

Article

Fire-Induced Changes in Geochemical Elements of Forest Floor in Southern Siberia

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Abstract: Wildfires significantly influence the environmental distribution of various elements through their fire-induced input and mobilization, yet little is known about their effects on the forest floor in Siberian forests. The present study evaluated the effects of spring wildfires of various severities on the levels of major and minor (Ca, Al, Fe, S, Mg, K, Na, Mn, P, Ti, Ba, and Sr) trace and ultra-trace (B, Co, Cr, Cu, Ni, Se, V, Zn, Pb, As, La, Sn, Sc, Sb, Be, Bi, Hg, Li, Mo, and Cd) elements in the forest floors of Siberian forests. The forest floor (Oi layer) samples were collected immediately following wildfires in Scots pine (*Pinus sylvestris* L.), larch (*Larix sibirica* Ledeb.), spruce (*Picea obovata* Ledeb.), and birch (*Betula pendula* Roth) forests. Total concentrations of elements were determined using inductively coupled plasma–optical emission spectroscopy. All fires resulted in a decrease in organic matter content and an increase in mineral material content and pH values in the forest floor. The concentrations of most elements studied in a burned layer of forest floor were statistically significantly higher than in unburned precursors. Sb and Sn showed no statistically significant changes. The forest floor in the birch forest showed a higher increase in mineral material content after the fire and higher levels of most elements studied than the burned coniferous forest floors. Ca was a predominant element in both unburned and burned samples in all forests studied. Our study highlighted the role of wildfires in Siberia in enhancing the levels of geochemical elements in forest floor and the effect of forest type and fire severity on ash characteristics. The increased concentrations of elements represent a potential source of surface water contamination with toxic and eutrophying elements if wildfire ash is transported with overland flow.

Keywords: wildfires; Siberian forests; forest floor; major; minor; trace and ultra-trace elements



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1. Introduction

Forest ecosystems periodically undergo wildfires, which can catastrophically affect natural resources and cause profound societal and economic impacts [1,2]. In recent decades, more than 70% of fires and up to 90% of the total area burned in Russia have occurred in the forests of Siberia. Approximately two-thirds of the Siberian territory is covered by forests, with the main tree species being larch (*Larix sibirica*, *L. gmelini*, and *L. cajanderi*), Scots pine (*Pinus sylvestris*), fir (*Abies sibirica*), spruce (*Picea obovata*), Siberian pine (*Pinus sibirica*), and birch (*Betula* spp.) [3]. Climate change has led to an increase in fire season length, wildfire frequency, and area burned in Siberia over the recent decades [4]. Changes in fire regimes have already led to vegetation shifts and transformation from forest to steppe ecosystems in some Siberian regions [5,6], with some drastic areas considered at high risk of fire-induced forest loss by the end of the century [7]. The total forest area affected by fires in Siberia varied from 1 to 12 Mha between 1996 to 2019 [3] depending on weather conditions and shifts in the Arctic Oscillation [8]. In the northern regions of Siberia,

where the population density is low, the main cause of fires (up to 90%) is lightning, whereas in the southern regions, more than 80% of fires are human-caused. Thus, the number of fires in Siberia increases southwards, and the fire return interval decreases accordingly [3]. The North American boreal forests support more high-intensity crown fires than Eurasia due to differences in the dominant tree species [9]. In Eurasia, the strongest upward trends in fire frequency were found in Central and Eastern Siberia [10]. Krasnoyarsk Krai, Central Siberia, is among the regions most affected by fires in Siberia [11]. Increased fire activity leads to significant destruction of vegetation cover and drastic changes in the physical, chemical, and biological properties of soils [12,13]. The main effects of wildfires on soils include loss of organic matter, deterioration of soil structure, decreased porosity, reduced water, cations retention, increase in pH and electrical conductivity, alteration of microbial and invertebrates' communities, increased soil water repellence, reduced infiltration, and increased runoff [14,15]. Wildfire impacts on ecosystems are expected to increase in the future due to changes in climate and land use [16]. Despite the effects of fire on properties of soil being well established, the effects on many chemical elements associated with ash, including potentially toxic ones, are not well studied and documented. High-severity and recurrent fires can impair the biogeochemical cycles of elements in soil [17,18]. Fire-induced geochemical changes in soils are of great importance in studying contaminant transport and human health [19].

During burning, the temperature at the soil surface typically rises to 200–300 °C, reaching 500–700 °C in the presence of heavy fuels such as slash (debris left from logging, thinning, and storms), and occasionally reaching 850 °C [13,14]. After a fire, residual ash is commonly left on the surface of burned soils from the consumed fuels (biomass and organic matter). Ash consists of mineral materials and charred organic components. The organic component comprises mainly pyrogenic compounds, which are highly aromatic, although it may also contain some uncharred material [20–22]. The mineral component of ash consists of silicates, oxides, phosphates, carbonates, and sulfates. The quantity and characteristics of ash produced during a fire depend on the total amount of fuel burned, fuel type, and combustion completeness. At lower temperatures ($T < 450$ °C), ash is organic-rich, while at high temperatures ($T > 450$ °C), most organic carbon is volatilized, leaving an ash rich with mineral residue [22]. Ash production increases with fire severity [23].

The relative proportions of elements may increase or decrease in ash depending on their temperatures of volatilization [22,24]. Fire temperatures are typically sufficient for the volatilization of Hg (100–200 °C) and decomposition of the Hg–humic acid complex (200–300 °C) [25,26]. The major volatilization of As occurs between 300 and 500 °C [27]. Nitrogen starts to volatilize at 200 °C, and its loss can reach 50–100% at 300 °C and above. The losses of K, Na, P, and S are only possible at temperatures higher than 760–880 °C. The volatilization temperatures of other elements are very high: Mg above 1107 °C, Ca above 1240 °C, Mn above 1962 °C, Al above 2467 °C, and Fe above 3000 °C [22,24,28,29]. Tuhý et al. [30] demonstrated in laboratory single-step combustion experiments that Cd, Cu, Pb, and Zn were released at temperatures above 550–600 °C. Therefore, redistribution of elements by fire involves a decrease in the concentration of combustible elements and an increase in levels of noncombustible elements [31]. Ash is rich in Si, Ca, Mg, K, and, to a lesser extent, in Na, P, and S. It also contains trace elements [19,22,28,32]. Increasing temperature during fire may have a greater impact than species type in the spatial variability of elements [33]. Ash is highly mobile; it can be incorporated into the soil or redistributed or removed from a burned site by wind and water [22,23]. Ash can release elements into the soil, sediments, or surficial waters even after long-range airborne transport [34]. The transfer of ash-derived potentially toxic and eutrophying constituents to surface water bodies can damage aquatic ecosystems and disrupt drinking water supplies, which entails environmental and socioeconomic costs [35]. Trace elements are of major concern due to their toxicity, persistence in the environment, and tendency to bioaccumulate in the food chain [36]. Even for the essential trace elements exerting biochemical and physiological

functions in plants and animals, there is a very narrow range of concentrations between beneficial and toxic effects [37].

Many previous studies reported elevated total concentrations of various elements in ash or burned soils after fires [23,34,38–40]. Several authors have found an increase in levels of some elements in ash and topsoil with fire severity [23,35,41]. According to Santín et al. [23], different fire severities result in various geochemical forms and chemical behavior of the elements in the ash, which, in turn, can affect their solubility in water. They found that solubility of Al, As, Cd, Fe, Pb, Si, Ca, Cu, P, K, and Mg in ash deposited during a severe wildfire in a dry sclerophyll eucalypt forest (Sydney, Australia) was less than 10% of the total element concentration, except for B (6–14%) and Na (30–50%). Pereira et al. [29] observed an increase in water-soluble Ca, Mg, and Na and a decrease in water-soluble Mn, Fe, and Zn in ash samples collected from plots composed from *Quercus suber* and *Q. robur* trees compared to unburned litter after a low-severity prescribed fire in the northeast part of the Iberian Peninsula. Our understanding of the behavior of trace elements in burned soils is still limited compared to our understanding of major and minor elements [19].

The total concentrations of elements in ash decrease during the first year after the fire due to rainfall and associated overland flow [40]. Moreover, as the pH of the ash decreases over time, certain elements that are present in cationic form in aquatic media (Cu, Fe, Mn, Ni, Zn, Pb, Cd, etc.) may become more mobile and be released into the soil water. Thus, after a fire, the elements can move vertically or laterally, constituting a risk of groundwater and surface water contamination [15,42]. Post-fire runoff can supply more trace elements in soluble forms than runoff from unburned areas [19]. The geochemical forms of various elements can change as ash is mobilized from production sites to suboxic/anoxic sediments in rivers and reservoirs. For instance, changes in redox conditions may result in the release of P and toxic metals from sediments into water [23].

While numerous studies [23,26,29,31,33–35,40–43] have been conducted worldwide to understand the fire-induced geochemical changes in soils, there is only limited information available on the concentrations and behavior of major, minor, and trace elements in soils of Siberian forests affected by fires of various severities [39,44–48]. There is also a lack of data on the levels of geochemical elements in wildfire ash for Siberia, partly due to its high mobility and therefore rapid redistribution after fire, which makes ash more challenging to collect than burned soils [35]. Bodí et al. [22] highlighted that studies of ash characteristics in large burned areas of Russia are underrepresented. To fill this gap, this present work aims to evaluate the effects of wildfires on the levels of major, minor, trace, and ultra-trace elements in the forest floors of Scots pine, larch, spruce, and birch forests in southern Siberia.

2. Materials and Methods

2.1. Study Area and Sampling Procedure

The study area is located in the south of the Krasnoyarsk Krai, Central Siberia, on the left and right banks of the Yenisey River (Figure 1). We evaluated fire impact on geochemical elements at four sites representing typical forest types in southern Siberia: a Scots pine (*Pinus sylvestris* L.) forest with litter as a dominant ground cover (Plot 1); a larch (*Larix sibirica* Ledeb.) forest with *Carex*, *Calamagrostis*, *Spiraea*, and *Rosa* spp. in the living surface vegetation (Plot 2); a spruce (*Picea obovata* Ledeb.) forest with *Carex* spp. and feather moss (*Pleurozium schreberi* (Willd. ex Brid.)) as a dominant ground cover (Plot 3); and a birch (*Betula pendula* Roth) forest with *Carex* spp., *Maianthemum bifolium* (L.) F. W. Schmidt, *Atragene sibirica*, and *Vicia cracca* L. dominating the living ground vegetation (Plot 4).

The climate of the study area is sharply continental. Mean annual temperatures between 2006 and 2022 varied from 0 to 2.3 °C for the sites studied, with daily minimum and maximum values reaching −44.4 and 36.9 °C, respectively. The lowest annual precipitation (372.9 mm) was recorded at Plot 1 in the forest-steppe and the highest precipitation (813.5 mm) at Plot 2 in the mountain taiga zone, while in Plots 3 and 4, annual precipitation averaged 532.5 and 518.2 mm, respectively. The average snow depths for Plots 1–4

were 7.1, 60.3, 29.4, and 22.7 cm, respectively, as reported by the nearest weather stations (<https://rp5.ru>; accessed on 1 March 2024).

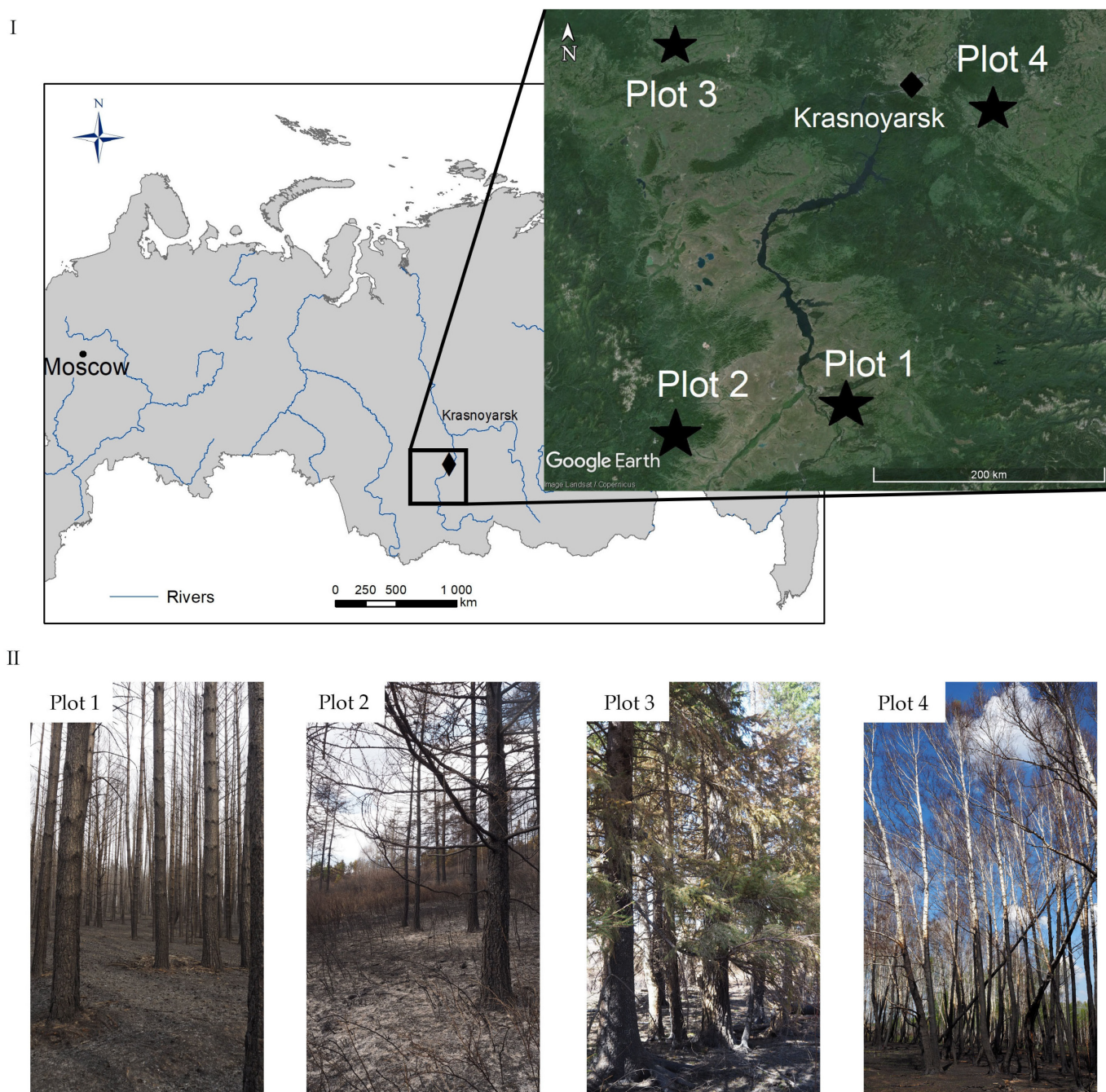


Figure 1. Location of study area (I) and view of burned sites (II) in Scots pine (Plot 1), larch (Plot 2), spruce (Plot 3), and birch (Plot 4) forests.

Average tree diameter varied among the sites studied from 23.3 to 32.7 cm, and height from 13.4 to 28.8 m. All sites were burned 2–7 May 2022, which is common for the study area, where spring fires with fire return intervals of 10 to 33 years predominate [49]. All fires were caused by human carelessness and were extinguished within 1–3 days of occurrence. We examined burned plots and adjacent unburned (control) plots within 3 to 10 days post fire. There was no rain between fires and sampling. We determined fire severity in situ based on the average char heights on the trees [50] and the completeness of combustion of ground fuels [51]. The Scots pine forest (Plot 1) was burned by high-severity crown fire with

total tree mortality. The larch (Plot 2) and birch (Plot 4) forests were burned by high-severity surface fires, while the spruce forest (Plot 3) was burned by surface fire of moderate severity. The detailed characteristics of the study sites are provided in Shapchenkova et al. [52].

In all burned forests, we carefully sampled only the charred forest floor layer (i.e., ash layer). This layer contained both organic and mineral residues resulting from the burning of the forest floor and aboveground vegetation. In all forests, the average burn depth across the site was up to 3 cm. In adjacent unburned plots, we sampled the layer of the forest floor that corresponded to the burned layer at plots exposed to fires. This layer (Oi) consisted of undecomposed or weakly decomposed needles/leaves, small twigs, cones, cured herbs, and grasses.

In the larch forest, the forest floor (Oi layer) was only 1–2 cm thick before the fire. During the fire, it was burned down to the mineral soil. So, we collected the whole burned Oi layer.

In the birch and spruce forests, only the upper part (Oi layer) of the forest floor was burned (1.2–3 cm of a pre-fire forest floor depth of 5.7–7.5 cm). Therefore, we sampled only the Oi layer of the forest floor in the unburned sites.

In the Scots pine forest, the burn depth across the whole plot was 0.8–2.2 cm, while around the tree stems, the forest floor was burned down to the mineral layer (up to 6–8 cm). So, we collected the samples of the burned layer of forest floor across the site and samples of ash near the tree stems separately. In the unburned site, we sampled the upper burned Oi layer.

All samples were collected in five replicates at each site. The mass of samples was circa 10–20 g. The samples were air-dried in the laboratory, ground, and sieved through a 0.5 mm sieve.

2.2. Analytical Procedures

The pH value was measured with a PP-15 Professional Meter (Sartorius, Göttingen, Germany) in a suspension of forest floor in distilled water (1:25 mass/volume). Organic matter and mineral residue (material) contents in the samples were determined from thermogravimetric data. Thermogravimetry was carried out using a TG 209 F1 thermal analyzer (Netzsch, Germany) in an air atmosphere from 25 to 850 °C at a heating rate of 10 °C/min with the gas flow of 20 mL/min in an aluminum oxide crucible. The organic matter content was estimated as a sample mass loss (%) in the temperature range of 170–850 °C, where complete combustion of organic matter occurs. The residual mass (mineral material) after combustion was determined at 850 °C.

Total concentrations of Ca, Al, Fe, S, Mg, K, Na, Mn, P, Ti, Ba, Sr, B, Co, Cr, Cu, Ni, Se, V, Zn, Pb, As, La, Sn, Sc, Be, Bi, Hg, Li, Mo, Sb, and Cd were analyzed after acid (HNO₃, HF, and HCl) digestions of samples by inductively coupled plasma-optical emission spectroscopy (ICP-OES) [53] with a Spectrometer ICAP-PRO X DUO ICP-OES (Fisher Scientific, Waltham, MA, USA).

Additionally, microscopic examination of burned forest floor samples from the Scots pine forest was carried out with a scanning electron microscope (TM-1000, Hitachi Ltd., Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (EDX).

2.3. Data Analysis

Mean values and standard deviations were calculated for each parameter studied. Student's *t*-test was used to estimate whether parameters for unburned and burned forest floor of Scots pine, larch, spruce, and birch forests were significantly different. The differences were considered significant at $p < 0.05$. The relationships between the parameters were determined with the Pearson correlation coefficient. The statistical analyses of the data were performed with STATISTICA 10 software (StatSoft Inc., Tulsa, OK, USA) and R [54]. The graphs were created using R packages 'ggplot2', 'ggbreak', and 'corrplot' [55–57].

3. Results

3.1. Physicochemical Characteristics of Forest Floor

At the unburned plots, the Scots pine and larch forest floors had a higher organic matter content and a lower proportion of mineral material (residue) compared to the spruce and birch forests. pH values ranged from very strongly acidic (pH 4.47) in the Scots pine forest floor to moderately acidic (pH 5.52–5.90) in the larch, spruce, and birch forests. The birch forest floor showed the highest pH (Figure 2).

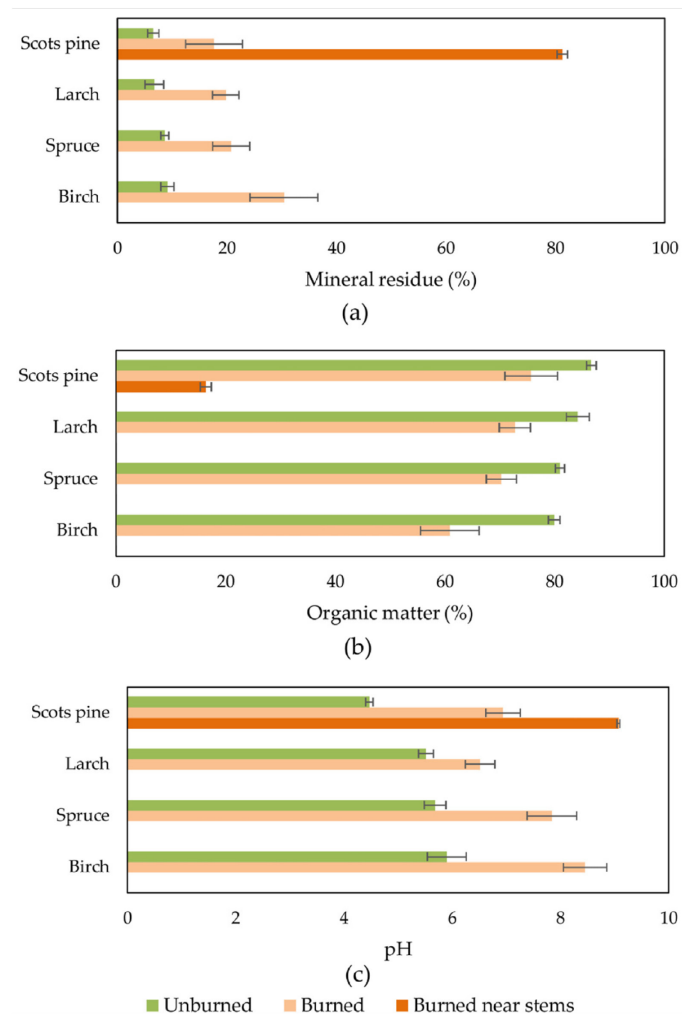


Figure 2. Mineral residue content (a), organic matter content (b), and pH (c) in unburned and burned forest floor at Scots pine, larch, spruce, and birch, forests (n = 5 for each site).

The wildfires we studied resulted in a decrease in organic matter content and an enrichment in mineral material (residue) as well as an increase in pH in the burned forest floors compared to those unburned. After a high-severity crown fire in the Scots pine forest, we found that forest floor near tree stems was completely burned to a mineral layer (Figure 3a). The SEM micrographs of burned forest floor samples from the Scots pine forest showed the presence of visually distinguishable wood fragments due to incomplete combustion (Figure 3b) and a finer texture after complete combustion of organic matter near tree stems (Figure 3c). The EDX spectra (Figure 3d,e) indicated that mineral particles mainly consisted of Ca, Si, and Fe. These samples differed considerably from each other in this forest, so we discuss them separately here.

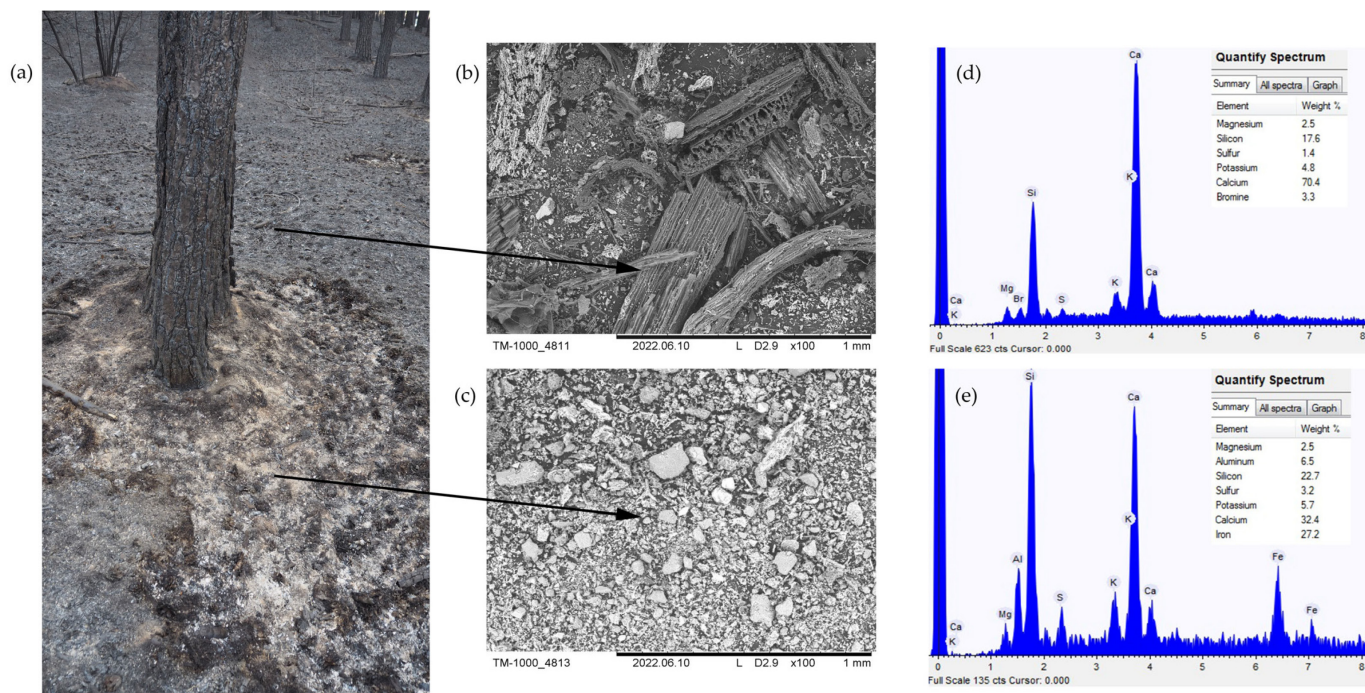


Figure 3. Photo (a) of burned Scots pine forest (Plot 1); SEM micrographs and EDX spectra of wildfire ash produced across the site (b,d) and near tree stem (c,e) where intense burning was observed.

The Scots pine forest floor after fire showed a decrease in organic matter content by 13% across the plot and by 81% near tree stems, while the spruce, larch, and birch forest floors showed decreases of 13, 14, and 24%, respectively. The increase in mineral material in forest floor was as follows: birch (by 233%) > larch (193%) > Scots pine (170%) > spruce (140%). In burned forest floor samples collected near the Scots pine stems, the proportion of mineral material increased 12-fold.

The pH values in burned forest floors of larch, spruce, and birch forests increased by 1.00–2.56 units (or 18–43%). The greatest increase in pH (by 55 and 103%) was observed for the forest floor in Scots pine forest. The forest floor in the larch forest showed the lowest shift in pH (Figure 2). The differences in physicochemical characteristics of forest floor samples before and after fire were statistically significant (at $p < 0.05$) for all forests studied.

3.2. Major and Minor Elements in Burned and Unburned Forest Floor

Among major and minor elements (Ca, Al, Fe, S, Mg, K, Na, Mn, P, Ti, Ba, and Sr), Ca attained in the highest concentrations (11,515–31,336 mg/kg) in the unburned forest floors of all the forests studied. The elements K, S, Mg, and Al were also abundant, ranging from 982 to 3914 mg/kg, 1449 to 3895 mg/kg, 1012 to 3225 mg/kg, and 1084 to 2059 mg/kg, respectively. The birch forest floor had the highest levels of Mg, Al, Fe, Na, P, Ba, and Ti, while the spruce forest floor was enriched by Ca, S, Mn, and Sr. The larch forest floor showed the highest concentration of K (Figure 4, Table S1).

After the fires, the levels of Ca, Mg, Al, Fe, Na, Ti, Ba, and Sr in all forest floors were statistically significantly higher ($p < 0.05$) compared to those at the unburned plots. The concentrations of these elements increased by 154–455% in the birch forest, by 35–1455% in the larch forest, and by 90–873% in the Scots pine forest after high-severity fires and by 116–371% in the spruce forest after moderate-severity fire. The elements concentrations increased by 5–64 times in the burned Scots pine forest floor near the tree stems. The concentrations of some elements, such as K (larch forest), S (birch, Scots pine, and larch forests), Mn (spruce and Scots pine forests), and P (larch forest), did not differ statistically significantly between the burned and unburned plots.

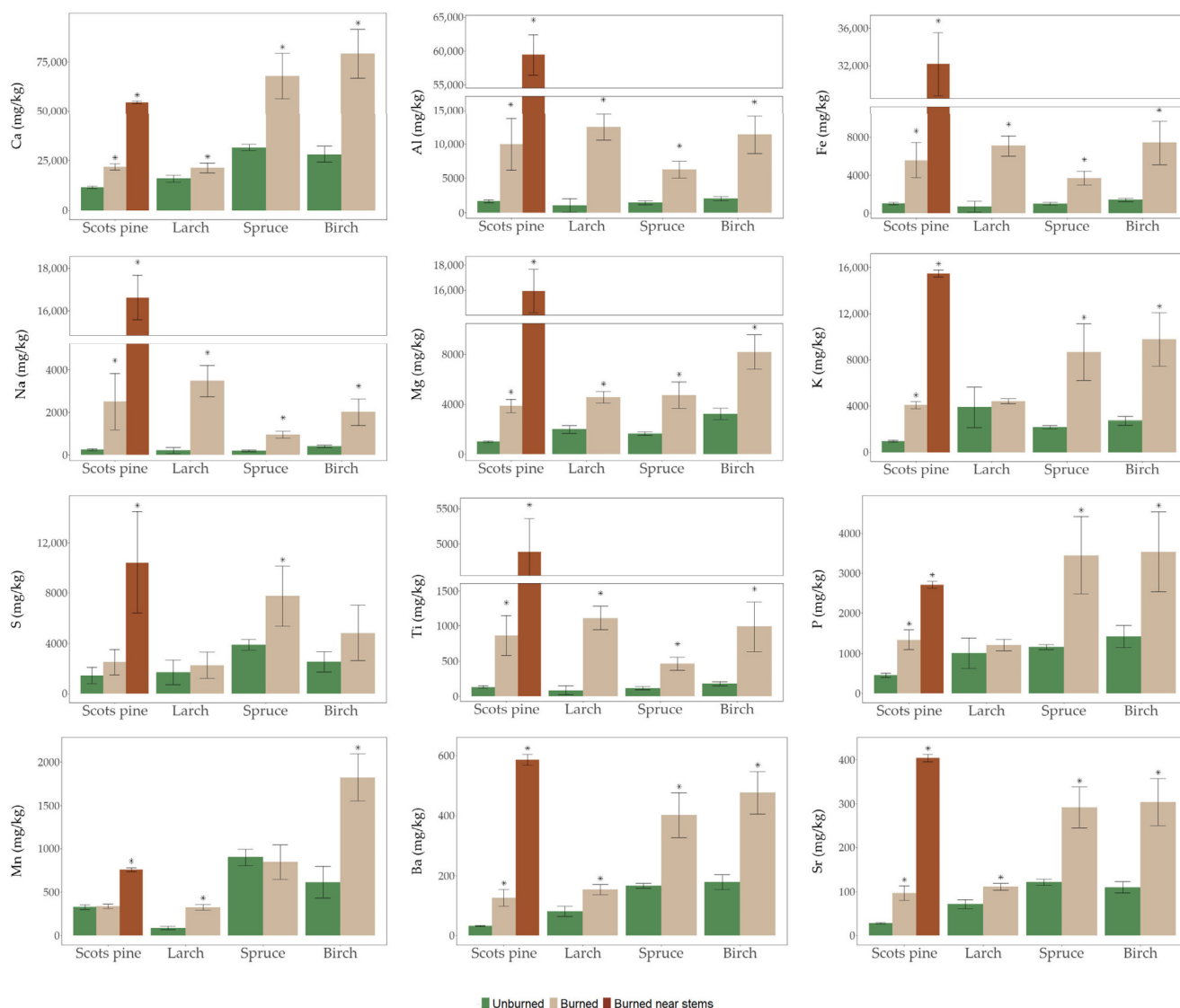


Figure 4. Total concentrations of major and minor elements in forest floor. Mean and associated standard deviation are given. Asterisks indicate significant differences ($p < 0.05$) between burned and unburned samples ($n = 5$ for each site).

3.3. Trace and Ultra-Trace Elements in Burned and Unburned Forest Floors

Trace elements such as Zn, B, Cr, Cu, and Ni were most abundant in the unburned forest floor of the studied forests, ranging over 15.5–83.2, 12.6–40.7, 5.5–7.9, 4.3–10.4, and 2.5–9.1 mg/kg. Low concentrations were found for Cd, Mo, Co, Li, Sb, Sc, Sn, and Bi. The levels of Be and Hg were below detection limits (Figure 5, Table S2). The birch forest floor was characterized by the highest concentrations of most trace elements.

In the burned forest floor, the concentrations of trace and ultra-trace elements increased by 69% (Se)–566% (Li) in the birch forest, by 43% (Cd)–663% (B) in the spruce forest, by 48% (As)–1500% (La) in the larch forest, and by 70% (Zn)–494% (V) in the Scots pine forest compared to the unburned samples. The greatest increase (by 4 (Zn)–36 (Sc, V) times) in element levels was observed in the burned forest floor near the Scots pine stems, where complete combustion of organic matter was observed. All reported differences in element concentrations between burned and unburned forest floors were statistically significant. Among the trace and ultra-trace elements analyzed, Zn, B, Cr, Ni, Cu, and V attained higher concentrations in burned forest floors. No statistically significant differences in Sb and Sn contents were found after the fires, except for samples near stems in Scots pine forest. The

difference in Se concentration was statistically significant only for the burned birch forest floor. B, As, and Bi showed statistically significant changes after the fires only in some plots.

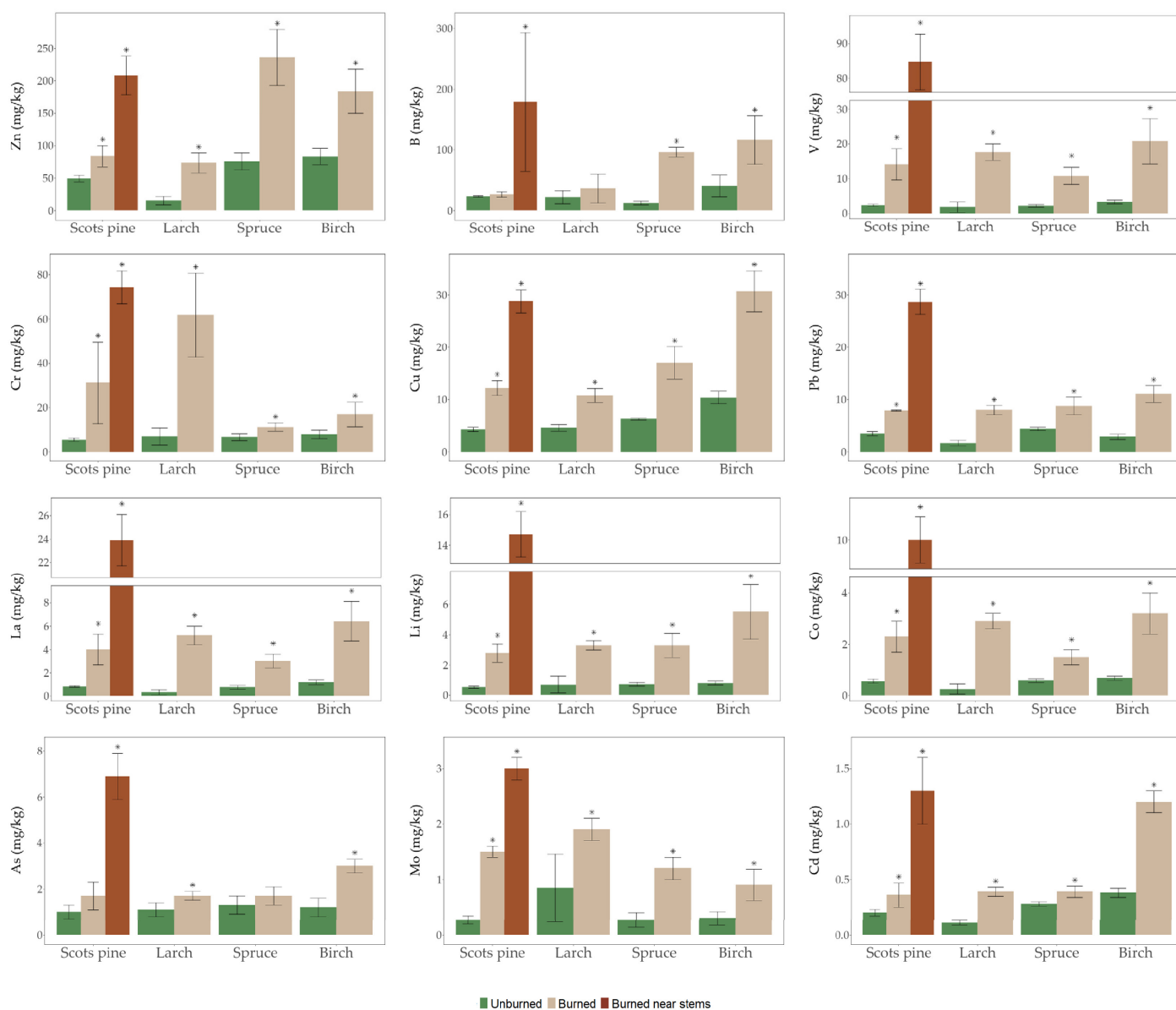


Figure 5. Total concentrations of trace and ultra-trace elements in forest floor. Mean and associated standard deviation are given. Asterisks indicate significant differences ($p < 0.05$) between burned and unburned samples ($n = 5$ for each site).

3.4. Correlations among Element Contents and Relationships of Elements with Physiochemical Characteristics of Forest Floor

The relationships between major and minor elements concentrations in unburned and burned forest floor with pH, organic matter, and mineral residue contents are shown in Table S2. Ca, Al, Fe, P, S, Mn, Ba, Sr, Ti, Cu, Zn, Co, Ni, Cd, Li, V, and La were positively correlated with mineral residue content ($r \in [0.51, 0.85]$ at $p < 0.05$) in unburned samples. Positive correlations were found between pH and Ca, Mg, P, S, Ba, and Sr ($r \in [0.57, 0.82]$ at $p < 0.05$). Many of the elements showed negative correlations with organic matter content. After fire, positive correlations ($r \in [0.44, 0.97]$ at $p < 0.05$) were found between most of elements (with exception of Ca, Mn, P, Zn Se, Sb, and Sn) and mineral residue content. In contrast, significant negative correlations were identified between most elements and

organic matter. Elements such as Ca, Mg, Al, Fe, K, P, S, Mn, Ba, Sr, Cu, Zn, Co, B, Se, Li, V, La, and Bi were positively correlated with pH ($r \in [0.45, 0.95]$ at $p < 0.05$).

Significant correlations between elements in unburned and burned samples are presented in Figure 6. In unburned samples, Al showed a strong relationship with Fe, Ti, Sc, La, Na, and V. Ca was closely related to Ba, Sr, and P. Cu was strongly associated with Cd, Mg, and Ni. B showed moderate correlations with Al, Fe, Ti, Na, Ni, La, and Sc. Mo revealed a strong negative correlation with Co and weak negative correlations with Al, Pb, and Zn. As was the only element that showed no significant correlation with any of the other elements. In burned samples, we observed a greater number of significant correlations among elements compared to unburned samples. For example, Al was strongly correlated not only to Fe, Ti, Sc, La, Na, and V but also to As, Co, Li, Mg, and Pb. Some elements in burned samples showed higher values of correlation coefficients compared to those in unburned samples. For example, Mg showed stronger correlations with Fe, K, La, and Li in burned samples. However, some significant associations among elements in unburned samples were not significant in burned samples (e.g., Al and Cu, Zn; Co and Zn). In general, the highest correlations were found among such elements as Al, Fe, Mg, Na, Ti, La, Li, V, Sc, Co, Pb, and As. Other elements (Ca, Cr, Mn, P, and Zn) in burned samples revealed negative relationships.

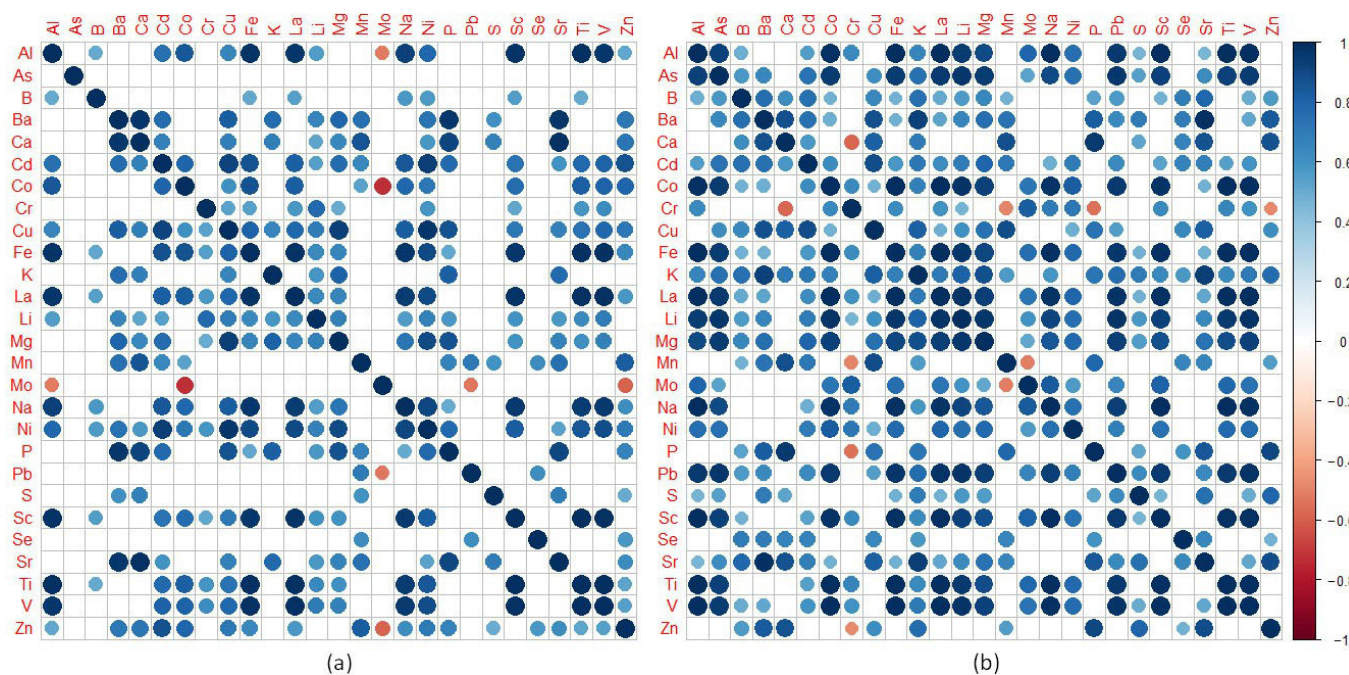


Figure 6. Pearson's correlation matrix among element concentrations for unburned (a) and burned (b) samples. Blue and red colors indicate positive and negative correlations, respectively. The darker the tone, the more significant the corresponding correlation (at $p < 0.05$).

4. Discussion

4.1. Wildfires Effects on Physicochemical Properties of Forest Floor

The degree of alteration in soil properties caused by wildfire depends mainly on its intensity and duration [19,58]. The forest floor is the most affected by fire and can account for up to 85% of the total fuel burned in forests, with down woody debris, stem bark, needles, and small branches in the crown contributing the remainder [58,59]. Depending on the intensity of the fire and the vegetation exposed to the fire, organic matter is charred or partially or completely oxidized [12,13].

In all studied forests, significant changes in the composition and pH of the burned forest floor (Oi layer) were observed. Thermogravimetry showed a loss of organic matter and an enrichment in mineral material for burned samples compared to those unburned

(Figure 2). The greatest loss of organic matter was found in samples collected near tree stems in Scots pine forest after a high-severity crown fire (Plot 1). This indicates that very high temperatures were reached near the tree stems, resulting in complete combustion of the organic matter present. SEM observations revealed that the burned layer even within a single site (Scots pine forest) had diverse compositions. Substantial consumption of organic matter begins between 200 and 250 °C and ends at around 460 °C [13]. Bodí et al. [22] stated that the particle size of ash depends on the combustion temperature; the ash particles become finer as the temperature increases from 350 to 500 °C due to increasingly complete combustion. We do not also exclude the contribution of some mineral material from the soil to these samples. Santín et al. [23] reported that the contribution of soil material to the ash layer can be significant, both in terms of ash load and ash composition. Soil inputs need to be considered in wildfire ash studies because they can have a significant impact on ash characteristics.

The burned forest floor in the birch forest (Plot 4) revealed the higher losses of organic matter compared to larch, spruce, and Scots pine (with exception of samples near tree stems) forests. Apparently, the upper layer of the forest floor in the birch forest was dry enough (mainly due to the lack of foliage in the crown and absence of grasses and herbs in the beginning of vegetation season) to be significantly consumed by a high-severity spring fire. Our previous study [52] indicated that these fires resulted in a significant decrease in the thermolabile fraction of organic matter, leaving the thermostable (recalcitrant) components, which are more resistant to microbial decomposition [60]. Our observations on organic matter loss are in agreement with Badía et al. [61], who reported that soil organic carbon content in topsoil (0–1 cm) decreased by 28% after wildfire in Aleppo pine (*Pinus halepensis* Mill.) forests in Spain.

The combustion of organic matter left, naturally, an increased level of mineral material content in burned forest floor samples. Krasnoshchekov [46] also reported that burned forest floor had higher mineral material content by 20, 40, and 231% even 5 years after low-, moderate-, and high-intensity fires in Scots pine forests (Baikal region, Siberia), respectively.

pH in the burned layer of forest floor was enhanced after fires in all the forests studied. The increase in pH is mainly attributed to the combustion of organic matter, which provided large quantities of ash containing base cations, and to the decrease in organic acids and acidic functional groups in organic matter during burning [19,40,41]. Ulery et al. [62] observed that the enhanced pH at the soil surface immediately after the fire was due to the formation of various oxides, hydroxides, and carbonates of K and Na. pH increases significantly at temperatures above 450 °C [14]. The greatest increase in pH was observed for burned forest floor in the Scots pine forest (by 55%) and especially near the tree stems (by 103%) due to the significant combustion of organic matter and the associated increase in mineral residue. In the burned forest floors, pH had a statistically significant positive correlation with concentrations of Ca ($r = 0.85$, $p < 0.05$), Mg ($r = 0.76$, $p < 0.05$), and K ($r = 0.92$, $p < 0.05$) (Table S2). Campos et al. [40] also reported pH values of 6.9–8.0 in eucalypt and pine ash samples collected immediately after fire. Sánchez-García [35] noted that pH values in ash samples ranged from 6 to 11.2. In general, alterations in the physicochemical properties of burned soils are strongly related to ash formation [40].

4.2. Wildfire Effects on the Chemical Elements

The chemical composition of forest floor (Oi layer) mirrors that of the vegetation cover [63]. In particular, forest floor chemistry is influenced by complex factors such as plant species, green leaf chemistry and the degree of element resorption prior to leaf fall, and availability of elements in the soil [64]. Among the elements studied, P, S, K, B, Ca, Cu, Fe, Mg, Mn, Mo, Ni, and Zn are considered as essential elements for all plants, as they are required to complete the plant life cycle. Al, Co, Na, Si, Se, and V are beneficial elements that are not required by all plants but can promote plant growth and may be essential for certain taxa [65–67].

Our results showed that not only essential and beneficial elements but also many other elements (La, Sc, Sb, Sn, etc.) were also taken up by plants from the soil and then redeposited in the forest floor (Oi layer). We found that Ca was the most abundant element, with K, S, Mg, and Al also present in high concentrations in the unburned forest floor. Our data are consistent with the earlier findings of Krasnoshchekov [46], who reported the following sequence of accumulation of chemical elements from the highest to the lowest: Ca, Si, and Fe and Mg, Al, K, and P in the forest floor of taiga Scots pine forests in the Baikal region, Siberia.

The concentrations of Be and Hg in most of our forest floor samples were very low, in particular below detection limits of the method used, which can be likely related to low uptake of these elements into vegetation. The concentration of Hg in crop plants has been reported to be less than 0.1 mg/kg [68], and about 90% of Hg in a forest ecosystem is stored in the soil rather than associated with vegetation [17]. Hg concentration in the upper soil layer is usually greater than in the subsurface horizons and related to the contents of organic carbon and sulfur; however, accumulation of Hg in the surface layer occurs quite slowly, even in the case of a small anthropogenic contribution [69]. Blackwell et al. [70] reported that Hg accumulation in the Oi/Oe and Oa horizons of the forest floor likely represents several years and decades of Hg deposition, respectively. The alkaline earth metal element Be is found in trace quantities in environmental materials. Most plants take up Be from the soil in small amounts, and the levels of Be in plants range from 0.0013 to 2.0 mg/kg [71,72].

The birch forest floor was characterized by higher levels of many elements (Al, Fe, Mg, Na, P, Ba, Ti, B, Zn, Cu, Ni, Cr, Co, Cd, V, La, Li, Sc, and Be) than the conifer forest floors. This might be due to the higher element contents of birch leaves compared to conifer needles. For example, Modrzewska et al. [73] and Kosiorek et al. [74] found higher concentrations of Ca, P, Mg, Ni, Mn, Fe, and Zn in birch (*Betula pendula*) leaves compared to Scots pine (*Pinus sylvestris*) needles. The spruce forest floor showed the highest concentrations of Ca, Mn, Sr, S, Pb, Se, Bi, and As, and the larch forest floor was the richest in K, Sn, and Mo. The highest content of Sb was observed in the Scots pine forest floor. Vesterdal and Raulund-Rasmussen [75] showed that the forest floors of the seven tree species had very variable element contents, indicating that tree species may have a significant effect on element immobilization in the forest floor.

Wildfires release elements associated with vegetation and organic matter [76]. Due to the high volatilization temperatures, most of the elements were not volatilized during the fires and therefore concentrated in the burned layer of the forest floor in the forests studied. Most of the elements analyzed showed marked differences in the concentrations in the burned layer of the forest floor under four forest types, which reflect a variety of factors, such as type, density and age of the vegetation, the parts of the plant burned (leaves, bark, etc.), the concentration of elements before the fire, maximum temperature reached, and the intensity and duration of the fire [17,23,33]. In our case, the forest floor was a major source of elements for the ash, as it contributed the most to the total fuel combustion during spring surface wildfires in Siberia [3]. In the Scots pine forest burned by the high-severity crown fire, the canopy also contributed to the ash.

We found a statistically significant increase in levels of major and minor elements (Ca, Mg, Al, Fe, Na, Ti, Ba, and Sr) as well as trace and ultra-trace elements (Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn, La, Li, and Sc) in the burned forest floor in all plots. K, S, Mn, P, B, As, and Se showed elevated significant levels only in some burned plots. We found no statistically significant accumulation of Sb and Sn in the forest floors studied after fires.

Similar to our results, other researchers also reported a significant influence of fire on element concentrations. For example, Santín et al. [23] found that the ash loads were positively related to fire severity and that the contents of Al, B, K, As, and Pb in ash increased with fire severity in a dry sclerophyll eucalypt forest in Australia. Campos et al. [40] reported that the levels of V, Mn, Ni, Cd, and Pb in burned soils were 1.7–13.4 times higher than in unburned soils, while Co and Cu showed no differences. Abraham et al. [17]

observed that the concentrations of As, Cd, Mn, Ni, and Zn increased by 1.1–1.9 times in burned soils, while Hg and Pb levels decreased after prescribed fire. According to Krasnoshchekov [46], the concentrations of Fe, Al, Ca, Mg, and P in the burned forest floors in Scots pine forests of Baikal region (Siberia, Russia) were higher by 7–20, 15–45, and 44–75%, respectively, compared to the unburned forest floor five years after low-, moderate-, and high-intensity fires. Bilichenko et al. [47] found that the concentration of Ca, Mg, Cr, Cu, Mn, Ni, Pb, and Co in the surface horizon of soils affected by wildfires in the Baikal region increased by 2–7 times. Chebykina et al. [48] reported a slight accumulation of Zn and Ni in soils due to a surface fire in the area around Yakutsk (Siberia, Russia).

It should be noted that the highest concentrations of most elements (except for Ca, P, Mn, Cu, Zn, and Se) were found in the samples collected around the Scots pine stems, which can be explained by the complete combustion of organic matter and, as mentioned above, the possible contribution of mineral material from the soil to the samples. The likely contribution of burned soil to these samples is also supported by the high concentrations of lithogenic elements such as Al, Fe, and Ti, which are mainly derived from mineral soils and are present in much higher levels in soils than in plant material [23]. In contrast, higher levels of Ca, P, Mn, Cu, Zn, and Se, which are considered biogenic elements and are mainly derived from biomass/necromass [23], were found in a burned layer of forest floor sampled across Plots 3 and 4.

The most abundant element in the burned forest floor samples of the studied forests was Ca, followed by Al, Fe, K, and Mg. In contrast, the elements found in low concentrations were Be, Bi, Sb, Sn, and Cd. Sánchez-García [35] also reported that Ca was the predominant element, and other important elements were Al and Fe in the wildfire ashes produced in various ecosystems (boreal, Mediterranean coniferous, temperate eucalyptus, and mixed forests). Harper et al. [43] also noted that Ca prevailed, and As, Cd, and Hg were found in the lowest concentrations in ash generated from wildfires in various vegetation types (U.K. grassland, Spanish pine forest, Spanish heathland, USA chaparral, Australian eucalypt forest, and Canadian spruce forest). Our results are consistent with those of Doufexi et al. [77], who studied the composition of wildfire ash collected from streams in

Greece and also found the dominance of Ca, Mg, Fe, and Al and the lowest contents of Be (0.7 mg/kg) and Sb (2 mg/kg). Similar to our findings, these authors also showed that elements such as Sc and La were present at concentrations of 4 and 12 mg/kg, respectively.

The concentration of Hg in the burned forest floor samples was below detection limits in all plots (except for near the Scots pine stems), indicating that Hg did not accumulate after the fire. This could be due to both the very low levels of Hg before the fire and probably its volatilization at relatively low temperatures during the fire. Some studies have shown that Hg concentrations decrease in ash compared to litter, with the decrease depending on fire intensity and vegetation type [26,78]. However, the detection of Hg at the average concentration of 0.49 mg/kg in burned samples collected near Scots pine stems was probably due to the presence of mineral particles from soils. According to the literature [15], Hg concentrations in mineral soils either decrease or show no significant change after burning. In contrast to Hg, the content of Be was also very low in the unburned samples, but it increased after fire.

In this study, significant positive correlations between most of the elements studied and the mineral residue content in the unburned and burned samples were found, which was expected since we are dealing with mineral elements. The elements studied showed only negative correlations with organic matter content before and after fires probably due to the fact that for organic matter such relationships do not assess the relevant reactive fraction of organic matter [40]. Boguta et al. [79] reported that the stable form of organic matter was negatively correlated with trace elements in bottom sediments and that their content depended on the labile form of carbon. Only a few elements were positively correlated with pH in unburned samples, and significantly greater number of elements showed this relationship after fires. Campos [40] also found positive correlations between Mn, Ni, Co, and Cd levels and pH in ash samples. Correlation analysis also revealed that a greater

number of elements were highly associated to each other in burned samples compared to those unburned. The correlations found indicate a wide variety of relationships between elements in unburned samples and a significant fire effect on them.

We found that not only the unburned forest floor of the birch forest but also the burned floor was characterized by the highest levels of many of the elements studied. This is likely related to the element concentrations in the forest floor before the fire and the high burn severity. Our results agree with findings of Campos et al. [40], who also observed consistent differences in the levels of elements in ashes derived from various forest types (eucalypt (*Eucalyptus globulus* Labill.) and maritime pine (*Pinus pinaster* Ait.)).

Our results indicated considerable variability in the accumulation of elements after fires in the forests studied. However, we observed some trends, so we grouped elements according to their post-fire change in concentration in burned samples compared to those unburned: (1) those that mostly increased by up to 200% – Ca, Ba, Mg, P, Mn, S, Sr, Cu, As, Se, and Bi; (2) those that mostly increased by more than 200% – K, Na, Al, Fe, Ti, V, Co, Ni, La, Li, and Sc; and (3) those that showed no statistically significant changes post fire – Sb and Sn. Concentrations of other elements (Zn, B, Cd, Pb, Mo, and Cr) varied greatly among the forests studied and showed no clear trends in post-fire accumulation. These differences in accumulation of the elements after fire, in our opinion, are mainly related to the amount and composition of the burned fuels and fire severity. When grouping the elements, we did not consider samples collected near the Scots pine stems because they differed significantly due to the contribution of mineral material from the soil.

We compared the levels of the elements in a burned layer of forest floor studied here with the available literature data on total concentrations of P, Ca, Mg, Na, Al, Fe, Mn, Ni, Cu, Zn, and Pb in ash produced after fires in boreal forests of Canada [35]. Concentrations of elements in our burned samples were mostly within their range in ash, except for Al, Fe, and Ni, which were significantly higher, and Ca, which was noticeably lower in some cases. Compared to ash collected immediately after fire in a pine (*Pinus pinaster* Ait.) forest in Portugal, our samples had lower levels of V and Pb and similar levels of Mn, Cu, Ni, Co, and Cd [40]. In comparison with data from Santín et al. [23] on the contents of the elements in ash from a dry sclerophyll eucalypt forest in Australia, our samples revealed significantly higher concentrations of Ca, K, Mg, Na, P, B, Cu, and Cd but lower concentrations of Al, Fe, and As, while Pb levels were similar.

Overall, the fires resulted in the input of considerable amounts of the elements in all studied forests. On the one hand, ash becomes an important source of nutrients such as N, P, and K for the soil, which are essential for plant growth and recovery [80,81]. High-severity fires in Siberia result in intensive colonization by pyrogenic herbaceous species such as fireweed (*Chamerion angustifolium*) and *Calamagrostis* spp. [82]. Fireweed is considered to be an indicator of more nutrient-rich soils [83]. Occupation of burned sites by fireweed promotes forest recovery after disturbance, whereas *Calamagrostis* spp. inhibit forest recovery. The proliferation of *Calamagrostis* on burned sites, along with the lack of nearby seed sources, hampers forest regeneration and leads to conversion to steppe vegetation [5].

Ash contains potentially toxic elements (Cd, As, Cr, Sn, Sb, Be, and others). These elements can have a negative effect on soil microorganisms, causing enzyme inactivation, cell damage, oxidative stress, and/or precipitation or chelation of essential metabolites [18]. The risks of contamination caused by fires are not limited to the in situ burned soils but can also include groundwater and especially surface water bodies [40] through ash transported off the slopes into rivers and reservoirs and by movement of water-soluble elements with subsurface flow [23]. In addition to the presence of potentially toxic elements, increased N and P post-fire runoff into water bodies can lead to eutrophication [20].

The greatest increase in runoff and soil erosion and, as result, transfer of ash and sediment to surface water bodies, occurs within 1 to 2 years after a fire. Thus, the increasing frequency of fires and their recurrence in previously affected areas accelerate the processes of soil degradation by enhancing the effect of water erosion [36].

5. Conclusions

The transformation of organic matter by fire is driven by a number of factors, such as vegetation structure and composition, soil type, and fire characteristics, and it affects many ecosystem properties and functions, such as nutrient cycle, vegetation succession, and microbial dynamics. We evaluated and compared, for the first time in Russia, the levels of 32 major and minor (Ca, Al, Fe, S, Mg, K, Na, Mn, P, Ti, Ba, and Sr) and trace and ultra-trace (B, Co, Cr, Cu, Ni, Se, V, Zn, Pb, As, La, Sn, Sc, Sb, Be, Bi, Hg, Li, Mo, and Cd) elements in the burned Oi layer of the forest floor collected immediately after moderate- and high-severity wildfires in Scots pine (*Pinus sylvestris* L.), larch (*Larix sibirica* Ledeb.), spruce (*Picea obovata* Ledeb.), and birch (*Betula pendula* Roth) forests in southern Siberia. Coniferous and deciduous forests exhibited marked differences in the levels of elements in unburned forest floor. The fires had a significant effect on total element concentrations in forest floors in comparison with those unburned. The positive correlations found between element levels and mineral material (residue) content in burned samples confirm a significant effect of fire severity. The increasing fire frequency and severity observed in Siberia may result in significant input of the chemical elements to soil, alteration of soil quality, and risks of surface water contamination. Our study allowed to determine only the short-term effects of wildfires on the levels of elements in the forest floor of Siberian forests. Therefore, further research is needed to fully understand the availability, mobility, and fate of elements in the soils of deciduous and coniferous forests in the long term. Knowledge of the characteristics of ash generated in different forest types under various fire severities is required for prediction of the potential for ash contamination from future wildfires under a changing climate in order to prevent and mitigate risks of post-fire contamination of surface water bodies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/fire7070243/s1>, Table S1: Total concentrations of trace and ultra-trace elements (mg/kg) in forest floor; Table S2: Pearson correlation coefficients between concentrations of major, minor, trace, and ultra-trace elements and organic matter content, mineral residue content, and pH for unburned and burned forest floor.

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