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**EFFECT OF SPECIES ON THE ELEMENTAL COMPOSITION OF WOOD ASHES
AND THEIR FERTILIZER VALUES ON AGRICULTURAL SOILS**

DIPLOMA THESIS

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DECLARATION

STUDENT'S DECLARATION

I, OLALEKAN MOSES AYODEJI, hereby declare that except for the reference to other people's work which has been duly cited and acknowledged, this Action Research is the result of my effort and that it has neither in whole nor in part been presented elsewhere.

SIGNATURE.....

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(OLALEKAN MOSES AYODEJI)

SUPERVISOR'S DECLARATION

I hereby certify that the preparation and presentation of this thesis were supervised following the guidelines binding the supervision of the Diploma Thesis laid down by the Czech University of Life Sciences.

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ABSTRAKT

Popel z dřevin byl po dlouhou dobu používán jako hnojivo na zemědělské půdě. Doposud není znám vliv druhů dřevin na prvkové složení popela a na to, zda je popel produkovaný v domácích podmínkách vhodný pro využití na zemědělské půdě jako hnojivo. Cílem studie bylo analyzovat prvkové složení popela *Betula pendula*, *Carpinus betulus*, *Fagus sylvatica*, *Larix decidua*, *Picea abies*, *Pinus sylvestris*, *Quercus robur* a *Tilia cordata* z lokalit Hlinsko a Mšec. Popele byly produkovány v běžném otopném zařízení v domácích podmínkách a uvedené dřeviny byly zvoleny proto, že se běžně používají jako palivové dřevo k vytápění domů. Prvkové složení popelů bylo stanoveno pomocí rentgenové fluorescenční spektrometrie. Obsah makro (P, K, Ca a S), mikro (Mn, Fe, Zn a Cu), stopových (Al, Si, Rb, Sr, Mo, Zr, Th a Se) a rizikových (As, Ni a Pb) prvků byl stanoven ve všech popelech, s významným vlivem druhu na obou lokalitách. Obsah P, K, Ca a S se pohyboval od (g kg^{-1}) 3,5 až 21,1, 30 až 135, 100 až 300 a 3,7 až 12 ve všech popelech. Obsahy Mn, Fe, Zn a Cu v popelu všech druhů se pohybovaly v rozmezí (v g kg^{-1}) 1 až 32, 0,2 až 4,5, 89 až 2050 mg kg^{-1} a 50 až 198 mg kg^{-1} . Obsah Cu, Sr a Pb v popelu *Carpinus betulus* významně dobře koreloval s obsahem těchto prvků v půdě na lokalitě Hlinsko. Významně vyšší obsah prvků v popelech z Hlinska ve srovnání s Mšecem vyplýval z obsahu prvků v půdě a částečně z absorpční kapacity druhu vyplývající z kořenového systému. Popel *Larix decidua* z lokality Mšec je nevhodným hnojivem pro zemědělské půdy pro nadlimitní obsah olova $> 100 \text{ mg kg}^{-1}$. Obsah dalších rizikových prvků (Ni a As) byl v popelích pod legislativním limitem. Popele dřevin, až na výjimku *Larix decidua* z lokality Mšec, jsou z hlediska obsahu prvků vhodné pro použití jako hnojivo na zemědělské půdě.

ABSTRACT

Wood ashes have been used as fertilizer on agricultural soil over a long period. So far, the effect of species from different localities on the elemental composition of wood ashes and whether home-made ashes are suitable for agricultural soil as fertilizers is not well-known. The study aimed to analyze the elemental composition of home-made ashes of *Betula pendula*, *Carpinus betulus*, *Fagus sylvatica*, *Larix decidua*, *Picea abies*, *Pinus sylvestris*, *Quercus robur*, and *Tilia cordata* from Hlinsko and Mšec localities, Czech Republic, commonly used for heating homes. The elemental composition of the studied wood ashes was determined using portable X-ray fluorescence spectrometry. The wood ashes were characterized by the accumulation of macro (P, K, Ca, and S), micro (Mn, Fe, Zn, and Cu), and other (Al, Si, Rb, Sr, Mo, Zr, Th, and Se) elements, with a significant effect among the species in both sites. The contents of P, K, Ca, and S ranged from (g kg^{-1}) 3.5 to 21.1, 30 to 135, 100 to 300, and 3.7 to 12, respectively, in all the ashes. The contents of Mn, Fe, Zn, and Cu in the ashes of all the species ranged from (in g kg^{-1}) 1 to 32, 0.2 to 4.5, 89 to 2050 mg kg^{-1} , and 50 to 198 mg kg^{-1} . The content of Cu, Sr, and Pb in the ash of *Carpinus betulus* significantly well correlated with content in the soil from Hlinsko, due to the influence of the soil elemental composition by an abandoned graveyard from past human settlement. The significantly higher content of the elements in the ashes from Hlinsko compared to Mšec resulted from the soil's elemental content and partly from the root absorptive capacity of the species. The ash of *Larix decidua* in Mšec is unsuitable fertilizer for agricultural soils- characterized by $> 100 \text{ mg kg}^{-1}$ Pb. The contents of other risk elements (Ni and As) were below the regulatory limit for Agricultural soils. Hence the studied home-made ashes are suitable to be used as fertilizers. The total content of P, K, Ca, Fe, Mn, Cu, Zn, and Pb in the ashes obtained by pXRF and *Aqua regia* followed by inductively coupled plasma optical emission spectrometry well correlated. Hence, the pXRF has adequate precision for tracing the elemental signatures. The accumulation of elements in wood ashes of the same species from different localities relates to the genetic makeup of the species, geology, as well as anthropogenic activities of the given location.

Keywords: Agricultural soil, *Betula pendula*, Fertilizer, Macro element, Micro element, Risk element

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CHAPTER ONE

1. INTRODUCTION

Wood ashes have been used since the Paleolithic period by humans, whether deliberately or unintentionally. Wood ashes were previously utilized as a source for potash production, liming agent, and source of nutrients for plants (Huang et al., 1992; Glaser 2007; Semelová et al., 2008; Šmejda et al., 2017). In most archeological sites, locations with ashy deposits were identified with high elemental content and biomass production, even after thousands of years of abandonment (Hejcman et al., 2011; Hejcman et al., 2013; Asare et al., 2020). Thus, the elemental composition of wood ashes in soils is preservable over a long period.

Although wood ashes commonly are used to fertilize contemporary agricultural soils mostly in subsistence farming as they are composed of major and minor elements that trees need for growth, the fertilizer values are not well-known. Notwithstanding, the use of wood ashes as fertilizer can pose problems due to the accumulation of risk elements that can affect soils and subsequent trophic levels (Obernberger et al., 1997; Lane et al., 2020). Risk elements in wood ashes can exceed the regulatory limit in agricultural soils, e.g., (mg kg^{-1}) As (20), Pb (100), Cd (3), Ni (50), Co (50), and Cr (100) (Chiroma et al., 2014). The accumulation of risk elements in wood ashes mostly relates to the kind of activities in the location of the tree species. For example, emissions from metal smelting, fossil fuel combustion, and the spreading of phosphate fertilizers are considered the cause for high levels of Cd in wood ashes (Narodoslawsky and Obernberger, 1996). Additionally, the content of Pb can be high in wood ashes from the Czech Republic due to the sub-recent and recent disposition through leaded gasoline from the 1930s to the 1950s (Novák et al. 2008). However, contaminated wood-combustion ashes with high levels of regulated environmental contaminants generally require only a basic level of treatment before being utilized for Agricultural soils. To identify the influence of anthropogenic elements in soils and their accumulation in trees, it is pertinent to establish a relationship between the content of elements in soils and ashes.

Other pertinent factors that influence the accumulation and depletion of elements in wood ashes are the condition of the combustion of the wood as well as the treatment of the wood before burning (Liodakis et al., 2005). For example, at temperatures $> 500\text{ }^{\circ}\text{C}$, carbonates, and bicarbonates increase, while oxides become more prevalent in temperatures above $1000\text{ }^{\circ}\text{C}$ (Naylor and Schmidt, 1986; Misra et al., 1993). The elemental compositions of wood ashes are

also related to the type of tree species and their ability to accumulate elements, as species may have different absorptive capabilities. Determination of elemental composition in the ash of leaves and stems was carried out to correlate nutrient uptake by plants with the nutrient content of the soil to monitor plant growth and the effect of fertilizer supplementation (Misra et al., 1993). Most of these analyses concluded that the minerals present in the ashes are oxides of different elements (Liodakis et al., 2005). Although several authors reported the chemical composition of wood ashes in the past, the focus was on the use of wood ashes to alleviate acidic soils (Campbell, 1990; Adekayode and Olojugba, 2010; Okmanis et al., 2016). Reportedly, ashes exhibit high pH ranging from 9-13.5 (Campbell, 1990; Okmanis et al., 2016). So far, the question which is still unanswered is whether different home-made ashes are suitable fertilizer for agricultural soils. The question stems from the assertion that wood ashes generated from homes often are obtained under an unspecified temperature range. Additionally, the effect of species on the elemental composition of wood ashes from different localities is not well-known.

Furthermore, many authors have used different analytical approaches to determine the elemental and molecular composition of mineral matter in wood ashes, e.g., thermal gravimetric analysis, differential thermal analysis, inductively coupled plasma emission spectroscopy, and X-ray diffraction (Rožić et al., 2005). However, the use of X-ray fluorescence spectrometry (XRF) has sparingly been used (Mahendra et al., 1993; Chand et al., 2009). We used the portable XRF (pXRF) spectrometry as a reliable and cost-effective approach to determine the total element content of wood ashes. Wood admittedly is still used for generating heat in homes, and the resultant ashes are used as fertilizers in agricultural soils by most farmers.

As the fertilizer values of home-made ashes are under-studied, we determined the elemental composition of 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. Therefore, the temperature adopted was unspecified, similar to the combustion of wood at homes. In this case, obtained ashes undergo total combustion without charcoal residues.

1.1. Main objectives:

- a) To determine the effect of species on the elemental composition of ashes from different localities in the Czech Republic.

- b) The extent of enrichment of macro, micro, other elements of wood ashes from two different localities.
- c) To determine whether home-made wood ashes are suitable to be used as fertilizers on agricultural soil.
- d) To determine the relationship between the content of selected elements in the soil and wood ashes.
- e) To find out whether pXRF has adequate precision for the determination of the elemental composition of wood ashes.

1.2. Research questions

- a) To what extent can the same tree species from different localities influence the elemental composition of wood ashes?
- b) What is the fertilizer value of obtained wood ashes of commonly used European tree species from home combustion?
- c) Can home-made wood ashes be used as fertilizer in agricultural soils?
- d) Among the studied species, which of the ashes are most suitable to be used as fertilizer for agricultural soils?
- e) Is there a relationship between the content of elements in the soil and the studied wood ashes?
- f) Can the use of the pXRF provide adequate precision for the geochemical tracing of the elemental composition of wood ashes?

CHAPTER TWO

2. LITERATURE REVIEW

This chapter of the thesis is composed of older and recent studies on biomass ashes, particularly wood ashes from different parts of the world. The chapter thoroughly discusses; the historical origin and use of biomass ashes, the chemical composition of biomass ashes, analytical approaches used in the elemental analysis of biomass ashes, and factors affecting the elemental composition of wood ashes.

2.1. Historical origin and use of biomass ashes

Biomass ashes were produced and used by humans since the paleolithic period. The timing of human claims for regular fire use by early people in Africa predates 1.6 million years ago (Wil et al., 2011). Archaeologists suggested that the colonization of areas outside Africa, especially of regions such as Europe where temperatures are at a time below freezing, was indeed tied to the use of fire (Albert et al., 2010; Wil et al., 2011). Evidence from Europe indicates that early hominins moved into the northern latitudes without the habitual use of fire. From ca 300,000 to 400,000 years ago onward, fire became a significant part of the hominin technological repertoire (Wil et al., 2011). In the second half of the Middle Pleistocene, spectacular cases of pyro-technological knowledge in the production of hafting materials emerged. The increase in the number of sites with high evidence of fire throughout the Late Pleistocene shows that European Neandertals had fire management, unlike that documented for Upper Paleolithic groups (Paola et al., 2011).

During prehistory, hominins all over the world subsisted as hunters and gatherers, with a generally highly mobile lifestyle (Wil et al., 2011). The overwhelming majority of their traces consist of woods, the debris of stone tool production, and often food remains. With few exceptions, preserved fireplaces are simple clusters of burnt materials occurring as flat lenses or in small hollows. The most common proxies for the use of fire consisted of various find categories that display locations been submitted to heating, e.g., the reddened sediments on which fire was built, tree branches, fragments of charred bones, and pieces of charcoal (Wil et al., 2011). Volcanic eruptions can also be a factor in driving the natural fire regime in volcanically active areas as well as lightning strikes (Christian et al., 2003). The remains of example grass and forest fires can become associated with archeological materials. Hence,

charcoal, charred bone material, and heated flints do not necessarily indicate anthropogenic fires (James, 1989). At open-air sites, direct evidence for human fires, such as charcoal, can be easily removed by natural processes, including erosion by water or wind (Sergant et al., 2006).

2.1.1. Historical evidence of the use of biomass ashes in Europe

The earliest traces of hominin presence in Europe come from its southern parts and date over one million years ago (Carbonell et al., 2008). Recent data from the Happisburgh site in England suggests that hominins may have adapted to the challenging environments of the boreal zone in the Early Pleistocene, ca 800,000 years ago (Parfitt et al., 2010). The fire would have been an important tool in such environments. However, evidence for use of fire in the Early and Early Middle Pleistocene of Europe was non-existent, until ~300 – 400 ka (Wil et al., 2011).

The early European sites show that the earliest possible evidence of the use of fire to burn biomass comes from two sites dated to ~400 ka, Beeches Pit in England, and Schöningen in Germany. At Schöningen, Germany, the evidence consists of some heated flints, although mostly natural pieces (Thieme et al., 2008) and charred wood, including wooden tools, with the studies of possible remains of former hearths still in progress (Maier et al., 2008). At Beeches Pit, dated to Marine Isotope Stage, the evidence consists of heated lithics and heated sediments (Preece et al., 2006), interpreted as the remains of hearths.

2.2. Uses of biomass ashes

Biomass-based energy systems for heat will have an important place in the overall energy setup to meet increasing consumer demands. However, growing interest in biomass energy (ashes) is driven by many factors, which includes, (a) restoration of unproductive and degraded lands, increasing biodiversity, and soil fertility (Best and Christensen, 2003) and (b) meet energy needs at all times, without expensive conversion devices. Woody biomass in the form of wood chips, wood residue, planer shavings, sawdust form the basis for most combustion processes that use the energy value of this waste material. All these combustion systems produce a significant amount of ash, which varies from 5-15% wt of biomass processed reported by Adrian et al. (2012). However, ash utilization is limited by the presence of heavy metals and other inorganic compounds, which are formed because of the thermochemical reactions that the biomass undergoes when combusted. For example, the variability in heavy metal content in the ash of feedstock according to Adrian et al. (2012) arises from the differences in

properties, and hence no singular inorganic composition profile for ash is true. Subsequently, no application will be suitable for all kinds of ash. Inefficiencies in boilers and furnaces also result in high percentages of unburned organic matter in ash. The carbon content may be recycled to the boiler or furnace to improve energy output and increase the process efficiency as clarified by Khan et al. (2009).

Ashes applied as agricultural fertilizers, have a vitalizing effect on their application to agricultural or forest soils (Olanders et al., 1994). Olanders et al. (1994) reported that the ash from biomass fuel contains only trace amounts of heavy metals, which makes them easy to dispose of and as good fertilizers. Gomez-Barea et al. (2009) optimized the operating conditions in achieving better ash quality and assessed the ash quality to explore its potential utilization as a fuel due to the presence of high unburned carbon content. The presence of alkali metals, alkaline earth metals, chlorine, sulfur, and silicon influences the reactivity and leaching to the inorganic phases (Wang et al., 2008). Ash may be utilized as a neutralizing and liming agent. Research also indicates that bottom ash has significantly lower contents of heavy metals compared to fly ash, as such, a mixture of fly ash and bottom ash may be suitable for application as a soil amendment to forest soils (Quaak et al., 2009). This should assist in maintaining nutrient cycling instead of landfilling such important nutrients. Unburned carbon present in ash allows for the exploration of using ash as a fuel. The unburned organic matter has been investigated as a fuel source in some studies that suggest recirculation of ash, increasing residence times, and increasing material turbulence inside the boiler (Ronald et al., 2012). The presence of carbon in ash limits its applications as it decreases its binding properties in construction material. The high carbon content also presents challenges for palletization and briquetting as it decreases the binding properties (Adrian et al., 2012). The need for other ash processing methods should be investigated. However, Ronald et al. (2012) in their study proposed sieve fractionation as a suitable method for the separation of unburnt carbon present in bottom ash obtained from a fixed-bed combustion system, followed by the application of the gasification technology to particle sizes of energy imports. The use of gasification technology in the reduction of ash-carbon content and the ability to recover useful energy in the combustion residue presents promising prospects. Sieve fractionation may also assist in identify fractions in bottom ash with high organic/carbon content and those with high mineral content as well their impact on the overall volume of ash stored or disposed of (Adrian et al., 2012). If ash is to be burnt, the likely conditions under which it softens, and melts must be known since this may cause severe negative impacts on the combustion equipment leading to corrosion. It is

expected that the production of bottom ash will increase greatly; therefore, continued research is needed to find suitable applications and processing technologies for ash.

Another important extended overview of the potential utilization of biomass ash and the related technological advantages and challenges was conducted by Vassilev et al. (2013). Biomass ash has many potential areas of application: in forest ecosystems to return nutrients to harvested fields or to counteract soil acidification, for agricultural and horticultural purposes as fertilizer (Aronsson et al., 2004) and geotechnical construction and industrial processes. Typical applications in this last field are the construction of roads, surface layer in landfills, and admixture of ash for concrete, brick, or cement production.

The possibility to use fly and bottom ash as raw materials for geopolymers has been studied by several authors (Kopljenovic et al., 2010), however, the typical $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the ash for producing good quality geopolymers has been determined to be between 3.3 and 4.5 (Tyni et al., 2012). The potential use of biomass ash as filler in a bituminous mixture has been recently investigated by (Melotti et al., 2013) biomass ash, if subjected to a sieving process, may be considered as a valid alternative to natural filler. Mortars produced by replacing natural sand with bottom bed ash comprised of sand, soil, small stones, and unburnt biomass fraction from forest biomass combustion showed similar properties of the standard ones as it was reported by (Modolo et al., 2013). High calcium wood ash has been used as partial cement replacement up to 15 wt-% (Cheah et al., 2012), thus obtaining mortars with higher compressive strengths as compared to the control mortar after 90-day curing. Concrete formulations produced by replacing up to 10% of cement with biomass ash from bark combustion showed mechanical properties comparable with the reference ones after 28 days and a very good leaching resistance in both marine and freshwater medium as stated from (Barbosa et al., 2013) research work. The high content of chlorides in this ash is still an open issue, and the durability of these mortars must be further investigated (Modolo et al., 2013).

Besides, biomass ashes have complicated alkali-silica reaction (ASR) performances because of their different chemical compositions and particle size (Wang, 2015). However, Wang has recently demonstrated that biomass containing fly ash increases strength and reduces ASR expansion in mortar even with their high available alkaline (Wang, 2015).

With the increasing attention towards CO_2 emission reduction and cost optimization in cement production, the replacement of the clinker quota with supplementary cementitious materials (SCMs) in cement and concrete production is becoming increasingly widespread (Lothenbach et al., 2011) explained. Also, the utilization of cement with increasing content of SCMs would allow the development of mortars and concrete with a reduced environmental impact and lower

embodied energy. Moreover, most of the SCMs used in concrete has a beneficial effect on the durability properties thanks to the densely packed hydrated silicate phases that are forming and give a high resistance to the concrete against chemical such as chloride and sulfate attack as well as very low porosity of the cement paste (Snelling et al., 2012).

It is very important to be aware that the recycling of biomass ash as construction materials meets the recommendations of the European Directive on waste 2008/98/CE and has significant environmental benefits related to CO₂ emission reduction and the reduction of waste carried to landfills. (Melotti et al., 2013).

2.3. Chemical composition of biomass ashes

Renewable energy sources play a key role in current global strategies to reduce greenhouse gas emissions and, partly, in efforts to replace fossil fuels and for agricultural purposes. The chemical composition of ash from biomass is an important feature allowing for evaluation of the behavior of elements during combustion and the use of ashes. Biomass is one of the most important sources of renewable energy (Stolarski et al., 2018). According to (Viktarovich 2016), the construction of intelligent energy systems based on biomass as a source of primary energy enables strengthening economic, environmental, and social benefits. However, Mirowski (2016) stated that the use of biomass potential for heating purposes in municipal and housing sectors should include not only compacted biomass fuel, but also biomass fuels with low heating value and bulk density as well as waste biomass generated during the production of high calorific value food.

Ash is one of the by-products generated during biomass burning. Combustion waste arising from the combustion of biomass in households is collected in a nonselective manner and exported to a landfill, thus constituting an additional and unnecessary burden for the environment as stated by Hawrot-Paw et al. (2017). Thus, the contents of ash-forming elements in biomass fuels vary greatly. Also, Demirbas (2005) stated that the major inherent ash forming elements in biomass ash include Ca, Si, Al, Ti, Fe, Mg, Na, K, S, and P. The composition of ash affects its behavior under high temperatures of combustion and gasification reactors (Quaak et al., 1999). These problems may include clogged ash-removal caused by slagging ash, sintering, deposition, erosion, corrosion, and pollutant emissions that are mainly created by the presence of alkali metals, alkaline earth metals, Si, Cl, and S in the ashes (Vamvuka, 2009). If the properties of ash are well recognized, it is possible to apply it to agriculture for fertilizing purposes (Antonkiewicz, 2009) clarified. It is important to note that biomass ash

consists of various proportions of Si, Al, Fe, Ca, Mg, Na, K, Ti, and Mn, with heavy metals as impurities (Kajda-SzczeŃniak, 2014; see also Table 1). And the return of ashes from the combustion of biomass to the soil is the most ecological and sustainable disposal method. In this way, a significant part of the macro and micronutrients taken by the plants returns to the soil, closing the circulation of minerals.

Table 1. The content (mg kg⁻¹) of elements in studied ashes at different temperatures according to Eitigni and Campbell (1991).

Element	Temperature (°C)					
	538	649	760	871	982	1 093
Aluminum	10415	12 825	13 115	10 115	13 415	11 015
Antimony	264	142	65	91	94	208
Arsenic	< 20	< 20	< 20	54	74	59
Barium	1 301	1 490	1 640	1 463	1 601	1 530
Beryllium	< 5	< 5	< 5	< 5	< 5	< 5
Bismuth	< 30	< 30	< 30	< 30	< 30	< 30
Cadmium	< 2	< 2	< 2	< 2	< 2	< 2
Calcium	187 480	187 480	241 180	216 080	238 980	264 580
Cerium	< 40	< 40	< 40	< 40	< 40	< 40
Chromium	52	37	49	20	39	622
Cobalt	< 3	< 3	< 3	< 3	< 3	< 3
Copper	345	620	588	380	437	422
Iron	8 796	11 951	9981	8 219	22 411	16 781
Lanthanum	< 10	< 10	< 10	< 10	< 10	< 10
Lead	51	75	200	39	43	685
Lithium	35	55	70	10	30	10
Magnesium	59 730	68060	76 970	69170	80 470	89 100
Manganese	10 549	11 789	13 489	11 859	16 609	21 680
Molybdenum	18	21	26	39	56	192
Nickel	59	64	151	63	497	8 979
Phosphorus	16 950	19 060	21 720	19 370	21 030	25 460
Potassium	110 500	86 590	47 720	79 860	51 970	4 026
Selenium	< 50	< 50	< 50	< 50	< 50	< 50
Silicon	33 867	39 777	42 647	31 997	46 477	35 267
Sodium	2 961	4 947	4 365	1 643	1 479	< 100
Titanium	780	1060	1 012	777	957	796
Vanadium	13	18	23	17	26	234
Ytterbium	3	3	3	2	5	3
Zinc	2 678	2 139	1 001	177	26	55
Zirconium	14	14	16	15	19	23

Some studies reported the content of valuable nutrients in the ash from the combustion of biomass, (Vassilev et al., 2014) and in support, Meller et al., 2012 stated that their use in higher doses may have a deacidifying effect and improve the physicochemical properties of light soils.

At the same time, ashes from biomass are characterized by a significant diversity of their properties, depending on the type of biomass burned and its origin. They can also contain harmful substances, such as heavy metals. It should be noted that, apart from the use of ashes as a fertilizer, the elements in ash may also cause problems during combustion in the furnace (Vassilev et al., 2014). Although the ash content in biomass is much smaller than in coals, their different origin and chemical nature affect the operation of boiler equipment causing, among others, increased deposition of slag and ash in the furnace or increased rate of wear of metal boiler elements due to corrosion (Eriksson et al., 2018). These problems can lead to increased operating costs and reduced efficiency and availability of the device. In addition to this, the assessment of the content of individual mineral components in ashes generated from the combustion of biomass becomes problematic. These analyses are necessary before the potential use of ash in agriculture and for determining the impact of ash during combustion, estimation of its impact on the boiler, or considering its use in other forms of recycling.

Another study to note according to Michalik et al. (2012), indicated that the chemical and mineral composition of biomass ashes differ significantly from coal ash. In the case of co-combustion, the composition and properties of fly ash and slag differ from the composition of ash and slag obtained during the combustion of coal. Modified composition of fly ash produced in co-combustion influences possibilities of its application. The composition of coal ash varies within a broad range, but silicates or aluminosilicates are dominant components. The variation of the chemical composition of biomass ash is very high (Michalik et al., 2012). The chemical composition of biomass ash results in its very variable mineral composition. Several samples are rich in K and Mg phosphates, other rich in carbonates e.g., calcite, fairchildite, kutnahorite, sulfates (arcanite) and lime beside other components as quartz or cristobalite, and Fe oxides (Michalik et al., 2012), however, the addition of these components to coal ash component results in high variability of composition and properties of ash obtained in co-combustion. And in support of this, (Kofman, 1987) noted that the characteristics and chemical composition of biomass ash may be different depending on the fuel incineration technique, additives, and storage conditions.

Biomass ash consists of inorganic minerals and organic compounds remaining in the ash because of incomplete combustion (Malle, 2005). And Nitrogen, which volatilizes during combustion, may be found only in very small amounts, but all the macronutrients occur in the ash (Malle, 2005). The major proportion of the minerals in the ash is a mixture of oxides, hydroxides, silicates, and carbonates of the base-forming cations. Some of the oxides and hydroxides in the ash dissolve easily in water and produce a strong alkaline reaction (liming

effect) as reported by Ljung and Nordin, (1997). In the work of (Haykiri-acma, 2013), thermochemical processes such as gasification, liquefaction, pyrolysis, and direct combustion are commonly employed for converting biomass wastes into higher heating value substances such as fuels. And after thermal-chemical processing, there still exist relatively large quantities of inorganic elements including K, Na, Ca, and P in the ash (Wang et al., 2008).

Biomass ash is easy to melt and volatilize because of the presence of these inorganic elements (Arvelakis et al., 2004). Hence, the types of biomass ash with relatively high volatility and complex composition often easily result in slagging, fouling, and corrosion; these problems are closely related to the high content of alkali metal and alkali earth metals (Xiao et al., 2011). Moreover, the primary properties of biomass ashes can significantly influence their potential utilization in various fields as well as affect the products of biomass gasification, combustion, and pyrolysis. From an economic and environmental point of view, it is, therefore, meaningful to investigate the physicochemical and slagging characteristics of biomass ash. There have been numerous studies characterizing various biomass ashes, such as cashew nut ash (Ogundiran et al., 2011), woody biomass ash (Skrifvars et al., 2004), seaweed biomass ash (Wang et al., 2008), bagasse fly ash (Batra et al., 2008), wheat hull ash (Terzioğlu et al., 2013), peanut hull ash (Liao et al., 2011), corn straw ash, sunflower husk ash (Quaranta et al., 2011), and bamboo ash (Fang and Jia, 2012).

These investigations revealed that the physicochemical properties of various biomass ashes are quite different. Additionally, there have been studies on various potential utilization of biomass ashes, including as a soil amendment (Pan and Eberhardt, 2011), a raw material for ceramic production (Abraham et al., 2013), a potential source of SiO₂ (Terzioğlu et al., 2013), as well as a bio-based material for biopolymers (Burgos et al., 2016). Therefore, it is crucial to note that there are impacts of biomass species and temperature on the physical and chemical properties of biomass ash. High temperature causes ash yield and the K, Na, and Cl contents to decrease but caused the Ca and Mg contents to increase (Yao et al., 2017). Yao et al. (2017) concluded that the physicochemical properties of biomass ashes from three types of biomass (rice straw, peanut shell, and corn cob) were comprehensively characterized in terms of their potentials to be transformed into eco-friendly and some high value-added products. Other indicators like free moisture content, electrical conductivity, organic matter content, and overall nutritional and toxic elements and their mobility in aqueous solutions also confirm that the wood ash is suitable for soil improvers production (Serafimova et al., 2011).

The ash content of wood chips normally depends on the bark content of the mixture since the minerals are usually more concentrated in that region (Olanders et al., 1994). Ash is the

inorganic incombustible part of fuel left after complete combustion contains the bulk of the mineral fraction of the original biomass (Khan, et al., 2009). Ash is an integral part of the plant structure and consists of a wide range of elements (Quaak et al., 1999). In woods, ash represents < 2%, while in agricultural crop materials it can be 5–10% and up to 30–40% in rice husks and milfoil. According to Adrian et al., (2012), biomass-based products produce solid residue ash, a result of thermochemical degradation. These thermochemical processes include combustion, pyrolysis, and incineration of woody biomass. Bottom ash and fly ash are usually the two types of ash produced and may vary in properties due to the different types of biomass available, operating conditions, and type of system used (Adrian et al., 2012). High ash contents significantly reduce the energy output derived from a specific biomass source.

2.4. Factors affecting the elemental composition of wood ash

It has been demonstrated that the ash from burnt wood could be used to improve soil fertility (Okoli et al., 2014). This is probably not a new concept as Morrison (1959) mentioned that wood ash has a Ca content of approximately two-thirds that of limestone. However, according to Campbell (1990), for the most part, 90% of ash is either land-filled or land-applied. The disposal of wood ash is a growing problem as environmental regulations become more stringent and landfill sites become less available and more expensive. For example, in the United States, from the 1700s through the early 1900s, wood was combusted to produce ash for chemical extraction (Campbell, 1990). The study of wood ashes from subtropical tree species in South Africa, and many other countries, revealed that wood ash primarily is a Ca source, though ash from a homestead fire may differ in composition if fire-making material other than wood is used (Ndlovu et al., 2018). However, there is wide variation in P, K, Ca, and Mg levels in wood ash compared to other sources such as feed lime (CaCO_3) and limestone. As it is typical of most waste and by-products the concentration of other elements, especially trace elements in wood ash, varies considerably, even within tree species (Van Ryssen et al., 2018). Meanwhile, it must be accepted that wood ash is primarily a waste product that could originate from a variety of sources such as discarded wood, wood fires in industrial boilers, or from fireplaces in rural homesteads. Wood ash is the inorganic residue that remains after plant materials have been subjected to high-temperature treatment, which burns away all organic parts, leaving behind only the inorganic component as mineral salts. However, the definition of wood in terms of its ash content is not specific, because, in many instances, firewood could consist of the wood, dry leaves, and bark of trees.

The chemical composition of ashes obtained from biomass combustion is usually very diverse, due to many different factors. Generally, these factors relate to the, (a) raw material the type of biomass, plant species or plant parts, growth processes and conditions, plant age, fertilization and applied dose of plant protection products, harvest time and techniques, transport and storage conditions, processing methods, as well as the process of combustion, (b) fuel preparation, combustion technology, and combustion conditions plus other technical conditions (Grzegorz et al., 2018). These factors can enrich or reduce the content of elements in biomass ash. Hence, due to the high diversity of ash quality, depending on the type of biomass being burned, a detailed analysis of the chemical composition of ash is required before indicating the direction of its management, especially the use as fertilizer as opined by (Joanna et al., 2018). Also (Van Ryssen et al., 2018) stated that tree species, tree components such as bark or wood ash, and the temperature when burning wood have a major influence on mineral composition in wood ash. Therefore, it is concluded that because of the wide variation in the composition of wood ash, it is advisable to perform chemical analyses on ashes.

The chemical composition of wood ash varies among tree species, growing conditions such as soil type and climate, and combustion methods as depicted by (Campbell, 1990), and Changes also occur during storage and varying environmental conditions. Lambert (1981) reported that factors such as the season of the year, age of the tree, decayed or non-decayed trees, and types of bark in tree species (decorticating or fibrous stringy barks) are causes of variation in the mineral composition of wood, reflected in the ash. Österås (2004) reported that fertilization, pollution, and interactions between mineral elements can affect the mineral composition of wood and bark of the Norway spruce, while Zule and Dolenc (2012) pointed out that some elements are mobile in trees, and can move from one part of the tree to another where there is an inadequate supply, while other are immobile as this would eventually influence the distribution of elements in wood ash.

Van Ryssen et al. (2018) concluded in their study that many by-products that have the potential to be utilized in animal nutrition show variation in the mineral composition of wood ash, especially that of trace elements. Furthermore, the temperature at which the wood is combusted affects the mineral content. It can be accepted that a variety of fire-making materials would be used in homestead fires. However, it cannot be simply accepted that the ash from homestead fireplaces is equal to the ash from burnt wood, since other fire-making materials such as cattle dung and maize cobs are used in some areas as depicted by (Ndlovu et al., 2018). According to (Serafimova et al., 2010) analysis, as a result of oxidation processes during combustion, the generated wood ash retains the overall composition of the mineral nutrients contained in the

waste wood except for nitrogen compounds, which are mainly released into the gas phase. It is, therefore, advisable to perform chemical analyses on ashes because of the wide variation in the elemental composition.

2.5. Analytical approaches used in the elemental analysis of biomass ashes

The solvent fraction is one of the approaches used in the elemental analysis of biomass ashes. Tagami et al., (2019) stated that this approach helps in obtaining the lignin fractions with tailored properties for application for certain materials. This method involves four common industrial solvents, namely, ethyl acetate, ethanol, methanol, and acetone, in various combinations, which were found to be efficient for separating spruce and eucalyptus kraft lignins into fractions with low polydispersities. The ethanol fraction of spruce and the ethyl acetate fraction of eucalyptus afforded the highest yields. Additionally, Gel-permeation chromatography analysis can be used to evaluate the efficiency of the chosen solvent combination for lignin fractionation. The composition and structure of the lignin material were then characterized by elemental analysis, analytical pyrolysis (Py-GC/MS/FID), and ¹³C NMR spectroscopy (Tagami et al., 2019). And Proximate analysis data (ash, volatile components, organic matter, and fixed carbon) can be obtained through the direct measurement of weight changes in each experimental curve, and the high heating values in MJ kg⁻¹ (Gioia et al., 2019). Another approach to note is the application of evolutionary algorithms. It is a hybrid model comprising of adaptive neuro-fuzzy inference system (ANFIS) and particle swarm optimization (PSO) called the PSO-ANFIS model. The model is based on the proximate values of biomass materials to predict their corresponding elemental compositions (Obafemi et al., 2019) a hybrid model comprising of adaptive neuro-fuzzy inference system (ANFIS) and particle swarm optimization (PSO) called PSO-ANFIS model. According to Obafemi et al., (2019), the model is based on the proximate values of biomass materials to predict their corresponding elemental compositions. And the coverage of the data points considered for the development of this correlation between ultimate and proximate value analysis includes the C, O, H, VM, and FC contents and the Ash in weight percentages (dry basis).

However, The ANFIS model, which was proposed by Jang, Jang (1993), supports the Takagi-Sugeno system (Takagi, 1985), although there are other types of fuzzy systems such as singleton and linguistic (Neil, 2013), the Sugeno fuzzy model is the most applied fuzzy inference system due to its ability to fit into an adaptive framework. It provides a systematic approach to develop a fuzzy rule from input and output variables. The data elements are divided

into different categories through a data clustering process. ANFIS model, however, utilizes the strengths of fuzzy logic and artificial neural network in one framework. This enables it to solve complex and nonlinear problems such that the optimal distribution of membership function is obtained from input to output mapping (Yaghoobi et al., 2016). ANFIS is a five-layer network consisting of two adaptive layers and three non-adaptive layers. Parameters of the first and fourth layer are adaptive and can be updated according to the learning technique used, which in this case is the Particle Swarm Optimization (PSO). For the prediction of the elemental composition, ANFIS model maps the three inputs (VM, FC, and Ash) to the elemental compositions (C, H, and O) as the output. The model is trained such that overfitting or underfitting is avoided by ensuring that the training stops when no further improvement is observed and the maximum iteration is reached (Jabbar et al., 2015). This means that the accuracy of the model is becoming static notwithstanding a few stochastic fluctuations.

The use of a differential thermal analyzer with an on-line inductively coupled mass spectrometer (ICP-MS) allows continuous and near-synchronous analysis of mass loss and elemental release patterns during pyrolysis of biomass ashes (Thy et al., 2017). Applied to a mixed-conifer softwood, the results show that the released elements can be divided into those that are dominantly released during decomposition (250–475 °C) and those dominantly released at high temperature (900–1300 °C), thus reflecting their different roles in the organic matrix. Production and analysis of a 950 °C pyrolysis wood ash allow the bulk partition between flue gas (including entrained particles) and solid char to be evaluated, mass balance, and a semi-quantitative calibration to be suggested as this demonstrates that the present approach can provide reliable insight and semi-quantitative modeling tools useful for explaining the role and behavior of many elements during thermal treatment of biomass (Thy et al., 2017). The use of dry analytical methods, e.g., portable X-ray fluorescence spectrometer to obtain the total content of elements in ashes has been conducted by many authors (Xing et al., 2016; Katarzyna et al., 2018). However, the use of wet analytical methods, e.g., extraction by different acids (Mehlich extractant for plant-available elements and *Aqua regia* for total elements) have the potential to influence the recovery of many elements. The assertion stems from the fact that the reaction between the acids and base (biomass ashes) can result in a complete neutralization.

CHAPTER THREE

3. METHODOLOGY

3.1. Location and sample collection

Eight (8) solid biomass fuelwoods initially were selected for this study, as commonly used wood for domestic heating in the Czech Republic. Samples of branches (wood and bark) of *Betula*, *Carpinus*, *Fagus*, *Larix*, *Picea*, *Pinus*, *Quercus*, and *Tilia*, were collected from two different localities, Hlinsko and Mšec in the Czech Republic. The reference names adopted for these sample fuelwoods are in Table 2.

Table 2. The names of selected tree species

Local name	Scientific name	Reference name
Silver birch	<i>Betula pendula</i>	<i>Betula</i>
European hornbeam	<i>Carpinus betulus</i>	<i>Carpinus</i>
European beech	<i>Fagus sylvatica</i>	<i>Fagus</i>
European larch	<i>Larix decidua</i>	<i>Larix</i>
Norway spruce	<i>Picea abies</i>	<i>Picea</i>
Scots pine	<i>Pinus sylvestris</i>	<i>Pinus</i>
European oak	<i>Quercus robur</i>	<i>Quercus</i>
Small-leaved lime	<i>Tilia cordata</i>	<i>Tilia</i>

Hlinsko (map reference; 49°45'44" N, 15°54'27" E) is in the Chrudim district belonging to the Pardubice region. The *Betula* from this locality was on an abandoned graveyard of a past settlement site. The altitude of the sampled area ranges from 550 – 670 m asl in the landscape area of the Iron Mountains, in the northern part of the Bohemian-Moravian Highlands. The site is on the Palaeozoic metamorphic rock, and the soil is Histic Stagnosol (Němeček and Kozák, 2005; Chytrý, 2012; Czech Geological Survey, 2012).

Wood samples of the same species also were collected from Mšec, as in the case of Hlinsko. The village Mšec (map reference; 50°12'24" N, 13°51'40" E) is in the Rakovník district in the Central Bohemian Region, approximately 5.5 km north of Nový Strašecí. The site has an elevation of 480 m asl. In Mšec, the soil is Luvic Cambisol on a Marlstone geology (Němeček and Kozák, 2005; Czech Geological Survey, 2012).

Additionally, we randomly collected four mixed soil samples from the surroundings of *Picea*, *Larix*, *Pinus*, and *Betula* from Hlinsko for further elemental analysis.

3.2. Sample preparation

Each branch wood measures approximately 100 cm long, with a diameter from 20-30 cm as such firewood is often used for heating households in the Czech Republic. Four branch samples were collected from each species in the two localities. Each branch sample was thoroughly washed with Ultrapure-deionized water (18 Ω) to prevent contamination by dust and soils. The samples were further dried in an open-air for 72 hours to total desiccation. After that 500 g of each dried sample was burnt independently in a furnace until complete combustion (without charcoal pieces). The obtained ash samples were homogenized and sieved through a 0.1-mm sieve and subsequently put into a labeled plastic bag. In total, we prepared 32 ash samples (8 species x 4 replications) for further laboratory analysis.

In the case of the elemental analysis of the soil, the samples were oven-dried for 48 hours. After the removal of plant materials and other debris, the samples were grounded and further homogenized by passing through a 2-mm sieve.

3.3. Analytical methods

Elemental analyses were performed by using a portable ED-XRF (pXRF) analyzer manufactured by Delta Professional Olympus, Waltham, MA, USA. The pXRF was successfully used in the elemental analysis of biomass ashes (Chand et al., 2009; Xing et al., 2016). The pXRF detects the total or near-total contents of elements (from Magnesium up to Uranium) in the matrix.

Operationally, the samples were irradiated with two beams for 1 minute –30 s of the 10-kV beam and 30 s of the 40-kV beam. Each ash sample was tested in triplicate with 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).

For the elemental analysis of the soil, the total content K, Ca, Mn, Fe, Cu, Zn, As, Rb, Sr, Zr, Mo, and Pb were determined by pXRF as in the analysis of the ashes but calibrated in the soil Geochem mode (Kalnický and Singhvi, 2001; Canti and Huisman, 2015; Asare et al., 2020). The content of P, K, Ca, Mn, Fe, Zn, Cu, Sr, Rb, Al, Si, Mo, Zr, Th, Se, As, Ni, and Pb were

pertinent in this study as elements above the detection limit by the pXRF in all the samples. The total contents of some elements were omitted from further analysis for either not detected or above the detection limit only in a few cases.

3.4. Quality control

The accuracy of the pXRF was determined by comparing the data with the elemental composition obtained by standard analyses. To calibrate the pXRF for the analysis of the elemental composition of wood ash, 2 g of certified reference material (CRM, fly ash) was weighed and transferred into a VWR® 115 PTFE Jar containing 60 ml of *Aqua regia* (3ml HCl and 1ml HNO₃, International Organization for Standardization - USEPA 3052).

Additionally, we placed the mixture on a hot plate at 120 °C until the volume was 40 ml. The solution was transferred to a conical flask and diluted to 100 ml using Ultrapure-deionized water (18Ω). Approximately 20 ml of the diluted solution was transferred into glass test tubes for the determination of the total content of elements using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700x, Agilent Technologies Inc., Santa Clara, CA, USA) in an accredited laboratory. The analysis was conducted with an emphasis on the total contents of P, K, Ca, Mn, Fe, Zn, Cu, As, and Pb. These elements were measured in three replicates. The elements were also determined using the pXRF and a calibration curve was made for each element.

3.5. Data Analysis

There was homogeneity of variance among obtained data for the contents of elements in studied ashes. Data for elemental contents of ashes were tested using the Shapiro-Wilk W-test for normality and met the assumptions for the use of parametric tests. Factorial ANOVA followed by posthoc comparison using Turkey HSD test was applied to identify significant differences among ashes of different species. To determine the relationship between the data obtained by pXRF and *Aqua regia* ICP-MS, as well as the content of elements in the ashes and the soil, Pearson's correlation was used. We performed all statistical analyses using STATISTICA 13.4 (www.statsoft.io).

CHAPTER FOUR

4. RESULTS

4.1. Reliability of analytical methods

From the analysis of the CRM (BCR – 176R), we obtained the following mass fraction of the following elements using the pXRF: (in mg kg⁻¹) 13414 ± 261 Fe, 1088 ± 17.4 Cu, 16709 ± 237 Zn, 56 ± 0.7 As, 118 ± 2.8 Ni, 24.5 ± 1.1 Co, and 4954 ± 498 Pb compared to the original values of 13100 ± 500 Fe, 1050 ± 70 Cu, 16800 ± 400 Zn, 54 ± 5 As, 117 ± 6 Ni, 26.7 ± 1.6 Co, and 5000 ± 500 Pb obtained by *Aqua regia* ICP-MS. The calculated recovery (mean value of element ÷ reference value) × 100, according to the Eurachem guide (Magnusson and Örnemark, 2014) was > 90% for all the analyzed elements.

The comparison of the data obtained from the pXRF and *Aqua regia* ICP-MS revealed a strong linear correlation among the studied elements: $r > 0.9$, $p < 0.001$ for P, K, Ca, Fe, Cu, Zn, Pb, and $r = 0.77$, $p = 0.026$ for Mn (Table 3).

Table 3. The relationship (Pearson's correlation) between data obtained by *Aqua regia* ICP-MS and pXRF.

Parameter	P	K	Ca	Mn	Fe	Cu	Zn	As	Pb
Regression equation	$y = 0.9 + 0.9*x$	$y = -1.2 + 0.9*x$	$y = -2.3 + 0.99*x$	$y = 0.28 + 0.81*x$	$y = -0.15 + 0.90*x$	$y = -15.9 + 1.04*x$	$y = 13.5 + 0.44*x$	$y = -20.7 + 0.27*x$	$y = -0.24 + 0.58*x$
Correlation coefficient (r)	0.97	0.99	0.99	0.77	0.95	0.99	0.99	0.25	0.99
p-value	< 0.001	< 0.001	< 0.001	0.026	< 0.001	< 0.001	< 0.001	0.470	< 0.001

However, there was no significant correlation for As ($r = -0.252$, $p < 0.547$). The control test indicates that the pXRF has adequate precision for this study and suitable for the tracing of geochemical signatures in wood ashes.

4.2. Elemental composition of wood ashes

The statistical description of the elemental composition of the ashes of this study is in Figs. 1 – 5. There was a significant effect among the contents of macro (P, K, Ca, and S), micro (Mn, Fe, Zn, and Cu), other (Al, Si, Rb, Sr, Mo, Zr, Th, Se, As, Ni, and Pb) elements in the ashes of all the species from all the localities (Figs. 1–5).

The content of the macro-elements in the ashes significantly differed among the species from the two localities (Fig. 1). The contents of P ranged from 7.2 – 21.1 g kg⁻¹ in Hlinsko and 3.5 – 8.1 g kg⁻¹ in Mšec (Fig. 1a). The P content was highest (21.1 g kg⁻¹) in the ash of *Pinus* from Hlinsko and the lowest (3.5 g kg⁻¹) in *Fagus*, obtained from Mšec. The content of K was from 67–135 g kg⁻¹ in Hlinsko and 30 – 70 g kg⁻¹ in Mšec (Fig. 1b). The content of K was highest (135 g kg⁻¹) in the ash of *Quercus* from Hlinsko and the lowest (30 g kg⁻¹) in *Tilia*, obtained from Mšec.

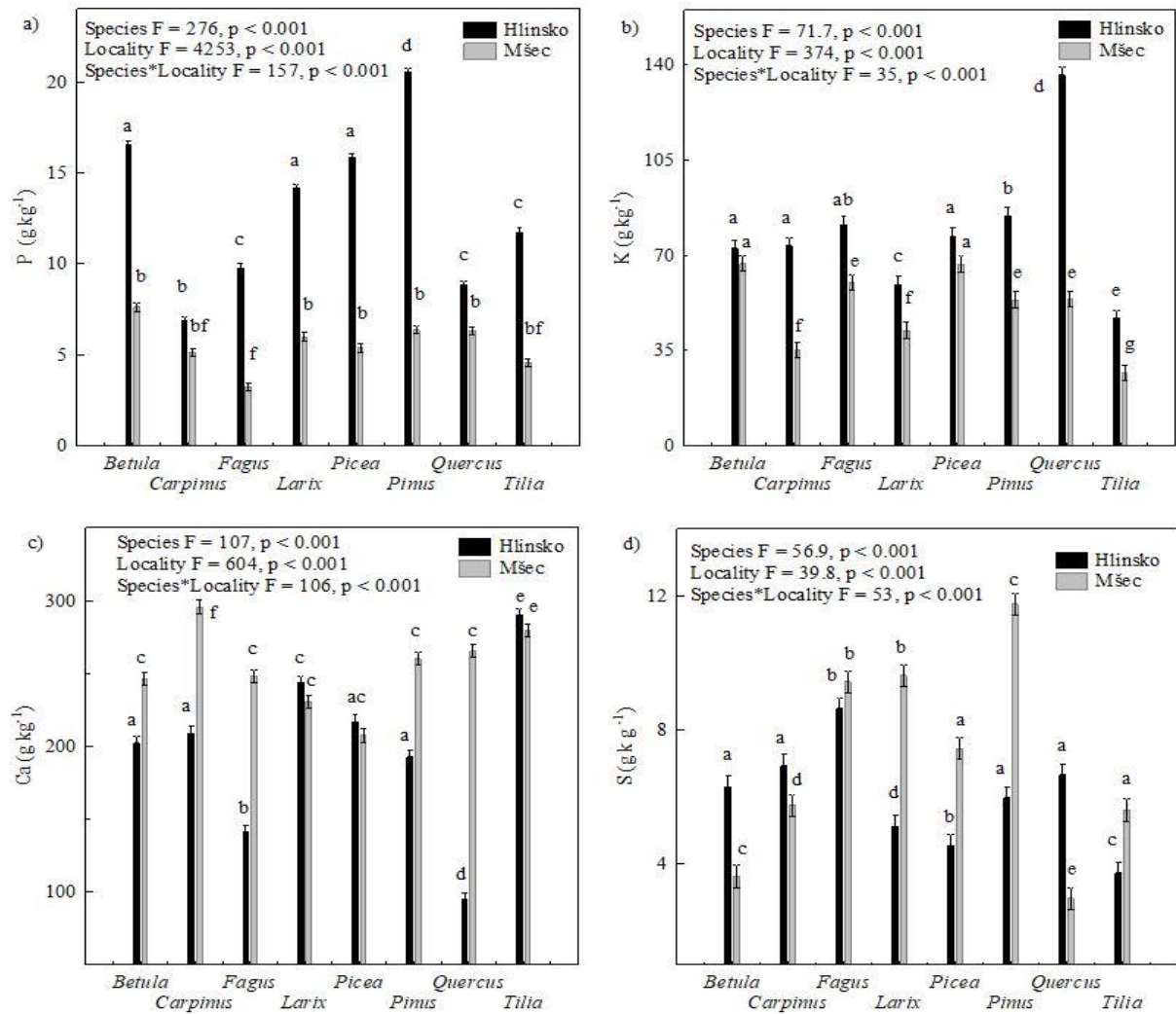


Figure 1. The effect of species on the total content of (macro elements) (a) P, (b) K, (c) Ca, and (d) S in the wood ashes from Hlinsko and Mšec in the Czech Republic. The *F* and *p* values were obtained from factorial ANOVA. Using Tukey *posthoc* HSD test, mean values with the same letters were significantly not different. The error bars indicate the standard error of the mean.

In the case of Ca, the content ranged from 100 – 299 g kg⁻¹ in Hlinsko and 215 – 300 g kg⁻¹ in Mšec (Fig. 1c). The highest (300 g kg⁻¹) content of Ca was in the ash of *Carpinus* from Mšec and the lowest (100 g kg⁻¹) in *Quercus* from Hlinsko. The content of Ca was highest compared

to all the studied macro elements. Among the macro elements, the least recorded was S, which ranged from 3.7 – 8.5 g kg⁻¹ in Hlinsko and 3.7 – 12 g kg⁻¹ in Mšec (Fig. 1d). However, the highest (12 g kg⁻¹) and lowest (3.7 g kg⁻¹) contents were in the ashes of *Pinus* and *Quercus*, respectively, from Mšec.

Furthermore, there was a significant effect on the content of microelements (Mn, Fe, Zn, and Cu) among the ashes of the species in all the two localities (Fig. 2). The content of Mn ranged from 1.2 – 20.1 g kg⁻¹ in Hlinsko and 1 – 32 g kg⁻¹ in Mšec (Fig. 2a). The highest content (32 g kg⁻¹) of Mn was in the ashes of *Larix* and *Picea* from Mšec and the lowest in *Tilia* from both sites. Moreover, the content of Fe was from 0.8 – 4.5 g kg⁻¹ in Hlinsko and 0.2 – 4.3 g kg⁻¹ in Mšec (Fig. 2b). The Fe content was highest (4.5 g kg⁻¹) in the ash of *Fagus* from Hlinsko and the lowest (0.2 g kg⁻¹) in *Carpinus* from Mšec. The content of Zn (in mg kg⁻¹) ranged from 89 – 2050 in Hlinsko and 102 – 1100 in Mšec (Fig. 2c). Zinc content was highest (2050 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) 72 – 198 in Hlinsko and 50 – 150 in Mšec (Fig. 2d). The Cu content was highest in the ashes of *Fagus* in Hlinsko and the lowest in *Carpinus* from Mšec.

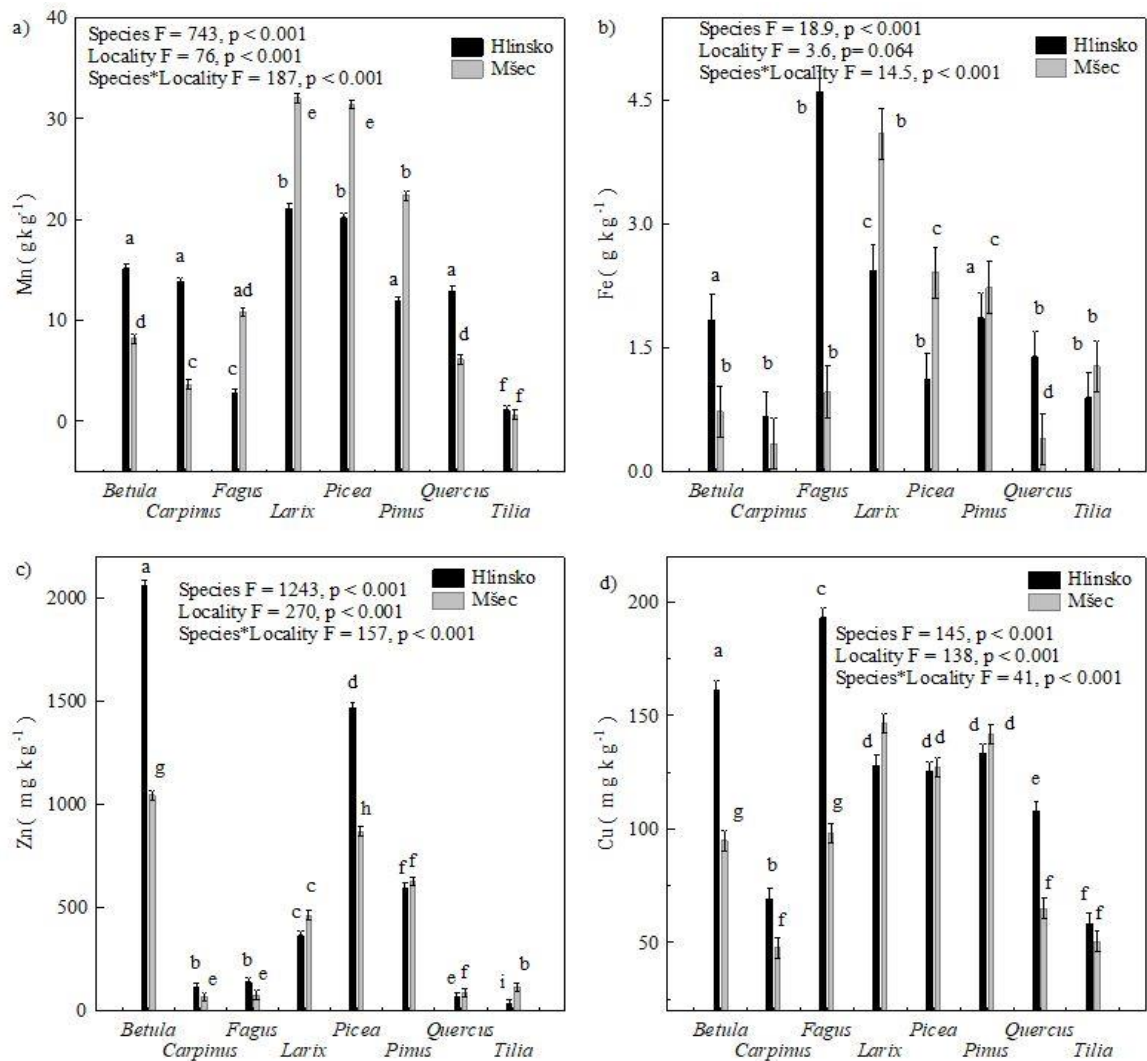


Figure 2. The effect of species on the total content of (microelements) (a) Mn, (b) Fe, (c) Zn, and (d) Cu in the wood ashes from Hlinsko and Mšec in the Czech Republic. The F and p values were obtained from factorial ANOVA. Using Tukey post hoc HSD test, mean values with the same letters were significantly not different. The error bars indicate the standard error of the mean.

Additionally, there was a significant effect on the content of other elements (Al, Si, Sr, Rb, Mo, Zr, Th, and Se) in the ashes from the different species of the two localities (Figs. 3 and 4).

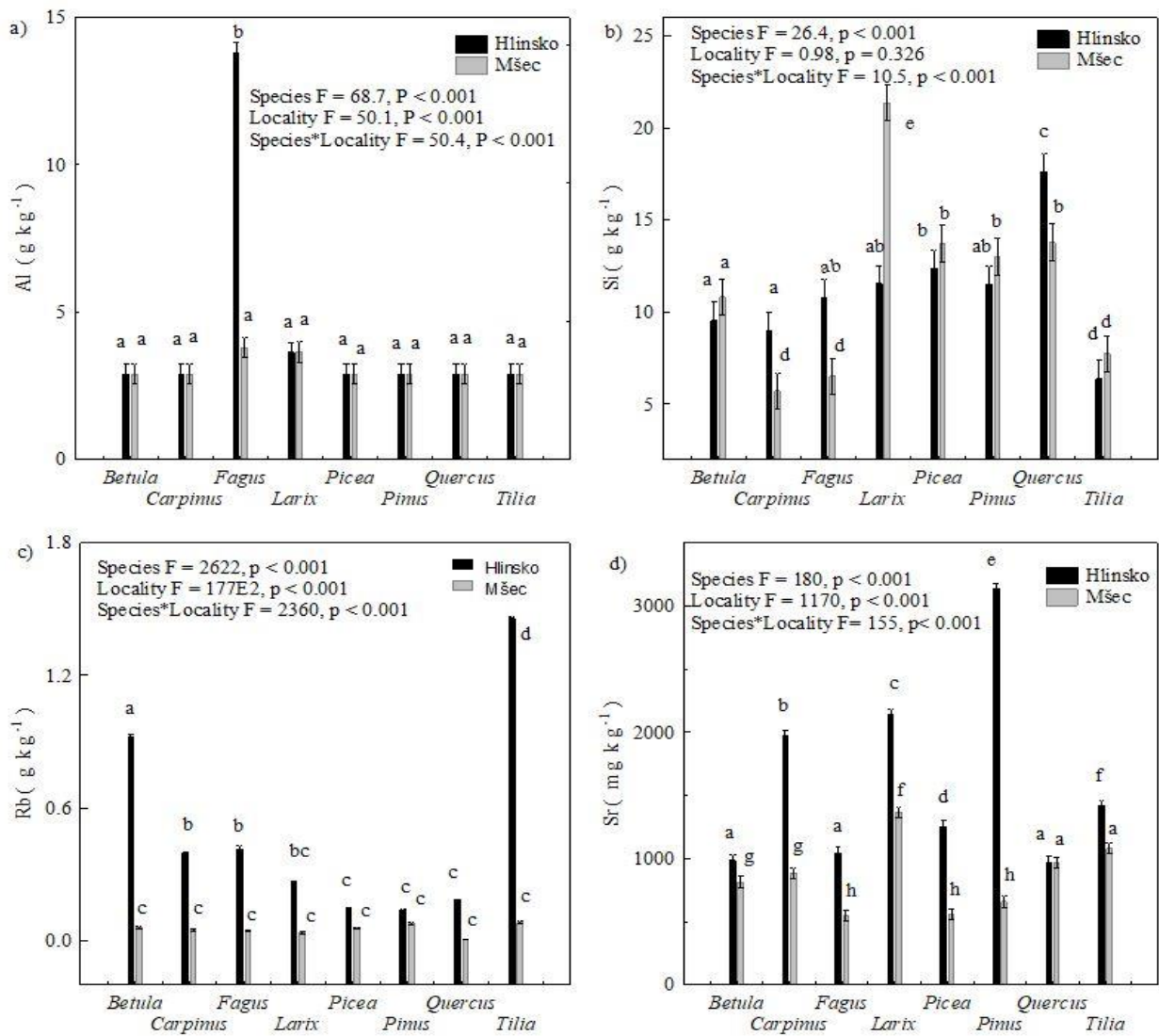


Figure 3. The effect of species on the total content of (other elements) (a) Al, (b) Si, (c) Rb, and (d) Sr in the wood ashes from Hlinsko and Mšec in the Czech Republic. The F and p values were obtained from factorial ANOVA. Using Tukey post hoc HSD test, mean values with the same letters were significantly not different. The error bars indicate the standard error of the mean.

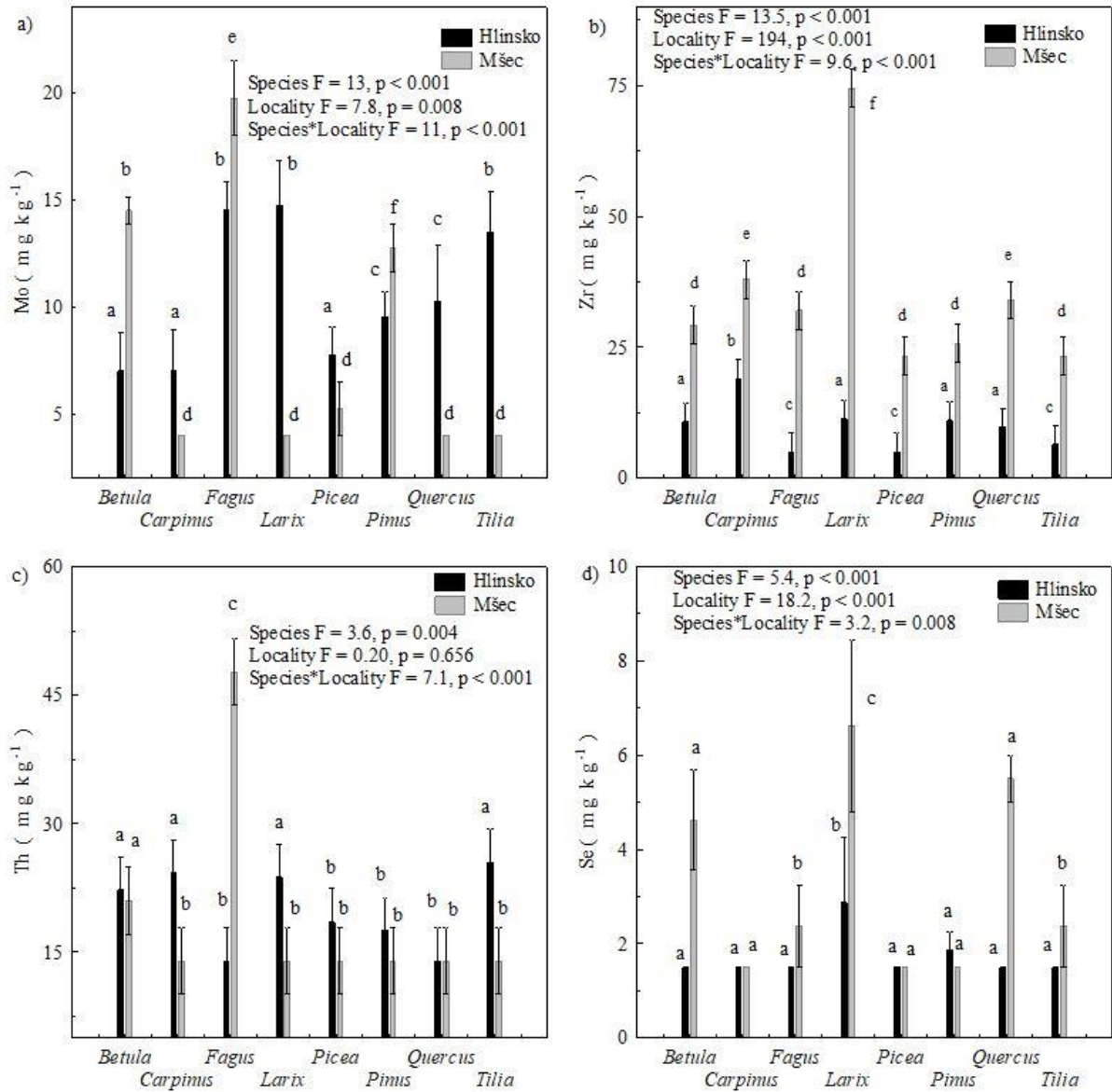


Figure 4. The effect of species on the total content of (other elements) (a) Mo, (b) Zr, (c) Th, and (d) Se in the ashes of selected tree species from Hlinsko and Mšec in the Czech Republic. The F and p values were obtained from factorial ANOVA. Using Tukey post hoc HSD test, mean values with the same letters were significantly not different. The error bars indicate the standard error of the mean.

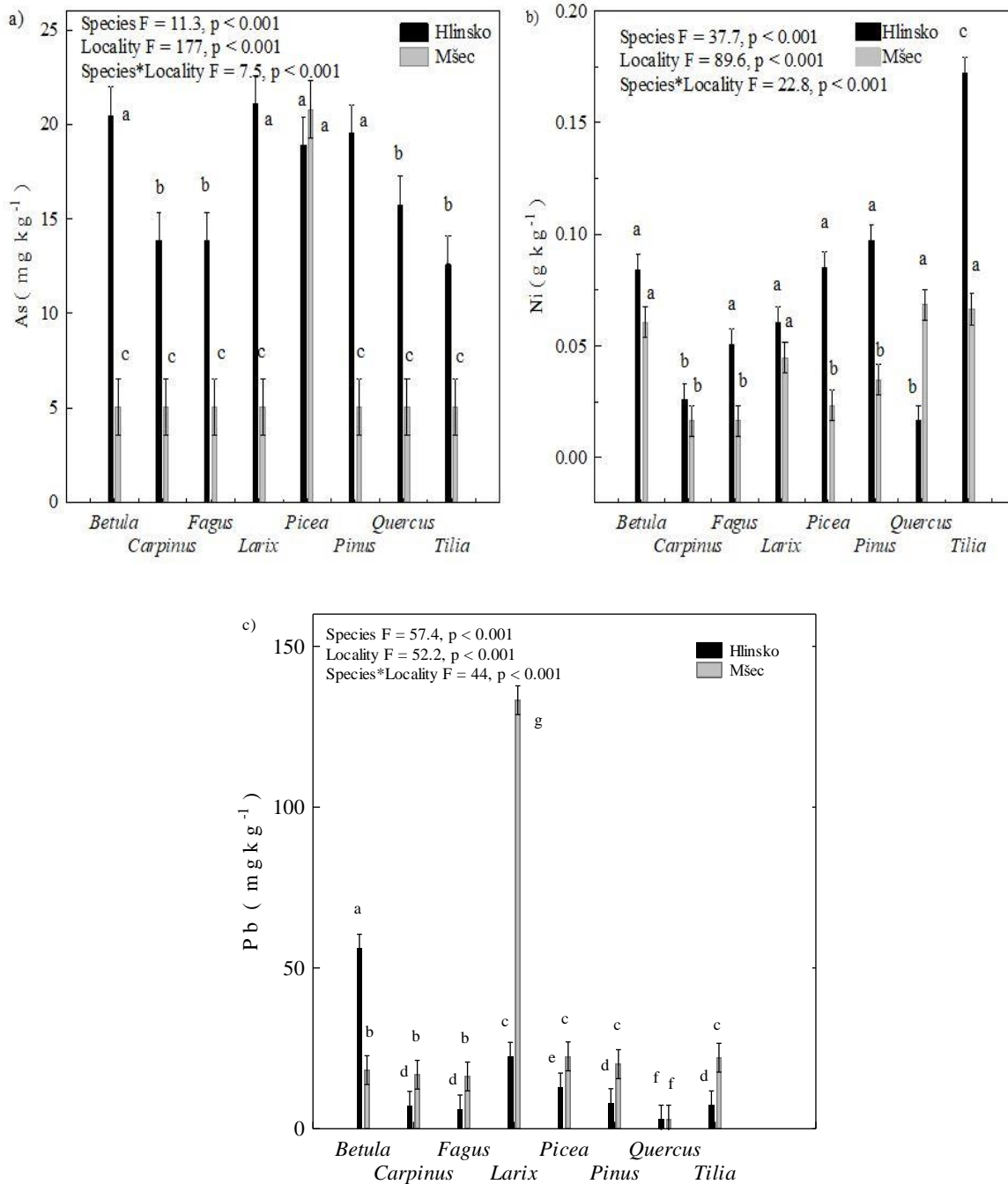


Figure 5. The effect of species on the total content of (risk elements) (a) As and (b) Ni in the wood ashes of from Hlinsko and Mšec in the Czech Republic. The F and p values were obtained from factorial ANOVA. Using Tukey post hoc HSD test, mean values with the same letters were significantly not different. The error bars indicate the standard error of the mean.

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 (Fig. 3a). Si content ranged from 7.2 – 18 g kg⁻¹ in Hlinsko and 6.3 – 21.2 g kg⁻¹ in Mšec (Fig. 3b). The content of Rb was from 0.2 – 1.6 g kg⁻¹ in Hlinsko and approximately 0.2 g kg⁻¹ in all the species in Mšec (Fig. 3c). The Sr

content was approximately $1000 - 3225 \text{ mg kg}^{-1}$ in Hlinsko and $500 - 1467 \text{ mg kg}^{-1}$ in Mšec (Fig. 3d).

In the case of risk elements (As and Ni), there was a relatively higher content in Hlinsko among all the ashes in comparison to Mšec (Fig. 5). Except for the content of Pb (132 mg kg^{-1}) in the ash of *Larix* from Mšec, all the risk elements were below the permissible limit in Agricultural soils (Fig. 5c).

4.3. Relationship between elemental content of soil and wood ashes

There was a significant correlation between the content of Cu, Sr, and Pb in the soil and the ashes of *Betula*, *Pinus*, *Larix*, and *Picea* ($r = 0.56 - 0.90$, $p < 0.05$; Fig. 6a-c) in Hlinsko. Conversely, there was no significant relationship between the content of Ca, Fe, Mn, Zn, As, Rb, Zr, and Mo in the soil and the ashes of all the species (Appendix 1).

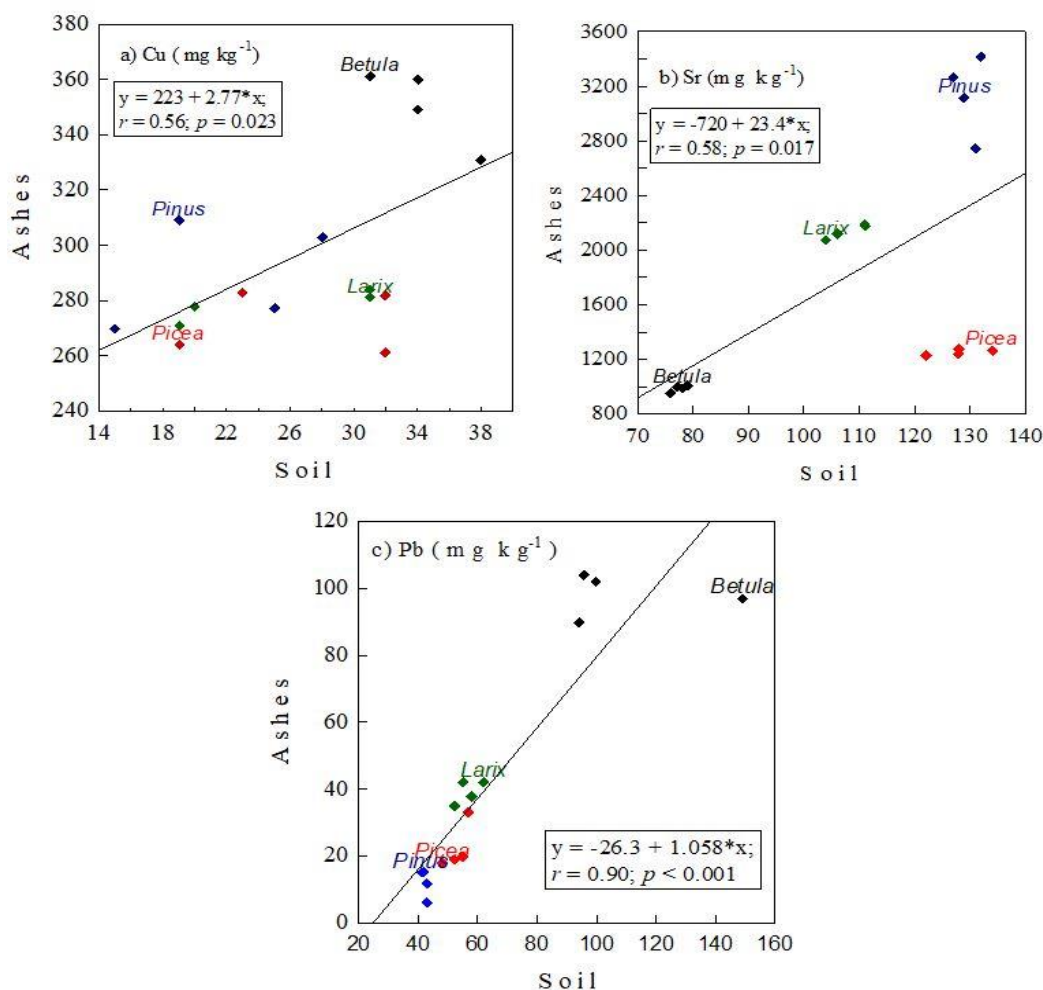


Figure 6. Relationship between the content of (a) Cu, (b) Sr, (c) Pb in the soil and ashes.

CHAPTER FIVE

5. DISCUSSION

Even though the studied ashes were of the same species from two localities, the content of elements was significantly different. The ashes in this study are suitable for macro (P, K, Ca, and S), micro (Mn, Fe, Zn, and Cu), and other (Al, Si, Rb, Sr, Mo, Zr, Th, and Se) elements deficient soils and agricultural soils at large. Notwithstanding, the ash of *Larix* in Mšec can pose a risk to Agricultural soils with $> 100 \text{ mg kg}^{-1}$ of Pb when applied as a fertilizer. However, the message is relevant for local farmers who apply home-made ashes on their arable fields, where wood is completely burnt without any specified temperature.

Additionally, the precision and recovery of the elements by the pXRF were adequate as the pseudo total content by *Aqua regia* extraction following the use of ICP-MS revealed a strong linear correlation. Therefore, pXRF offers a time-efficient and inexpensive approach in the geochemical exploration of wood ashes to determine their practical applicability on Agricultural soils.

The ashes in this study are suitable fertilizers in P deficient soils. The most suitable source of P was ash from *Pinus* in Hlinsko. However, the ashes from all the species from Hlinsko were more suitable for P fertilizer compared to Mšec, according to their significantly higher contents (Fig. 1a). The application of wood ash as fertilizer shows the best results in stands with visual symptoms of P deficiency, especially on N-rich drained peat soils (Okmanis et al., 2016). The P contents in most of the ashes from Hlinsko were within the ranges from 0.85 - 2.19% recorded by Etiégni et al. (1991), Huang et al. (1992), and Górecka et al. (2006) for ashes of some European woody species. Comparatively, ashes from Mšec was low in P, due to its content in the geology and probably nutrient absorptive capabilities of each species.

Considering the content of P in wood ash is comparatively lower to most macroelements (e.g., K and Ca), K content is mostly responsible for the positive impact of wood ash when applied as fertilizer (Okmanis et al., 2016). Hence, the ashes obtained by burnt branches of *Quercus* is much suitable to be used as mineral K supplements in soils with high K demand. Soil K levels increase with the application of wood ash which is attributed to the release of K by wood ash as well as to the replacement of K on soil exchange sites by Ca and other exchangeable cations released directly from wood ash into the soil suspension (Górecka et al., 2006). The solubility and potential availability of the macronutrients to plants in wood ash are high, and K has the highest bioaccumulation relative 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 highest content of macroelements in all the ashes was Ca and gives ash properties similar to agricultural lime (Naylor and Schmidt, 1986). The wood ashes from the selected species can be applied to Ca demanding soils according to their high levels. However, ashes from Mšec were more suitable, especially the ash of *Carpinus*. The relatively high content of Ca in Mšec is related to the Marlstone geology and the ability of the species to absorb maximum Ca for their growth. The Ca contents in the ashes of all the species of this study were within the range (10.9 – 36.1%) reported by Etiégni et al. (1991), Huang et al. (1992), and Górecka et al. (2006) among ashes of different woody species. Wood ashes have been reported previously to have the same liming effects as commercial lime and comparatively provide better plant growth responses than limestone because of the additional nutrients in ashes (Adekayode and Olojugba, 2010). However, adding wood ashes which usually contain 25% CaCO₃ and as a result are very alkaline with a pH of 10 – 12, increases soil alkalinity which creates an adverse condition for growing plants (Lannotti, 2020). Hence, ashes above this concentration of Ca are more suitable for acidic soils as many plants prefer a slightly acidic environment (pH < 7.0) to absorb nutrients from the soil. When soil alkalinity increases and the pH rises, necessary minerals such as P, Fe, B, Mn, Cu, Zn, and K become chemically tied to the soil and are not available for plant use.

The relatively lower contents of S compared to the other studied macro element is due to the high volatility of this element during the combustion process, especially in temperatures > 500 °C (Misra et al., 1993; Dibdiakova et al., 2015). Consequently, if wood ash is applied to arable fields as the fertilizer, S content in the ashes of the species, especially *Pinus* from Mšec is most suitable.

Furthermore, soil deficient in Mn and Fe can be fertilized by all the ashes of this study, more especially from *Larix* and *Fagus* in Mšec and Hlinsko, respectively. The comparatively higher content of Cu, especially in the case of the ash of *Betula* in Hlinsko is connected with the contents in the soil (Fig 6a). Typically, the ashes from *Betula* in Hlinsko according to the correlation model indicated that the elemental composition of the soil increases with increasing Cu content in the ash. Notably, the *Betula* was located on abandoned graves from a previous settlement and this can affect the elemental composition of the soil (e.g., Cu Pb, and Sr) and subsequent accumulation through the root system (Fig. 6a–c).

Additionally, the Zn content in the ash of *Betula* from Hlinsko was higher among all the species but within the maximum allowable content (> 2000 mg kg⁻¹) of in biomass ash (Reimann et al.,

2008; Brandón et al., 2017). 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.

The effect of species on the content of other elements (Al, Si, Rb, Sr, Mo, Zr, Th, and Se) in the ashes were varied in the two sites. Meanwhile monovalent ion impurities such as Rb⁺ have been reported in natural apatite and other bedrocks (Young et al., 1969; Hughes et al., 1991; Simonetti et al., 2008). Rubidium can substitute for K in higher plants, which implies that due to a similar monovalent charge, plants can take up Rb (Goldschmidt, 1954). This probably 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 has been reported by some authors (Wedepohl and Simon, 2010; Oroian et al., 2015). Tree species such as *Fagus sylvatica*, *Picea abies*, and *Pinus spp* contain elements including Sr and Rb (Oroian et al., 2015; Simniškytė-Strimaitienė et al., 2017).

The main challenge of using ashes for Agricultural soils is related to the accumulation of risk elements. However, the studied ashes contained levels unrelated to soil contamination except for the content of Pb in *Larix* from Mšec. We can conclude that the studied ashes are well suitable as fertilizers in Agricultural soils, however, a thorough elemental analysis must be conducted as the content can be influenced by anthropogenic activities.

CHAPTER SIX

6. CONCLUSIONS

The comparative elemental analysis of wood ashes of the studied species from different localities revealed the following inferences,

1. The comparative elemental analysis of ashes of the same species from different localities revealed that the content of elements in the soil has a significant effect on ashes. The ashes obtained from *Betula*, *Carpinus*, *Fagus*, *Larix*, *Picea*, *Pinus*, *Quercus*, and *Tilia* commonly used for heating in the Czech Republic were characterized by a high content of macro (P, K, Ca, and S), micro (Mn, Fe, Zn, and Cu), and other (Al, Si, Rb, Sr, Mo, Zr, Th, and Se) elements. Although the temperature adopted in the combustion of the wood was unspecified, we conclude that home-made ashes are suitable as fertilizer on agricultural soils.
2. Ashes of *Betula*, *Carpinus*, *Fagus*, *Picea*, *Pinus*, *Quercus*, and *Tilia*, are suitable to be used as P, K, Ca, S, Mn, Fe, Cu, and Zn fertilizers for Agricultural soils. The elemental composition of ashes of the same species from different localities is different owing to varied geology and anthropogenic activities.
3. The content of risk elements was below the regulatory limits in soils, except for the content of Pb ($> 100 \text{ m kg}^{-1}$) in the ash of *Larix* from Mšec. Thus, the ash of *Larix* from Mšec is unsuitable fertilizer for agricultural soils.
4. The use of the pXRF has enough precision for the determination of the elemental composition of wood ashes. Spreading wood ashes in the soil may interfere with the natural biogeochemical cycles, due to risk elements accumulation. Detailed elemental analysis of ashes is, therefore, recommended.

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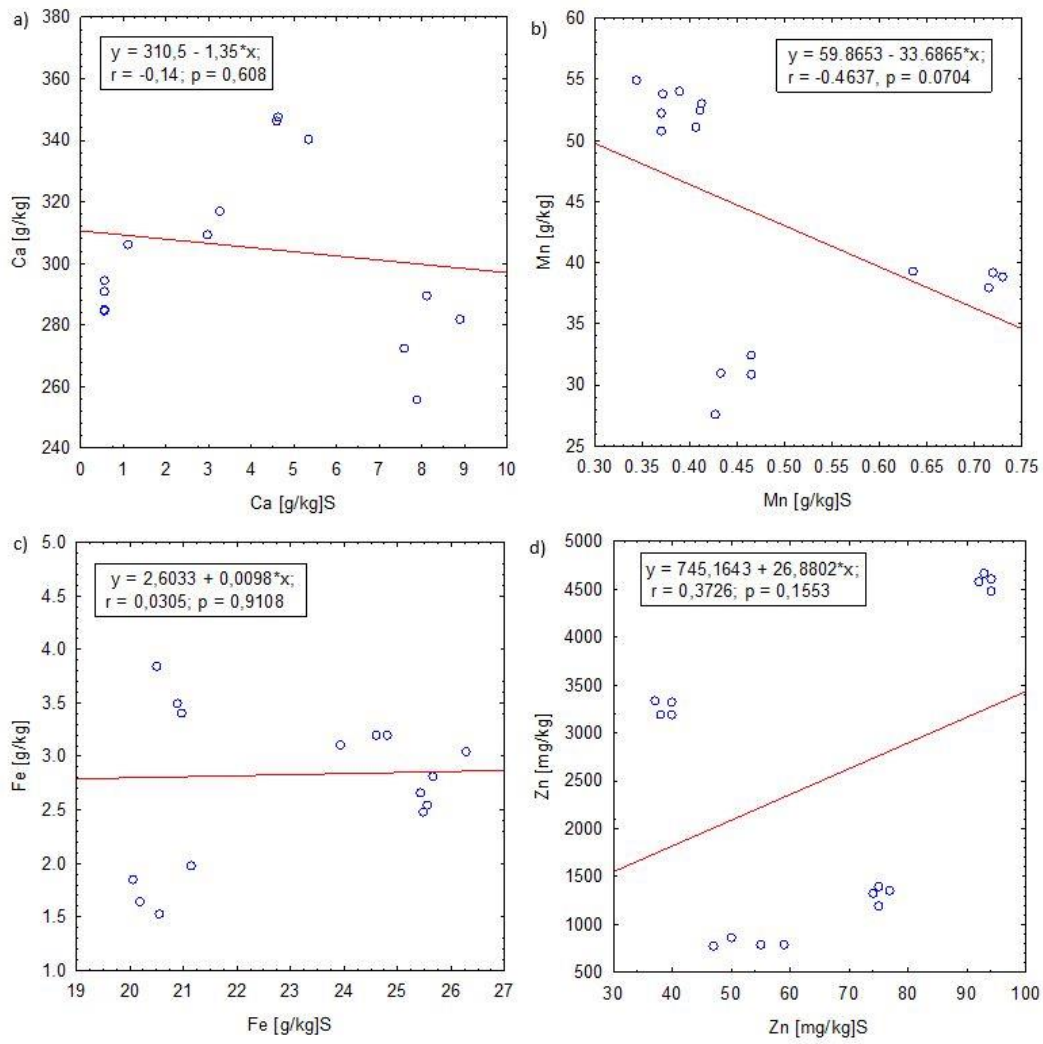
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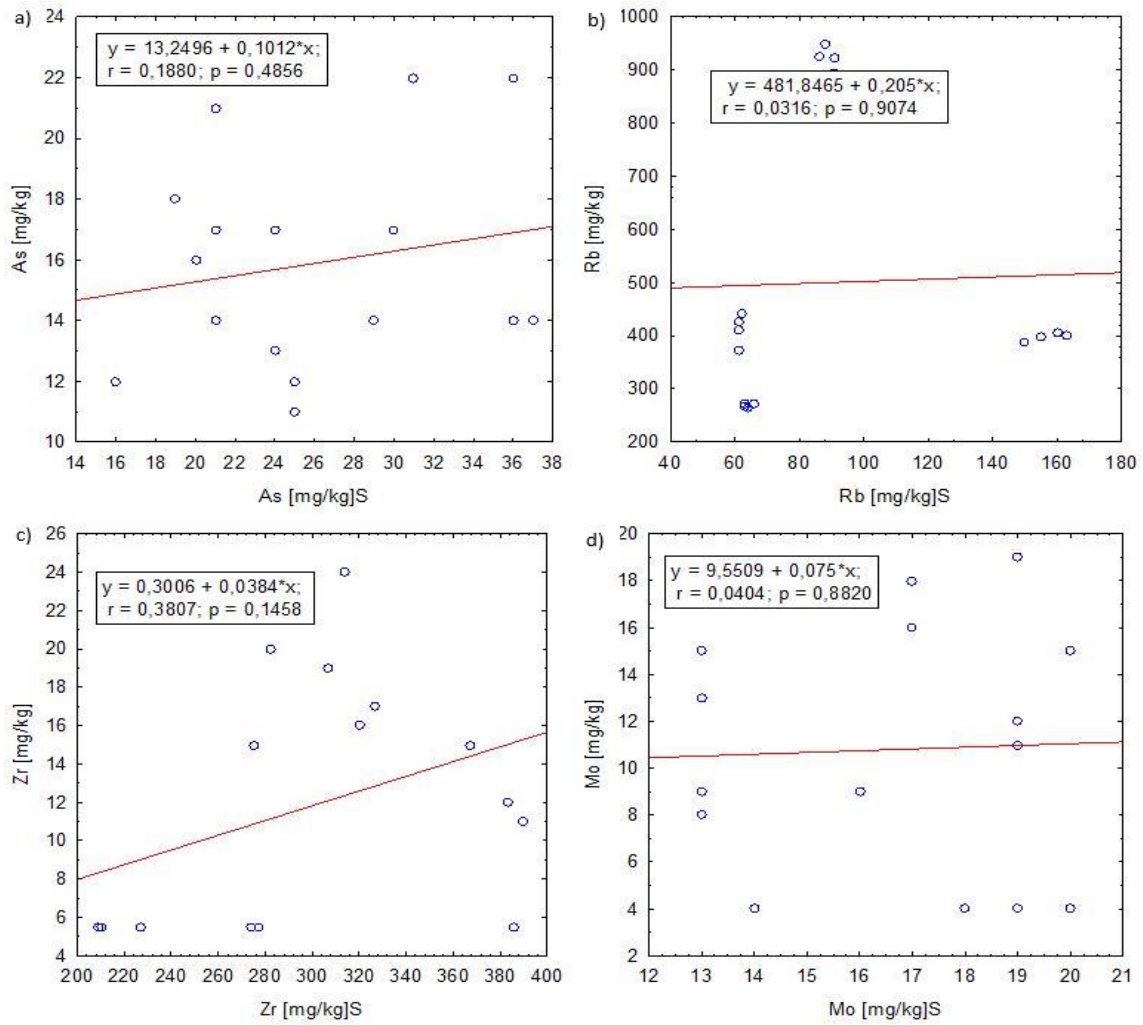
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APPENDIX 1



Relationship between the content of (a) Ca, (b) Mn, (c) Fe, and (d) Zn in the soil and ashes from Hlinsko.



Relationship between the content of (a) As, (b) Rb, (c) Zr, and (d) Mo in the soil and ashes from Hlinsko.

APPENDIX 2

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