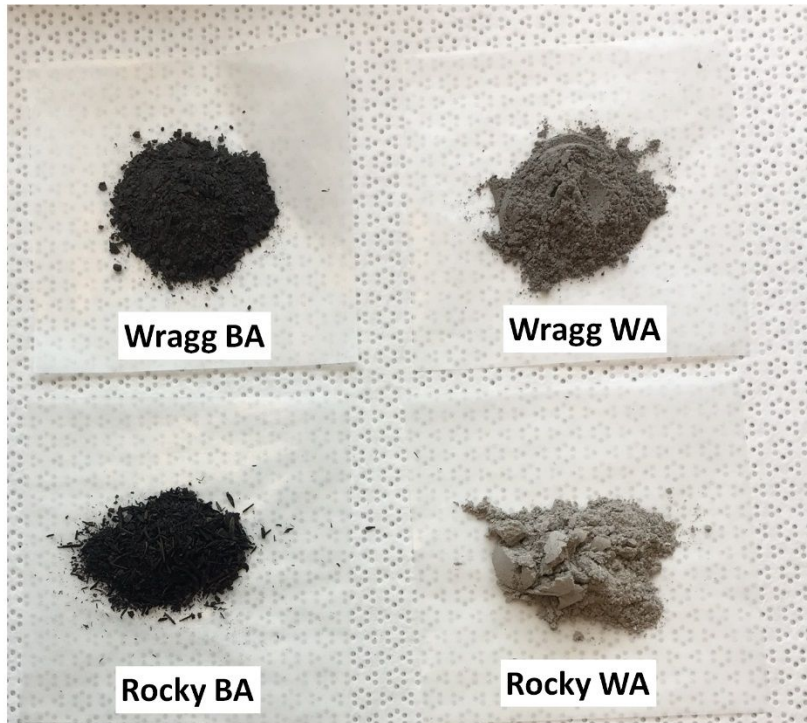|	Sulfidic smell	pH	DOC (mg/L)	SUVA$_{254}$ (L/mg/m)	TDN (mg/L)	Filtered Hg (ng/L)	Filtered MeHg (ng/L)	%MeHg
Water-only	-	8.0±0.0	7.6±0.2	2.0±0.1	0.9±0.0	0.7±0.1	<0.02±0.0	2.9
CA-Litter	+	5.0±0.0	277.7±3.2	1.5±0.0	7.2±0.4	11.6±0.9	0.57±0.44	4.9
WR1-BA	+	8.5±0.2	62.6±5.0	3.7±0.1	4.9±0.6	0.7±0.3	<0.02	2.9
WR3-BA	+	7.9±0.2	66.0±5.5	3.9±.1	7.1±0.6	2.3±0.2	0.22	9.6
WR4-BA	+	7.9±0.1	42.3±1.7	3.7±0.2	5.6±0.3	2.1±0.2	<0.02	1.0
WR5-BA	+	7.8±0.1	75.3±7.5	3.4±0.3	6.7±0.5	1.6±0.1	0.08	5.0
WR7-BA	+	7.9±0.1	49.3±5.4	3.5±0.1	5.5±0.5	1.7±0.2	0.19	11.2
WR1-WA	+	10.0±0.1	19.5±0.2	4.7±0.1	2.7±0.1	1.1±0.2	<0.02	1.8
WR2-WA	+	11.1±0.0	9.0±0.4	2.7±0.1	1.8±0.1	0.5±0.0	<0.02	4.0
WR3-WA	+	10.5±0.0	11.9±0.4	2.4±0.1	1.9±0.0	0.7±0.1	<0.02	2.9
WR6-WA	+	9.4±0.1	13.7±0.2	3.5±0.0	2.1±0.1	1.1±0.1	<0.02	1.8
WR7-WA	+	10.0±0.0	15.3±1.6	3.0±0.1	2.0±0.1	0.7±0.3	<0.02	2.9
RO1-BA1	+	7.6±0.0	43.8±3.1	3.6±0.3	4.3±0.1	0.7±0.1	<0.02	2.9
RO1-BA2	+	7.5±0.1	23.3±1.4	3.3±0.1	3.3±0.2	0.7±0.3	<0.02	2.9
RO1-BA3	+	7.4±0.0	42.1±6.6	2.8±0.2	3.9±0.2	0.9±0.2	<0.02	18.9
RO2-BA1	+	7.3±0.1	142.9±2.9	1.8±0.0	12.7±0.2	3.6±0.2	0.38	10.6
RO2-BA2	+	7.1±0.0	76.0±26.2	2.3±0.9	6.5±1.2	1.2±0.1	0.08	6.7
RO2-BA3	+	7.2±0.1	47.4±1.6	3.2±0.2	5.7±0.2	3.0±0.3	0.22	7.3
RO3-BA1	+	7.3±0.1	52.0±1.1	4.3±0.2	6.2±0.0	5.2±0.4	2.33±0.14	44.8
RO3-BA2	+	7.2±0.0	59.9±3.4	3.4±0.1	6.1±0.3	2.2±0.1	0.20	0.9
RO3-BA3	+	7.0±0.1	57.6±3.0	3.1±0.1	5.1±0.1	3.4±0.6	0.23	6.8
RO1-WA1	+	9.4±0.1	5.9±0.4	2.5±0.2	1.3±0.0	0.6±0.0	<0.02	3.3
RO1-WA2	+	8.9±0.2	6.4±0.3	3.0±0.2	1.5±0.1	0.7±0.2	<0.02	2.9
RO1-WA3	+	8.7±0.1	8.8±0.2	4.3±0.0	1.5±0.1	1.6±0.1	<0.02	1.3
RO2-WA1	+	10.9±0.0	7.6±0.5	1.8±0.1	1.4±0.1	0.5±0.1	<0.02	4.0
RO2-WA2	+	11.0±0.0	6.2±0.4	1.9±0.1	1.4±0.0	1.7±0.1	0.08	4.7
RO2-WA3	+	11.0±0.0	5.8±0.4	1.0±0.1	1.2±0.0	0.4±0.1	<0.02	5.0
RO3-WA1	+	10.1±0.0	5.5±0.1	2.2±0.0	1.2±0.0	0.4±0.1	<0.02	5.0
RO3-WA2	+	10.1±0.1	11.3±1.3	4.4±0.4	1.6±0.1	3.3±0.3	<0.02	0.6
RO3-WA3	+	10.2±0.0	7.1±0.7	2.5±0.2	1.4±0.1	0.6±0.1	<0.02	3.3

247

248 **Table S7** Summary of results of sealed incubation experiments after 12-weeks. Results are means ± S.D.,
249 except for MeHg in which we pooled the majority of samples from replicates for analysis. All dissolved
250 constituents represent <1.0-μm fraction. *Note:* smell is sulfide, "rotten" egg smell present (+) or absent (-);
251 COND=conductivity; DOC=dissolved organic carbon; SUVA$_{254}$=specific ultraviolet absorbance at 254 nm
252 (proxy of DOC aromaticity); TDN=total dissolved nitrogen; Hg=mercury;
253 MeHg=methylmercury; %MeHg=percent of Hg as MeHg.

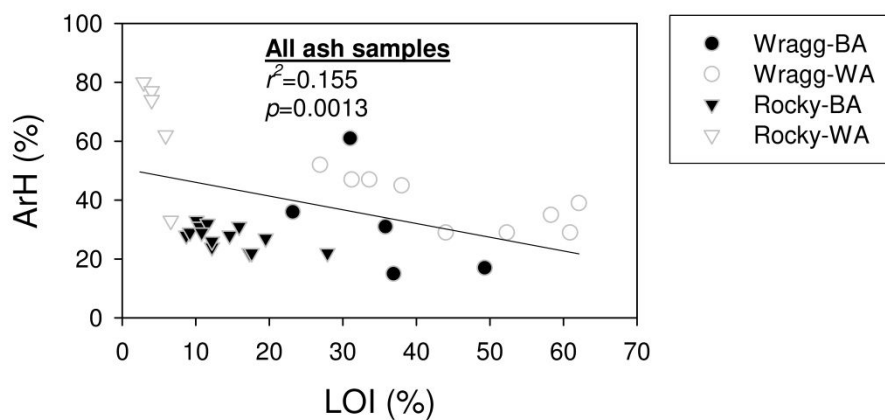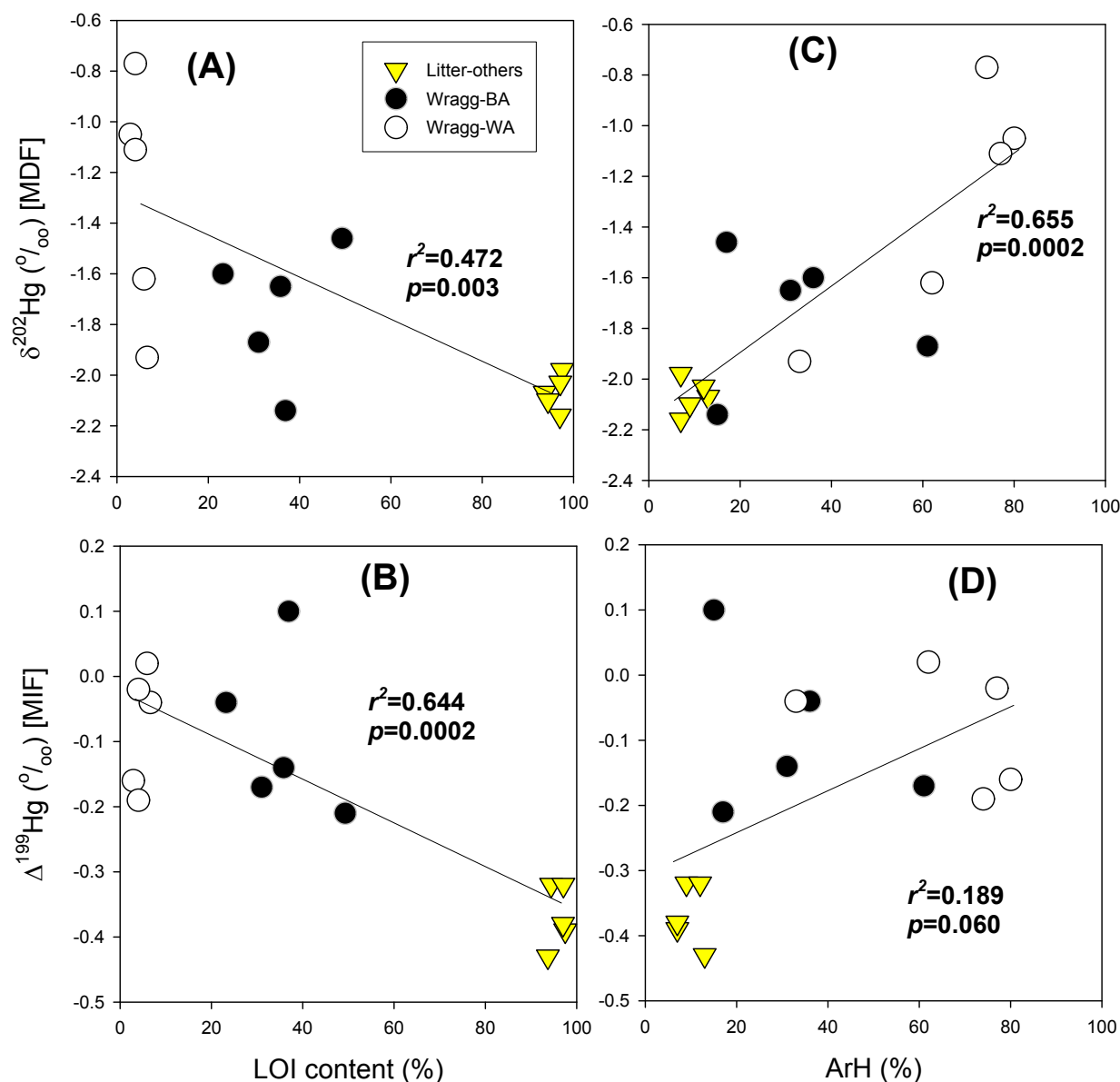|	Sulfidic smell	COND (μS/cm)	pH	DOC (mg/L)	SUVA$_{254}$ (L/mg/m)	TDN (mg/L)	Filtered Hg (ng/L)	Filtered MeHg (ng/L)	%MeHg
Water-only	-	124±3	6.6±0.3	7.0±0.5	2.8±0.3	0.3±0.0	0.4±0.1	<0.02	0.0
CA-Litter	+	387±4	6.8±0.4	305.6±3.6	1.5±0.1	3.6±0.5	2.8±0.2	0.13	4.8
WR1-BA	+	645±17	7.7±0.0	76.6±8.2	3.9±0.2	4.8±0.3	0.5±0.1	<0.02	3.3
WR3-BA	+	715±18	7.7±0.0	79.5±3.7	3.9±0.1	9.5±0.4	1.1±0.1	0.10	9.2
WR4-BA	+	540±38	7.8±0.0	53.1±7.8	3.7±0.2	6.5±1.1	1.3±0.1	0.06	4.4
WR5-BA	+	864±22	8.0±0.1	72.4±1.9	3.7±0.0	8.1±0.2	0.9±0.0	0.04	4.3
WR7-BA	+	607±34	7.9±0.1	57.1±3.5	3.5±0.2	6.3±0.1	1.0±0.2	0.10	10.0
WR1-WA	+	258±1	9.3±0.3	18.3±0.3	5.4±0.1	2.7±0.1	1.1±0.0	0.06	5.5
WR2-WA	+	906±86	11.2±0.1	7.9±0.3	3.5±0.2	1.7±0.1	0.6±0.1	0.04	6.9
WR3-WA	+	363±28	10.1±0.1	8.2±0.5	4.1±0.4	1.7±0.0	0.9±0.2	0.05	6.2
WR6-WA	+	432±6	9.0±0.1	8.4±0.4	5.7±0.1	2.1±0.1	0.7±0.3	0.05	6.5
WR7-WA	+	497±42	9.7±0.1	9.3±1.0	5.2±0.3	1.9±0.1	0.5±0.2	<0.02	4.3
RO1-BA1	+	493±28	8.2±0.2	37.2±3.5	5.3±0.1	4.8±0.2	0.4±0.1	0.05	11.8
RO1-BA2	+	391±29	8.0±0.1	16.3±0.5	4.4±0.1	3.0±0.1	0.4±0.0	0.03	6.7
RO1-BA3	+	422±35	7.8±0.0	29.9±1.1	4.9±0.1	3.7±0.1	0.4±0.1	0.06	13.0
RO2-BA1	+	715±23	7.8±0.1	78.8±1.3	3.4±0.0	13.8±0.3	1.6±0.1	0.05	3.1
RO2-BA2	+	641±10	7.8±0.1	56.0±0.7	3.3±0.0	7.9±0.1	0.7±0.1	0.03	4.2
RO2-BA3	+	557±5	8.0±0.2	52.6±2.6	3.4±0.1	8.8±0.3	1.6±0.2	0.05	3.3
RO3-BA1	+	598±6	7.9±0.0	54.7±1.2	4.6±0.1	8.0±0.2	1.9±0.1	0.35	18.4
RO3-BA2	+	621	8.1	52.5	3.8	8.1	1.0	0.03	3.0
RO3-BA3	+	605	8.0	53.2	3.6	7.9	1.6	0.14	8.8
RO1-WA1	+	214±3	9.0±0.0	5.0±0.2	3.0±0.0	1.1±0.1	0.5±0.1	<0.02	3.0
RO1-WA2	+	183±12	8.2±0.3	5.1±0.1	3.5±0.0	1.3±0.0	0.5±0.1	<0.02	4.7
RO1-WA3	-	306±21	8.0±0.1	7.6±0.4	4.7±0.1	1.1±0.1	1.0±0.2	<0.02	2.2
RO2-WA1	-	3,113±201	10.8±0.0	7.2±0.4	2.0±0.1	1.3±0.1	0.3±0.1	<0.02	5.0
RO2-WA2	-	948±35	11.2±0.1	6.5±0.2	2.4±0.1	1.4±0.1	5.3±1.0	0.12	2.3
RO2-WA3	+	664±50	11.1±0.1	5.0±0.2	1.4±0.1	1.0±0.0	0.3±0.1	0.04	13.6
RO3-WA1	+	1,168±42	10.0±0.0	5.1±0.1	2.4±0.1	1.0±0.1	0.4±0.1	<0.02	3.3
RO3-WA2	+	853±68	9.8±0.1	10.4±0.2	4.8±0.1	1.6±0.2	3.0±0.4	0.03	0.9
RO3-WA3	-	711±31	10.1±0.0	6.2±0.1	2.8±0.0	1.1±0.0	0.5±0.1	0.05	8.5

254

pre-sieved

2-mm sieved

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257 **Fig. S1** Top-pictures of pre-sieved surface (0-5 cm depth) ash samples -- black ash (BA) and white ash
258 (WA) from the Wragg Fire (2015). Bottom-pictures of 2-mm sieved surface (0-5 cm depth) ash samples -
259 - black ash (BA) and white ash (WA) from the Wragg Fire (2015), and the Rocky Fire (2015). Pictures
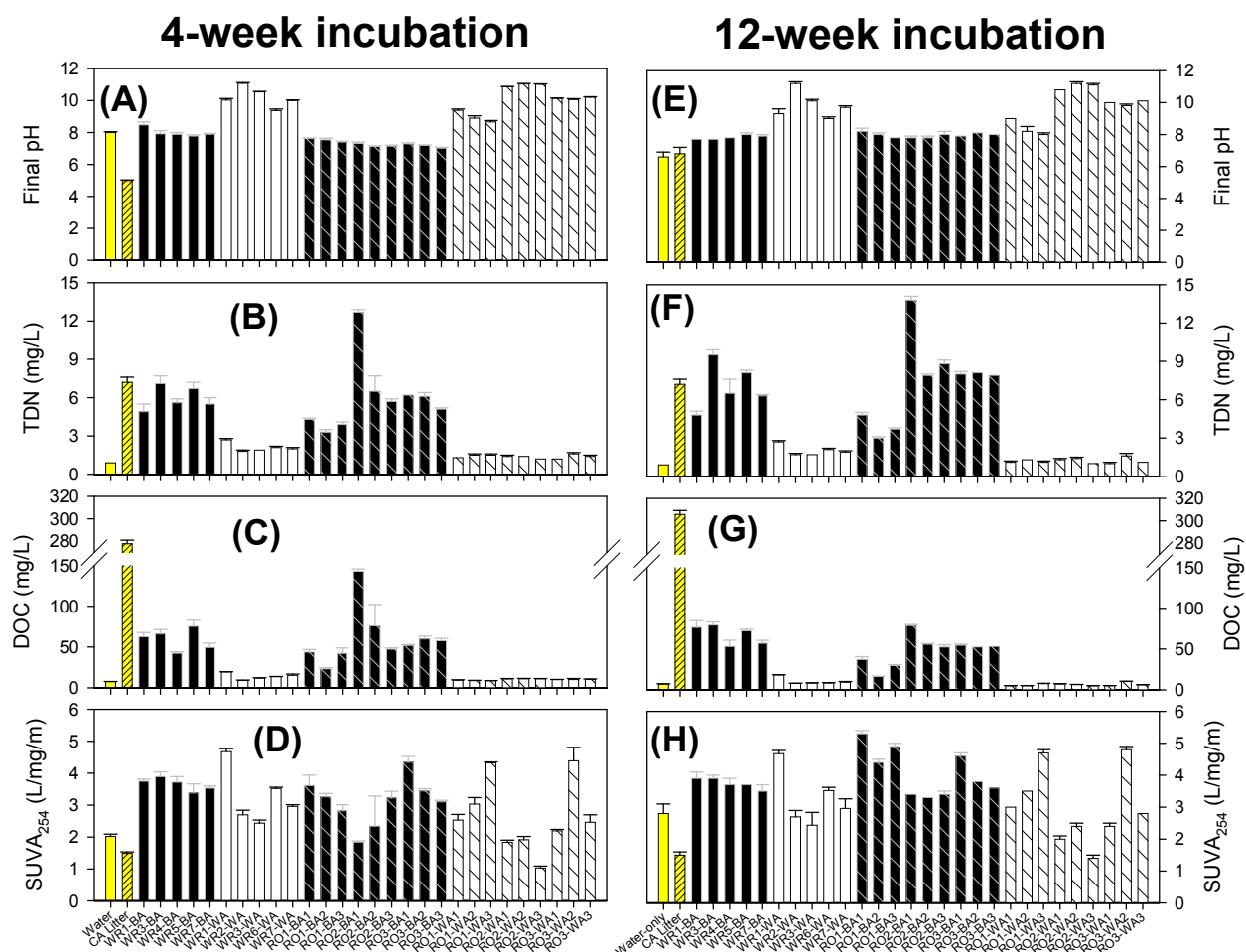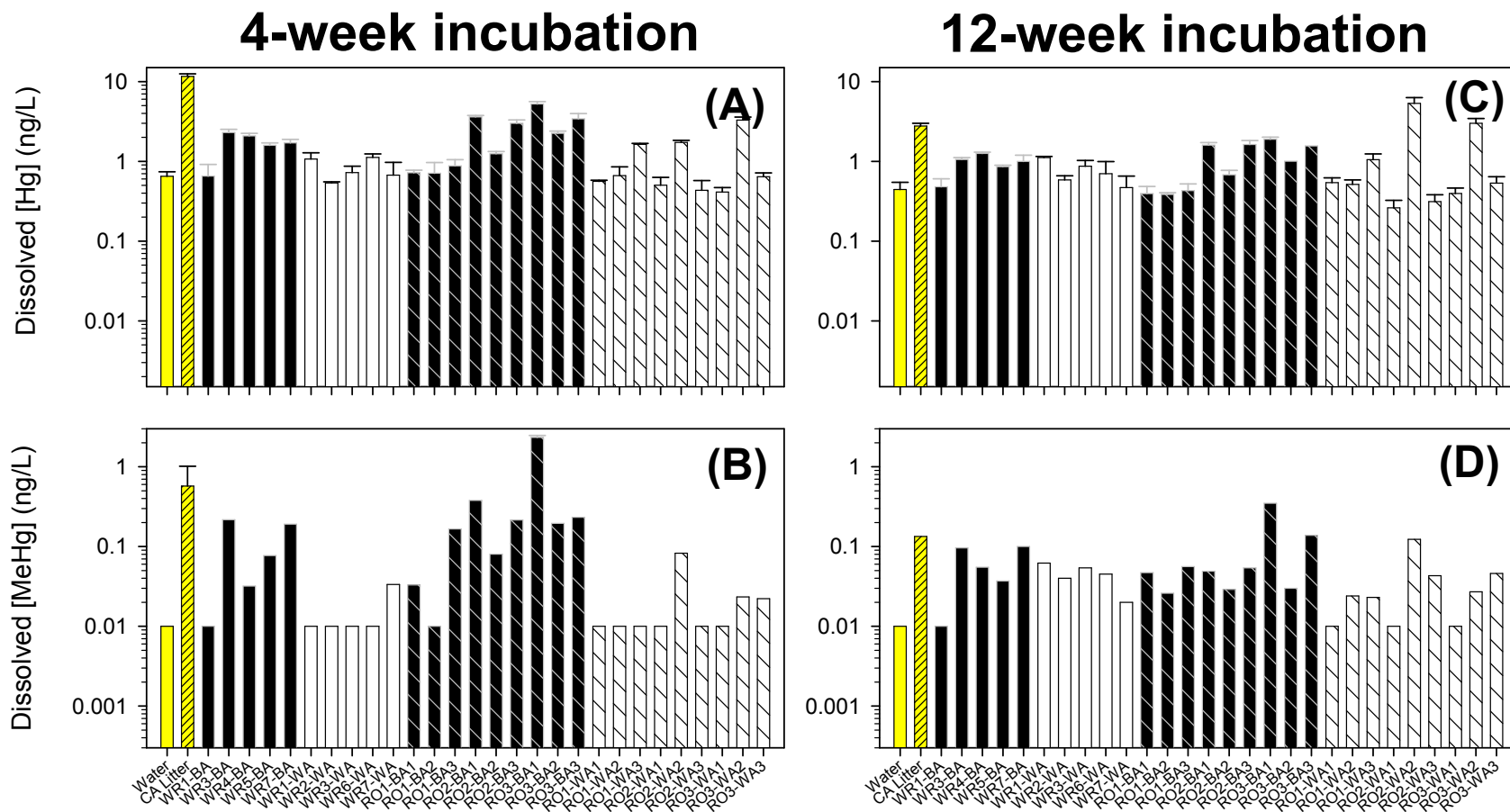260 taken by P. Ku and M. Tsui.

Fig. S2 Variation of percent aromatic hydrocarbon (ArH) of pyrolysis products as a function of loss-on-ignition (LOI) of black ash (BA) and white ash (WA) from the Wragg Fire and the Rocky Fire.
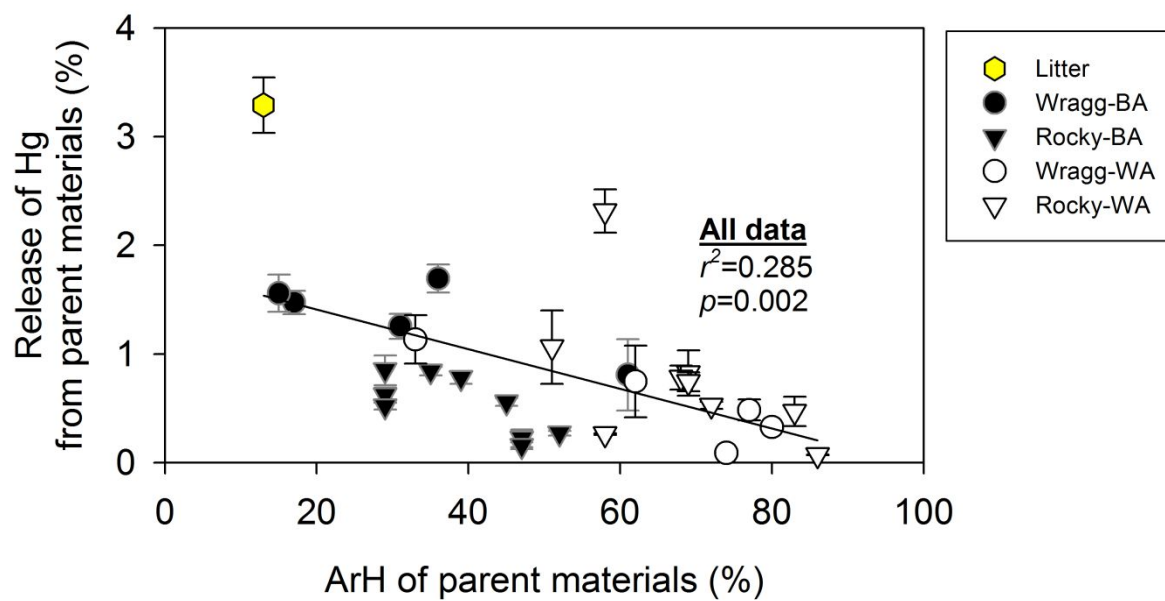
Fig. S3 Relationships between loss-on-ignition (LOI) and **(A)** δ^{202}Hg (mass-dependent fractionation [MDF]), and **(B)** Δ^{199}Hg (mass-independent fractionation [MIF]) of Hg isotopes among different unburned litter and ash samples. Relationships between percent of aromatic hydrocarbon (ArH) of pyrolysis products content and **(C)** δ^{202}Hg (mass-dependent fractionation [MDF]), and **(D)** Δ^{199}Hg (mass-independent fractionation [MIF]) of Hg isotopes among different unburned and ash samples. Published isotope data of foliage was not included as that particular study[15] did not provide information on LOI and ArH.
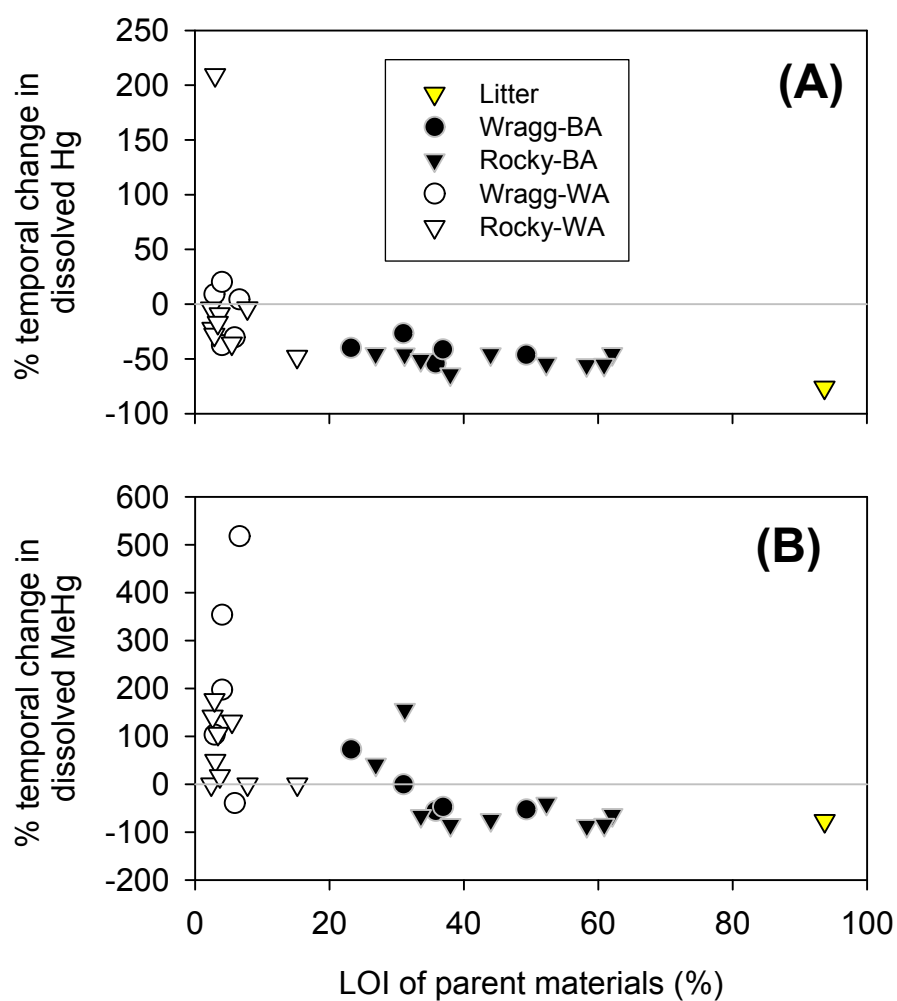
4-week incubation

12-week incubation

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Fig. S4 Data from incubation experiment for 4-week and 12-week, data are mean±s.d. (n=3; except RO3-BA2 and RO3-BA3 where n=1). **(A, E)** final pH at 4- and 12-week; **(B, F)** total dissolved nitrogen (TDN) at 4- and 12-week; **(C, G)** dissolved organic carbon (DOC) at 4- and 12-week; and **(D, H)** proxy of DOC aromaticity (SUVA$_{254}$) of the aqueous phase at 4- and 12-week. Note: Yellow: water-only; Hatched yellow: unburned litter from a northern California forest (Angelo Reserve); Black: BA from Wragg; White: WA from Wragg; Hatched black: BA from Rocky; Hatched white: WA from Rocky.

281

Fig. S5 Concentrations of dissolved (<1-μm) mercury concentrations ([Hg]; **A** and **C**) and dissolved methylmercury concentrations ([MeHg]; **B** and **D**) after 4- or 12-weeks of sealed incubation from water only (filtered stream water only, no solid materials added), unburned California litter (CA Litter), Wragg Fire black ash (WRX-BA), Wragg Fire white ash (WRX-WA), Rocky Fire black ash (RO#-BA), and Rocky Fire white ash (RO#-WA), where # is the site locations. Data are mean±s.d. (*n*=3 for Hg data while *n*=1 for most MeHg data).

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289 **Fig. S6** Relationships among parameters after 4 weeks of sealed incubation experiment. Release of Hg
290 from parent materials as a function of percent aromatic hydrocarbon (ArH) content of pyrolysis products.

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Fig. S7 Temporal percent changes of dissolved **(A)** mercury (Hg) and **(B)** methylmercury (MeHg)

concentrations in incubation bottles from 4-weeks to 12-weeks among incubation materials of different

loss-on-ignition (LOI).

SI References

1.   Olund, S. D.; DeWild, J. F.; Olson, M. L.; Tate, M. T. Methods for the preparation and analysis of solids and suspended solids for total mercury. Chapter 8 of Book 5, Laboratory Analysis Section A, Water Analysis. 2004. U.S. Geological Survey, Reston, Virginia.

2.   Song, J., Peng, P. A. Characterisation of black carbon materials by pyrolysis–gas chromatography–mass spectrometry. *J. Anal. Appl. Pyrolysis* **2010**, *87*, 129-137.

3.   Chen, H.; Blosser, G. D.; Majidzadeh, H.; Liu, X.; Conner, W. H.; Chow, A. T. Integration of an automated identification-quantification pipeline and statistical techniques for pyrolysis GC/MS tracking of the molecular fingerprints of natural organic matter. *J. Anal. Appl. Pyrolysis* **2018**, *143*, 371-380.

4.   Blum, J. D.; Bergquist, B. A. Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* **2007**, *388*, 353-359.

5.   Demers, J. D.; Blum, J. D.; Zak, D. R. Mercury isotopes in a forested ecosystem: Implications for air-surface exchange dynamics and the global mercury cycle. *Glob. Biogeochem. Cycles* **2013**, *27*, 222-238.

6.   Tsui, M. T. K.; Blum, J. D.; Kwon, S. Y.; Finlay, J. C.; Balogh, S. J.; Nollet, Y. H. Photodegradation of methylmercury in stream ecosystems. *Limnol. Oceanogr.* **2013**, *58*, 13-22.

7.   Tsui, M. T. K.; Blum, J. D.; Finlay, J. C.; Balogh, S. J.; Nollet, Y. H.; Palen, W. J.; Power, M. E. Variation in terrestrial and aquatic sources of methylmercury in stream predators as revealed by stable mercury isotopes. *Environ. Sci. Technol.* **2014**, *48*, 10128-10135.

8.   Woerndle, G. E.; Tsui, M. T. K.; Sebestyen, S. D.; Blum, J. D.; Nie, X.; Kolka, R. K. New insights on ecosystem mercury cycling revealed by Hg isotopic measurements in water flowing from a headwater peatland catchment. *Environ. Sci. Technol.* **2018**, *52*, 1854-1861.

9.   Balogh, S. J.; Huang, Y.; Offerman, H. J.; Meyer, M. L.; Johnson, D. K. 2002. Episodes of elevated methylmercury concentrations in prairie streams. *Environ. Sci. Technol.* **2002**, *36*, 1665-1670.

10. Tsui, M. T. K.; Finlay, J. C.; Nater, E. A. Effects of stream water chemistry and tree species on release and methylation of mercury during litter decomposition. *Environ. Sci. Technol.* **2008**, *42*, 8692-8697.

11. Blum, P. W.; Hershey, A. E.; Tsui, M. T. K.; Hammerschmidt, C. R.; Agather, A. M. Methylmercury and methane production potentials in North Carolina Piedmont stream sediments. *Biogeochemistry* **2018**, *137*, 181-195.

12. Parker, J. L.; Bloom, N. S. Preservation and storage techniques for low-level aqueous mercury speciation. *Sci. Total Environ.* **2005**, *337*, 253-263.

13. Mitchell, C. P. J.; Branfireun, B. A.; Kolka, R. K. Spatial characteristics of net methylmercury production hot spots in peatlands. *Environ. Sci. Technol.* **2008**, *42*, 1010-1016.

14. Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37*, 4702-4708.

15. Zheng, W.; Obrist, D.; Weis, D.; Bergquist, B. A. Mercury isotope compositions across North American forests. *Glob. Biogeochem. Cycles* **2016**, *30*, 1475-1492.