Effect of tree species on the elemental composition of wood ashes and their fertilizer values on agricultural soils

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Abstract
Wood ashes obtained from household heating and cooking are often applied to home gardens and arable fields by farmers. The effect of tree species and their locations on the elemental composition of wood ashes derived from domestic cooking and heating is unknown. The study aimed to discover the fertilizer values of wood ashes obtained from Betula pendula, Carpinus betulus, Fagus sylvatica, Larix decidua, Picea abies, Pinus sylvestris, Quercus robur, and Tilia cordata from two different localities, Hlinsko and Mšec, Czech Republic. The total element content in the ashes of dry wood samples (wood and bark) burnt at 460°C with a wood stove interfaced with a thermometer was determined using portable x-ray spectrometry. The content (in g kg⁻¹) of P (3.23–20.53), K (26.79–136.22), Ca (94.89–295.56), and S (2.97–11.75) in the ashes varies according to the tree species, locality, parent rock, and anthropogenic activities in the location of trees. Additionally, trace element contents ranged from 0.63–32.07 g Mn kg⁻¹, 0.34–4.6 g Fe kg⁻¹, 32.4–2062 mg Zn kg⁻¹, 47.61–193.09 mg Cu kg⁻¹, 3.99–21.53 mg Mo kg⁻¹, and 1.50–6.62 mg Se kg⁻¹. The pH of the ashes ranged from 8.71 to 11.54, suitable to alleviate soil acidity and a condition satisfying soil additive. A significant positive correlation between the contents of Cu, Sr, and Pb with the ashes of Picea abies, Larix decidua, Pinus sylvestris, and Betula pendula at Hlinsko is indicative of ancient anthropogenic activities input in the soil. The combustion of wood under home heating temperatures resulted in the concentration of most risk metal(loid)s, below permissible limits in agricultural soils. Application of wood ashes on arable fields requires considerable caution due to potentially toxic elements (Zn and Pb).

KEYWORDS
arable field, combustion temperature, macro element, risk element, total element, trace element, X-ray fluorescence spectrometry
1 INTRODUCTION

Wood ashes are often treated as waste in many households, neglecting their relevance in recent crops and herbage production when applied as fertilizers. Meanwhile, wood ashes served as a source of potash production and nutrients for plants during prehistory (Hejcman et al., 2011, 2013; Šmejda et al., 2017). For example, locations with ash deposits of current arable fields on ancient localities are well characterized by high element contents (Asare, Apoh, et al., 2020), biomass growth, and crop yields (Hejcman et al., 2011).

Many studies on the elemental composition of wood ashes demonstrated wide variability in their contents due to different plant species, parts, and combustion temperatures (Huang et al., 1992; Semelová et al., 2008; Smolíková-Danielowska & Jabłońska, 2022). The contents of soil nutrients, for example, P, Ca, K, Cu, and Zn, are often reported in different wood ashes, providing a basis for the recent use of wood ashes in some agricultural fields (Semelová et al., 2008; Wierzbowska et al., 2020). The high contents of Ca and K and sometimes Na provide the characteristic alkaline nature (pH 7.8–13.5) of wood ashes from many tropical (Adekayode & Olojugba, 2010; Asare et al., 2022) and European plant species (Campbell, 1990; Okmanis et al., 2016); hence, they are used to alleviate soil acidity.

Notably, the elemental composition of wood ashes is directly dependent on the parent rock, plant species, and anthropogenic activities in the locations of species (Asare et al., 2022). Therefore, wood ashes of the same tree species but different locations can differ in elemental compositions, while such studies are so far not well known. Additionally, burnt plant parts, for example, bark, wood, leaf, and root (Saarela et al., 2005), and combustion temperature remain important factors that significantly affect the content of specific elements (Zhou et al., 2021). For example, C, H, O, and S may volatilize at high temperatures >500°C (Naylor & Schmidt, 1986; Serafimova et al., 2011). Mineral substitutes are, therefore, recommended during the management of arable fields. Again, wood samples need no moisture content during burning to avoid incomplete combustion and generation of smoke, which contains many chemical compounds, such as carbon monoxide (CO), methane (CH₄), and hydrocarbons (Curkeet, 2011). However, complete combustion of wood produces mainly CO₂ (absorbed by plants) and H₂O but under different temperatures.

Besides the possibility of losing vital nutrients during the combustion process, the use of biomass ashes as soil fertilizer can potentially release toxic elements (e.g., As, Cd, Ni, and Pb) above allowable limits in soils and may relate to locations with emissions from metal smelting, long-term intensive fertilizer application (Lane et al., 2020; Obernberger et al., 1997). For example, emissions from metal smelting, fossil fuel combustion, and the spread of phosphate fertilizers are considered the cause of high levels of Cd in wood ashes (Narodoslawsky & Obernberger, 1996). Meanwhile, contaminated wood–combustion ashes with high levels of regulated environmental contaminants generally require only a basic level of treatment for utilization on agricultural soils. Plants possess different mechanisms of soil nutrient uptake. For example, some plants exhibit restrictive root–shoot translocation, making wood ashes obtained from the shoot less toxic to risk elements. Hence, the elemental compositions of wood ashes are a direct function of the plant genotype, uptake, translocation, and accumulation of elements by plants. Determination of elemental composition in the ash of leaves and stems was carried out to well-correlated nutrient uptake by plants with the nutrient content of the soil (Misra et al., 1993).

To determine the effects of anthropogenic activities on element contents in soils and tree species, we tried to establish a relationship between the elements in soils and wood ashes. Other important factors influencing the accumulation and depletion of elements in wood ashes include the condition of wood combustion and the treatment before burning (Liodakis et al., 2005). For example, decomposition and volatilization of CaCO₃ and CaO may occur during combustion. Some studies have shown that at temperatures of 350–450°C and 500–600°C, Ca/Mg hydroxides, and CaCO₃, respectively, occur (e.g., Liodakis et al., 2005; Sanders & André, 1997), which may decrease between 800 and 1000°C. Thus, the solubility of minerals during combustion can result in volatilization.

The question which is still unsatisfactorily resolved is, are wood ashes from domestic heating and cooking suitable enough as fertilizers? These household wood ashes often are obtained at different temperatures. Hence, empirical analyses are needed to confirm the suitability of such wood ashes as fertilizers in arable fields from an extreme variety of tree species. Additionally, the effect of species on the elemental composition of wood ashes from different localities is not well known.

As x-ray fluorescence spectrometry (XRF) has been sparingly used (Chand et al., 2009; Misra et al., 1993), we adopted this analytical approach as a reliable and cost-effective approach to determine the total element content of wood ashes.

As the fertilizer values of the homemade wood ashes are not studied, we determined the elemental composition of the ashes of Betula pendula, Carpinus betulus, Fagus sylvatica, Larix decidua, Picea abies, Pinus sylvestris, Quercus robur, and Tilia cordata from different localities in the Czech Republic.

In this study, we aim to answer the following research questions: (a) To what extent can different localities
influence the elemental composition of wood ashes of the same tree species? (b) What is the fertilizer value of wood ashes obtained from the combustion of commonly used European tree species? (c) Are wood ashes generated from home combustion temperatures of wood species suitable fertilizers for agricultural soils?

2 | MATERIALS AND METHODS

Eight (8) solid biomass fuelwoods were selected from two sites (Hlinsko and Mšec, Czech Republic; Figure S1) for this study, as commonly used species for domestic heating. Hlinsko is characterized by Palaeozoic metamorphic rock and Histic Stagnosol soil (Czech Geological Survey, 2012; Němeček & Kozák, 2005). The site has an altitude ranging from 550 to 670 m a.s.l. At Mšec, the soil is Luvic Cambisol on a Marlstone geological substrate (Němeček & Kozák, 2005), with an altitude of 480 m a.s.l.

2.1 | Location and sample collection

2.1.1 | Wood sampling

The reference names adopted for the sample fuelwoods are in Table 1. We collected samples of branches (wood and bark) of *Betula, Carpinus, Fagus, Larix, Picea, Pinus, Quercus*, and *Tilia* for both sites in August 2018. All samples were cut as log discs during forest felling or from living trees at the sites. The location of *Betula* from Hlinsko represented a visible relic of an abandoned graveyard from an ancient settlement. We collected four branch wood from each tree species per individual localities. Each branch of wood measured about 100 cm long, with a diameter from 20 to 30 cm: as firewood size used for heating households in the Czech Republic.

2.1.2 | Soil sampling

We collected soil samples in the surroundings of *Picea, Larix, Pinus*, and *Betula* at Hlinsko: locations marked with evidence of ancient human activities. To cover the variability of soil, we randomly collected four samples around each selected tree species. Each soil sample represented 10 sub-samples randomly collected and mixed into one representative sample per tree species. Soil samples from each stand were collected from the upper 10 cm depth using a soil probe (Purchhauer type, core diameter: 30 mm).

We collected 32 wood samples for each locality (Table 1), in addition to 16 soil samples only from the Hlinsko site.

| Local name      | Scientific name  | Reference name | Distribution                                                                 | Branch wood per site |
|-----------------|------------------|----------------|------------------------------------------------------------------------------|----------------------|
| Silver birch    | *Betula pendula* | *Betula*       | It occurs naturally throughout most of Europe up to central Siberia           | 4                    |
| European hornbeam | *Carpinus betulus* | *Carpinus* | The natural range extends from the Pyrenees to southern Sweden and eastwards to Iran. Widespread in central Europe | 4                    |
| European beech  | *Fagus sylvatica* | *Fagus*        | The natural range extends from southern Scandinavia to Sicily, from Spain in the west to northwest Turkey in the east | 4                    |
| European larch  | *Larix decidua*  | *Larix*        | It occurs in the central and eastern mountains of Europe                      | 4                    |
| Norway spruce   | *Picea abies*    | *Picea*        | Dominates the Boreal forests in Northern Europe and the subalpine areas of the Alps and the Carpathian Mountains | 4                    |
| Scots pine      | *Pinus sylvestris* | *Pinus*       | Found across Eurasia. The huge pine forests of Siberia are the largest stands | 4                    |
| European oak    | *Quercus robur*  | *Quercus*      | In Europe, found from Scandinavia to the Iberian Peninsula                    | 4                    |
| Small-leaved lime | *Tilia cordata* | *Tilia*        | Native to Europe                                                             | 4                    |
| Total samples   |                  |                |                                                                              | 32                   |
2.2 | Sample preparation

Each branch wood sample was washed thoroughly with Ultrapure-deionized H₂O (18Ω) to prevent dust and soil contact. The fresh wood samples were first dried in the open air in summer (avg. temp. of 31°C and 44% air humidity) for 72 h.

Individual branch wood samples were chopped into small slides of 0.5 cm thick and then oven-dried for 3 days at 60°C to total desiccation: this contributes to complete and fast combustion. After, 500 g of each dried sample per species was burnt independently in a wood stove interfaced with a thermometer (manufactured by Mingle Development, Shen Zhen Co., Ltd. China) until complete combustion. The combustion temperature did not exceed 460°C. The ash samples were homogenized through a 0.1-mm sieve and put into labeled plastic bags.

All the soil samples were initially oven-dried for 48 h. After removal of plant materials and other debris, samples were ground and homogenized through a 2-mm sieve.

2.3 | Analytical methods

The total element compositions of the wood ashes and soil samples were determined with a portable ED-XRF (pXRF) analyzer manufactured by Delta Professional Olympus, Waltham, MA (USA). In both cases, the pXRF device was in mining mode (for wood ashes) and Geochem-mode for soils.

The pXRF was previously successfully used for the elemental analysis of wood ashes (Xing et al., 2016) and different types of soils (Canti & Huisman, 2015; Šmejda et al., 2017). The device measures the total or near-total contents of magnesium to uranium in different matrices.

Each sample measurement was in triplicate, the final value as the arithmetic average of the three results. The quality of the pXRF results was tested successfully by BAS Rudice Ltd. Company, Czech Republic (https://www.bas.cz/) on 55 reference materials (e.g., SRM 2709a, 2710a, 2711a, OREAS 161,164, 166, RTC 405, 408). The content of P, K, Ca, Mn, Fe, Zn, Cu, Sr, Rb, Al, Si, Mo, Zr, Se, As, Ni, and Pb were pertinent in this study as elements above the detection limit by the pXRF in all the samples. The contents of some elements were omitted from further analysis for either not detected or above the detection limit only in a few cases (e.g., Ag, Cd, Sn, Sb, Ni, and Ti).

We determined the pH (H₂O) in two replicates for all ash samples at a ratio (ash-water) of 1:2 using a Voltcraft PH-100 ATC pH meter (pH 212) manufactured by I & CS spol. sr. o. (Czech Republic).

2.4 | Quality control

The precision of the pXRF was assessed by comparing the data with the elemental composition obtained by standard analyses. The contents of the total elements of certified reference material (CRM, BCR—176R-fly ash) were extracted using the USEPA 3052 extraction procedure (International Organization for Standardization, USEPA, 1996) with an extraction mixture of 65% HNO₃, 36% HCl, and 38% HF.

Procedure: A mass of 0.25 g of fly ash was mineralized in a mixture of 9 ml HNO₃, 3 ml HCl and 1 ml HF and heated in a sealed 60 ml VWR® PTFE Jar on a hot plate at 150°C for 24 h. After 24 h, 1 ml of 30% of H₂O₂ again added to the sample and evaporated on a hot plate at 50°C for 24 h. The evaporated sample was diluted to 20 ml by 2% HNO₃ for 2 h and filtrated. Next, the content of elements was determined with an inductively coupled plasma–optical emission spectrometry (ICP–OES; 720 Series, Agilent Technologies Inc., USA) and obtained in triplicates. We analyzed with an emphasis on the total contents of P, K, Ca, Mn, Fe, Zn, Cu, As, and Pb. The elements were also determined using the pXRF, and a calibration curve was made for each element.

2.5 | Reliability of analytical methods

The overall recovery of Ni, Co, Fe, Cu, Zn, As, and Pb from the CRM using Aqua regia ICP-OES and the pXRF was >90% (Table 2a). Moreover, the comparison of the data obtained from the pXRF and Aqua regia ICP-OES revealed a strong linear correlation for P, K, Ca, Mn, Fe, Cu, Zn, Pb ($r = 0.60–0.99, p < 0.01$) except for As, with a negative correlation ($r = −0.25, p = 0.547$) (Table 2). The control test indicates that the pXRF has adequate precision for this study and offers a cost-effective approach for the elemental analysis of wood ashes.

2.6 | Data analysis

There was relatively homogeneity of variance among obtained data for the contents of elements in studied ashes and soils. Data for elemental contents of ashes and soil were tested with the Shapiro–Wilk W-test for normality and met the assumption for the use of parametric tests. Factorial ANOVA followed by post hoc comparison using the Turkey HSD test was applied to identify significant differences among elements in wood ashes from different localities. The relationship between obtained dataset by pXRF and Aqua regia ICP-OES and the content of elements in selected ashes and soils furthermore was evaluated using Pearson’s correlation. We performed all
statistical analyses using STATISTICA 13.4 (www.statsoft.io).

3 | RESULTS

3.1 Chemical composition of wood ashes

The statistical description of the pH[H2O] and elemental composition of the studied ashes are in Table 3 and Figures 1–5. The pH value of the ashes under analysis was defined as alkaline, ranging from 8.71 to 11.54 (Table 3), indicating their suitability for highly acidic soils. There was a significantly negative relationship between pH and the content of S (r = −0.27, p = 0.027; Figure S2a) and vice versa with Ca (r = 0.67, p < 0.001; Figure S2b), which indicate that an increase S and Ca content reduces and increases pH of wood ashes.

There was a significant effect among the contents of macro (P, K, Ca, and S; Figure 1), trace (Mn, Fe, Zn, Cu, Al, Si, Rb, Sr, Mo, Zr, and Se; Figures 2–4), and risk (As and Pb; Figure 5) elements in the ashes of all the species among the localities. The contents of macro-elements in the ashes were significantly different among the species from the localities except for a few cases where the ashes from Betula (K), Picea (K), Larix (Ca), and Tilia (Ca) were similar in both sites (Figure 1). The contents of P in Hlinsko ranged from 6.85 to 20.53 g kg⁻¹ and in Mšec, 3.23 to 7.62 g kg⁻¹ (Figure 1a). The highest P content (20.53 g kg⁻¹) was in Pinus ash and the lowest, 3.23 g kg⁻¹ in Fagus. The content of K was from 46.85 to 136.22 g kg⁻¹ in Hlinsko and 26.75 to 66.94 g kg⁻¹ in Mšec (Figure 1b). The highest content of K (136.22 g kg⁻¹) was in the ash of Quercus and the lowest (26.75 g kg⁻¹) was in Tilia. The Ca content ranged from 94.89 to 280 g kg⁻¹ in Hlinsko and 207.36 to 295.56 g kg⁻¹ (Figure 1c). The highest Ca content (295.56 g kg⁻¹) was in Carpinus with the lowest (94.89 g kg⁻¹) in Quercus. The content of Ca was the highest compared to all the macro elements, which contributed to the high pH of the wood ashes. Among the macro elements, S recorded the least 3.74 – 8.64 g kg⁻¹ in Hlinsko and 3.7–12 g kg⁻¹ in Mšec (Figure 1d). We recorded 11.75 g S kg⁻¹ in Pinus and the lowest (2.97 g kg⁻¹) contents in Quercus from Mšec.

There was a significant effect on the content of Mn, Fe, Zn, and Cu among the ashes of the species in the localities (Figure 2). The Mn content ranged from 1.09 to 21.05 g kg⁻¹ in Hlinsko and 0.63 to 32.07 g kg⁻¹ in Mšec (Figure 2a). The highest Mn content (32.07 g kg⁻¹) was in the ashes of Larix and the lowest (0.63 g kg⁻¹) in Tilia.

Moreover, the Fe content ranged from 0.66 to 4.60 g kg⁻¹ in Hlinsko and 0.34 to 4.09 g kg⁻¹ in Mšec.
The highest (4.60 g kg\(^{-1}\)) content of Fe was in the ash of *Fagus* with the lowest (0.339 g kg\(^{-1}\)) in *Carpinus* from Mšec. The content of Zn (in mg kg\(^{-1}\)) ranged from 32 to 2062 in Hlinsko and 65.93 to 1044.68 in Mšec (Figure 2c). Zinc content was highest (2062 mg kg\(^{-1}\)) and lowest (89 mg kg\(^{-1}\)) in the ash of *Betula* and *Carpinus*, respectively, from Hlinsko. The content of Cu ranged from (in mg kg\(^{-1}\)) to 58.31–193.09 in Hlinsko and 47.61–146.51 in Mšec (Figure 2d). Copper content was highest in the ashes of *Fagus* from Hlinsko and the lowest in *Carpinus*, Mšec.

Additionally, there was a significant effect on the content of Al, Si, Rb, Sr, Mo, Zr, and Se in the ashes from different species among the localities (Figures 3 and 4). Except for the ash of *Fagus* in Hlinsko (14 g kg\(^{-1}\)), the content of Al was relatively similar (approx. 5 g kg\(^{-1}\)) for all the species from both sites (Figure 3a). Si content ranged from 7.2 to 18 g kg\(^{-1}\) in Hlinsko and 6.3 to 21.2 g kg\(^{-1}\) in Mšec (Figure 3b). Rubidium content in Hlinsko was from 0.2 to 1.6 g kg\(^{-1}\) and 0.2 g kg\(^{-1}\) in the ashes from Mšec (Figure 3c). The Sr content was from 1000 to 3225 mg kg\(^{-1}\) in Hlinsko and 500 to 1467 mg kg\(^{-1}\) in Mšec (Figure 3d).
In the case of risk elements (As and Ni), there was a relatively higher content in Hlinsko among all the ashes compared to Mšec (Figure 5). Except for Pb content (132 mg kg⁻¹) in the ash of Larix from Mšec, other risk elements were below permissible limits for agricultural soils according to Decree No. 13/1994 Sb. of Ministry of Environment in the Czech Republic (mg kg⁻¹) 20 for As and 60 for Pb (Figure 5c; Carlon, 2007) and European Commission (Brandón et al., 2017; Table 5).

3.2 Chemical composition of soils and the relationship with wood ashes

The content of elements in the soils around the selected tree species is in Table 4. The content of P, K, Cu, Zn, Mo, and Pb was significantly higher in the soils around the Betula compared to the other sample locations. There was a significant positive correlation among Cu, Sr, and Pb contents in soils and ashes of Betula, Pinus, Larix, and Picea (r = 0.56–0.90, p < 0.05) (Figure 6a–c). Conversely, there was no significant relationship between the content of Ca, Fe, Mn, Zn, Rb, Zr, and Mo in the soil and the ashes of all the species (Figures S2 and S3).

4 DISCUSSION

Even though the wood ashes were of the same tree species, the content of many elements differed with localities. The contents of macro (P, K, Ca, and S) and trace (Mn, Fe, Zn, Cu, Mo, and Se) nutrients pertinent to
plants were sufficiently enough compared to other ashes from European tree species, for example, pine, aspen, alder, poplar, spruce, hornbeam, hazel (Dibdiakova et al., 2015; Górecka et al., 2006; Okmanis et al., 2016; Someshwar, 1996), and renders them suitable for deficient arable soils. Positive plant growth after wood ashes application is well documented (Demeyer et al., 2001). Additionally, different plant species possess diverse mechanisms in the uptake, translocation and accumulation of elements evident from the content of the individual wood ashes. The wide distribution of the content of elements in the wood ashes of the tree species provides an opportunity to select the most suitable ashes according to soil needs. For example, the ashes of *Tilia* are more suitable for Ca deficient soils regardless of the locality (Figure 2c). The study supports the use of wood ashes to alleviate soil acidity according to the basic pH. Additionally, the influence of high Ca content from the Marl parent rock from Mšec contributed to higher pH than Hlinsko (Figure S2b).

The effects of mineral properties of soils are well shown according to the elemental contents. For example, the influence of the Marl parent rock at Mšec in the high content of Ca in the ashes of *Betula, Carpinus, Fagus, Pinus*, and *Quercus* compared to Hlinsko (Table S1). Other minerals found in wood ashes, including hematite (*Fe₂O₃*), albite (*Ca, Ca*)Al(Si, Al)₃O₈, and dolomite (*CaMg[CO₃]₂*) are either in small quantities in the wood or bark or absent, with mostly higher calcite due to the high concentration of Ca (Ndlovu, 2007; Symanowicz et al., 2018). These relate to the mineralogical composition of parent bedrocks, while the crystalline phase of minerals in wood ash changes as combustion temperature increases (Olanders & Steenari, 1995). The influence of anthropogenic sources of elements in the ashes of *Picea, Larix, Pinus*, and *Betula* was well reflected in the significant positive correlation...
between the content of Cu, Sr, and Pb. Besides their comparatively higher content than the other trace elements, each species has different uptake and accumulation strategies (Mleczek et al., 2019) regardless of how abundant the elements are in the soil. The high content of P, K, Cu, Zn, Mo, and Pb in the ashes of Betula in Hlinsko was significantly higher than in the same species in Mšec, resulting from the high element content due to anthropogenic elements input. Although we expected a relatively similar ability of nutrient uptake by the plant. The exact location of the Betula had an ancient grave: decomposition of dead human bodies releases many elements (Asare, Šmejda, et al., 2020), where plants can take them up.

The content of Pb in the ashes of Larix at Mšec renders it risky to adopt as fertilizer according to the high level above permissible limits in arable fields and mostly connected with the species in proximity to automobile roads. However, there were low contents of Pb in Hlinsko, with some increases in the ashes of Betula. Locations with high organic matter sorb Pb and probably be taken up by the plant (Thompson & Goyne, 2012). Ashes generated from home may not be adversely affected, but the condition of the growing species can render them unsafe to apply on arable soils. Wood ashes generated from temperatures used in heating households are suitable to maximize element contents, while the pXRF offers a time-efficient and inexpensive approach to the geochemical exploration of wood ashes to determine their fertilizer value. However, this message is relevant for local farmers who apply household wood ashes on their arable fields without adequate elemental analysis.

The most suitable source of P was ash from Pinus in Hlinsko. However, ashes from a Hlinsko were more suitable P fertilizer compared to Mšec. The P contents in most of the ashes from Hlinsko were up to 21.9 g kg⁻¹, recorded for ashes of most European woody species (Etiégni &

FIGURE 4 Effect of species on the total concentration of (trace elements) (a) Mo, (b) Zr, and (c) Se in the ashes of selected tree species from Hlinsko and Mšec, Czech Republic. The F and p-values were obtained from factorial ANOVA. Using Tukey posthoc HSD test, mean values with the same letters were significantly not different. The error bars indicate the standard error of the mean.
Comparatively, the ashes of Quercus in Hlinsko are more preferred fertilizer than the other species. K contents increase with the application of wood ashes attributed to the release of K by wood ash and the replacement of K on soil exchange sites by Ca and other exchangeable cations released into the soil suspension (Górecka et al., 2006). The solubility and potential availability of the macronutrients to plants in wood ashes are high, and K has the highest bioaccumulation compared to P, Ca, and S (Mandre, 2006). Since K fertilizers are usually expensive, the ashes from all the studied species can be good alternative sources of mineral K fertilizers for soils with K deficiency.

The wood ashes of the studied tree species are applicable for Ca-demanding soils according to their high contents. However, ashes from Mšec were more suitable, especially in the ash of Carpinus. The Ca contents in the ashes of all the species in this study were within the range (109–361 g mg⁻¹) of ashes of different woody species (Etiégni & Campbell, 1991; Huang et al., 1992; Górecka et al., 2006). Wood ashes have the same liming effects as commercial lime and comparatively provide better plant growth responses than limestone because of the supplementary nutrients in ashes (Adekayode & Olojugba, 2010). However, adding wood ashes which usually contain 25% CaCO₃, with a pH of 10–12, increases soil alkalinity and creates an adverse condition for growing plants (Lannotti, 2020). Hence, ashes above this Ca content are more suitable for acidic soils as many plants like a slightly acidic environment (pH < 7.0) to absorb nutrients. Although wood ashes have a high effect on liming soils due to CaO (lime), their proportion during application needs proper attention to prevent leaching (Vassilev et al., 2013). However, the process of obtaining high CaO during wood combustion (calcination) can reduce at temperatures < 800°C of totally dried wood (Kumar et al., 2007). When soil alkalinity increases and the pH rises, nutrients, for example, P, K, Fe, Mn, Cu, and Zn, can chemically adsorb to soil and become less available for plant uptake. The relatively lower contents of S compared to other macro elements are due to the high volatility during combustion, especially > 500 °C (Dibdiakova et al., 2015). Consequently, if wood ash is applied to arable fields, S content, especially in ashes of Pinus from Mšec, is most suitable. However, the lowest macro element content in the studied ashes was S. At high pH, metalloid(s) in wood ashes often leach into soils. Meanwhile, a negative correlation between the pH and S indicates a decreasing effect on pH (Figure S2a), which can affect the solubility of metalloid(s), thereby preventing extreme leaching. Hence, the application of this acid with a relatively low content of S will not result in high acidity after oxidation in the soil.

The content of Fe in all the studied ashes was relatively within most recorded values (3–4 g kg⁻¹) for many different species and organs of plants (Vassilev et al., 2013). Furthermore, soil deficient in Mn and Fe can be fertilized by all the ashes of this study, especially from Larix and Fagus in Mšec and Hlinsko, respectively. The comparatively high content of Cu, especially in the case of the ash of Betula in Hlinsko, relates to the level in the soil.
The Zn content in the ash of *Betula* from Hlinsko was higher among all the species, with *Pinus* and *Quercus* above the allowable limit for arable soils. However, Zn content in the ashes of birch and spruce, according to Reimann et al. (2008), was as high as 14,300 and 5350 mg kg\(^{-1}\), respectively (Reimann et al., 2008). Meanwhile, *Betula* spp. is also known as a Zn hyperaccumulator (Van Nevel et al., 2011). The content of Zn, especially in the *Betula* and *Picea* ashes, leaves concerns about their hyperaccumulation abilities in both sites, even though these localities are not contaminated. Thus, another pertinent aspect to consider during the selection of wood ashes for arable soil.

The composition of wood ashes varies because each tree species has its specific origin and formation conditions, which can cause enrichment or depletion of different elements (Pazalja et al., 2021; Vassilev et al., 2013, 2014). The element contents in wood ashes also depend on biomass resources, including types of biomass, plant species or parts, growing processes and conditions, plants’ age, fertilizer/pesticide doses, collection technique, storage, and processing. The effect of species over the accumulation of Zn content (>500 ppm) per this study is visible in *Betula*, *Picea*, and *Pinus*. Meanwhile, the Zn contents besides *Betula* and *Picea* were within the mean range in the ashes of world reference plants (Cohen & Dunn, 2004). Zinc contents in all plants were within the limit values given by EU directives and regulations (Silva et al., 2019). Biomass combustion: fuel preparation, combustion technology, conditions, collection, and cleaning equipment can also contribute to a high content of trace elements above the permissible limits. However, it is necessary to consider the allowable limit of risk elements in soils before applying wood ashes to avoid further leaching. Leaching tests using common mineral and water fertilizers showed that ammonium sulfate and potassium nitrate mobilize Cu, Zn, and Pb in wood ashes. According to studies by Pędziwiatr et al. (2021), 30% of total Zn content in wood ashes from home can potentially leach into groundwater. It is of great concern to closely monitor the content of essential metal nutrients in wood ashes, for example, Cu and Zn, to remain within allowable limits in soils.

Mineral composition of soils and plant-mineral uptake can result in high trace element contents and subsequent accumulation in wood ashes (Vassilev et al., 2014). The presence of elements such as Sb in household wood ashes may also result from the co-combustion of plastics with wood, which contaminate ashes. Knowledge about the origin, abundance, and mode of element occurrences (including mineral composition) is among the factors to consider during the combustion and utilization of wood ash.

The effect of tree species on the contents of Al, Si, Rb, Sr, Mo, Zr, and Se in the wood ashes differed with the
FIGURE 6  Relationship between the concentration of (a) Cu, (b) Sr, and (c) Pb in the soil and ashes of *Picea abies*, *Larix decidua*, *Pinus sylvestris*, and *Betula pendula* at Hlinsko.

TABLE 5  Content (mg kg\(^{-1}\)) of some trace elements in the studied sites and their regulatory limits

| Trace element | Study site | EU directives and regulations (ash)* | Soil permissible limit |
|---------------|------------|--------------------------------------|------------------------|
|               | Hlinsko    | Mšec                                 | Finland\(^b\) lower higher guideline limit guideline Czech Republic\(^c\) |
| As            | 12.9−20.05 | 5.04                                 | 50\(^f\) 100\(^e\)     | 20                      |
| Cr            | 300        |                                       | 200\(^f\) 300\(^e\)     | 90                      |
| Cu            | 58.31−193.09 | 47.61−146.51                        | 700                    |                          |
| Pb            | 2.85−56    | 2.85−133.23                          | 150                    | 70                      |
| Zn            | 32.4−2062  | 65.93−1044.68                        | 4500                   | 60                      |

\(^a\) Silva et al. (2019)

\(^b\) MEF (2007)

\(^c\) Decree No. 13/1994 Sb. of Ministry of Environment in the Czech Republic.

\(^d\) Health risk.

\(^e\) Ecological risk.
locality. The content of Al in all the ashes of this study may remain non-toxic even to sensitive plants in the soil owing to the alkaline nature (increased pH) of ash (Bojorquez et al., 2017). Meanwhile, monovalent ion impurities such as Rb\(^+\) also were reported in natural apatite (Hughes et al., 1991; Simonetti et al., 2008). Rb can substitute for K in higher plants due to a similar monovalent charge. Thus, plants can take up Rb to replace K (Goldschmidt, 1954). However, this partly accounted for the high Rb contents in the ashes from all species. Strontium content in continental plants is 26 mg kg\(^{-1}\) (Pais, 1984), and their accumulation in biomass ashes was reported (Oroian et al., 2015). Species such as Fagus sylvatica, Picea abies, and Pinus spp contain elements including Sr and Rb (Simniškyté-Strimaityienė et al., 2017). The relatively high content of Se in the species (e.g., Betula, Fagus, Larix, Quercus, and Tilia) in Mšec relates to its content in the Marl parent rock, which may contain <0.1–7.4 mg kg\(^{-1}\) and the uptake potential ability (Connor & Schaklette, 1975).

Although the element contents of wood ashes can improve the nutrient needs of agricultural soils, the applications must follow agronomic rates (Symanowicz et al., 2018) and regulatory limits (Table 5). We can conclude that the studied ashes are suitable as fertilizers in agricultural soils. However, a thorough elemental analysis must be conducted as the content of elements can be influenced by anthropogenic activities.

## 5 | CONCLUSIONS

Comparative chemical analysis of homemade wood ashes from the same tree species from different localities revealed wide variability in the content of elements. The content of elements in wood ashes is a function of the type of soil, the parent rock, and the ability of the species to accumulate elements. Different localities have a significant effect on the fertilizer values of wood ashes.

The obtained ashes from Betula, Carpinus, Fagus, Larix, Picea, Pinus, Quercus, and Tilia were characterized by a high content of macro (P, K, Ca, and S) and trace (Mn, Fe, Zn, Cu, Al, Si, Rb, Sr, Mo, Zr, and Se) elements. The ashes of Betula, Carpinus, Fagus, Picea, Pinus, Quercus, and Tilia are suitable to be used as P, K, Ca, S, Mn, Fe, Cu, Zn, Mo, and Se fertilizers for agricultural soils according to their allowable limits. Wood ashes from the tree species have high pH, suitable to alleviate high soil acidity. The content of risk elements was below the regulatory limits for soils, except for Pb in the ash of Larix from Mšec and Zn in Betula, Pinus, and Quercus in both localities.

Differences in plant species, local parent rock, and anthropogenic interferences in the location of trees affect the content of elements in wood ashes. Many other environmental conditions, including the moisture content of wood, conditions during combustion, and soil chemical properties, at different geographical locations, affect the composition of wood ashes. A detailed chemical analysis of ashes is recommended, with strict adherence to permissible limits in soils.

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## CONFLICT OF INTEREST

There is no conflict of interest.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in Dryad at https://doi.org/10.5061/dryad.69p8c9z55.

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