Immediate and Long-Term Fire Effects on Total Mercury in Forests Soils of Northeastern Minnesota

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Within the Boundary Waters Canoe Area Wilderness in northeastern Minnesota, soils were collected from 116 sites in areas of primarily virgin forest with fire-origin stand years (year of last recognizable stand-killing wildfire) that range from the 1759 to 1976. Median concentrations for total mercury in soils for this span of 217 years range from 0.28 ± 0.088 ppm (1759) to 0.09 ± 0.047 ppm (1976) for A-horizon soils and from 0.23 ± 0.062 ppm (1759) to 0.09 ± 0.018 ppm (1976) for O-horizon soils. A separate study of soils collected from 30 sites within an area that burned in a 2004 wildfire at Voyageurs National Park, northern Minnesota, suggested that high soil burn severity resulted in significant mercury loss from both organic and mineral soils. Integrated data from these two studies and additional regional soil data demonstrate that older forests have progressively higher mercury concentrations in O-horizon soils ($r^2 = 0.423$) and A-horizon soils ($r^2 = 0.456$). These results support the hypotheses that an important factor for mercury concentrations in forest soils is time since stand-replacing fire and that high soil burn severity has the potential to reduce the concentration of mercury in burned soils for tens to hundreds of years.

Introduction

Soil geochemistry surveys in northern Minnesota demonstrate that organic soil materials (O horizon) have median total mercury (Hg) concentrations of 0.12 ± 0.062 ppm and mineral organic soils (A horizon) have median mercury concentrations of 0.13 ± 0.078 ppm (*1, 2*). Deeper soils (B or C horizons) have much lower mercury concentrations, typically about 0.03 ppm (*1, 2*). This distribution of mercury in forest soils is consistent with the hypothesis that in the Upper Midwest atmospheric deposition supplies more mercury to terrestrial ecocosystems than geologic sources (*2, 3*). Atmospheric mercury is deposited directly through wet and dry deposition and indirectly via sequestration by foliage and subsequent inputs by throughfall and litterfall (*4–7*). Much of the mercury deposited to forest soils volatilizes back to the atmosphere, but because mercury has the ability to form strong bonds with soil organic matter, a small portion is retained in soils. Grigal (*8*) suggests that if mercury sequestration in upland forest soils is linearly related to deposition with time, then sequestration rates were about $1.4\ \mu\text{g m}^{-2}\ \text{a}^{-1}$ in preindustrial times and currently are about $5.0\ \mu\text{g m}^{-2}\ \text{a}^{-1}$. Thus, with ongoing atmospheric deposition through time, the concentration of total mercury in forest

soils will continue to increase unless the forest floor is somehow disturbed.

The bulk of the atmospherically deposited mercury in upland forest soils is retained at or near the forest floor with little movement of mercury down the soil profile (*8, 9*). Therefore, the vertical and spatial distribution of mercury in forest soils is dependent on factors that control mercury deposition, such as climate and canopy structure, and factors that control organic carbon contents in soils, such as climate, microbial activity, and landscape disturbances. One such disturbance is forest fire. Combustion of forest floor organic soils by fire will instantaneously release mercury in gaseous or particulate form (*10–17*). Relatively few studies have successfully documented additional releases of mercury from underlying mineral soils resulting from fire, but several recent studies suggest that some portion of this large pool of stored mercury can be mobilized if soils are heated to sufficiently high temperatures (*2, 18*). Numerous studies of effects of fire on carbon, which is highly correlated to mercury in forest soils, show widely varying effects, including both gains and losses and no change following fire with outcomes largely dependent on fire type and fire severity (summarized in refs *19–21*). Only a few studies of high intensity fires have documented significant losses of carbon from mineral soils. Sands (*22*) estimated carbon losses of 40 to 50% from soils 24 years after a high intensity fire in radiata pine in Australia. Forest soils that burned in the high intensity 2002 Biscuit fire in Oregon had estimated carbon losses of about 23% from combined organic and mineral soils (*23*).

Here we integrate soil geochemical data from several study areas in northeastern Minnesota. The main emphasis of this work is the loss of mercury in both organic and mineral soils with fire, but because of the close relation between mercury and carbon in soils and the potential for similar effects from fire, both elements are considered. This analysis indicates that significant mercury and carbon contained in organic and mineral soils can be mobilized by wildfire if soil burn severity is sufficiently high and that evidence of mercury and carbon loss from soils resulting from high intensity, high severity fires that may result in destruction of a forest canopy and deep burning at the forest floor may persist for many decades.

Materials and Methods

Study Area. In northeastern Minnesota, high mercury levels in soils, lake waters, and aquatic animals are found throughout the region, including within the Boundary Waters Canoe Area Wilderness (BWCAW), a wilderness recreation area in the Superior National Forest in northeast Minnesota, and Voyageurs National Park (VNP), located along the Minnesota-Ontario international border (Supporting Information (SI) Figure S1). Studies of dated lake sediment cores in the region (*24–26*) and geologic materials (*1, 27*) have consistently shown that atmospheric deposition is the major pathway for mercury deposition to wetlands, lakes, and soils. Swain et al. (*24*) estimate that annual deposition of atmospheric mercury in Minnesota has increased from $3.7\ \mu\text{g m}^{-2}$ in 1850 to $12.5\ \mu\text{g m}^{-2}$ in the 1990s.

Soils throughout northeastern Minnesota are typically shallow Inceptisols, developed on thin deposits of loamy until or glacial outwash overlying Precambrian bedrock. Vegetation in the region is typical of southern boreal and Laurentian mixed conifer-hardwood. European earthworms have invaded many of the previously earthworm-free regions in Minnesota. In some areas, earthworm activity has resulted

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in profound changes in soil structure and texture, including the loss of an organic O horizon and development of a thick, well-mixed mineral A horizon by relocation of organic matter from the forest floor into underlying mineral soils (28).

Much of the virgin forests in the BWCAW and VNP had been either burned or logged by the 1920s. In VNP, large stand-killing fires broke out in 1917−1918, 1923, and 1936, with fire years following times of severe drought (29). The BWCAW was historically subject to crown fires with a mean fire rotation period of between 50 and 100 years (30). Because of topography and a complex landscape of lakes and wetlands in the BWCAW, natural fires created a mosaic of relatively young, even-aged stands and older stands that escaped fires for centuries (30, 31). Using a combination of tree-dating, fire scars, historical data, and air photos, Heinselman (30) created year-of-origin maps for forest stands in the BWCAW that captured four centuries of fire history. One limitation of Heinselman's stand-origin maps is that evidence is not preserved for hundreds of creeping surface fires that may have burned through the region and potentially had an impact on soil chemistry. However, his remarkably detailed maps represent the most reliable fire history record for the region.

This study combines data from four sampling events in northern Minnesota to evaluate both the short- and long-term influence of fire on mercury in northern forests:

(1) Soil samples were collected in May 2001 and May 2002 in VNP as part of an investigation of mercury in bedrock, soils, lake waters, and age-one yellow perch in selected watersheds across the Park (1, 3).

(2) For a study of the Section 33 wildfire in VNP, soils were collected two weeks after a wildfire burned approximately 4 km² in the interior of the Park in July to August 2004 (2). The Section 33 fire was a stand-replacement fire killing much of the above ground vegetation in a predominantly spruce/fir/aspen forest. Fire behavior was variable and created a mosaic of fire effects on the landscape. Most of the area burned at high intensity, and other areas burned with low intensity through the duff layer (S. Weyenberg, NPS, personal communication, 2010). Sample sites were established within the footprint of the wildfire along 10 separate transects that each had similar vegetation and slope characteristics. Along each of the 10 transects, three sites were selected with varying soil burn severity (unburned, light/moderate, deep burning) determined by applying the fire severity matrix described in Keeley (32) to field observations of the extent of combustion to the soil organic layer. At unburned sites, plants were green and there were no direct effects of fire; at light/moderate sites, the soil organic layer was scorched but not totally consumed; and at deep burning sites, surface litter and the soil organic layer were completely consumed, exposing bare mineral soil.

(3) Soil samples were collected in September 2004 and September 2005 from nine to ten sites within ten watersheds in or immediately adjacent to the BWCAW for a regional evaluation of potential effects of prescribed fire on mercury in soils, lake waters, and fish. All samples were collected before any fire treatment. Forest stand-origin years were determined for the 116 sample sites by overlaying sample locations with stand-origin maps from Heinselman (30). Soils from the ten watersheds fell into seven fire stand-origin age groups, ranging from 1759 to 1894, and two logging-history groups, 1895 to 1915 and 1898 to 1921. During these logging periods, Minnesota state law required the burning of slash in logged areas (30), so soils from the logging groups are included in this analysis of fire effects.

(4) In September 2006 soils were collected from an area of the BWCAW burned in 1976 (Roy Lake wildfire), postdating Heinselman's stand-origin analysis, to fill a time gap between the early 20th century and more recent data. For the Roy Lake wildfire study, soils were collected from twelve sites in areas where the original forest had been destroyed in the 1976 wildfire and from twelve sites in adjacent areas that had not had a stand-replacing fire since 1801.

For all sampling events, soil samples were collected by soil horizon designations rather than by depth and from upland sites rather than lowlands or wetlands. Where present, an O horizon, consisting of organic material in varying states of decomposition (but not forest litter), was collected within a fixed area and weighed in the field. The underlying A horizon, a mixture of humified organic material mixed with mineral soil, was collected from a measured volume and weighed in the field. In the field the distinction between an O horizon and an A horizon was based on estimated mineral content and texture; some A-horizon samples had organic carbon contents that were greater than 20%, and so those samples would be more accurately classified as an Oa horizon. The base of an Oa or A horizon was easily defined by a color change at the top of an E or B horizon. Soils from all four sampling events described above were collected and processed in a consistent manner. Soil densities determined by volumetric sampling permitted calculation of element inventories (mass per unit area).

Analytical Techniques. All geochemical analyses were completed by the USGS geochemistry contract laboratory, SGS Minerals. Analytical techniques and quality control/quality assurance requirements are described in detail in ref 33. O-horizon soils were air-dried (<25 °C) and reweighed to calculate densities. Soils were then milled and split, with one portion set aside for total mercury analysis and the remainder of the sample ashed at 500 °C for 13 h at the USGS analytical laboratory in Denver, CO. Percent total carbon in O-horizon soils was estimated as (100 - % ash). Mineral soils were air-dried and sieved to <2 mm, with the sieved fraction weighed for density calculations. Total carbon was determined by an automated carbon combustion analyzer. For total mercury analyses of organic and mineral soils, aliquots were digested using a mixture of nitric and hydrochloric acids, with potassium permanganate, sulfuric acid, and potassium persulfate added to the solution, followed by a NaCl-hydroxylamine solution. Mercury analyses of the diluted digested samples were completed using a Perkin-Elmer Flow Injection Mercury System-100 cold-vapor atomic absorption mercury analyzer, with a lower limit of detection of 0.02 ppm.

Statistical Methods. Differences in soil chemistry for burned and unburned soils were evaluated using the Kruskal−Wallis one-way analysis of variance for multiple groups and the Mann−Whitney U-test to compare two groups (SYSTAT 11.0 statistical software package). These nonparametric tests evaluated the null hypothesis that there were no significant differences for mercury and carbon concentrations and inventories among soils collected in burned and unburned areas. Rejection of the null hypothesis at the 95% confidence level ($p \leq 0.05$) was taken as evidence that there existed significant differences for these elements among samples classified by varying fire impacts.

Results and Discussion

Median and mean mercury and carbon concentrations and inventories from 126 soil samples collected in VNP and the BWCAW used in this analysis are available in SI Table S1. Mercury concentrations from all sites range from 0.03 to 0.29 ppm in O-horizon soils and from 0.01 to 0.35 ppm in A-horizon soils. The Spearman rank-order correlation coefficient for mercury and carbon concentrations in A-horizon soils is 0.866; the correlation coefficient for mercury and calculated carbon concentrations in O-horizon soils is 0.398.

Immediate Effects of Wildfire on Soil Mercury and Carbon. Loss of carbon in soils by fire should result in loss of mercury because of the close association between the two
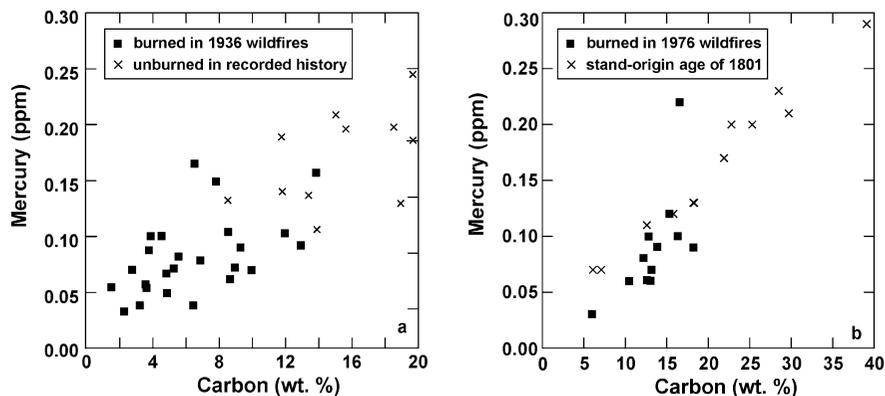
FIGURE 1. Scatterplot of mercury versus carbon concentrations for A-horizon soils from a) areas in the Kabetogema Peninsula, VNP, that burned in 1936 wildfires and are unburned in recorded history and b) areas in the BWCAW burned in the 1976 Roy Lake wildfire and adjacent areas with a stand-origin year of 1801.

elements (5). The 2004 Section 33 wildfire burn area in VNP supports the supposition that mercury and carbon are mobilized from both O- and A-horizon soils if soil burn severity is sufficiently high (2). Total combustion of O-horizon soils at deep burning sites released approximately 0.25 mg Hg m^{-2} and 1000 g C m^{-2} (2). Importantly, exposure and apparent heating of underlying mineral soils (Oa and A horizons) at deep burning sites also had the potential to mobilize significant quantities of mercury and carbon. Median inventories for mercury and carbon from unburned sites (1.02 mg Hg m^{-2} and 1180 g C m^{-2}), light/moderate sites (0.77 mg Hg m^{-2} and 1013 g C m^{-2}), and deep burning sites (0.13 mg Hg m^{-2} and 420 g C m^{-2}) indicated significant ($p \leq 0.005$) reductions of both elements at deep burning sites when compared to unburned sites (2). There was variability in the soils data collected along the 10 transects in the Section 33 wildfire study, but the overall pattern for 7 of the 10 transects strongly supported loss of mercury and carbon from both organic and mineral soils in areas where soil burn severity was described as deep burning.

Long-Term Effects of Wildfire on Soil Mercury and Carbon. We surmise that mercury losses from soils in areas immediately following wildfires are likely to be gradually ameliorated by continued atmospheric deposition of mercury and sequestration in soils, eventually restoring mercury levels toward or beyond prefire levels. However, the time required for this may be decades or even hundreds of years. Soil data from the integrated studies described here provide several lines of evidence supporting this assertion.

The principal landscape factor that best explained a heterogeneous distribution of mercury in A-horizon soils across the Kabetogama Peninsula, a small area of VNP with a relatively homogeneous climate and forest structure, was the wildfire history of the region. A-horizon soils from the 2001 to 2002 regional soil survey in VNP showed a large range of concentrations for both mercury (0.03 to 0.28 ppm) and carbon (2.7 to 36.3 wt %) (1). A plot of mercury concentrations versus carbon concentrations for A-horizon soils within and outside of areas burned during the severe fires that swept across the Kabetogama Peninsula in 1936 suggest decades-long impact on both mercury and carbon concentrations in burned and unburned soils (Figure 1a). A similar distribution of mercury and carbon for A-horizon soils in the area of the 1976 Roy Lake fire in the BWCAW verified the pattern observed for VNP soils (Figure 1b). Soils collected within the 1976 fire footprint under stands of even-age jack pine have statistically significant lower mercury ($p < 0.006$) and carbon ($p < 0.035$) concentrations than mercury and carbon concentrations of soils within a nearby spruce-aspen forest with a stand-origin year of 1801.

To expand the time range of the analysis, soil data from the Roy Lake wildfire and the Section 33 wildfire were combined with the large soil data set from the BWCAW. The 2004 VNP Section 33 wildfire mercury and carbon data from deep soil burning sites represent a recent end point documenting immediate effects of high soil burn severity, with complete combustion of O-horizon soils, and reduced mercury and carbon in A-horizon soils. The Section 33 wildfire data were designated as year 1 in this analysis and merged with mercury and carbon data in O- and A-horizon soils from the BWCAW classified by the forest stand age from the maps of Heinselman (30). The two logging intervals were combined and assigned a year of 1905, near the middle of the time span for logging/slash burning activities in those areas. Figure 2 is a plot of the mercury concentrations in O- and A-horizon soils against time in years since last the recognizable stand-killing fire for the integrated soil data.

There is considerable spread in the data in Figure 2, as would be expected for soils collected within large areas defined by mapped stand-origin age that on the ground are a heterogeneous landscape with multiple gradients of fire styles, effects, and long-term recovery following fire. The fact that Heinselman's maps only record major stand-replacing fires and not the hundreds of other probable fires that may have had local impacts on soil chemistry has to be of concern. In addition to landscape variations, forest canopy type, and variable fire effects, many other factors influence mercury delivery and retention in forest soils. All of these factors certainly contribute to the observed variability in mercury concentrations for forest soils in Figure 2. However, even with these caveats, Figure 2 shows that the concentrations of mercury in forest soils were lowest immediately following fire and increased with time since the last recognizable stand-replacement wildfire.

This trend indicates that fire history plays a critical role for the concentration of mercury in relatively undisturbed forest soils for tens to hundreds of years. These results are consistent with findings from other studies in forested areas. A study in Acadia National Park, Maine, showed that soils in a watershed that burned in 1947 exhibited lower mercury concentrations than soils in a comparable but unburned watershed (11). In an upland boreal forest plot in Saskatchewan, Canada, Friedli et al. (34) measured mercury inventories in organic soils of 2.92 ± 0.87 mg Hg m^{-2} for a boreal forest with a stand age of 139 years and 1.01 ± 0.28 mg Hg m^{-2} for a boreal forest with a stand age of 39 years.

Total soil inventories of mercury and carbon for VNP and the BWCAW were determined by adding together inventories calculated for O- and A-horizon soils collected from each of the 126 sites (Figure 3). This approach is used because at a number of sites in the BWCAW, especially in watersheds with easy recreational access, an O horizon is thin or missing because of earthworm activity. For sites where the O horizon has been consumed by earthworms, it is assumed that
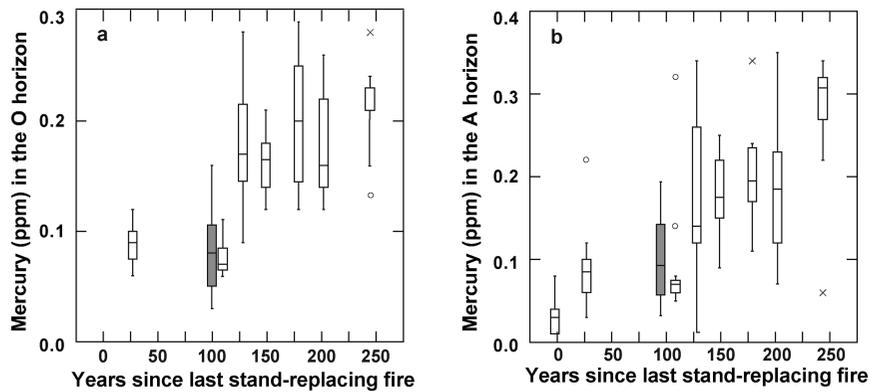
FIGURE 2. Box plots of mercury concentrations in a) O- horizon and b) A-horizon soils collected from the BWCAW and from high soil burn severity sites within the 2004 Section 33 wildfire area in VNP plotted against time since last major stand-replacement fire. Soils from the Section 33 wildfire defined as year 1. Shaded box from areas in the BWCAW that were logged and then burned in slash fires.
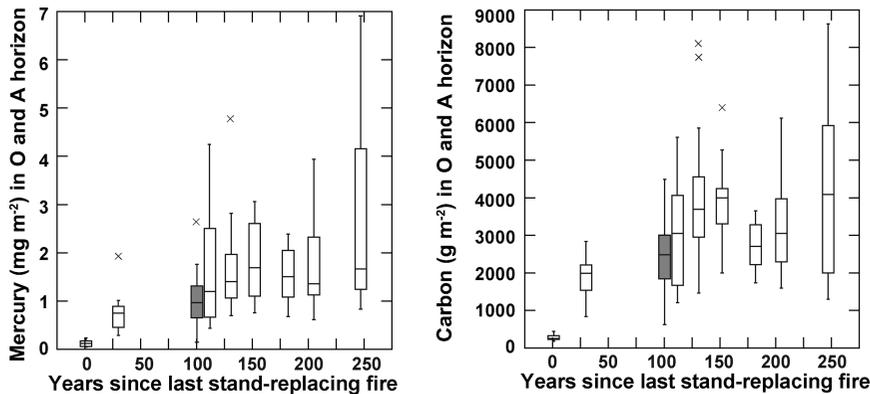

FIGURE 3. Box plots of a) total mercury inventories and b) carbon inventories in combined O- and A-horizon soils from the BWCAW and from high soil burn severity sites within the 2004 Section 33 wildfire in VNP plotted against time since last major stand-replacement fire. Soils from the Section 33 wildfire defined as year 1. Shaded box from areas in the BWCAW that were logged and then burned in slash fires.

mercury originally contained in O-horizon materials was incorporated into underlying mineral soil. The combined inventories in Figure 3 represent the total quantity of mercury and carbon at individual sites in soils collected above the top surface of either an E horizon or a B horizon, which in this region typically contain low concentrations of mercury and carbon (1, 2, 27). Soil mercury and carbon inventories in combined O- and A-horizon soils both increase with increasing time following stand-killing wildfire, but accumulation rates for the two constituents seem to be somewhat different (Figure 3). Mercury increases continuously during the 250-year time span, while carbon inventories flatten out after approximately 150 years. However, the variability in the data and a lack of data for other factors that control mercury and carbon cycling in soils makes interpretation of these accumulation rates somewhat problematic.

An important factor in all our observations about mobilization of mercury and carbon from soils by fire, especially mineral soils, is the impact of the heat pulse of the fire on the soil surface. In the VNP Section 33 wildfire study, we were able to evaluate visually soil burn severity extent. Mercury and carbon were mobilized by combustion of organic soils at both light/moderate and deep burning sites but were mobilized from mineral soils only at deep burning sites. Many of the major wildfires in the region have been described as high intensity and high severity fires that burned large areas. The 1936 fires in VNP broke out after three years of drought and burned through some areas that had previously burned in 1923. The 1936 fires are described as 'a hard burn, consuming all vegetation and soil down to bedrock in some places' (29). The majority of the soils from

the BWCAW were collected from areas where the last recognizable stand-replacement fire mapped by Heinselman (30) occurred following times of prolonged drought, including 1976, 1894, 1875, 1863−1864, and possibly 1755−1759 (31). In such extreme dry conditions forest floor litter and humus layers have very low moisture contents and can become part of the fuel load (31). When the forest floor burns, underlying mineral soils may be especially susceptible to the effects of combustion, which may have been the situation for some of the sites sampled in the BWCAW study. Slash fires through logged areas can also be of high fire severity if the fuel load is heavy (31).

Additional factors other than time may also have roles in mercury inputs and outputs to soils following fire. Volatilization rates of residual mercury from charred organic soils and exposed mineral soils in burned areas could possibly rise because of increased surface light intensity and resulting higher soil temperatures following loss of the insulating organic layer and a forest canopy (35). Destruction of a forest canopy will dramatically alter mercury delivery to the forest soil because this eliminates mercury additions from litterfall and throughfall. Grigal (5) estimated that mercury delivery to the forest floor under a mature forest canopy is approximately four times higher than fluxes to open areas with no canopy. Changes in forest type from coniferous to deciduous following fire, often because of pH changes in burned soils, also can have a major impact on mercury additions to the forest floor and eventual movement into soils (11, 36). Conifers efficiently capture mercury from the atmosphere and with a coniferous canopy, throughfall dominates mercury flux to the forest floor; in deciduous

forests, litterfall represents the largest input of mercury to forest soils (35).

This difference in mercury cycling behavior for coniferous versus deciduous forests may contribute to observed differences in mercury concentrations interpreted to reflect stand age for two adjacent small watersheds in the BWCAW. Soils from a watershed dominated by large white pine with a stand-origin year of 1759 have the highest median mercury concentrations in this analysis. Immediately adjacent to this watershed, a white birch/balsam/aspen forest has a stand-origin year of 1894, and soils have mercury levels somewhat lower than expected if mercury additions to soils are linear with time. It is possible that mercury accumulation rates for soils in these two watersheds are different because of their different forest types. However, an additional complicating factor is observed earthworm activity in soils within the dominantly deciduous watershed. Invading earthworms prefer litter from deciduous species to pine and spruce litter (37). The rapid processing of forest litter by earthworms and incorporation of organic materials into mineral soils has an unknown influence mercury cycling.

Soil mercury data integrated for this analysis demonstrate that areas in northeastern Minnesota burned in stand-replacing fires have reduced soil mercury concentrations relative to prefire conditions and that mercury losses from soils are concomitant with carbon losses. This relationship could have important implications for resource managers in areas where mercury contamination of aquatic resources is of concern. One outcome from the regional BWCAW study was the observation that methylmercury in age-1 yellow perch was correlated with total mercury concentrations in O- and A-horizon soils (38). If watershed soils play a role in mercury delivery to lakes and streams, long-term, reduced mercury in soils following major stand-replacing fires may result in lower potential for mercury contamination to aquatic organisms within the burned area. This hypothesis is currently being tested with data from the BWCAW regional study.

Many forested regions that have not had major fires that resulted in combustion of the forest floor still retain large inventories of atmospherically deposited mercury. Average annual mercury emissions from wildfires for the conterminous United States are estimated to be approximately 31 t per year for current conditions (39). The bulk of this mercury is assumed to have been released from combustion of organic soils and vegetation rather than from heating of mineral soils. However, the largest inventory of mercury sequestered in forests is within mineral soils (40). If climate change results in larger, more frequent high severity wildfires (41, 42), it is possible that mercury currently stored in organic as well as mineral soils will be increasingly vulnerable to mobilization by fire. As a result, reduction of atmospheric mercury emissions from anthropogenic sources mandated by legislation may be offset by increased natural emissions from wildfires.

Supporting Information Available

The location of the study areas and median and mean mercury and carbon concentrations and inventories used in this analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES100544D