

**The impact of forest fires on the chemistry of forest soils with emphasis
on mercury sequestration-north central U.S.**

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Abstract

A geochemical soil survey in Voyageurs National Park, Minnesota reveals a pattern of variations in many elements that correlates well with the landscape pattern of severe wildfires that burned across the region in 1936, about 65 years prior to the present study. Organic carbon and strongly correlated elements such as Hg, S, Se, Pb, and P are deficient in mineral soils within areas that burned in severe fires in 1936 relative to surrounding areas that have not burned for a considerably longer time. We interpret this pattern to illustrate a long-lived influence of severe fires on the chemical character of soils, an influence which appears to be greater than geological influences in many cases. Of particular interest is an apparent long-lived deficiency in Hg in burned areas relative to adjacent unburned forests, which implies that severe wildfires may have a long-lasting cleansing effect on Hg in these forests. A comparable soil survey of Isle Royale National Park, Michigan shows a similar spatial pattern with higher concentrations of carbon and correlated elements outside of areas that burned in 1936, although in detail this pattern is complicated by variations in geology, vegetation, and climate. Preliminary results from a study on the effect of prescribed fire on soil chemistry within a small watershed in Minnesota define short-term effects of fire on Hg distribution in mineral soils and help clarify the processes that result in the observed long-term changes.

1. Introduction

Forest soils are generally a sink for atmospherically deposited mercury (Hg) and increasingly have become a storehouse of the anthropogenically-enhanced Hg deposition of recent decades (see reviews by Grigal, 2002; 2003, and references therein). Within the conterminous United States there are an estimated 1,350 tons of Hg in the forest floor (forest duff or O-horizon) and 28,700 tons in the upper 1 meter of underlying mineral soil (Grigal, 2002). Forest soils in the north central United States show regional variability in Hg contents, but average about 150 $\mu\text{g/kg}$ Hg in organic forest floor material and about 25 $\mu\text{g/kg}$ Hg in the upper 25 cm of the mineral soil (Nater and Grigal, 1992). The corresponding mass of Hg averages about 1 mg/m^2 for forest floor organics and 6 mg/m^2 for mineral soil. The degree and rate at which this large store of Hg could be mobilized within forested ecosystems is in large part dependent on the nature and behavior of forest soils. Forest disturbances, including wildfires, may play a significant role in the Hg cycle in northern forests (Garcia and Carrigan, 1999; Caldwell et al., 2000; Amirbahman et al., 2004). Forest fires have the potential to affect Hg stored in soils in two distinct ways. Combustion of forest floor organic material, which contains about 15% of the total Hg forest soil pool, can instantaneously release Hg in gaseous or particulate form. The remaining 85%, the much larger pool of Hg in mineral soils, may also be affected by burning, but the processes that might control the behavior of Hg in mineral soils during and after forest fire are poorly known.

Documentation of Hg release by wildfires is provided by both laboratory combustion of forest fuels (Friedli et al., 2001) and measurement of Hg in smoke plumes from a fire in which both standing vegetation and a substantial amount of forest floor organics were burned (Friedli et al., 2003). Long range transport of Hg in smoke plumes from wildfires in Canadian boreal forests has been documented by Sigler et al. (2003). These studies confirm that combustion of forest floor organic material releases much of the contained Hg, but do not provide additional information on the behavior of Hg in mineral soils. A component of Hg release by heating of mineral soils was inferred by Friedli et al. (2003) because observed Hg release from studied fires was greater than could be accounted for solely by combustion of fuels as determined by laboratory combustion measurements.

The fate of the large pool of Hg contained in the upper mineral soil of forests and the role that forest fires might play in determining its fate seems a critical factor in modeling Hg cycles in forested watersheds. We present here soil geochemical data from three study areas in the Lake Superior region (Figure 1). Although the soil surveys within Voyageurs and Isle Royale National Parks were not designed and conducted to study fire effects of Hg in forest soils, the observed distribution of soil chemistry reveals striking patterns of relative element depletions and enrichments that correlate with patterns of historic severe wildfires. We document that areas within Voyageurs National Park that were severely burned in 1936, about 65 years before we began collecting soil samples, show depletions in total Hg, as well as strongly correlated elements including organic C, P, Pb, Se, and S, compared to soils from adjacent unburned areas. We interpret the relative Hg depletions within burned areas to indicate that mineral soils were substantially affected by the severe fires of 1936 in a manner which resulted in Hg loss, and that much of the variability of Hg concentrations and correlated elements in forest soils within Voyageurs can be traced back to this 65-year old event. We also present preliminary results from a study on short-term fire effects from a small prescribed burn near Snowbank Lake in northern Minnesota. These investigations are used to develop two possible and potentially linked scenarios to explain Hg depletions in forest soils following fire. The first is a simplistic model of Hg loss by volatilization concurrent with combustion to account for all Hg depletions within a burned area. A second scenario presents a more complex model in which Hg losses from forest soils may be prolonged following severe fire because of fundamental changes to the character of the forest and consequent, significant alterations in the Hg cycle within forest soils.

2. Methods

Details of soil sampling, preparation, and digestion methods, as well as analytical techniques, analytical quality control, and complete files of all geochemical soil data from Isle Royale and Voyageurs National Parks are available digitally from the U.S. Geological Survey (Woodruff et al., 2002; Woodruff et al., 2003). Soil data from the Snowbank Lake study are unpublished, but the sampling and analytical methods used are

similar to those techniques applied in the studies within the parks, which are summarized below.

2.1 Field studies

The USGS conducted geochemical soil surveys in both Voyageurs and Isle Royale National Parks in the Lake Superior region of the north central United States. Collection of soil samples within the two parks was from 1999 to 2002. Research within both parks was designed to determine Hg concentrations of watershed soils for lakes exhibiting varying levels of Hg in fish rather than a study on the effects of forest fires. As a result of the original study design, the distribution of sample sites is skewed toward certain lake basins of particular interest for our initial studies. We also are currently conducting a small study of fire effects on soil chemistry in a prescribed burn area near Snowbank Lake in the Superior National Forest. The study area at Snowbank Lake was burned by prescribed fire in 2000. Soil samples were collected preburn, and at various times following the fire from 2000 to 2003. Field protocols in the Snowbank study were the same as used for the sampling in the two national parks.

At all sites soil samples were collected by soil horizons, rather than by depth, and from upland sites rather than lowlands or wetlands. Soils within the study areas are young and formed from glacial materials deposited approximately 12,000 to 10,000 years ago. At each sample site, soil pits were dug by hand to 50 to 75 cm and generally extended to about 100 cm with a bucket auger, although in some cases, shallow bedrock or extremely rocky soils limited sampling depth. After collection and removal of organic forest floor material, mineral soil samples were collected from the A- and C-horizons. Soil profiles were described and measured and the vegetation and physiographic setting of each site were recorded. All sites were located by GPS.

2.2 Analytical techniques

Mineral soils were air-dried in the laboratory and sieved to recover the silt + clay fraction ($<63\ \mu\text{m}$) for analysis. Material that did not pass through the sieve was discarded. All results presented here are from this fine fraction of the soils. The sieved soil samples were ground and totally digested using a variety of multi-acid methods.

Mercury analyses were performed by cold vapor-atomic absorption spectroscopy. Total C was determined by an automated carbon analyzer and carbonate C by coulometric titration. Organic C is calculated by subtracting carbonate C from total C. Total S was determined by an automated sulfur analyzer. Arsenic and selenium were analyzed by hydride generation-atomic absorption spectroscopy (HG-AAS). In addition, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) provided data for 40 elements, discussed below.

Analyses were done at XRAL Laboratories, Toronto, Canada, using USGS-developed techniques, and at USGS laboratories in Lakewood, Colorado. Quality control was monitored by the USGS Analytical Chemistry Services Group in Lakewood, Colorado. Duplicate samples were submitted at a rate of 10% of total samples. Data were accepted if recovery was $\pm 15\%$ at five times the limit of detection and the relative standard deviation was less than 15% for duplicate samples.

The ICP-AES technique provides data for a suite of 40 elements, 27 of which can be interpreted quantitatively. Thirteen elements reported below the limit of detection for all or most samples analyzed and are not further considered in this report. These thirteen elements with their limits of detection are Ag (2 ppm), Au (8 ppm), Be (1 ppm), Bi (10 ppm), Cd (2 ppm), Eu (2 ppm), Ho (4 ppm), Mo (2 ppm), Nd (9 ppm), Sn (5 ppm), Ta (40 ppm), Th (6 ppm), and U (100 ppm). The remaining 27 elements (Al, Ca, Fe, Ga, K, Mg, Na, P, Ti, Ba, Ce, Co, Cr, Cu, La, Li, Mn, Nb, Ni, Pb, Sc, Se, Sr, V, Y, Yb, Zn) occur in quantifiable concentrations in all or a large majority of samples. For samples reporting an element below the limit of detection a value of 2/3 the detection limit was assigned for purposes of calculations and geographic portrayal.

3. Study areas

3.1 Voyageurs National Park

Voyageurs National Park, stretching for 50 km along the Minnesota-Canada border, was established in 1975. Following an initial logging frenzy for white pine in the late 1800s, extensive logging continued until the area's designation as a National Park. The park is 60% land and 40% water, mostly contained within four large lakes. The interior of

the park is now somewhat remote with water-access only and a few foot-trails, and is in part administered as wilderness. The climate of Voyageurs is mid-continental.

Voyageurs is underlain by Neoproterozoic rocks of the Superior Province (Table 1). Bedrock in the northern part of the park is fine- to medium-grained biotite-rich metasediments (Day et al., 1990). Several small leucogranite and dioritic intrusions cut the metasediments. In the southern and eastern part of the Park metasediments grade into schist-rich migmatites and then into more granite-rich migmatite. Large areas of pink to gray biotitic, massive to weakly foliated Lac La Croix granite are predominant in the eastern end of the Park (Day et al., 1990).

Bedrock in the western third of the park is covered by ground moraine of the Des Moines lobe (Hobbs and Goebel, 1982). Des Moines lobe tills were derived from shales and limestones in the lowlands of Manitoba, and are generally clayey and carbonate-rich, and contain abundant limestone clasts. In the eastern two-thirds of the park thin, sandy glacial deposits of the Vermillion moraine overly bedrock and are part of the Rainy lobe, derived from rocks of the Superior Province, a greenstone-granite terrane.

Bedrock outcrops in Voyageurs are abundant and many ridge tops are bare rock. The soils of Voyageurs are generally inceptisols developed on gravelly and sandy till or outwash. Loamy, sandy soils are typically thin, often less than 20 cm to underlying bedrock (U of MN, 1981). The composition and structure of forests in Voyageurs have been altered by the long history of logging, but are typical of the southern boreal or Laurentian mixed conifer-hardwood region with much of the park forested by spruce, fir, and aspen (USGS, 2000). An outbreak of spruce budworm disease has decimated the white spruce population in a number of areas.

3.2. Isle Royale National Park

Isle Royale National Park is an archipelago of nearly 400 islands in northern Lake Superior. The bulk of the park is the single large island of Isle Royale, which is 72 km long and 15 km wide, oriented with the long axis northeast-southwest. Isle Royale has a long history of human use, including commercial fishing, sporadic native copper mining in the 1800's, and unprofitable logging operations in the early 1900s. Concerns about

plans for extensive logging in the 1920s resulted in a long effort to preserve the island. Isle Royale was established as a National Park in 1941. Designation of most of the land mass as a wilderness in 1976 has greatly reduced human impact. The climate of Isle Royale is mid-continental and somewhat moderated by Lake Superior (Hansen et al., 1973).

The Mesoproterozoic bedrock of Isle Royale is mostly basalt with a small area of conglomerate and sandstone overlying basalt in the southernmost part of island (Huber, 1975). The stacked basalt flows run the length of the island and dip to the southeast, creating a series of long bedrock ridges and intervening valleys. Bedrock on the island is covered by Pleistocene deposits of the late Wisconsinan Superior lobe, which occupied the present basin of western Lake Superior and advanced from the northeast. In the northern two-thirds of the island basalt bedrock is covered by a thin, discontinuous sheet of lodgement till, but an apparent still-stand of the ice margin resulted in development of several recessional moraines and deposition of a thick till across the southern third of the island (Huber, 1973). Glacial transport directions for much of Isle Royale are nearly parallel to the bedrock trends along the length of the island, except in southern part of the island where ice movement was slightly oblique to the strike of the bedrock ridges (Huber, 1973). Outcrops of bedrock are abundant, especially in the northeastern half of the island, where bare rock ridges are common.

Soils developed on tills, outwash, lacustrine deposits, and raised beaches lines, which are remnants of former glacial lake-levels. Soils on the northern part of the island are poorly developed spodosols; soils are better developed on the thick tills of the southern third of the island (ESRI, 2000). Forested uplands on Isle Royale vary from boreal mixed and conifer forests in the north to a maple-yellow birch hardwood forest on the better soils of the south (ESRI, 2000). Much of the island's hardwood forests were converted to an aspen-birch forest by severe fire in 1936 (Cole et al., 1997). Heavy browsing by moose has altered the natural forest succession on the island, such that aspen and balsam fir are being replaced by white spruce (McInnes et al., 1992).

3.2 Snowbank Lake

A 92-acre area near Snowbank Lake, 120 km southeast of Voyageurs National Park in the Superior National Forest, was burned in a fuel reduction prescribed fire by the USDA Forest Service on October 11, 2000. Bedrock and the glacial deposits in the Snowbank area are similar to those found in much of Voyageurs. Soils are mainly inceptisols developed on sandy or gravelly till. The forest around Snowbank Lake is a mixed stand of older-aged balsam fir, spruce, aspen, red pine and jack pine. Many trees, particularly mature balsam and spruce, were blown down by a severe storm in July 1999.

4. Soil chemistry and fire

4.1 Soil chemistry of Voyageurs and Isle Royale National Parks

Soil samples collected from Voyageurs and Isle Royale typically consist of an O-horizon (not always present) as much as 10 cm thick, underlain by an A/O- or A-horizon, generally only 5 to 10 cm thick, in places with an underlying E-horizon. Beneath the organic mineral topsoils, B-horizon soils grade downward into a parent C-horizon material, rarely deeper than 40 to 75 cm.

Compositions of O-horizon samples are not considered in this study because of high variability in sample chemistry, in part a result of the heterogeneity of sample material (e.g., pine needles vs. deciduous leaves) and a range of decomposition (previous year's litter vs. older highly decomposed fibric material). Analyses of O-horizon samples from Voyageurs and Isle Royale are given in Woodruff et al. (2002) and Woodruff et al. (2003). An additional confounding factor determining the presence or absence of an O-horizon, as well as the character and composition of the forest floor, has been the introduction and radiation of exotic earthworms throughout the Upper Midwest (Hale, 2004). We have visually identified earthworm presence at a number of our sites in both Voyageurs and Isle Royale. One of the consequences of high earthworm activity is destruction of the organic forest floor, with incorporation of organic material into mineral soil. To minimize chemical changes that may have resulted from this accelerated mixing of forest floor with mineral soil, an attempt was made to use data for plots and statistical testing from soil sites with recognizable, coherent decomposing forest floor material

rather than just fresh, undecomposed litter on bare mineral soil, often an indication of pervasive earthworm activity.

Table 2 gives the mean composition for all elements from all samples from the A- and C-horizons from the two parks. Soils classified as A-horizon are generally dark gray/black mineral soils with some organic matter; soils with organic C concentrations greater than 20% may be more accurately classified as A/O. Rarely, lighter gray E-horizon material was incorporated by sampling, but these samples have not been differentiated from other A-horizon samples in our statistical analysis. A-horizon soils are generally less rocky than the C-horizon soils, although angular pebbles are common. Roots and woody debris are also abundant, and were removed by sieving prior to chemical analysis. Typically A-horizon soils display a sharp lower boundary with reddish brown B-horizon soils.

The mean compositions of A- and C-horizon soils from the two parks in Table 2 demonstrate the influence of geology on soil compositions. C-horizon soils on Isle Royale typically have higher concentrations of Ca, Fe, Mg, Ti, and especially Cu, compared to C-horizon soils in Voyageurs, reflecting the predominantly basaltic source of the glacial deposits on the island. Higher concentrations of elements such as Al, K, Na, Pb, and Sr in Voyageurs soils result from the more granitic/alkalic source rocks for glacial deposits from the Rainy Lobe. Most of the compositional differences between A- and C-horizon soils at individual sites can be related to either soil-forming processes, effects of vegetation, or anthropogenic influence. Many major and trace elements in both A- and C-horizon soils do show significant internal correlations that can be attributed to expected mineral associations; e.g., Fe, Mg, Ti and Sc from pyroxene, or K, Na, Ba, and Sr from feldspars.

It is apparent from the data presented in Table 1 that the underlying bedrock in both Isle Royale and Voyageurs have little or nondetectable quantities of Hg (detection limit = 20 ppb). This lack of a geologic source of Hg is reflected in the compositions of the C-horizon soils from both parks, which have much lower Hg concentrations than A-horizon soils (Table 2). This distribution of relatively high Hg concentrations in A-horizons compared to either bedrock or parent soil material is taken as evidence that the bulk of

the Hg present in forest soils within the parks is a result of atmospheric deposition rather than geological sources.

As for many mineral soils in the Upper Midwest (e.g., Grigal and Nater, 1989; Cannon and Woodruff, 2003) A/O- and A-horizon soils from the two parks show a strong correlation between organic C and Hg (Figure 2A). Sulfur is also positively correlated with organic C (Figure 2B) and Hg, consistent with the finding of Skyllberg et al. (2000) that Hg is bound largely to reduced sulfur in soil organic matter. A lack of correlation in our data between Hg and elements characteristic of clay minerals, such as Al, indicates that adsorption of Hg onto clays is of secondary importance to soil organic matter as a site for Hg in A-horizon soils. Other elements which have at least moderate correlations with organic C and Hg, including P, Pb, and Se, also are probably adhered to soil organic compounds. In general, both Se and Pb can be commonly bound in sulfide minerals and therefore could be controlled in part by percentage of sulfide minerals in soil. However, sulfide minerals are not abundant in bedrock of either of the parks and the presence of sulfides in any appreciable amount in the rather well oxidized soils of the region is unlikely. We discount, therefore, the role of sulfide minerals in influencing the concentration of these elements in the soils. We conclude that the concentrations of Hg, P, Pb, S, and Se A-horizon soils are a reflection of the concentration of organic matter and that all 5 elements, in major part, are components of organic molecules.

4.2 1936 fires in Voyageurs and Isle Royale National Parks

Following three years of extreme drought much of the Upper Midwest, large, severe stand-replacing forest fires throughout the summer of 1936 broke out across the region, including areas within what is now Voyageurs and Isle Royale National Parks. The fires on Isle Royale began in July from three ignition points (two lightening and one human-caused) and spread quickly through logging slash, eventually burning over 26,000 acres, about 20% of the main island (NPS, 2003) (Figure 3A). The fires were only extinguished by rains and snow in October. The same summer, fires also broke out throughout northern Minnesota and southern Ontario, also fueled in part by logging slash and timbering activity. Within Voyageurs, the fires were confined to the Kabetogama Peninsula, which makes up the bulk of the dry land in the heart of the park. The fires

burned across two large sections of the peninsula, from lakeshore to lakeshore, burning more than 35,000 acres, almost half of the land area (Figure 3B).

Since 1936, both parks, especially Voyageurs, document a number of small fires that were typically contained by aggressive fire suppression. Our soil geochemical studies in the parks sampled areas within the 1936 fire footprints, areas that burned after 1936, and in areas where the fire history is unknown (Figure 3). To avoid potentially confounding effects from post-1936, often low severity, fires we have examined soil data from both parks that compare only sites within areas documented to have burned during the severe 1936 fires with sites that apparently did not burn in 1936 or at any known time since then.

4.3 Fire patterns in soils of Voyageurs National Park

From the larger Voyageurs soil data set, we selected 50 mineral soil samples sites on the Kabetogema Peninsula to compare for fire effects; 26 sites are within the areas burned in 1936, 24 sites are in areas not obviously burned either in 1936 or within recorded history (Table 3). Selecting sites only within the Kabetogema Peninsula minimized the variability of several of the major factors that control soil properties. Because mineral topsoil are most likely to reflect a severe fire signature, we concentrated on A-horizon soil chemistry in this analysis.

For A-horizon soils, the spatial distribution of elements typically associated with organic carbon in upland forest sites (e.g., Hg in Figure 4) for ‘burned’ sites (soil sample locations within the mapped boundaries of the 1936 fires) and ‘unburned’ sites (sample locations outside the 1936 fire perimeter) first suggested a connection between soil chemistry and severe fire. This was further verified by a plot of organic carbon vs. Hg for the subset of samples from the Kabetogema Peninsula, which shows distinct groupings for samples within the two categories (Figure 5).

To test for differences in soil chemistry between burned and unburned areas, a series of plots were constructed. Of all the elements, organic C and associated elements Hg, P, Pb, S, and Se seemed to have the greatest distinction between 1936 burned and unburned sites (Figure 6). The significance of these differences was statistically tested using the nonparametric Kurskall-Wallis one-way analysis of variance. For these six elements the Kurskall-Wallis test showed significant differences between burned and unburned sites

for C, Hg, P, Pb and S (probability level <0.001); the distribution for Se was not sufficient to fit the requirements for testing. We propose, and discuss in more detail in following sections, that the strong depletions in organic C, Hg, P, Pb and S, and possibly Se, observed within the 1936 burn areas in A-horizon soils are the result of either loss of these elements by direct combustion in the 1936 fires, or, perhaps more significantly, post-fire depletions initiated by longer term wildfire-induced forest disturbance. It is our interpretation that the 1936 fires were of such severity that post-fire forest recovery has not fully ameliorated fire effects on soil compositions during the 65 years between the fires and our sampling. The strong relative depletions in organic C, Hg, P, Pb, and S may be a characteristic and long-lasting signature of severe wildfires on mineral topsoils.

4.3.1 Other possible causes of soil variability

We have also examined possible controls on soil chemistry other than severe fire. Other spatial factors commonly interpreted to cause soil variability, such as changes in bedrock composition and varying character of glacial deposits, seem much less significant than the fire history in explaining the variable compositions. Within the limited geographic area of the Kabetogema Peninsula in Voyageurs National Park, several of the major factors that control soil properties, such as climate and soil age, are similar and should not exert undue influence. For other factors, including bedrock composition, and vegetation, we extracted a variety of variables for each sample site from field notes and digital data sets to test their significance using the same analysis of variance approach used for fire history.

Bedrock geology The composition of bedrock, the source of till and other glacial deposits that are the parent materials of mineral soils in this region is a widely recognized factor in controlling soil composition. In areas of very thin tills, such as in Voyageurs, a strong correlation between bedrock composition and the composition of soil parent material is highly expectable. A digital geologic map of the park (Hemstad et al., 2002) shows a total of 31 rock units. Within the area of our soil sampling the bedrock geology can be simplified into three general rock types -- leucogranite, biotite schist, and migmatite. However, Kruskal-Wallis testing shows no significant correlation between both A- or C-horizon soil compositions (Table 3) and the composition of underlying

bedrock (Table 1). Because the bulk compositions of the three rock types are somewhat similar, it is probable that homogenization of the different rock types during glacial transport and deposition minimized strong correlations between underlying bedrock and the soils developed over it. In any case, it is clear that within Voyageurs bedrock geology is a much less significant factor in causing variations in A-horizon soil composition than is fire history.

Vegetation characteristics Because the nature of forest cover has the potential to influence soil composition, particularly the input and character of organic matter, we examined numerous variables related to forest vegetation for significant correlations. In addition to variables extracted from a recent digital vegetation map of the park (USGS, 2001), we used our own site-specific field observations of tree species, size, and percent canopy. Analysis of variance tests were performed to search for significant correlations between variables defined by forest type, species mix, percent canopy, and modal stand height. In many cases it was necessary to generalize the detailed information in the vegetation map in order to achieve a sufficiently small number of variable classes. Analysis of variance testing which includes a large number of classes becomes counterproductive as it results in insufficient data points in some classes to yield statistically reliable results.

Numerous analyses found no strong correlations between vegetation characteristics extracted from the digital vegetation map and compositions of A-horizon soils. Using our site-specific observations we did find minimally significant correlations between a simple variable defined by a three-fold classification of dominantly deciduous forest, dominantly conifer forest, mixed conifer-deciduous forest; Ni and Cr in A-horizon soils are enriched in sites that are dominantly coniferous vs. deciduous or mixed sites. There were no significant differences for organic carbon or associated elements. Although it is possible that further, more detailed analyses of vegetation could yield some additional correlations with soil composition, we conclude that the analyses of variance reported here indicate that variations in forest characteristics do not have as great an influence on soil chemistry as fire history.

In summary, examination of some of the factors most likely to result in variable soil chemistry, in addition to forest fires, has not revealed significant correlations in most

cases. We are left with the conclusion that the impact of the severe 1936 wildfires remains the most important determinant in the compositional variability of A-horizon soil within Voyageurs National Park.

4.4. Fire patterns in soils of Isle Royale National Park

The major wildfire season of 1936 also affected Isle Royale National Park, with the severity of the fires resulting in stand-replacement in nearly all of the burned areas (Hansen et al., 1973; Cole et al., 1997). For the soil survey of Isle Royale we sampled soils at 119 upland sites across the burned and unburned parts of the island (Woodruff et al., 2003). However, because our original studies focused on watersheds northeast of the parts of the island that burned in 1936 and were not intended to study fire effects, our samples are strongly skewed toward that area. Overall, only 15 of our sites were burned in 1936, as well as a site that also burned in 1948 (Figure 3). There are 86 unburned sites northeast of the burned area and 17 unburned sites to the southwest.

Unlike the Kabetogema Peninsula of Voyageurs, which has similar climate, vegetation, and glacial cover across the study area, these factors are variable across Isle Royale. The Lake Superior shoreline and low-lying islands are typically cooler and wetter than the upland ridges, with distinct boreal vegetation (ESRI, 2000). In the interior of the island, the northeast is dominated by spruce-fir-paper birch-aspen, while the southern part is mostly a sugar maple-yellow birch northern hardwood forest, a distribution controlled in part by the varying thickness of glacial material. The central area of the island within the 1936 burns is now dominantly paper birch-aspen-spruce (Hansen et al., 1973).

As done for soil data from Voyageurs, we initially used visual comparison of element concentrations with fire history to identify compositional patterns that might be related to severe fire (Figure 7). A simple comparison of sites that are above and below the mean composition for all Hg data from Isle Royale shows that while Hg contents are highly variable in unburned areas, with only two exceptions, areas within the 1936 burn are below the mean Hg concentration. But, this apparent visual trend is not as statistically robust as in Voyageurs. Complicating factors in interpreting the soil chemistry data on Isle Royale are regional trends in the geochemical composition of soil parent material (C-

horizon), varying climate between shorelines and the island interior, and the forest type distribution.

There are significant compositional differences between A- and C-horizon soils from the northeast end of Isle Royale compared to soils from the southwest. In the northeast, C-horizon soils are significantly higher in Al, Cr, and Cu, and lower in As, K, Na, Li, Pb, and Sr. These differences are likely the result of contrasting bedrock influence, with greater chemical influence from basaltic bedrock in the northeast where glacial deposits are thin. To the southwest, in the area of thick till and glacial transport oblique to the bedrock trends, the glacial material contains a higher percentage of material derived from sandstones that overlie basalt in the southeast part of the island and extend under Lake Superior to the east of the island.

Selection of soil sample subsets that minimize climatic, glacial and vegetation differences between burned and unburned areas failed to yield the highly significant correlations between burned and unburned soils obtained from the Voyageurs soil data subset. A-horizon soil data on Isle Royale do not consistently show the notable decreases in organic C, Hg, Pb, P, and S within the fire footprint areas as seen with the Voyageurs data. There may be a number of reasons we are unable to resolve the fire footprint. The smaller number of sample sites that can be selected to minimize climatic, forest cover, and geologic differences handicaps statistical testing. Also, the highly variable, yet persistent moose population on Isle Royale has had a major influence on vegetation (Krefting, 1974), and consequently soil nutrient cycling (McInnes et al., 1992; Pastor et al., 1993). It is interesting to note that for the complete soils data sets for the two parks, on average A-horizon soils from Voyageurs have higher concentrations of both C and Hg than soils samples collected from Isle Royale, although there is a wide spread of the data (Table 2). Pastor et al. (1988) documented that moose browsing on Isle Royale has apparently resulted in, among other factors, decreases in soil carbon. The influence of landscape variability and disturbances other than fire apparently makes the identification of a chemical signature of the 1936 fires in Isle Royale soils ambiguous.

4.5 Snowbank Lake

At ten sites within the area of a planned prescribed fire samples from the O- and A-horizons were collected prior to the burn. Two days following the fire, prior to any rainfall, the sites were reoccupied and comparable samples were collected. Fire severity was high-moderate (100% of organic forest floor material consumed, mineral soil exposed) at 4 sites and low-moderate at 4 sites (some forest floor material combusted or charred, mineral soil not exposed). Two sites were untouched by the fire. At the high-moderate sites, exposed mineral topsoils were desiccated down to 2 cm, but no color change was apparent. Soil samples from the 10 sites were also collected 6 months following the fire, and twice in the following two years.

The average concentration of Hg in O-horizon soils was 0.24 ppm. Complete combustion of forest floor material within moderate-severe fire areas would release the bulk of contained Hg. At sites where fire severity was moderate-high and mineral soils were exposed and desiccated, two separate soil samples from the A-horizon were collected to look for differences between desiccated soils and underlying soils. No apparent differences in either organic C or Hg concentrations were noted between pre-fire soil samples and samples collected immediately following the fire, or between desiccated topsoils and soils immediately underlying. However, subsequent soil sampling at the same sites and at the same depths revealed an unexpected trend in Hg concentrations in A-horizon soils. Figure 8 shows a plot of organic C vs. Hg in all A-horizon soils for the moderate-high Snowbank sample sites with time. Six months following the fire (May, 2001) there was an apparent increase in Hg concentrations for similar organic C contents. This seeming increase in Hg was not observed in soil samples collected one and two years later; in fact, there may be a subtle decrease in Hg, compared to original values, in the final samples analyzed.

5. Interpretations

Our data for Voyageurs show patterns for some elements in of A-horizon soils that are not readily related to geologic variables. The pattern imposed by the 1936 fires on A-horizon soil chemistry appears to be the dominant factor in controlling the spatial variability of many elements that are related to organic carbon content. The patterns for these elements may reflect both short- and long-term changes in geochemical mobility

produced by burning. The soil data from Voyageurs suggests that the history of severe fires which occurred as much as 65 years prior to our study remains a major determinant of the spatial geochemical patterns within the park and, for many elements, outweighs geological causes of variability. We suggest, therefore, that fire history, even fires decades prior to sampling, should be considered as an important variable when interpreting the geochemistry of northern forest soils.

Accelerated erosion following fire can play a major role in removal of soils in areas of steep topography. We have not observed significant post-fire erosion at our study sites at Snowbank Lake, as a consequence of the intentionally less severe impact of prescribed fire on soils is preservation of an intact fine-root system, inhibiting post-fire erosion and the relatively subdued, rolling landscapes of the Upper Midwest. Within the 1936 burn areas, large areas of exposed bedrock suggest enhanced erosion following severe fire. A reasonable presumption for our studies in the two national parks is that the 1936 fires were of adequate severity to establish conditions in which post-fire erosion removed much of the A-horizon from areas of thin soil cover over bedrock, and that in many areas the present-day A-horizons within the 1936 burned areas have re-established only within the intervening years. However, erosion following fire played an insignificant role in controlling the present day spatial distribution of organic carbon and associated elements. Rather, in the following sections we specifically emphasize the potential effects of forest fire on C and associated elements, especially Hg. Fire may have both short-term and longer-term effects on soil compositions, which are especially important for organic material (see review by Gonzalez-Perez et al., 2004). The short-term effects of fire include combustion of forest floor organic material and immediate volatilization of Hg and other elements contained in organic matter. Longer-term effects may result from perturbations in forest structure and processes consequent to destruction of mature forest stands and initiation of new stands, and the effects this progression may have on C and Hg deposition and sequestration rates.

5.1. Combustion and short-term effects

Severe fires, especially those occurring during drought as was the case with the 1936 fires, may consume a high percentage of the forest floor organic layer and volatilize

much of the Hg contained in it. A survey of Hg in soils of the north central United States indicates that O-horizon soils, on average, contains about 1 mg Hg/m² whereas the underlying 25 cm of mineral soils contains about 5 mg Hg/m² (Nater and Grigal, 1992). Thus, combustible O-horizon soils contain roughly 15-20% of the total Hg load in the near-surface forest soils that is subject to immediate loss during fires. Based on post-fire observations at our Snowbank Lake study site, we estimate that roughly 50% of the total Hg load in the O-horizon was probably lost instantaneously during the fire from the 92 acre prescribed burn area.

The fate of the Hg sequestered in underlying mineral soils following fire is not as clear, and the processes by which Hg might be released from mineral soils because of forest fires are poorly defined. Certainly, a pulse of heat having the potential to volatilize Hg contained in the mineral soil may be transmitted into the ground, but there is little documentation of the degree to which this occurs. At Snowbank Lake mineral topsoils at moderate severity sites did not show any immediate decrease in Hg, even though the overlying O-horizon was completely combusted and the top 2 cm of mineral soil were desiccated. The apparent short-term increases in Hg concentrations for A-horizon soils six months following the fire may have resulted from incorporation of Hg retained on ash or residual organic material into the mineral topsoils. However, subsequent changes in organic C vs. Hg with time suggest that the apparent short-term higher Hg values were perhaps linked to short-term changes in the quality of the carbon following the fire. The combustion of the organic layer and heating of organic carbon in mineral soils can produce negatively charged organic molecules which condense on cooler mineral soils, resulting in the hydrophobicity often noted for burned soils (DeBano, 1981). For exposed, burned soils at high-moderate severity sites at Snowbank Lake, it is possible that formation of organic coatings may have enhanced short-term adsorption of atmospheric Hg. After a year's time between sampling (May 2001 to May 2002), the fire-induced organic coatings may have dissipated resulting in the loss of this adsorbed Hg. In any case, a principal conclusion of the Snowbank Lake study is that there has been no substantial loss of Hg from A-horizon soils either immediately after the prescribed fire or within 3 years following the burn, which suggests that the relative Hg depletions between

burned and unburned sites in the 1936 fires in Voyageurs are not simply a residual result of Hg loss during the actual burning.

5.2. Longer-term effects

We have documented significant compositional changes in Hg, organic C and other potentially volatile elements related to 65 year-old fires, particularly in A-horizon soils in Voyageurs National Park. Similar effects are not apparent in the relatively short term post-fire sampling at Snowbank Lake. We suggest that severe fires initiate long-term changes in cycles of Hg, C, and other elements that can produce compositional changes in A-horizon soils during a period of multiple years or decades after a fire.

The high correlation of organic C and Hg concentrations in our soil data (Figure 2) suggests that both elements respond in a similar way to fire and post-fire recovery processes. Thus, the rather extensive literature on fire effects on C can give some insights into the behavior of Hg. Numerous studies of effects of fire on carbon sequestration in soils have been conducted and show widely varying effects, largely dependent on fire type and severity (see reviews by Johnson, 1992 and Gonzalez-Perez et al., 2004) and references therein). Short-term loss of soil carbon or organic matter in severe fires has been documented in Russia (Czimczik et al., 2003), Washington (Grier, 1975), Alaska (Dyrness et al., 1989) and Maine (Fernandez et al., 1989). Longer-term effects of severe fires on soil carbon and organic matter are not as extensively documented but changes persisting for at least 10 years have been documented by Johnson and Curtis (2001). Fire effects may mirror the effects of clear-cutting, which simulates, to some extent, the stand-replacing aspects of fires. Long term decreases in soil organic matter after clear-cutting are documented in New England by studies of Covington (1981) and Johnson et al (1995). Soil carbon was shown to continue to decline for as much as 15 years after cutting and then slowly recover to pre-cutting levels over a period of greater than 60 years. The decline can be related to a number of factors including increased rates of decomposition and decreased rates of leaf and wood litterfall in the earlier post-fire years, with the result that decomposition exceeds input. By comparison, long-term losses of carbon and soil organic matter by stand-replacing fire may be more pronounced than

similar losses documented for clear-cut areas because of the additional, initial loss of soil organic matter during combustion of the forest floor.

For the observed decreases in Hg in the 1936 burns areas in Voyageurs, two general factors may be involved. First, in regions where atmospheric deposition has enriched the forest floor in Hg, combustion of O-horizon soils during severe fire will remove this source Hg (and C) that otherwise might have been incorporated into the A-horizon by soil-forming processes. This loss of surficial soil organic matter could be further exacerbated by stand-killing fires that destroy the forest canopy, resulting in reduced inputs of leaf or needle litter that may persist for the years or decades required to restore a forest and allow reestablishment of an O-horizon.

Second, destruction of mature forest stands by fire results in drastically decreased input rates of numerous elements scavenged from the atmosphere (e.g., Hg, Pb) by the pre-fire forest canopy. We propose that, as with C, the loss of forest canopy after a stand-replacing fire can potentially lead to a long-term decline in soil Hg because of the absence of a mature forest canopy and its importance in controlling Hg deposition rates. The efficiency of canopy vegetation in augmenting Hg deposition rates to the forest floor has been documented in many recent studies in a variety of settings (see review by Grigal, 2002) and references therein). Although overall estimates of Hg fluxes vary considerably between studies, all show higher Hg deposition rates beneath forest canopy than in adjacent openings. Grigal (2002) has estimated mean values for various flux terms which, in total, result in Hg deposition rates to the forest floor under a mature canopy being about four times higher than rates at sites with no canopy. Figure 9 is based on these estimated mean fluxes and illustrates the potential impact of loss of canopy by a stand-replacing fire. The combined throughfall and litterfall in the forest is nearly four times the rate of precipitation-delivered Hg in openings because it includes dry deposition of Hg to foliar surfaces between precipitation events, which is either washed-off by subsequent rain or carried to the forest floor with autumn litter fall. The throughfall-litterfall Hg input is largely offset by volatilization of newly deposited Hg and by export in surface-water or shallow groundwater, so that net annual sequestration at the forest floor is about $5 \mu\text{g m}^{-2}$. A stand-replacing fire will result in a dramatic reduction in Hg deposition until a canopy is restored and again becomes an efficient collector of

atmospheric Hg. A critical question is the extent to which Hg export by volatilization changes after a fire. If the volatilization flux of about $32 \mu\text{g m}^{-2} \text{a}^{-1}$ remains higher than $10 \mu\text{g m}^{-2} \text{a}^{-1}$, the Hg deposition rate in openings, the burned area will be a net emitter of Hg for the period, probably years, required to restore canopy-influenced Hg deposition. Thus, the loss of canopy by a stand-replacing fire could result in a prolonged period of declining soil Hg, and an even longer period in which burned soils would have lower Hg content than adjacent unburned soils.

6. Discussion

Our soil geochemical surveys in northern forests of the Lake Superior region show empirically that there is a strong statistical correlation between the concentrations of organic carbon and associated elements in A-horizon soils and stand-replacing wildfires that burned parts of our study areas in 1936. In Voyageurs National Park variations in element concentrations correlate with fire history far more strongly than with any other geologic, forest, or physiographic variable that we have examined. These results indicate that at a scale of our study area, roughly 1000 km^2 , fire history is a variable that should always be examined in interpreting the significance of geochemical patterns.

The striking magnitude and longevity of the fire-dependent geochemical variations seen in Voyageurs raises the question of why this area has preserved the signature of fire-induced changes in such a pronounced way when this effect has not been reported elsewhere. Mercury depletions resulting from a 1947 fire in Acadia National Park in the northeastern U.S. was presented by Amirbahman et al. (2002), but similar descriptions are rare. We suggest three possible factors which might contribute to the prominent fire signature seen within Voyageurs. First, although there are only anecdotal descriptions for the 1936 fires in the Upper Midwest, we infer that the fires in Voyageurs and Isle Royale, which burned during a time of extreme drought and were stand-replacing fires nearly everywhere, were of very high severity, having a profound impact on the forest floor. Thus, these fires may represent an end-member of a spectrum of fire severity and fire effects on soils and record an intensity of soil alteration not widely duplicated in more typical fires of the region. Second, our studies were in a relatively remote wilderness area where there has been little anthropogenic disturbance since the fires, which might

otherwise obscure natural variations. Third, our study area in Voyageurs has relatively uniform climate, bedrock, and glacial till compositions which minimizes geological variability of soil compositions and allows other soil chemistry indicators to be more readily distinguished. This last factor may play a role in our inability to clearly distinguish the fire signature in the Isle Royale soil data.

Atmospheric deposition of Hg to remote lakes in the upper Midwest has caused widespread concerns for human and wildlife health (Sorensen et al., 1990). Past research on Hg contamination has focused on chemical and biologic processes within lakes to understand the factors that control Hg accumulation in biota. Little research has been directed at terrestrial processes in lake watersheds that may influence the accumulation of Hg in soils, plant detritus, and biota in these systems, or about the effects of drastic changes in the terrestrial environment (such as fire or logging) on the aquatic Hg cycle in a lake..

We have emphasized the long-term reduction in the total Hg load in soils of burned areas of Voyageurs National Park, a factor which might be significant in understanding the highly variable levels of Hg contamination in lakes throughout the park. There is some indication that methylmercury concentrations in fish in individual lakes within Voyageurs may correlate with total Hg concentrations in soils within a lake's watershed (Woodruff and Cannon, 2002). Because stand-initiating fires seem to reduce total Hg loads in forest soils for decades, we speculate that severe fire might result in long-term beneficial effects within watersheds that have high initial levels of total Hg in O- and A-horizon soils. On the other hand, studies in Acadia National Park (Amirbahman et al., 2002) suggested that any potentially beneficial total Hg reductions produced by burning were offset by changes in other chemical characteristics which produced higher methylmercury within the burned watershed. We are currently investigating short- and long-term effects of forest fires on the distribution of total mercury in soils and methylmercury production in lakes in the Lake Superior region. Results of these new studies should aid in developing a more complete understanding of potential links of fire-induced geochemical changes and the larger Hg cycle.

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Table 1. Mean composition of bedrock samples for Isle Royale and Voyageurs National Parks. (values for Al through Ti are percent; trace elements are parts per million).

	Isle Royale basalt	Isle Royale sandstone	Voyageurs migmitite	Voyageurs granite	Voyageurs schist
Al	8.80	4.54	7.56	7.30	8.76
Ca	6.27	0.15	1.86	0.63	1.63
Fe	7.91	1.61	0.92	0.89	4.49
K	0.61	2.91	0.83	3.14	2.29
Mg	4.02	0.28	0.34	0.14	1.88
Na	2.27	1.29	3.44	2.74	2.40
P	0.09	0.02	0.04	0.02	0.07
Ti	1.01	0.32	0.09	0.07	0.42
As	0.94	2.89	<0.6	<0.6	1.4
Ba	240	947	175	373	742
Ce	44	89	15	72	38
Co	47	3	4	3	17
Cr	133	11	<2	4	49
Cu	122	65	6	4	32
Hg	<0.02	0.06	<0.02	<0.02	<0.02
La	14	29	7	33	19
Li	13	12	13	53	40
Mn	1259	286	122	184	654
Ni	137	2	11	<3	63
Pb	24	90	14	34	16
Sc	31	6	3	3	17
Se	0.2	0.2	<0.2	<0.2	<0.2
Sr	298	90	379	122	325
V	279	48	20	13	125
Zn	94	84	23	34	70

Table 2. Mean composition of A- and C- horizon soils (values for Al through Ti, C and S are percent; trace elements are parts per million) and comparative elemental ratios for Isle Royale and Voyageurs National Parks.

	Isle Royale A n = 134	Voyageurs A n = 104	IR/Voy A	Isle Royale C n = 144	Voyageurs C n = 122	IR/Voy C
Al	4.92	4.75	1.04	6.70	7.52	0.89
Ca	2.01	1.04	1.93	2.91	1.32	2.20
Fe	4.14	1.61	2.57	5.35	3.02	1.77
K	1.04	1.18	0.88	1.17	1.77	0.66
Mg	1.18	0.41	2.88	1.99	0.90	2.21
Na	1.04	1.19	0.87	1.50	1.90	0.79
P	0.064	0.062	1.03	0.051	0.056	0.91
Ti	0.612	0.223	2.74	0.682	0.302	2.26
As	3.45	2.89	1.19	2.48	3.49	0.71
Ba	373	456	0.82	333	479	0.70
Ce	35	39	0.90	46	49	0.94
Co	17	9	1.89	24	12	2.00
Cr	80	39	2.05	80	55	1.45
Cu	72	19	3.79	109	27	4.04
Hg	0.103	0.141	0.73	0.056	0.050	1.12
La	16	20	0.80	16	24	0.67
Li	12	16	0.75	13	34	0.38
Mn	1177	892	1.32	730	369	1.98
Ni	42	27	1.56	70	38	1.84
Pb	27	31	0.87	11	18	0.61
Sc	12	6	2.00	19	10	1.90
Se	0.70	0.51	1.37	0.49	0.51	0.96
Sr	130	178	0.73	160	250	0.64
V	131	51	2.57	164	85	1.93
Zn	86	61	1.41	58	53	1.09
Total C	10.58	14.19	0.75	n.a.	n.a.	
S	0.053	0.062	0.85	n.a.	n.a.	

Table 3. Means and standard deviations for mineral soils from A- and C-horizons from the Kabetogema Peninsula in Voyageurs National Park divided into areas that burned in 1936 and areas that were unburned. Values for Al through Ti and for C and S are in percent; other elements are in parts per million

	A-horizon		C-horizon	
	1936 burn	Unburned	1936 burn	Unburned
Al	5.22 (0.84)	4.06 (1.41)	7.60 (0.50)	7.36 (0.60)
Ca	1.00 (0.17)	1.09 (0.42)	1.31 (0.25)	1.27 (0.18)
Fe	1.72 (0.54)	1.49 (0.69)	2.94 (0.76)	2.67 (0.87)
K	1.34 (0.25)	0.94 (0.29)	1.74 (0.30)	1.87 (0.30)
Mg	0.43 (0.12)	0.35 (0.13)	0.86 (0.19)	0.79 (0.29)
Na	1.32 (0.31)	0.88 (0.35)	1.94 (0.52)	2.03 (0.39)
P	0.05 (0.02)	0.07 (0.02)	0.06 (0.09)	0.03 (0.02)
Ti	0.28 (0.08)	0.18 (0.07)	0.31 (0.08)	0.26 (0.76)
As	2.95 (1.44)	2.6 (0.8)	2.9 (1.4)	2.4 (1.8)
Ba	485 (70)	410 (100)	465 (57)	473 (60)
Ce	37 (12)	31 (20)	53 (31)	38 (26)
Co	9 (6)	10 (6)	13 (5)	11 (5)
Cr	44 (17)	30 (14)	53 (29)	33 (22)
Cu	19 (9)	15 (9)	27 (12)	20 (13)
Hg	0.10 (0.06)	0.19 (0.05)	0.05 (0.03)	0.03 (0.02)
La	19 (6)	21 (19)	23 (8)	20 (12)
Li	18 (10)	11 (7)	31 (12)	23 (12)
Mn	530 (556)	1133 (942)	346 (71)	324 (87)
Ni	22 (8)	19 (9)	39 (16)	33 (13)
Pb	29 (8)	37 (11)	19 (3)	16 (3)
Sc	6 (1)	5 (2)	10 (2)	9 (3)
Se	0.44 (0.21)	0.65 (0.41)	0.67 (0.46)	0.35 (0.22)
Sr	189 (35)	149 (43)	243 (49)	245 (31)
V	57 (16)	45 (24)	81 (24)	77 (39)
Zn	46 (19)	66 (36)	48 (18)	43 (19)
Organic C	8.7 (6.6)	22.4 (7.5)	n.a.	n.a.
Total S	0.05 (0.02)	0.08 (0.04)	n.a.	n.a.

Figure Captions

Figure 1. Map showing location of study areas in Voyageurs National Park and Snowbank Lake, Minnesota and Isle Royale National Park, Michigan.

Figure 2. Plot of organic carbon versus mercury (A) and sulfur (B) for all A-horizon soil samples from Isle Royale (open circles) and Voyageurs National Parks (X's). A slight random jitter was applied to make overlapping points easier to display.

Figure 3. Maps of Isle Royale and Voyageurs National Parks showing the footprints of the 1936 fires within the parks and the distribution of all soil samples from park surveys.

Figure 4. Map showing the extent on the 1936 burns and relative concentrations of Hg (in ppm) in A-horizon soils across the Kabetogema Peninsula in Voyageurs National Park. For simplicity, Hg concentrations are classified as above or below the mean concentration for the whole park soil data set.

Figure 5. Plot of organic carbon versus mercury for A-horizon soils from moderate-high severity fire sites at Snowbank Lake. Samples were collected at approximately the same sites over a 3 year period.

Figure 6. Comparison of element concentrations in soils from burned and unburned sites on the Kabetogema Peninsula, Voyageurs National Park. Elemental concentrations for Hg, P, Pb, S, and Se are recalculated on an organic carbon-free basis [element concentration = measured element concentration $\times$ (100%) / (100% - organic carbon %)].

Figure 7. Map showing the extent of the 1936 burns and relative concentrations of Hg (in ppm) in A-horizon in Isle Royale National Park. For simplicity, Hg concentrations are classified as above or below the mean concentration for the whole Park data set. For simplicity, Hg concentrations are classified as above or below the mean concentration for the whole park soil data set.

Figure 8. Plot of organic carbon versus mercury for A-horizon soils within burned (X's) and unburned (open circles) sites on Kabetogema Peninsula, Voyageurs National Park. Confidence ellipses are at a probability of 0.7.

Figure 9. Estimated mean fluxes of total Hg in forests as reported by Grigal (2003). The importance of the forest canopy is shown by the combined throughfall and litterfall deposition of $38 \mu\text{g m}^{-2} \text{a}^{-1}$ compared to $10 \mu\text{g m}^{-2} \text{a}^{-1}$ in open areas where deposition is solely from precipitation. Wildfires which destroy the forest canopy result in a nearly four-fold decrease of Hg deposition rates.

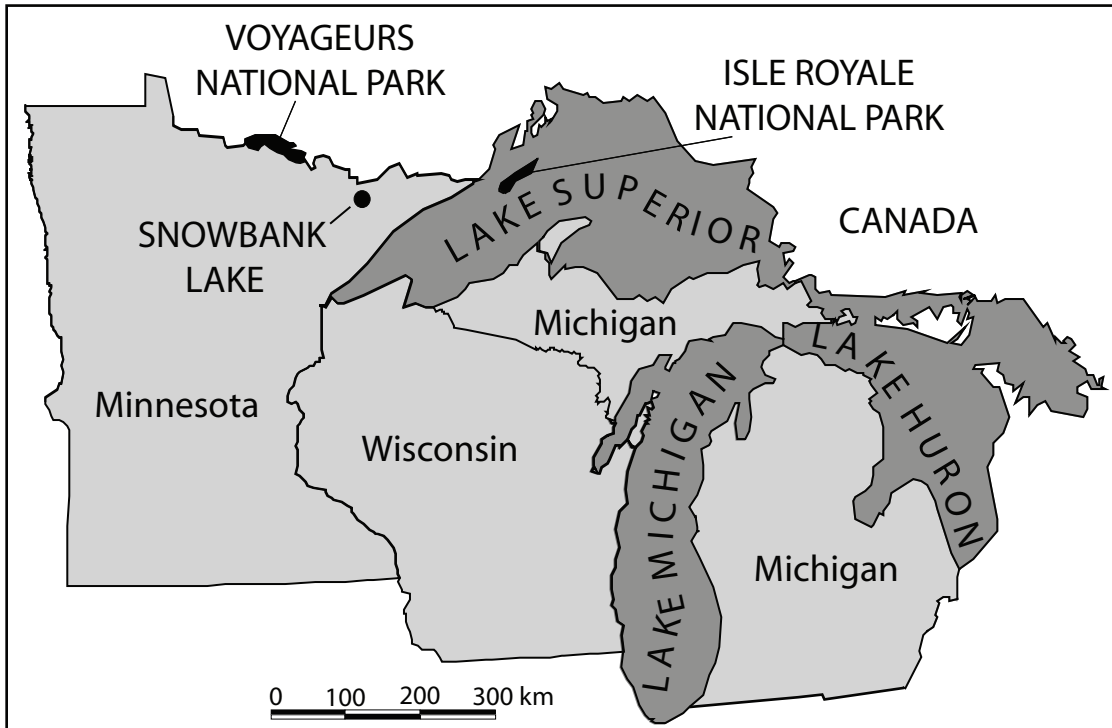


Figure 1

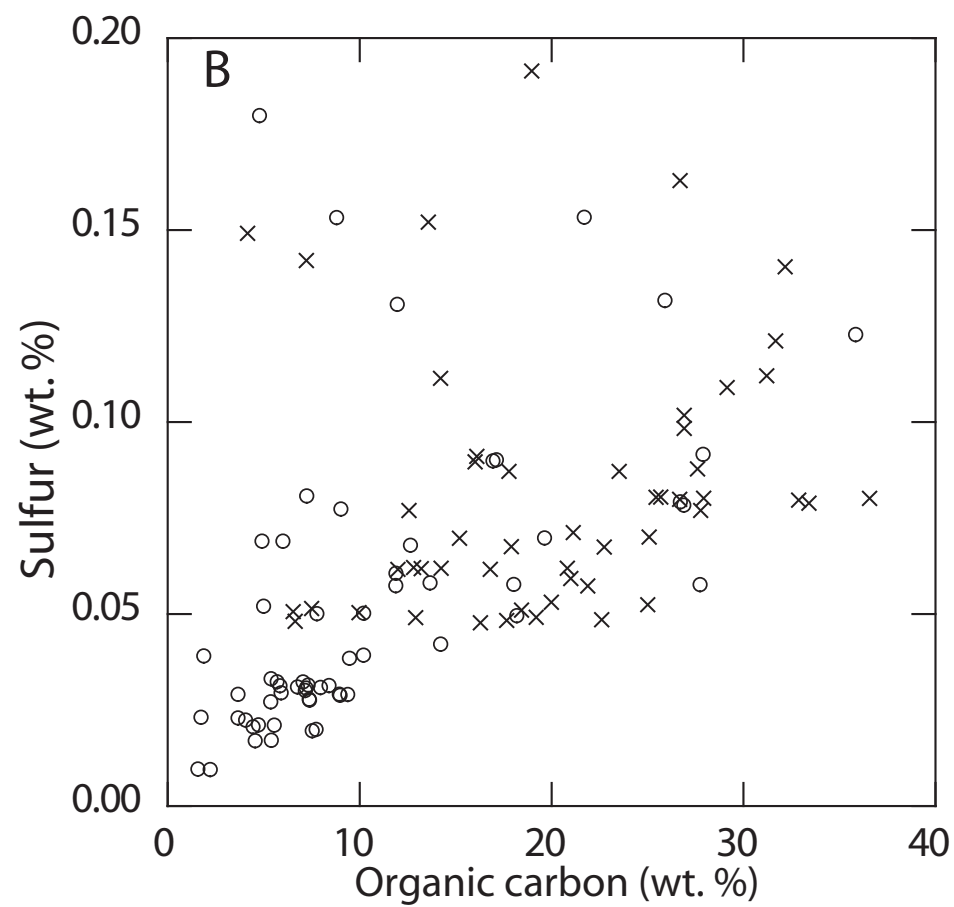
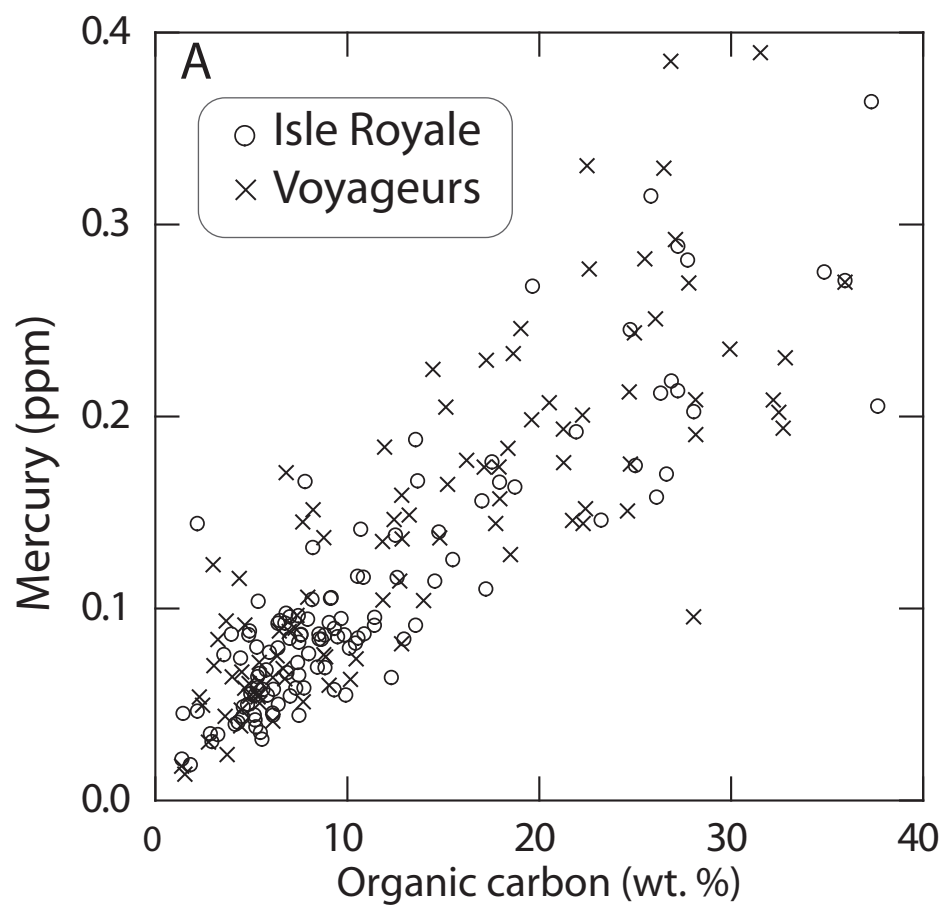


Figure 2

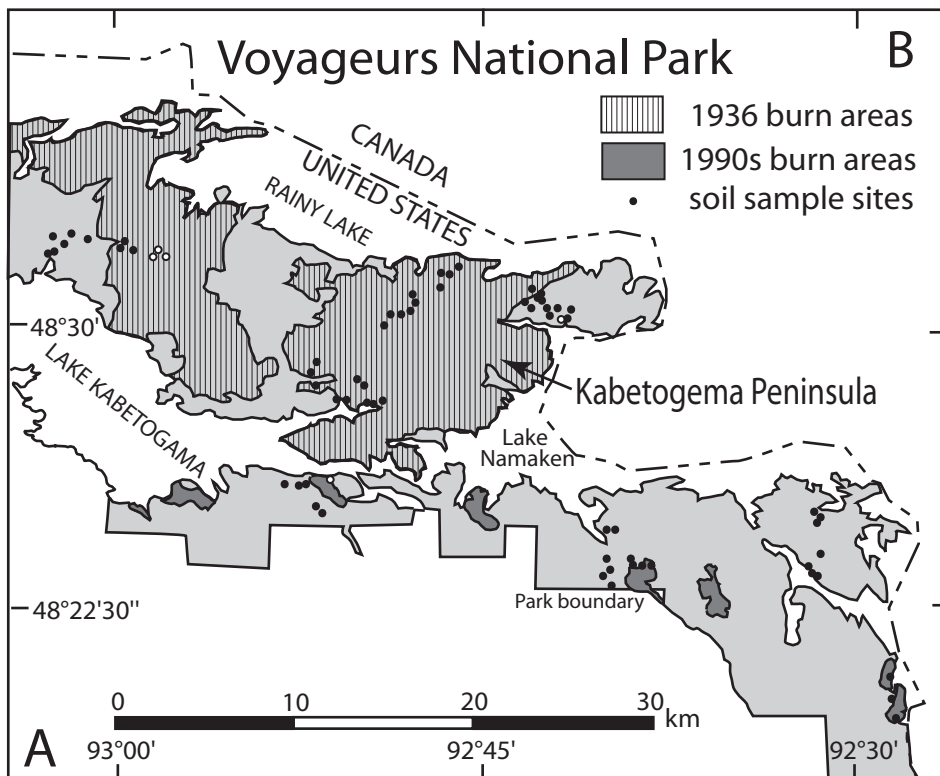
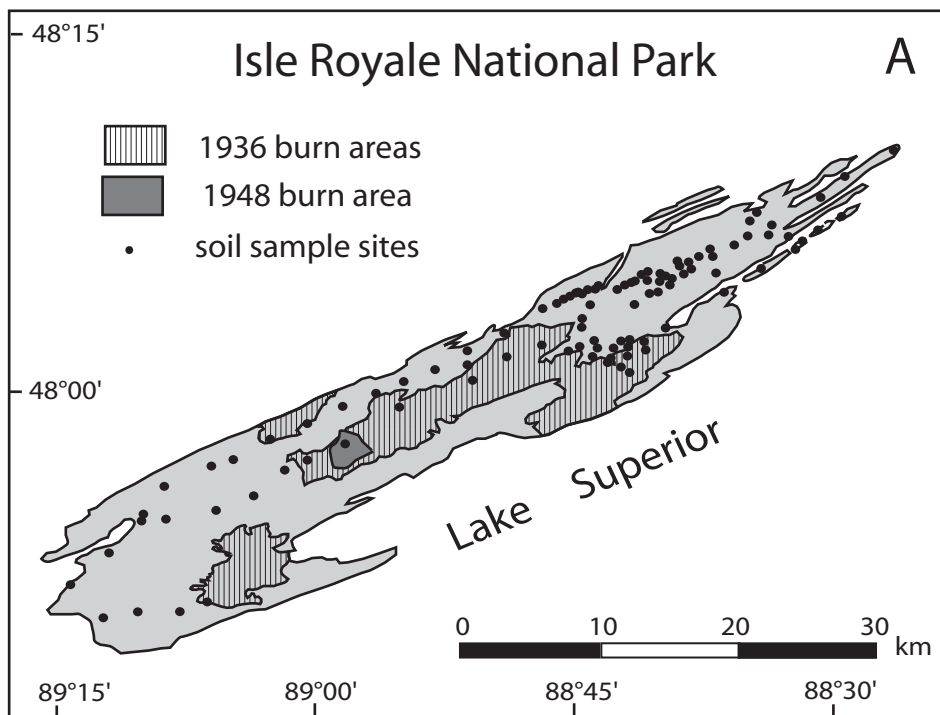


Figure 3

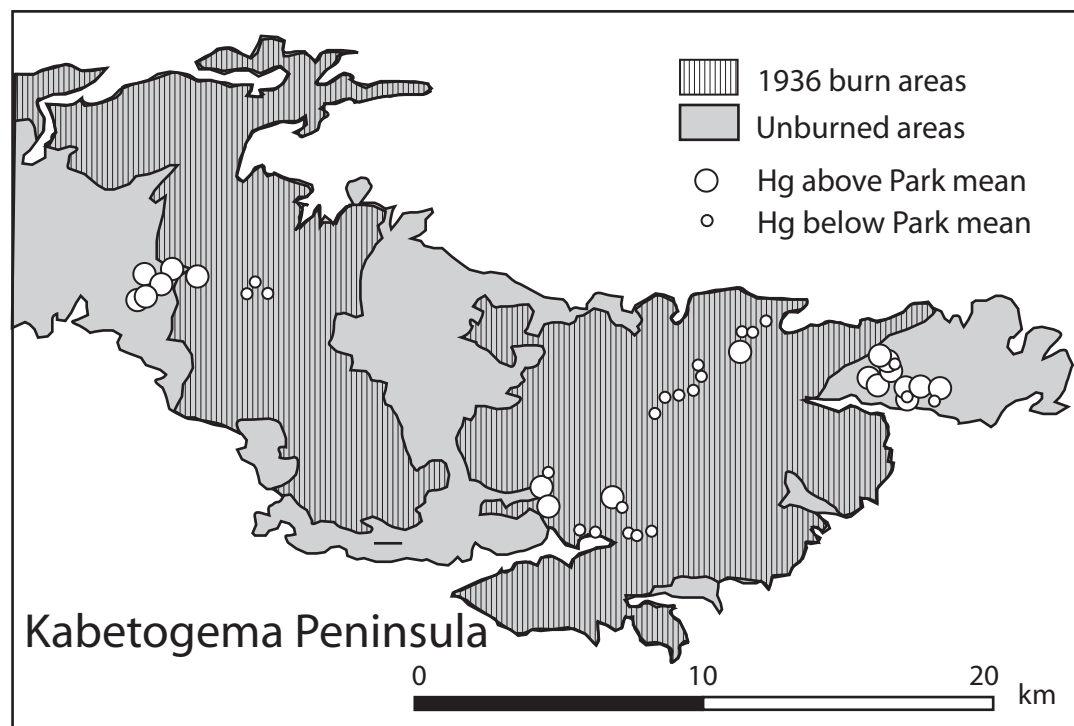


Figure 4

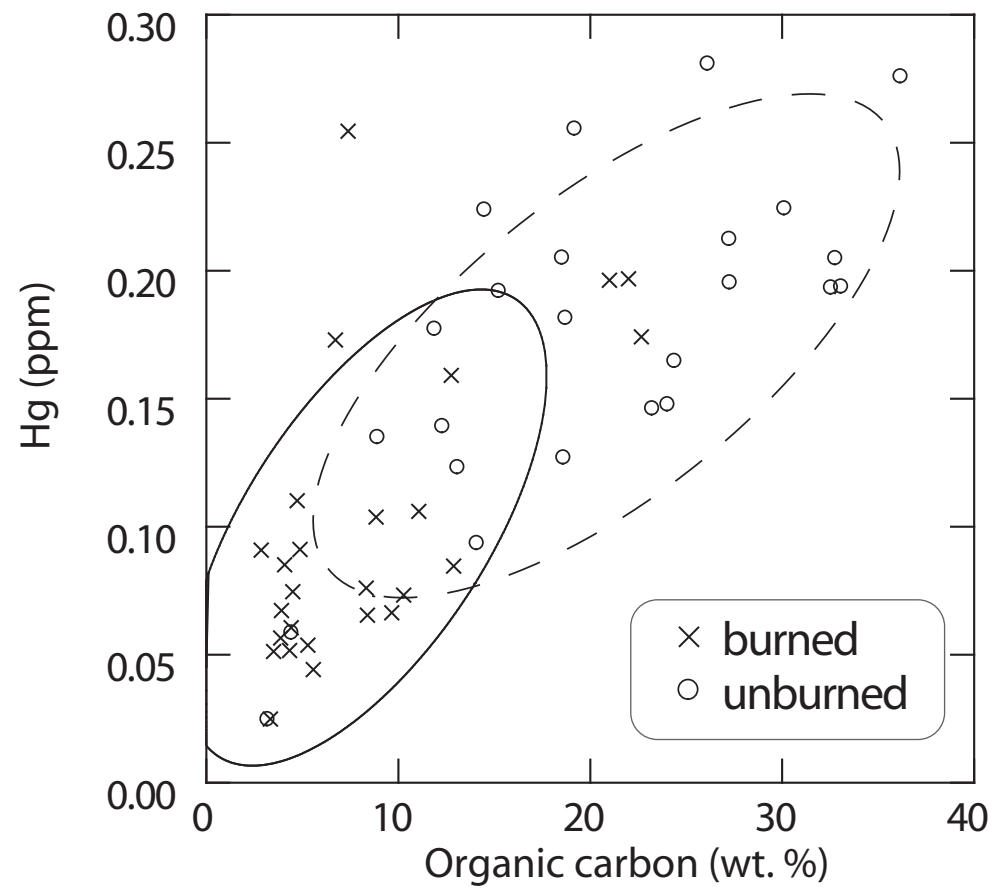


Figure 5

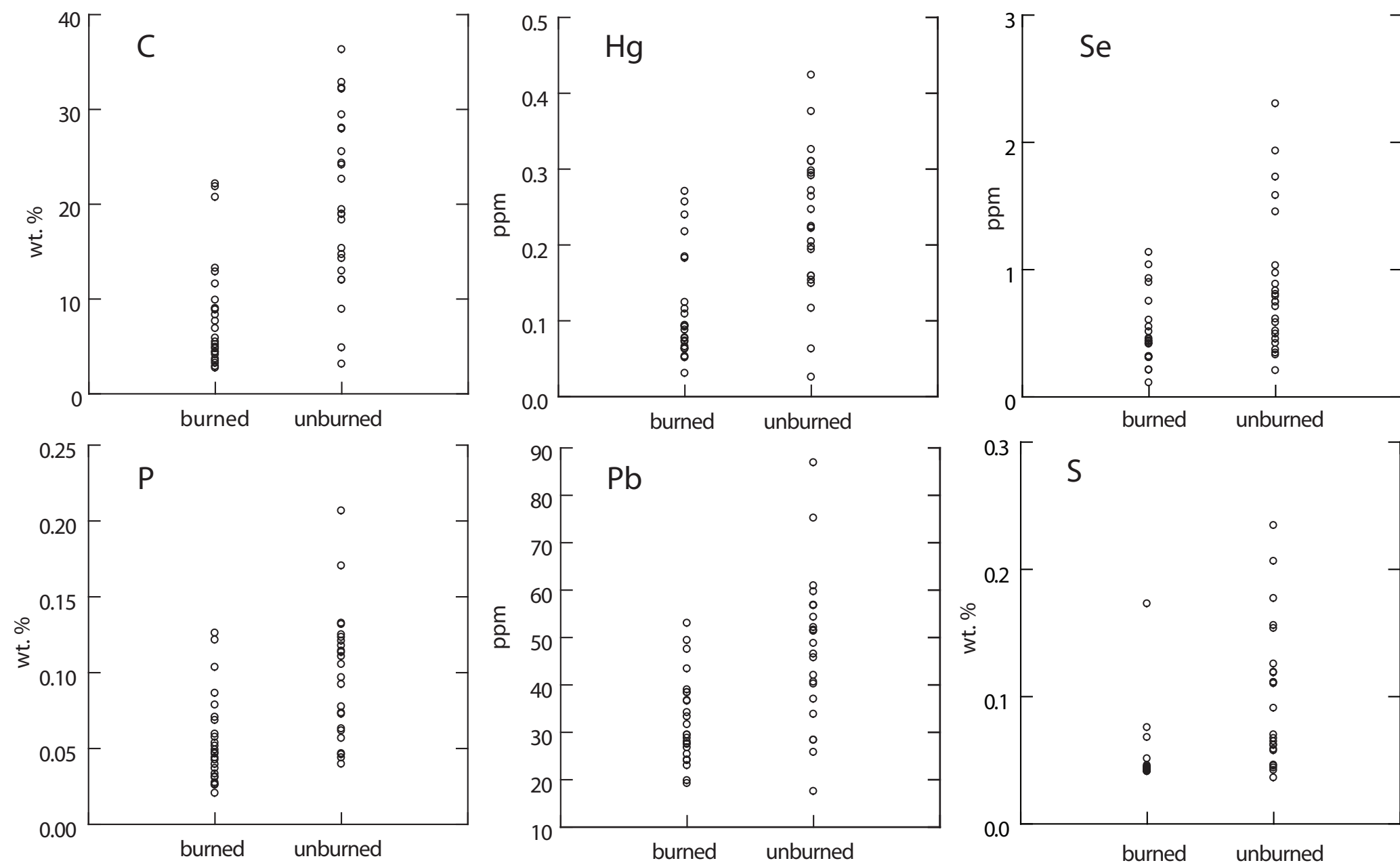


Figure 6

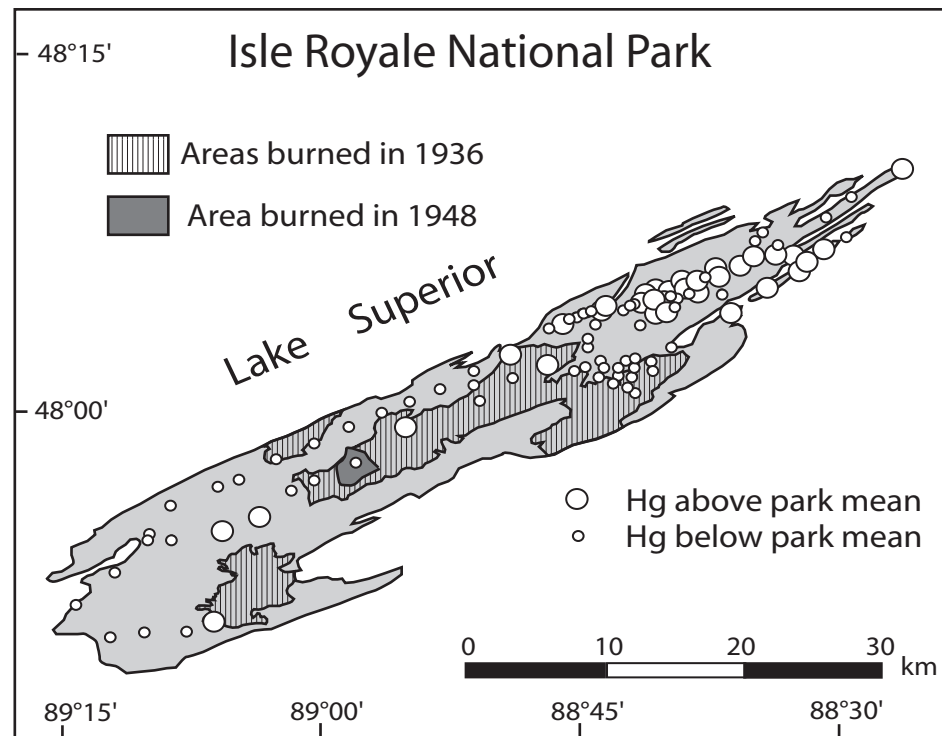


Figure 7

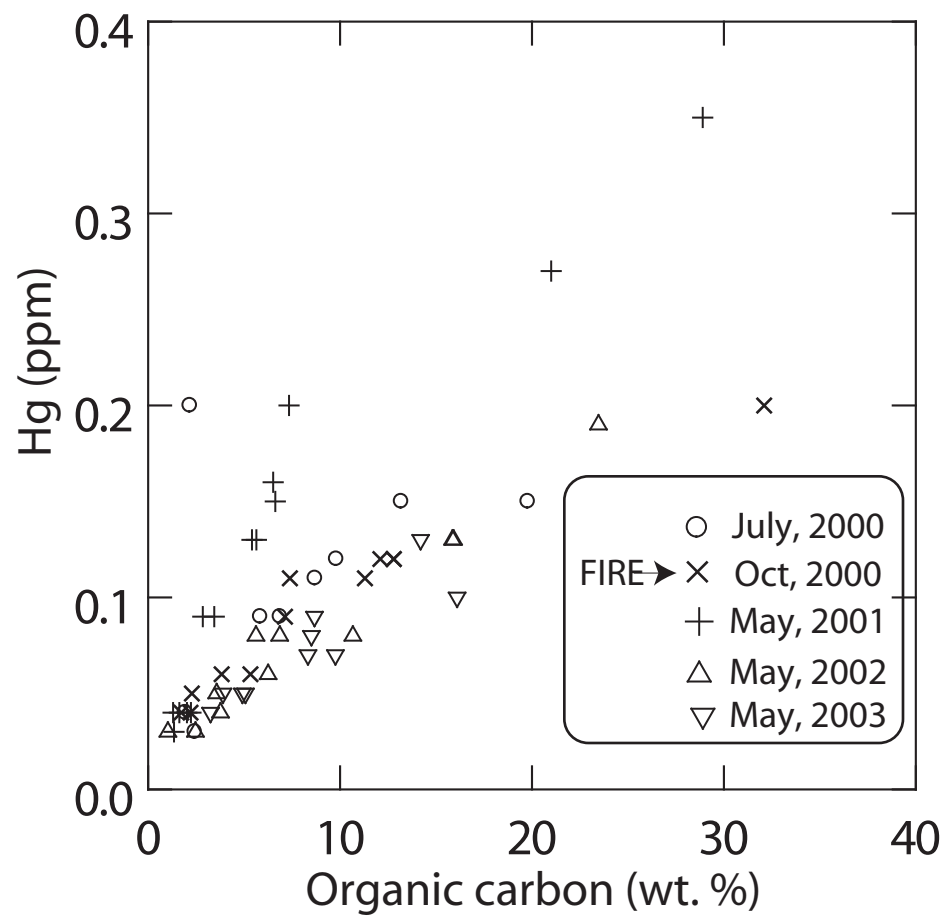


Figure 8

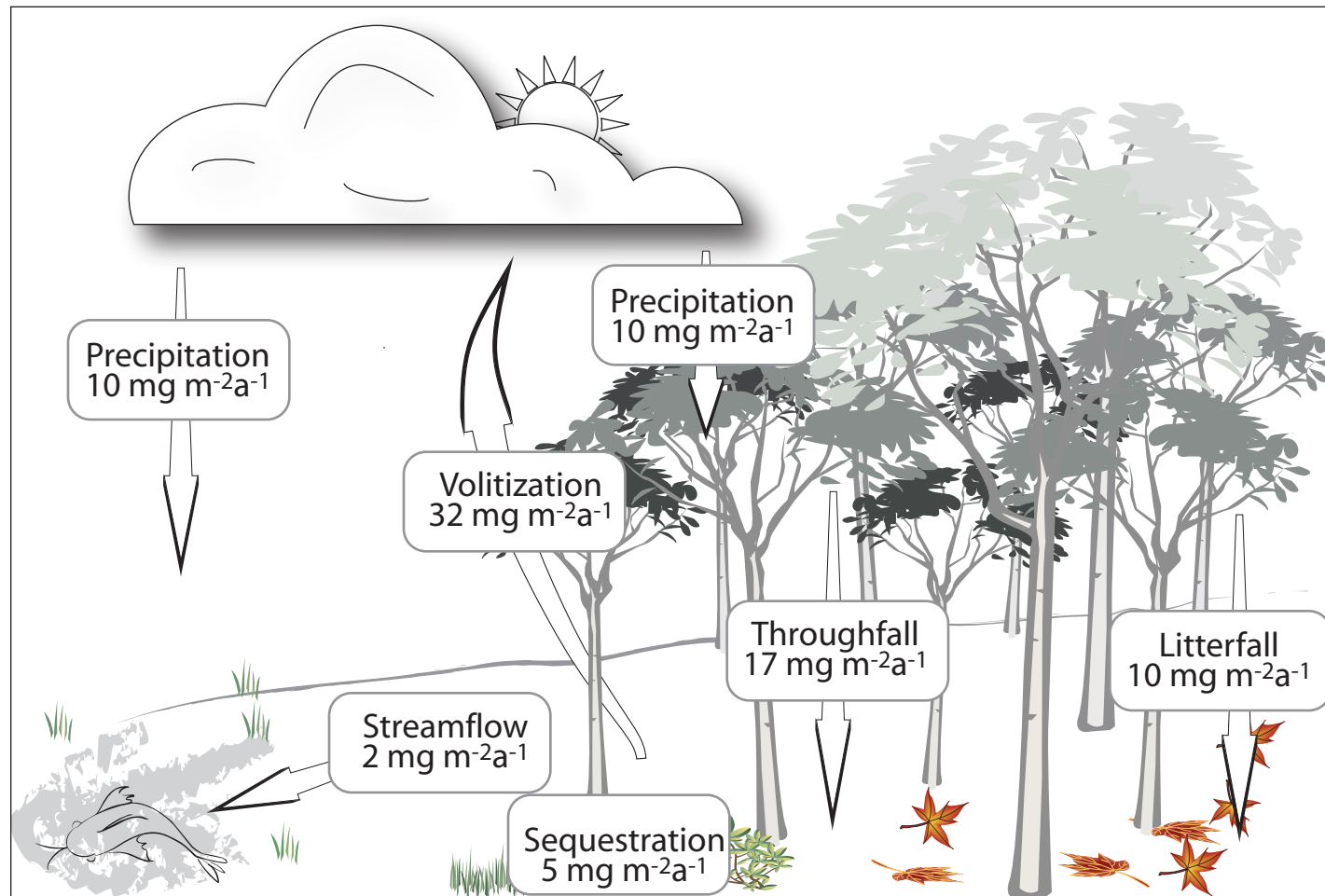


Figure 9