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Impact of Wood Ash and Sewage Sludge on Elemental Content in Hybrid Alder Clone

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Abstract: In this study, the focus was on evaluating the effects of the initial treatment of wood ash and sewage sludge on hybrid alder clones' aboveground biomass and elemental content. To measure the element concentrations in the tree rings, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) was utilized, which is a valuable tool for dendrochemistry research, albeit with some challenges in accurate quantification. One important aspect of the study was the development and comparison of different "in-house" matrix-matched standards for the precise quantification of element concentrations in tree rings. It was found that the commercially available reference materials, IAEA 413 (algae) and IAEA 392 (algae), were the best choices due to their homogeneity. The study also revealed that the use of sewage sludge and wood ash as soil improvers significantly benefited the increase in hybrid alder biomass. However, no significant increase in element content was found in the obtained wood mass, and for some elements, there was a decrease in concentration.

Keywords: hybrid alder; tree rings; LA-ICP-MS; wood ash; sewage sludge

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Citation: Bertins, M.; Paiste, P.; Makovskis, K.; Ansone-Bertina, L.; Busa, L.; Lazdina, D.; Lazdins, A.; Kirsimäe, K.; Klavins, M.; Viksna, A. Impact of Wood Ash and Sewage Sludge on Elemental Content in Hybrid Alder Clone. *Sustainability* **2023**, *15*, 7242. https://doi.org/10.3390/su15097242

Academic Editors: Monika Żubrowska-Sudoł and Beata Karolinczak

Received: 31 March 2023
Revised: 22 April 2023
Accepted: 25 April 2023
Published: 26 April 2023

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1. Introduction

The growth in the world economy in its current form is largely based on the use of raw natural resources that are processed into various types of goods. According to the European Commission, the global consumption of materials such as biomass, fossil fuels, metals, and minerals is expected to double in the next four decades, while annual waste generation is expected to increase by 70% by 2050 [1].

By maintaining such a development trend, in which resources are extracted and processed, increases in the emission of greenhouse gases, the problems of water availability and reductions in biological diversity are promoted [2]. Recently, there has been growing interest in the circular economy (CE) as a necessary component in solving resource and waste problems. In Europe, the goal is to strive for a climate-neutral, resource-efficient, and competitive economy, ensuring sustainable development. The European Union (EU) Circular Economy Action Plan aims to introduce a growth model that gives more to the planet than it takes [1]. Although there is not one definition of CE, overall, the aim of CE is to keep resources in use in the economy as long as possible, preserving and increasing their value from one cycle to the next, while reducing the waste generation [2,3].

In this context, it is also important to mention the bioeconomy, which, according to the definition of the European Commission, is considered as an integrated approach to the use of biological resources to ensure sustainable development, using biotechnical applications in all economic and industrial sectors that use biological resources and processes to produce food, feed, biological products, energy, and services [3]. Considering the principles of both of these approaches, it is possible to define a circular bioeconomy that includes the activities of both approaches. In the studies carried out so far, the concept of a circular bioeconomy has been proposed, which is based on three main components, including (a) improvements in the efficient use of resources in production processes; (b) the recovery and enhancement of wastes/residues from production processes and (c) reductions in greenhouse gas (GHG) emissions along all phases of the production processes [3,4].

The geopolitical events of the last year have significantly affected the economic development of Latvia, Europe, and the world. Recently, more and more attention has been paid to energy prices, as well as to the promotion of the use of renewable energy resources, thereby reducing dependence on fossil resources. In Latvia, wood is considered one of the most valuable resources. Forests in Latvia dominate the landscape, covering more than half (52%) of the country's territory, which equates to around 3.4 million hectares [5]. The forested area is expanding naturally, which is also through the afforestation of abandoned agricultural land and former mining sites. To improve tree growth conditions and increase the competitiveness of planted seedlings with the forest environment vegetation, forest soil fertilization is utilized after regenerative felling to add nutrient elements that may be lacking. In terms of the economy, timber harvesting is a vital contributor, with approximately 12 million cubic meters of timber harvested from Latvian forests each decade [5–7].

The concept of the circular bioeconomy has gained attention in the forestry sector, where the selection of suitable tree species is critical for achieving optimal results. Hybrid alder (*Alnus x. spaethii*) has emerged as a promising species due to its potential economic value and fast growth rate. This species is a hybrid of European black alder (*A. glutinosa*) and Caucasian alder (*A. subcordata*), known for its adaptability to different soil types and tolerance to harsh environmental conditions [8–10]. In Latvia, a hybrid of *Alnus glutinosa* and gray alder (*Alnus incana)* is also recognized as a promising fast-growing species for wood production [11].

Recent studies have shown that hybrid alder has high yield potential, making it a suitable option for bioenergy and biomass production [12,13]. Additionally, hybrid alder has been found to be effective in phytoremediation, specifically in the removal of heavy metals from contaminated soils [14,15]. This ability to tolerate and accumulate heavy metals makes it a useful tool for restoring polluted environments.

To maximize the benefits of hybrid alder, the effectiveness of fertilizers should be evaluated, taking into account the species' requirements and growth rate. Hybrid alder is a versatile tree species that can contribute to various environmental and economic applications. Its potential to sequester carbon, produce renewable energy, and restore contaminated environments makes it an attractive option for sustainable forestry practices.

The concept of the circular economy (CE) has led to the exploration of new methods for enhancing soil quality and the disposal of bioenergy residues. One such method is the application of wood ash (WA) to soil, which has shown promising results. Forest soil fertilization is another effective technique used to improve the growth and yield of forest stands. Extensive research in Europe and North America has shed light on the benefits and limitations of this method, making it a crucial tool for sustainable forest management [16].

By adding nutrients to the soil through forest stand fertilization or WA application, forest managers can provide optimal growth conditions for trees, which can result in the increased competitiveness of planted seedlings and enhanced stand productivity. This approach not only contributes to the economic viability of the forestry sector but also concurs with the principles of the CE, promoting the efficient use of resources and waste reduction. Therefore, it is crucial to continue exploring and implementing sustainable forest management practices that prioritize the health and productivity of forest ecosystems.

In Latvia, the availability of mineral fertilizers has become complicated due to recent geopolitical events, which has led to increased interest in studying and developing the use of waste products and by-products, such as sewage sludge and wood ash. Wood ash, a by-product of energy production from logging residues, has proven to be an effective forest soil amendment, especially in boreal stands on organic soil, where it can reduce deficiencies of potassium (K) and phosphorous (P) [17]. Additionally, studies have shown that wood ash has the potential to increase growth on mineral soils as well. While wood ash provides a significant input of macronutrients and micronutrients, it typically contains low levels of nitrogen (N), which is abundant in organic soils but limited in mineral soils. Therefore, the use of N-containing mineral fertilizers may improve growth on mineral soil in boreal forests [18]. Combining wood ash fertilization with mineral fertilizers can enhance the supply of other nutrients, leading to improved growth in planted boreal forests on afforested mineral soil.

Numerous experiments have been conducted to examine the impact of fertilization on various ecological parameters in forests, including ground vegetation, soil and foliage chemistry, as well as nutrient leaching into groundwater and surface water [19]. However, evaluating the effectiveness of added fertilizer in terms of plant uptake, soil storage, and nutrient loss has received less attention. While some studies have focused on changes in plant nutrient concentrations, this approach fails to identify the source of N uptake. Alternatively, researchers have used $\delta^{15}N$ (the normalized ratio of two stable nitrogen isotopes: ^{15}N:^{14}N) values to determine the source of N uptake by plants from the mineral fertilizer, soil, and plants themselves. This approach offers valuable insights into the N uptake process and can help to optimize fertilization practices for sustainable forest management.

When designing experiments to evaluate the effect of fertilization or other silvicultural practices on plant nutrient uptake, including unfertilized control plots is essential, particularly in the absence of pre-treatment measurements [20]. However, it is important to acknowledge that natural variability and heterogeneity in soil properties and moisture conditions may complicate the interpretation of results, even within a single forest stand [21]. In studies using $\delta^{15}N$ values to estimate N-fertilizer uptake efficiency, control plots become even more critical [22]. Moreover, the application of wood ash to improve forest soil generally increases the pH in the forest floor [19,23,24] as well as in the upper mineral soil layer [24,25], while the use of ammonium-nitrate fertilizers can induce soil acidification [26]. Soil pH can have a significant impact on the availability of N and other nutrients to plants. Therefore, the selection of appropriate control plots and the careful monitoring of soil pH changes are crucial when interpreting the results of experiments on forest soil fertilization.

The ability of plants to accumulate both essential nutrients and harmful pollutants from soil makes them an effective passive sampling tool. Utilizing plants for the remediation of polluted areas is recognized as a cost-effective and environmentally friendly approach. Numerous studies have demonstrated that several plant species have the potential to accumulate heavy metals, which makes them ideal for stabilizing, treating, and phytoremediating problematic soils [27,28].

Hybrid alder has been shown to have a high accumulation capacity for heavy metals, such as cadmium, lead, and zinc [29]. These properties make hybrid alder a valuable tool for the restoration and remediation of degraded lands, including abandoned mines and industrial sites. Furthermore, the ability of hybrid alder to grow in nutrient-poor soils and adverse climate conditions makes it a low-cost and environmentally friendly option for phytoremediation projects [30].

Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) is a useful analytical technique for tree ring analysis due to its ability to provide high-resolution data with minimal sample preparation requirements and the capacity to measure a wide range of elements and isotopes. LA-ICP-MS is widely used in dendrochemistry research, including investigations into environmental pollution, environmental changes, and tree physiology [31]. However, one of the main challenges of this method is the accurate quantification of the obtained data, which can be affected by a range of factors such as laser-induced matrix effects, the non-homogeneous distribution of elements in the tree ring and matrix-matched calibration standards [32].

While the use of in-house matrix-matched standards for the calibration of LA-ICP-MS in tree ring analysis is necessary, it can also introduce additional sources of error due to the potential variability in sample preparation and the difficulty in accurately quantifying the amount of added elements. Therefore, it is crucial to properly validate the accuracy and precision of in-house standards through inter-laboratory comparison and comparison with certified reference materials, such as those provided by the International Atomic Energy Agency. Additionally, careful consideration should be given to the selection of the matrix-matched material to ensure its suitability for calibration purposes and to minimize any potential matrix effects that could impact the accuracy and precision of the analysis [32].

Light-stable isotope ratio mass spectrometry (IRMS) is a widely used method for investigating the nitrogen cycle and is highly effective in measuring ^{14}N, ^{15}N, ^{12}C and ^{13}C isotopes simultaneously [33,34]. This makes IRMS an invaluable tool for tracking N flow in different ecosystems through isotopic labeling. However, a significant challenge when using IRMS to study N-cycling is isotopic fractionation resulting from plant physiological processes [35]. Even when different $\delta^{15}N$ values are present in various supply sources, such as fertilizers and soil, it can be difficult, if not impossible, to determine the source of N in the plant due to this fractionation.

The objective of this study was to evaluate the effects of soil treatment with wood ash and sewage sludge on hybrid alder tree biomass and elemental content. Additionally, the study aimed to develop and compare different "in-house" matrix-matched standards for the precise quantification of element concentrations in tree rings. The findings of this study provide valuable insights into the reuse of waste materials for the production of new, high-value products, which aligns with the circular bioeconomy goals. Furthermore, the study results offer practical implications for the forestry industry, specifically in terms of wood sample research. The new information presented in this study has the potential to benefit both researchers and practitioners, contributing to a more sustainable and efficient use of natural resources.

2. Materials and Methods

The main aim of this research visit was to study element distribution in tree rings of hybrid alder (*A.x hybrida A.Braun ex Rchb.*). Stem disc samples were collected from hybrid alder trees, which were 11 years old, growing on an experimental plot (Figure 1) located in the central region of Latvia (56.6919 N, 25.1370 E based on the geodetic coordinate system of Latvia (LKS92), Transverse Mercator projection). The experimental site was considered to be marginal due to unfavorable biophysical conditions such as excess soil moisture, unsuitable texture, and stony soil. The plot was set up in the spring of 2011.

Figure 1. Experimental plot during sampling in March 2022.

In the beginning of the experiment, hybrid alder (clone No. 4) seedlings were cultivated in a laboratory for in vitro propagation situated in the SFRI Silava Climate house in Latvia. The tree seedlings were planted in an experimental plot with an average spacing of 2.0 × 2.0 m. The experimental plot was a part of a large-scale plantation that covered an area of 16 hectares, consisting of deciduous trees and short-rotation energy crops. The soil in the experimental area was classified as Luvic Stagnic Phaeozem (Hypoalbic) or Mollic Stagnosol (Ruptic, Calcaric, Endosiltic) as per the Food and Agriculture Organization of the United Nations classification (2006). The soil texture was primarily loam at a depth of 0–20 cm and sandy loam at a depth of 0–20 cm and 20–80 cm.

To conduct the experiment, three fertilization subplots were created, each with four replications: a control (no fertilization), sewage sludge, and wood ash. Each subplot was sized at 30 × 24 m and was established in the spring season of 2011. The sewage sludge used was classified as Class I (according to the regulations of the Cabinet of Ministers of the Republic of Latvia No. 362) and was sourced from "Aizkraukles ūdens" (Aizkraukle Water). A dose of 10 t_{DM} ha^{-1} was applied for the sludge. Additionally, stabilized wood ash from a boiler house located in Sigulda was used as fertilizer with a dose of 6 t_{DM} ha^{-1}. Further details on the dose and characteristics of the applied fertilizers are in Table 1.

Table 1. The major nutrient content in the applied fertilizers.

Fertilizer	Origin	Dose	Application Form	The Input of Major Nutrients through Fertilization, kg ha^{-1}		
				N_{tot}	P_{tot}	K_{tot}
Wood ash	Boiler house, Sigulda	6 t_{DM} ha^{-1}	Mechanically	2.6	65	190
Sewage sludge	Municipal wastewater treatment plant, "Aizkraukles ūdens"	10 t_{DM} ha^{-1}	Mechanically	259	163	22

The chemical analysis of soil was conducted immediately after the application of fertilizers to determine the concentration of major elements and heavy metals. A mixture of concentrated HNO_3 and HCl was used for extraction, and the samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). The results showed that there were no significant statistical differences ($p > 0.05$) in the content of major elements (K, Ca, Mg, and P) and toxic heavy metals (Cd and Pb) between the fertilized soils and the control plots. It is worth mentioning that previously used fertilizers contain both nutrients and heavy metals; however, the concentration of heavy metals in the fertilized soils did not exceed the heavy metal target values and precautionary limits established by legislative regulations for soil and ground quality [36].

In order to carry out the study, a total of three trees were chosen from three distinct fertilization subplots—sewage sludge, wood ash, and a control (no fertilization). The characteristics of chosen trees are shown in Table 2.

Table 2. The characteristics of hybrid alders from different subplots.

Subplot	The Average Height of Trees, m	The Average Mass of Stem (Fresh Biomass), kg	The Average Mass of Branches (Fresh Biomass), kg	Average Diameter at 1.3 m Height, mm
Control	9.0 ± 0.2	28.2 ± 4.7	4.1 ± 0.6	100 ± 5.6
Sewage sludge	10.0 ± 0.4	40.5 ± 5.5	5.6 ± 1.3	116 ± 15
Wood ash	9.3 ± 0.4	33.8 ± 5.7	4.9 ± 2.0	106 ± 7.6

The stem discs were sawed at a height of 0.20 m, with the aim of incorporating all the tree rings in the samples, as illustrated in Figure 2. The thickness of the tree discs was roughly 1 cm.

After air-drying, the stem discs were smoothed using trace-metal-free sandpaper with varying grit sizes (P120, P240, and P800) and then cut into pieces no larger than 4.0 cm. Various analytical techniques such as ICP-MS, LA-ICP-MS, and IRMS were used to analyze the samples. To prepare for ICP-MS analysis, the samples underwent pretreatment using microwave-assisted digestion.Each individual tree ring was analyzed separately, with a sample size of approximately 0.2 g taken from each ring. The samples were mineralized using microwave-assisted acid digestion. In this process, each sample was placed in a Teflon microwave digestion vessel and treated with 6 mL of 65% HNO_3 (trace metal grade, Fisher Scientific) and 2 mL of concentrated 36% HCl (trace metal grade, Fisher Scientific) sequentially. The vessels were sealed and heated in a Milestone Start E microwave oven using a programmed method, involving heating to 160 °C over 15 min and holding at 160 °C for 35 min. After digestion, the samples were diluted to a volume of 25 mL with deionized water obtained using Millipore water deionization equipment. To ensure the accuracy of the measurements, multiple certified reference materials (CRMs)—IAEA 336 (lichen), IAEA 413 (algae), IAEA 392 (algae), BRC 692 (white cabbage) and BCR-060 (Aquatic plant *Lagarosiphon major*)—were used. The analysis of the CRM produced results that were in good agreement with the certificate values, with differences not exceeding 10%.

Figure 2. Prepared hybrid alder tree disk (Ø = 114 mm) with visible radial increment rings.

A standard procedure was used to determine element concentrations in the samples. The elements Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Rb, Sr, and Zn were analyzed using an Agilent 8900 ICP-QQQ ICP-MS equipped with a MicroMist nebulizer. The ICP-MS settings were as follows: RF power—1.550 W; sampling depth—8 mm; auxiliary gas flow—0.90 mL min^{-1}; plasma gas flow—15 L min^{-1}; and He cell gas flow—5 mL min^{-1}. All analytical standard stock solutions were TraceCert (Sigma-Aldrich) for ICP (100 mg L^{-1}). A calibration graph was created using six different standard solutions in the concentration range from 0.1 µg L^{-1} to 500.0 µg L^{-1}, prepared from stock standard solutions, with blank correction. An Internal Standard Mix solution from Agilent Technologies (10 mg mL^{-1}) was used as an internal standard. The ICP-MS system was checked for stability after every ten samples by using two standard solutions. The MassHunter workstation program, including its Instrument control and Offline data analysis subprograms, was used to obtain and analyze measurement data.

In order to determine the $\delta^{15}N$ and $\delta^{13}C$ values, the samples were weighed and placed into tin capsules, with each sample weighing approximately 4 mg. These samples were then analyzed in duplicate using an EA3000 elemental analyzer (EuroVector) that was coupled to a Nu-horizon continuous-flow isotope ratio mass spectrometer (Nu Instruments). To ensure the accuracy of the stable isotope ratio determination, a sample of glutamic acid (Sigma Aldrich) was used as an internal standard. Certified reference materials, USGS-40 and USGS-41 (L-Glutamic acid), were also used for this purpose. The $\delta^{15}N$ values were expressed in ‰ relative to air N_2, while the $\delta^{13}C$ values were expressed in ‰ relative to VPDB (Vienna Pee Dee Belemnite).

The direct analysis of sample tree rings was performed via laser ablation (LA) ICP-MS using Cetac LSX-213 G2 + LA, HelEx 2- vol ablation cells coupled to Agilent 8800 ICP-MS. Helium was used as the carrier gas at a combined flow of 0.8 L min^{-1}. In-house-made doped cellulose pellets were used for quantification, and NIST612 were used for quality control measurements. Carbon (13C) was used as an internal standard element for the analysis of the wood matrix. Single spot analyses with spot sizes of 80 µm and laser energy outputs of 1.46–1.48 J cm^{-2} at a frequency of 10 Hz were used. For mapping, movement speeds of 160 μm s^{-1} were employed.

To identify significant differences in element content between the wood samples obtained from the differently fertilized subplots, an analysis of variance (ANOVA) was utilized. The F value was used as a criterion for determining the significance of the differences, and differences were considered significant if $F > F_{crit}$ at a 95% confidence level ($p \leq 0.05$) for the comparison of the results obtained from different subplots and the determination of the effects of the various fertilization methods on the elemental content of the wood samples. In addition, a principal component analysis (PCA) was performed using the CAT (Chemometric Agile Tool) software to identify the most important variables that explained the variance observed in the elemental content of the wood samples. This approach allowed for the reduction in the dimensionality of the data and visualization of the relationships between the different variables in a more comprehensive way [37].

3. Results

3.1. Calibration of LA-ICP-MS

For the quantification of data obtained via LA-ICP-MS analysis, different approaches was used, including analyses of dissolved samples with ICP-MS and the preparation of matrix-matched reference materials.

Cellulose, as the primary component of wood, was used to create in-house reference materials. For this, three types of microcrystalline cellulose powders were mixed with various elements and compressed into pellets of 10 mm in size. The accuracy of the element content was ensured by analyzing the pellets with ICP-MS after acid digestion. In addition, certified reference material powders, IAEA 336 (lichen), IAEA 413 (algae), IAEA 392 (algae), and BRC 692 (white cabbage), were also analyzed to provide a basis for comparison.

The results were analyzed using PCA (Figure 3), revealing that the consistency of the prepared standards was influenced by the particle size of the material used for pellet preparation and the element concentration. Moreover, the IAEA 413 (algae) and IAEA 392 (algae) powder reference materials could be directly pressed into pellets, producing sufficiently homogeneous material that can be used as matrix-matched standards.

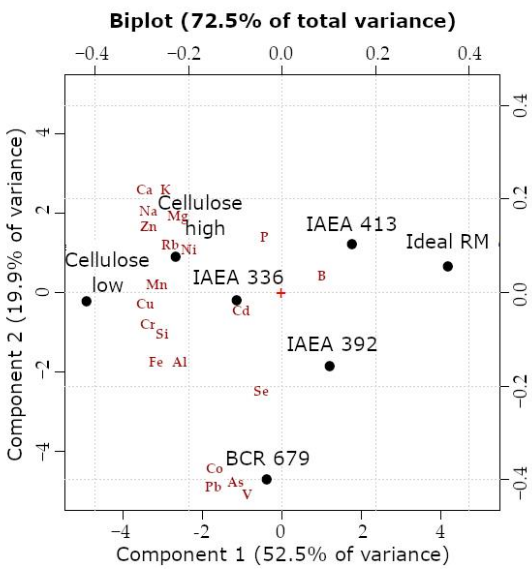

Figure 3. Comparison of homogeneity of different prepared RM pellets.

3.2. N and C Isotope Ratio Measurements

Based on the results presented in Table 3, the N and C content did not show significant variations among different tree rings. Specifically, the mass fraction of N was approximately 0.15%, and that of C was 47%. However, the isotope ratio values displayed a relatively wide range, with a $\delta^{13}C$ value ranging from −28.6 to −26.4 ‰ and a $\delta^{15}N$ value ranging from −18.3 to −11.0 ‰.

Table 3. The δ15N and δ13C values and mass fractions of N and C in hybrid alder stem wood tree rings from different years (mean values ± SD).

	$\delta^{15}N$, ‰			wN, %			$\delta^{13}C$, ‰			wC, %		
2012	−13.0	±	0.6	0.20	±	0.02	−26.7	±	0.3	48.7	±	0.3
2013	−13.0	±	0.4	0.19	±	0.01	−27.8	±	0.8	47.8	±	0.1
2014	−13.0	±	0.3	0.16	±	0.03	−28.6	±	0.2	47.3	±	0.1
2015	−18.3	±	0.7	0.12	±	0.01	−28.4	±	0.2	48.3	±	0.9
2016	−11.0	±	0.7	0.19	±	0.07	−26.9	±	0.6	48.5	±	0.7
2017	−15.3	±	1.1	0.11	±	0.01	−26.4	±	0.9	46.5	±	0.7
2018	−17.0	±	0.5	0.14	±	0.03	−27.6	±	0.6	47.7	±	0.7
2019	−15.9	±	1.4	0.13	±	0.02	−27.2	±	0.2	46.4	±	0.2
2020	−15.0	±	0.7	0.13	±	0.04	−27.7	±	0.7	47.5	±	0.6

Previous research has suggested that the $\delta^{13}C$ value is primarily determined by the plant species and the photosynthetic pathways employed [38]. Variations in $\delta^{13}C$ values between different tree rings can also be attributed to specific weather conditions during those years. On the other hand, the factors influencing variations in $\delta^{15}N$ values are more complex, as this value is influenced by both external factors such as fertilization practices and internal processes related to the natural nitrogen cycle [39].

3.3. Laser Ablation Measurements of Alder Tree Rings

In the course of this study, LA-ICP-MS measurements were made to map different elements in the hybrid alder tree rings (Figure 4) using an external matrix-matched standard calibration approach. The results were also compared to ICP-MS measurements and were in good agreement. Tree samples were measured together with different prepared matrix-matched standards, and ^{13}C was used as an internal standard to counteract the effect of different ablation characteristics between samples and reference material pellets. For example, in Figure 4b, the obtained map of Ca distribution in the ablated area of the hybrid alder tree sample is shown.

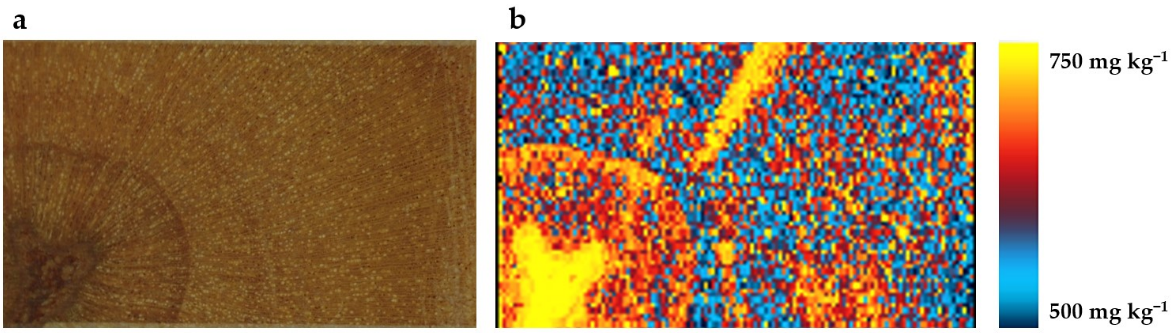

Figure 4. (**a**) Ablated area of hybrid alder tree (10 × 17 mm); (**b**) Ca distribution in hybrid alder.

3.4. Concentrations of Major and Minor Elements in Hybrid Alder Stem Wood

In Table 4, the concentrations of 22 different elements in hybrid alder wood are shown, which were measured under various fertilizer treatments. Among these elements, K, Ca, and P were the most abundant, with concentrations ranging from 724 to 1006 mg kg^{-1}, 530 to 743 mg kg^{-1}, and 133 to 187 mg kg^{-1}, respectively. The statistical analysis of the data revealed that the fertilizer treatments did not have a significant effect on the average levels of Ca and P in the wood. These results are consistent with previous studies [40,41] that have reported similar levels of K, Ca, P, and Mg in hybrid alder wood. Furthermore, the analysis showed that there were no significant differences in the levels of heavy metals such as Cr and Zn between the different treatments. However, some slight increases in the concentrations of several elements were observed in the samples treated with wood ash, including Li, Mg, Al, P, Ca, Mn, Co, Ni, Zn, Rb, Sr, Cd, Ba, and Pb. In contrast, the use of sewage sludge as fertilizer resulted in lower levels of certain elements, including B, Al, P, K, Ca, V, Cr, and Cu, than in the control samples.

Table 4. Element concentrations in hybrid alder stem wood from different fertilization subplots (mean ± SD, mg kg^{-1}) (Fcrit = 3.40; p = 0.05; significant differences between groups denoted with letters a, b, and c).

Element	Control	Wood Ash	Sewage Sludge	F
Li	0.008 a ± 0.004	0.014 b ± 0.007	0.007 a ± 0.004	3.81
B	4.7 a ± 0.3	4.5 a ± 0.3	3.6 b ± 0.3	26.8
Na	3.1 a ± 1.2	3.3 a ± 1.1	8.0 b ± 1.4	33.9
Mg	132 ± 24	160 ± 22	135 ± 31	2.53
Al	2.2 a ± 1.7	1.6 a ± 1.1	0.4 b ± 0.2	7.94
P	158 ± 31	187 ± 41	133 ± 58	3.16
K	1006 a ± 231	874 b ± 100	724 c ± 85	7.62
Ca	666 ± 127	743 ± 201	530 ± 74	2.29
V	0.09 a ± 0.01	0.08 a ± 0.01	0.06 b ± 0.01	10.69
Cr	0.04 ± 0.04	0.03 ± 0.01	0.02 ± 0.01	2.84
Mn	1.7 a ± 0.15	16.1 b ± 3.5	9.9 c ± 2.8	69.9
Fe	7.3 ± 3.1	6.5 ± 1.2	6.4 ± 1.1	0.56
Co	0.006 a ± 0.04	0.017 b ± 0.007	0.018 b ± 0.005	15.1
Ni	0.04 a ± 0.01	0.08 b ± 0.02	0.05 a ± 0.03	12.5
Cu	2.65 a ± 0.59	2.73 a ± 0.67	1.63 b ± 0.19	12.1
Zn	4.97 ± 1.58	7.12 ± 4.06	4.35 ± 0.95	2.87
As	0.023 a ± 0.004	0.019 a ± 0.003	0.015 b ± 0.004	12.4
Rb	0.32 a ± 0.07	0.56 b ± 0.06	0.42 c ± 0.05	33.2
Sr	2.18 a ± 0.43	7.46 b ± 2.24	3.59 a ± 0.45	37.4
Cd	0.02 a ± 0.01	0.04 b ± 0.01	0.02 a ± 0.01	15.8
Ba	1.44 a ± 0.36	2.64 b ± 0.7	1.53 a ± 0.16	18.6
Pb	0.13 a ± 0.04	0.37 b ± 0.15	0.17 a ± 0.02	16.5

As depicted in Figure 5, the level of Mg remained relatively constant across different tree rings, as evidenced by the standard deviation in elemental content among various samples. Similar patterns were observed for both P and Ca. These results can be attributed to consistent growth conditions, where fertilizer was solely applied at the time of planting, and the subsequent growth conditions remained stable.

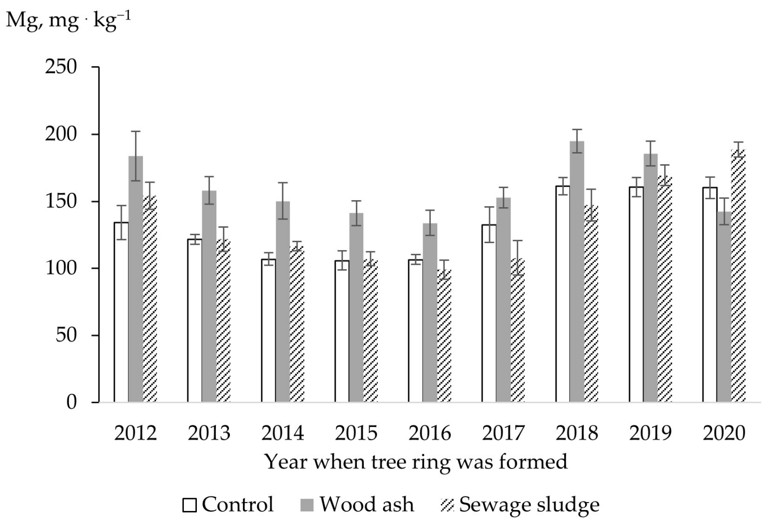

Figure 5. The magnesium content in hybrid alder stem wood tree rings in a nine-year period.

The findings from this study reveal that in all samples, irrespective of the fertilization method, there is a noticeable decrease in the potassium (K) concentration in the more recently formed tree rings (as shown in Figure 6). This can be attributed to the high mobility of K, which facilitates its effective transportation to the actively growing parts of the tree [42].

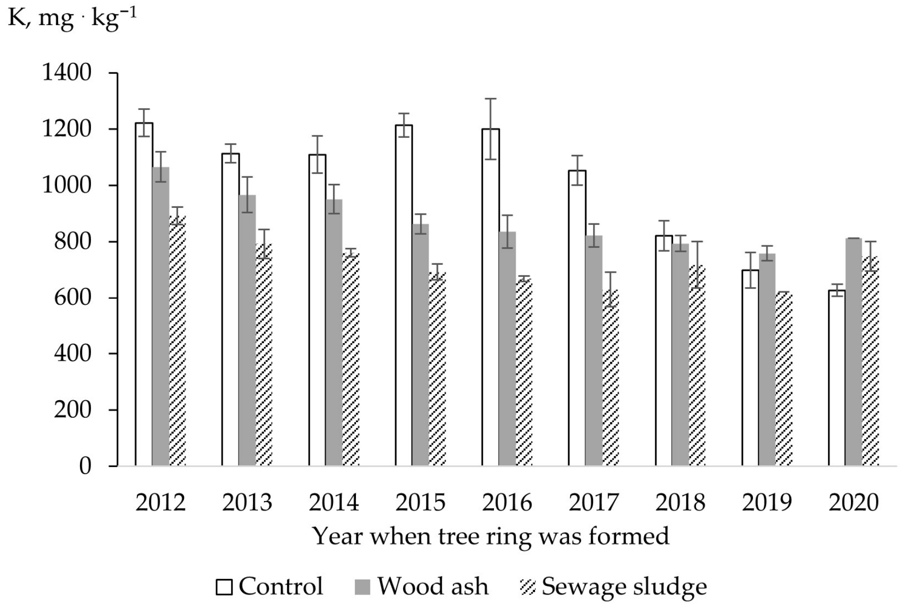

Figure 6. The potassium content in hybrid alder stem wood tree rings in a nine-year period.

As shown in Figure 7, there was a decrease in the concentration of Ca in the more recently formed tree rings. This can be attributed to the low mobility of Ca, which is predominantly located inside cells and thus immobilized in the wood as old cells die and new cells are formed [43,44]. The decreasing trend of Ca concentration in the tree rings can be explained by the fact that Ca is not readily translocated from older to newer tissues.

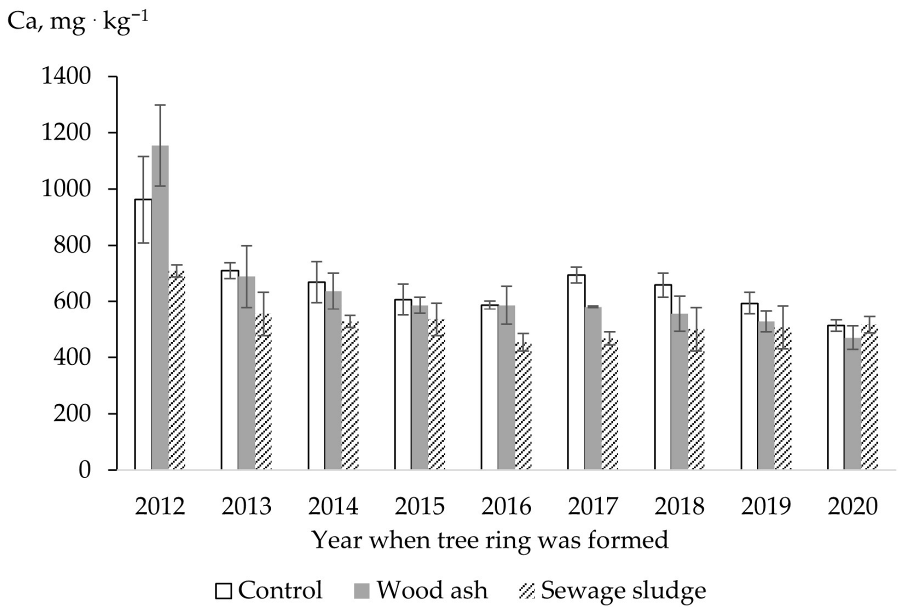

Figure 7. The calcium content in hybrid alder stem wood tree rings in a nine-year period.

The results of the principal component analysis (PCA) conducted on the studied samples indicate that the overall variation between the samples can be explained by two components, which together account for 58.4% of the total variance (33.8% and 24.5% for the first and second components, respectively). The PCA plot (Figure 8) shows that samples from plots with different types of fertilization form distinct clusters. Samples from the control plots are richer in Fe, Ca, Cu, Cr, K, Al, B, V, and As, while those from the wood-ash-fertilized plots tend to accumulate more P, Li, Zn, Mg, Cd, Ba, Ni, Pb, Rb, Sr, Co, and Mn. Samples from the sewage sludge treatment have higher levels of Na, which is the only element that shows a significant difference between the treatments.

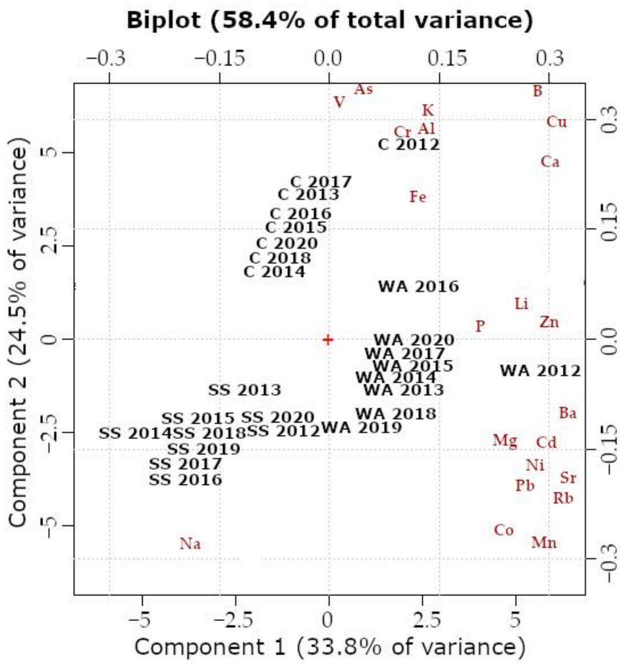

Figure 8. Principal component analysis of element distribution in differently fertilized samples (C—control, WA—wood ash, SS—sewage sludge).

4. Discussion

Laser ablation (LA) has become a popular technique for the analysis of trace elements in various materials, including tree rings. The LA technique offers a number of advantages over traditional methods such as solution-based analyses, including high spatial resolution and minimal sample preparation requirements. In the case of tree rings, the LA-ICP-MS analysis of elements can provide a detailed record of environmental and climatic changes over time. Some research results showed that the analysis of tree rings with the LA-ICP-MS technique was able to provide high-resolution records of past fire events in forest ecosystems [45]. Another study demonstrated that the LA-ICP-MS analysis of tree rings could provide a means to study historical mercury (Hg) pollution, as Hg accumulation in tree rings was found to correlate with historical industrial activities [46]. Moreover, besides LA-ICP-MS, other LA techniques such as laser ablation–inductively coupled plasma–optical emission spectrometry (LA-ICP-OES) have also been used for the analysis of tree rings. It was also found that the LA-ICP-OES analysis of tree rings could provide a record of lead (Pb) pollution in a highly industrialized region [47].

To sum up, the chemical composition of tree rings is essential to judge the influence of various environmental conditions on the specific object under study. The obtained results show that the direct analysis of tree rings using laser ablation-ICP-MS and the quantification of chemical elements using matrix-matched reference materials is an effective tool for evaluating the chemical composition of the studied material.

One of the main challenges in quantifying LA-ICP-MS data is the potential for matrix effects, which can arise from differences in the physical and chemical properties of the sample and the reference material used for calibration. This can lead to the inaccurate quantification of element concentrations in the sample, as the mass spectrometer response may not be proportional to the true concentration of the element of interest. Several approaches have been developed to mitigate these effects, including the use of matrix-matched reference materials, internal standardization, and mathematical correction algorithms [48]. Another issue that can arise in LA-ICP-MS analysis is the variability in the laser ablation process, which can result in uneven sampling and measurement errors. To address this, multiple ablation spots are often analyzed, and the results are averaged to improve the accuracy of the measurements. Additionally, the careful calibration of the laser power and ablation rate can help to minimize these sources of error [49]. In this study, microcrystalline cellulose powders were used as a solid support for constructing calibration curves, using doping with aqueous solutions of different elements.

Cellulose is an abundant organic compound on Earth and is the main constituent of plant cell walls, including those of wood. Cellulose molecules are long chains of glucose (sugar) units that are linked together by beta-1,4-glycosidic bonds. Wood is composed primarily of cellulose, hemicellulose, and lignin, with cellulose being the most abundant component, accounting for approximately 40–50% of the dry weight of wood. Cellulose provides strength and rigidity to the cell walls, making it an essential structural component of plants [50]. The obtained results after processing using PCA (Figure 3) showed that the homogeneity of the prepared standards directly depends on the particle size of the material used for the preparation of the granules and the concentration of the elements. The results of this study are comparable to the results of Santos Moreao et al., where filter paper was used as a solid support of a calibration standard [32].

To sum up, it was found that the LA-ICP-MS analysis of tree rings can be, in practice, performed using any available powdered reference material with a similar matrix, as in the studied sample, which can be pressed into a pellet, and if ^{13}C is used as an internal standard, the force of pressing becomes negligible. However, it was found that commercially available reference materials IAEA 413 (algae) and IAEA 392 (algae) exhibit the best homogeneity and can be used as RMs without additional milling of the sample. The typical laser beam size for the analysis of tree samples is set to about 100 µm, which means that even cellulose with a particle size of 50 µm is sufficient for the preparation of spiked matrix-matched reference materials.

Overall, the mineral content of tree stem wood is influenced by the chemical composition of xylem sap, which reflects the availability of elements in the soil during the year when the ring was formed. Therefore, the elemental content of each tree ring can serve as a proxy for the properties and characteristics of the soil at that time, making dendrochemistry a powerful tool for investigating historical changes in soil chemistry.

Our study showed that the use of sewage sludge and wood ash as soil improvers significantly enhanced the increase in the obtained biomass of hybrid alder, and at the same time, an insignificant increase (for some elements, even a decrease) in heavy metallic element content in the obtained wood mass was observed.

Based on the experimental results (Table 4) (Figures 5–8), the element content of hybrid alder stem wood samples exhibited a notable increase in the following order: control, sewage sludge, and wood ash. This trend can be attributed to the fertilizer production process. The sewage sludge, which was collected from a municipal wastewater treatment plant in Aizkraukle, a small town with low levels of trace elements and no heavy industry, had the highest proportion of organic matter to element content since it was not subjected to any further processing. On the other hand, wood ash had the lowest ratio of organic matter to element content due to its minimal organic matter content [51].

The study results showed that the hybrid alder actively accumulates macroelements found in ash (Mg, Ca, and P). There is decrease in K, which most likely is related to the pH changes in soil. The obtained results did not show significant impacts on the accumulated elements in the hybrid alder from sewage sludge; for some elements, there was an observed decrease in concentration (Al, Cr, Zn, and As) which was due to a significant increase in obtained biomass. The highest increase in biomass was obtained when sewage sludge was used for soil improvement, but the use of wood ash also benefited the biomass of the hybrid alder in comparison to control plots.

Dendrochemistry has been increasingly recognized as a valuable tool for detecting and reconstructing environmental changes that affect soil chemistry throughout a tree's life. One recent study demonstrated the potential of the dendrochemical analysis of tree rings for identifying long-term trends in soil contamination with heavy metals in polluted regions [52]. By examining the elemental composition of tree rings, dendrochemistry allows researchers to infer information about soil characteristics and the presence of different elements during specific growth periods. This approach enables conclusions to be drawn about changes in nutrient availability in soil over time, providing insights into the impact of environmental shifts on tree growth and development [31].

Our findings demonstrate that discernible differences can be observed between samples that have undergone different treatments. The results of the PCA showed that it was possible to distinguish between the control plots and those treated with wood ash and sewage sludge. This suggests that the application of these materials had a measurable impact on the elemental content of the trees, which could have implications for their growth and development.

Additionally, advancements in analytical techniques have allowed for more precise measurements of trace elements and isotopes in tree rings, providing further insights into the biogeochemical processes that influence soil chemistry [53]. Moreover, dendrochemistry has been shown to be useful in detecting subtle changes in soil chemistry resulting from land-use practices such as deforestation and agriculture [54,55].

The findings of this investigation revealed that there was a consistent elemental composition among various tree rings. For instance, there was no substantial variation in the levels of magnesium across different rings (Figure 5). The degree of fluctuation in elemental content between distinct samples was illustrated by the standard deviation. This uniformity in the levels of phosphorus and calcium was also observed. The reason for these results could be attributed to the stable conditions in which the trees were grown. Fertilizers were only administered during planting, and the subsequent growth conditions remained largely unchanged.

In conclusion, the study found that any available powdered reference material with a similar matrix as the sample can be used for the LA-ICP-MS analysis of tree rings. The use of sewage sludge and wood ash as soil improvers significantly increased the biomass of hybrid alder, but there was an insignificant increase in element content in the wood mass. The use of sewage sludge did not significantly impact accumulated elements in hybrid alder, and there was a decrease in concentration for some elements. The highest increase in biomass was obtained when sewage sludge was used for soil improvement, but the use of wood ash also benefited the biomass of the hybrid alder.

Furthermore, the study's findings support the circular bioeconomy goals by providing insights into the reuse of waste materials for high-value product production. The results have practical implications for the forestry industry and wood sample research, contributing to the more sustainable and efficient use of natural resources.

Author Contributions: Conceptualization, M.B. and D.L.; methodology, A.V., P.P. and K.K.; software, M.B. and P.P.; validation, D.L., A.L., M.K. and A.V.; formal analysis, M.B., P.P., K.M. and L.B.; resources, A.V. and A.L.; writing—original draft preparation, M.B. and L.A.-B.; writing—review and editing, M.B., L.A.-B., D.L., M.K. and A.V.; visualization, M.B., P.P. and L.A.-B.; supervision, D.L., K.K., M.K. and A.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Regional Development Fund's (ERDF's) project, "Climate change mitigation potential of trees in shelter belts of drainage ditches in cropland and grassland" (No. 1.1.1.1/21/A/030) and European Social Fund's project "Strengthening the doctoral capacity of the University of Latvia within the framework of the new doctoral model", identification No.8.2.2.0/20/I/006, UL registration No. ESS2021/434.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This research is supported by the "Strengthening the doctoral capacity of the University of Latvia within the framework of the new doctoral model" project with the project identification No.8.2.2.0/20/I/006, LU registration No. ESS2021/434, co-financed by the European Social Fund. Trees were measured with the aim to determine the growth rate and potential of accumulation of elements on the shelter belts on dich side in the European Regional Development Fund's (ERDF's) project, "Climate change mitigation potential of trees in shelter belts of drainage ditches in cropland and grassland" (No. 1.1.1.1/21/A/030).

Conflicts of Interest: The authors declare no conflict of interest.

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